Luminant

Dynegy Midwest Generation, LLC
1500 Eastport Plaza Drive
Collinsville, IL 62234

December 20, 2024

Illinois Environmental Protection Agency
DWPC – Permits MC#15
Attn: 35 I.A.C. § 845.650(e) Alternative Source Demonstration Submittal
1021 North Grand Avenue East
P.O. Box 19276
Springfield, IL 62794-9276

Re: Vermilion Power Plant New East Ash Pond; IEPA ID # W1838000002-04

Dear Mr. LeCrone:

Dynegy Midwest Generation, LLC (DMG) is submitting this Alternative Source Demonstration (ASD) for potential exceedances observed from the Q3 2024 sampling event at the New East Ash Pond identified by Illinois Environmental Protection Agency (IEPA) ID No. W1838000002-04.

As originally conveyed to the agency in 2021, it has been the DMG's position that an approved groundwater monitoring program is a prerequisite to detecting an exceedance, which is the trigger for an alternative source demonstration under Title 35 of the Illinois Administrative Code (35 I.A.C.) Section (§) 845.650(e). DMG submitted an operating permit application including a proposed groundwater monitoring program for the New East Ash Pond on October 25, 2021. The application is still under review by IEPA. However, IEPA has requested that DMG evaluate groundwater and implement a groundwater corrective action program prior to the issuance of a final operating permit.

While an actual exceedance cannot occur until IEPA issues an operating permit establishing a groundwater monitoring program (*see Section 845.650 and 845.120*), in response to IEPA's requests DMG evaluated the Q3 2024 groundwater samples for exceedances of the groundwater protection standards (GWPS) as described in Section 845.600 and is submitting this ASD for potential exceedances detected.

In accordance with 35 I.A.C. 845.650(e), this ASD is being submitted within 60 days from the date of determination of a potential exceedance and the ASD was placed on the facility's website within 24 hours of submittal to the agency.

Sincerely,

Dianna Tickner

Dianna Tickner
Sr. Director – Decommission and Demolition

Enclosures
Alternate Source Demonstration, Quarter 3 2024, New East Ash Pond Vermilion Power Plant

Intended for
Dynegy Midwest Generation, LLC

Date
December 20, 2024

Project No.
1940110241-008

35 I.A.C. § 845.650(E): ALTERNATIVE SOURCE DEMONSTRATION

NEW EAST ASH POND

VERMILION POWER PLANT

OAKWOOD, ILLINOIS

IEPA ID: W1838000002-04

RAMBOLL Bright ideas. Sustainable change.

CERTIFICATIONS

I, Eric J. Tlachac, a qualified professional engineer in good standing in the State of Illinois, certify that the information in this report is accurate as of the date of my signature below. The content of this report is not to be used other than for its intended purpose and meaning, or for extrapolations beyond the interpretations contained herein.

Eric J. Tlachac
Qualified Professional Engineer
062-063091
Illinois
Ramboll Americas Engineering Solutions, Inc.
Date: December 20, 2024

I, Brian G. Hennings, a professional geologist in good standing in the State of Illinois, certify that the information in this report is accurate as of the date of my signature below. The content of this report is not to be used other than for its intended purpose and meaning, or for extrapolations beyond the interpretations contained herein.

Brian G. Hennings
Professional Geologist
196-001482
Illinois
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Date: December 20, 2024

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Appendix A-3	Kelron Environmental (Kelron), 2003. Regional and Local Hydrogeology and Geochemistry, Vermilion Power Plant, Illinois. Dynegy Midwest Generation, LLC, November 2003
Appendix A-4	Panno, S.V., and K.C. Hackley, 2010. Geologic influences on water quality. In Geology of Illinois, ed. D.R. Kolata and C.K. Nimz, 337-350. Champaign, Illinois: Illinois State Geological Survey
Appendix B	Plots of Groundwater Elevation Data from Pressure Transducers Installed in Monitoring Wells 22, 70S, 70D, 71S, and 71D
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ACRONYMS AND ABBREVIATIONS

35 I.A.C.	Title 35 of the Illinois Administrative Code
^{14}C	carbon-14
ASD	Alternative Source Demonstration
BCU	Bedrock Confining Unit
CCR	coal combustion residuals
CMA	Corrective Measures Assessment
cm/s	centimeters per second
DMG	Dynegy Midwest Generation, LLC
E001	Event 1, Quarter 2, 2023
E003	Event 3, Quarter 4, 2023
E004	Event 4, Quarter 1, 2024
E006	Event 6, Quarter 3, 2024
EPRI	Electric Power Research Institute
GWPS	groundwater protection standard
HCR	Hydrogeologic Site Characterization Report
IEPA	Illinois Environmental Protection Agency
ISGS	Illinois State Geological Survey
IPCB	Illinois Pollution Control Board
LGU	Lower Groundwater Unit
LOE(s)	line(s) of evidence
mg/L	milligrams per liter
MGU	Middle Groundwater Unit
Middle Fork	Middle Fork of the Vermilion River
NAP	North Ash Pond
NAVD88	North American Vertical Datum of 1988
NEAP	New East Ash Pond
NGVD	National Geodetic Vertical Datum of 1929
OEAP	Old East Ash Pond
PCA	principal component analysis
PMP	Potential Migration Pathway
Q2	second quarter
QA/QC	quality assurance/quality control
Ramboll	Ramboll Americas Engineering Solutions, Inc.
RYBP	Radiocarbon Years Before Present
SEP	Sequential Extraction Procedure
SI	surface impoundment
SPLP	synthetic precipitation leaching procedure
TDS	total dissolved solids
TU	tritium units
UCU	Upper Confining Unit
USEPA	United States Environmental Protection Agency
UU	Upper Unit
VPP	Vermilion Power Plant

EXECUTIVE SUMMARY

Groundwater samples collected at the Vermilion Power Plant (VPP) New East Ash Pond (NEAP) during July and August 2024 for the Quarter 3, 2024 compliance sampling event (Event 6 [E006]) were evaluated for potential exceedances of the groundwater protection standards (GWPS) described in Title 35 of the Illinois Administrative Code (35 I.A.C.) § 845.600. This Alternative Source Demonstration (ASD) has been prepared to provide pertinent information regarding the detections of elevated lithium and chloride at well 71D pursuant to 35 I.A.C. § 845.650(e) for the VPP NEAP.

The four lines of evidence (LOEs) listed below, with elaboration provided herein, demonstrate that the NEAP, OEAP, and NAP did not contribute to the elevated lithium and chloride detected in well 71D. The alternative source of the elevated lithium and chloride is natural variation in groundwater quality due to groundwater interactions with the bedrock.

1. The ionic composition of bedrock groundwater is different than the ionic composition of NEAP, OEAP, and NAP porewater and consistent with published observations for Pennsylvanian bedrock.
2. Concentrations of chloride in the NEAP, OEAP, and NAP porewater are lower than those observed in groundwater from compliance well 71D.
3. A bedrock solids and geochemical evaluation identified naturally occurring shales as the source of elevated lithium and chloride at compliance well 71D.
4. Bedrock groundwater is only slightly connected or completely isolated from the groundwater in the Quaternary deposits based on isotopic analysis, observed hydraulic conditions, and hydraulic conductivity of associated hydrostratigraphic units.

This information serves as the written ASD prepared in accordance with 35 I.A.C. § 845.650(e). Based on the facts and evidence included and referenced herein, natural variation in groundwater quality due to interactions with bedrock caused the elevated lithium and chloride observed at well 71D during the E006 sampling event and the VER NEAP, OEAP, and NAP did not contribute to the elevated lithium and chloride. Therefore, assessment of corrective measures is not required for lithium and chloride at the VER NEAP.

1. INTRODUCTION

This ASD has been prepared on behalf of Dynegy Midwest Generation, LLC (DMG) by Ramboll Americas Engineering Solutions, Inc. (Ramboll), to provide pertinent information pursuant to 35 I.A.C. § 845.650(e) for the VPP NEAP (*i.e.,* Site) located near Oakwood, Illinois. All documents referenced in this ASD are either included in **Appendix A** as noted in the text or are considered incorporated by reference and may be found at publicly accessible internet addresses provided in the References section (**Section 5**).

The E006 sampling event was completed on August 1, 2024, and analytical data were received on August 30, 2024. In accordance with 35 I.A.C. § 845.610(b)(3)(C), evaluation of results to determine potential exceedances of the GWPSs described in 35 I.A.C. § 845.600 was completed by October 29, 2024, within 60 days of receipt of the analytical data (Ramboll, 2024a). The comparison identified the following potential GWPS exceedances in Bedrock Confining Unit (BCU) (*i.e.,* potential migration pathway [PMP]) groundwater monitoring wells:

- Chloride at wells 35D, 70D, and 71D
- Lithium at wells 35D, 70D, and 71D
- Sulfate at wells 35D
- Total dissolved solids (TDS) at wells 35D and 70D

The comparison identified the following GWPS potential exceedances in Upper Unit (UU; PMP) compliance groundwater monitoring wells:

- Sulfate at well 70S

These are similar to potential GWPS exceedances determined during previous quarterly sampling events, with the exception of the potential lithium exceedance at well 71D, which was a new potential exceedance determined after the E006 sampling event. A potential exceedance of the GWPS for TDS at well 70S was also observed prior to the E006 sampling event.

Three previous ASDs were submitted for the BCU potential GWPS exceedances referenced above (except for the potential lithium exceedance at well 71D addressed by this ASD) and are summarized in **Table A** below.

Table A. Summary of VPP NEAP ASDs.

ASD Year/Quarter (Q)	Potential Exceedances
2023 Q2 (E001) (Ramboll, 2023a)	Chloride and lithium (35D, 70D); sulfate and TDS (35D) (Ramboll 2023b)
2023 Q4 (E003) (Ramboll, 2024b)	Chloride (71D) (Ramboll, 2024c)[1]
2024 Q1 (E004) (Ramboll, 2024d)	TDS (70D)

1. The chloride potential exceedance at 71D is also addressed in this ASD with additional supporting information as described herein.

The Illinois Environmental Protection Agency (IEPA) communicated in written correspondence (IEPA, 2023; IEPA, 2024a; IEPA, 2024b; provided in **Appendix A-1**) that they did not concur with the previous ASDs. As allowed in 35 I.A.C. § 845.650(e), DMG subsequently filed timely petitions asking the Illinois Pollution Control Board (IPCB) to review the IEPA's denials of the

E001 and E004 ASDs. The IPCB accepted the petitions for appeal and for each appeal approved a partial stay, with no objections by the IEPA, of the requirements of 35 I.A.C. § 845.650(d), 35 I.A.C. § 845.660, 35 I.A.C. § 845.670, and 35 I.A.C. § 845.680, which pertain to corrective actions for the parameters with potential exceedances referenced in the ASDs, pending final action by the IPCB.

While the previously submitted ASDs each sufficiently demonstrated by a preponderance of the evidence that the NEAP, OEAP, and NAP are not the cause of or contributing to the prior detected potential exceedances and that an alternative source was responsible for the potential exceedances, this ASD provides the following information in response to concerns raised by IEPA:

- In response to IEPA's concern regarding evidence that draw water from the bedrock is completely isolated from the local groundwater flow system, hydrogeologic information is provided in **Sections 2.3.1 and 3.3** demonstrating the lack of a hydraulic connection between the bedrock and overlying shallow, unlithified soils that comprise the local groundwater flow system in the vicinity of the NEAP.
- In response to the IEPA's concern regarding evidence of the interaction of bedrock groundwater and the OEAP, hydrogeologic information is provided in **Section 2.3.1** regarding groundwater flow in the vicinity of the OEAP; and, the ionic compositions of porewater collected from both the OEAP and NAP are included in the comparison of the ionic composition of CCR porewater to that of bedrock groundwater collected from the monitoring wells in the vicinity of the NEAP presented in **Sections 3.1 and 3.2**.
- In response to IEPA's concerns regarding CCR characterization, specific references to the USEPA 2014 Human and Ecological Risk Assessment of Coal Combustion Residuals are provided in **Section 2.4** to demonstrate the scientific basis for considering CCR source water collected from porewater wells screened near the base of ash, rather than laboratory leach tests, to represent the best CCR source term for impoundments.
- In response to IEPA's concerns regarding underlying documentation associated with sample collection and analysis, underlying data including but not limited to sampling methodology, sample handling, analytical procedures, laboratory reports, and quality and control documents have been attached to this ASD or incorporated by reference and are discussed further in **Section 2.5**.

Pursuant to 35 I.A.C. § 845.650(e), the LOEs presented in **Section 3** demonstrate that natural variation in groundwater quality due to interactions with the bedrock are the cause of the lithium and chloride potential GWPS exceedances at **well 71D** listed above and the NEAP, OEAP, and NAP have not contributed to the potential exceedances.

This ASD was completed by December 28, 2024, within 60 days of determination of the potential exceedance (October 29, 2024), as required by 35 I.A.C. § 845.650(e). This ASD has been completed in conformance with guidance provided in the Electric Power Research Institute (EPRI) guidance for development of ASDs at CCR sites (EPRI, 2017; provided in **Appendix A-2**), and the Solid Waste Disposal Facility Criteria: Technical Manual (USEPA, 1993). An ASD uses a multiple LOE approach to demonstrate that a potential exceedance is more likely related to the alternative source and not the regulated unit (USEPA, 1993). The goal of a weight of evidence approach is to provide robust support for a causal relationship based on many smaller individual qualitative or quantitative pieces of evidence (USEPA, 2016). Critically, no individual LOE will be

completely conclusive, and the final determination of a conclusion is based on the totality of the evidence provided (USEPA, 2016).

The sulfate and TDS GWPS potential exceedances at **well 70S** are being addressed in accordance with 35 I.A.C. § 845.660, and an associated CMA was initiated on December 31, 2023. A request to extend the 90-day CMA completion deadline specified in 35 I.A.C. § 845.660(a)(2) by 60 days was submitted to IEPA on January 2, 2024, and approved in a written response from IEPA dated January 3, 2024. The CMA was completed and submitted to IEPA on May 29, 2024. Activities currently ongoing in support of corrective action are detailed in the Semiannual Remedy Selection Progress Report (Ramboll, 2024f).

2. BACKGROUND

2.1 Site Location and Description

The former VPP is located four miles northeast of the Village of Oakwood in Vermilion County. The NEAP lies in the bottomlands of the Middle Fork of the Vermilion River (Middle Fork) and is bordered to the west by bluffs, to the south by unimproved DMG land, and to the north and east by the Middle Fork. Several underground coal mines and one surface mine were historically operated both beneath the NEAP and in the vicinity of the VPP.

2.2 Description of New East Ash Pond CCR Unit

The NEAP is a 29-acre inactive, unlined CCR surface impoundment (SI) constructed overtop a thick shale formation using berms constructed with a low-permeability clay core and cutoff walls keyed into the underlying shale formation.

The original East Ash Pond (1989 pond footprint) was constructed in 1989 and expanded in 2002 to form the present-day NEAP. The 1989 pond footprint was built overtop a thick shale formation which is greater than 80 feet thick in the vicinity of the ash ponds. The earthen berms on the north, east, and south sides of the 1989 pond footprint were constructed with a low-permeability clay core and cutoff walls keyed into the underlying shale formation. The cutoff walls extended approximately 8 feet into the underlying shale. A natural earthen bluff composed of low-permeability native clays formed the west side of the 1989 pond footprint.

New berms were constructed in 2002 to expand the capacity of the 1989 pond footprint, forming the footprint of the present-day NEAP. The new berms raised the height of the original berms and were constructed with clay liners keyed into the underlying clay core. A cutoff trench backfilled with low permeability fill was placed along the western side slope of the enlarged NEAP. The low-permeability materials surrounding the footprint of the present-day NEAP form the existing containment system. The secondary pond was not expanded or modified as part of the 2002 NEAP expansion. The VPP ceased operations in 2011 when the power plant was retired.

2.3 Geology and Hydrogeology

2.3.1 Site Hydrogeology

Significant site investigation has been completed at the VPP to fully characterize the geology, hydrogeology, and groundwater quality as provided in the October 2021 operating permit applications for the NEAP, (Geosyntec Consultants, 2021a) and NAP and OEAP (Geosyntec Consultants, 2021b), which included Hydrogeologic Site Characterization Reports (HCRs) for these units as Appendix N of each document (Ramboll, 2021a; Ramboll, 2021b); and the January 2022 construction permit application for the NEAP (Geosyntec Consultants, 2022a). Additional supporting documents are referenced in the text and either provided in **Appendix A** as noted in the text or are considered incorporated by reference and may be found at publicly accessible internet addresses provided in the References section (**Section 5**). A site conceptual model has been developed and is summarized below.

In addition to the CCRs present in the NEAP, there are two different types of unlithified material present above the lithified bedrock, which were categorized into three hydrostratigraphic units in this report as follows:

- **Upper Unit (UU):** includes mixed Quaternary alluvial deposits of the Cahokia Alluvium described as sand with occasional layers of silty clay. The alluvial sand is generally a fine to medium sand that contains silts, clays, and gravels in varying amounts. This unit is present outside of the NEAP and in the bottomlands of the Middle Fork.
- **Upper Confining Unit (UCU):** consists of predominantly low permeability silty and clayey diamictons (glacial till) of the Wedron Formation with intermittent sand layers and lenses. This unit is present outside of the NEAP and along the western bluff of the Middle Fork.
- **Bedrock Confining Unit (BCU):** lowermost unit identified at the site and underlies all unlithified deposits. This unit occurs within Pennsylvanian shale which is the uppermost lithified unit at the Site.

None of the hydrostratigraphic units described above have been identified as an aquifer. However, the UU and BCU have been identified as PMPs.

The groundwater present in the unlithified and lithified materials present around the NEAP is isolated from the groundwater present in the vicinity of the NAP and OEAP. Interpreted groundwater flow direction and gradients toward the Middle Fork (Ramboll, 2021a) have not changed significantly since the hydrogeologic study of the NEAP completed in 2003 (Kelron, 2003; provided in **Appendix A-3**), and recent data supports the existing conceptual site model. A groundwater elevation map for the BCU for July 29, 2024, is presented in **Figure 1.** Groundwater elevations in BCU monitoring wells 70D and 71D were observed to be consistently increasing before and after the E004, E005, and E006 sampling events based upon data obtained from pressure transducers deployed in those wells (**Appendix B**). Groundwater elevations in those monitoring wells have not reached static equilibrium following each sampling event, thus yielding groundwater elevations that are not representative of the potentiometric surface at these locations. However, groundwater elevations at wells 10 and 22 are screened within the UU and BCU, respectively, and are considerably higher than groundwater elevations at or near the OEAP (**Figure 2**); therefore, the NEAP bedrock wells are not downgradient of the OEAP.

No BCU groundwater elevation data is collected and available to complete a potentiometric surface map for the BCU in the area of the NAP and OEAP. However, a calibrated groundwater flow model was completed as part of the January 2022 construction permit application (Geosyntec Consultants, 2022b) for the NAP and OEAP, which included the BCU within the model domain. The simulated potentiometric surface map, which includes the area of the NAP and OEAP, for the BCU from the calibrated groundwater model is provided in **Appendix C**. Simulated groundwater elevations in the shale are highest in the topographically highest areas, such as in the vicinity of the NEAP, and the lowest groundwater elevations occur at wells located adjacent to the Middle Fork, consistent with the HCRs for the NEAP and the NAP and OEAP (Ramboll, 2021a; Ramboll, 2021b) and as previously reported by Kelron (2003) for the NEAP. The simulated potentiometric surface indicates groundwater in the BCU does not flow from the OEAP to the area of the NEAP. The Middle Fork is the receiving body of water in the region, including for both the NAP and OEAP via a different hydrostratigraphic unit, referred to as the Middle Groundwater Unit (MGU) and described further below, and NEAP via the underlying BCU, consistent with the conceptual site model.

As described in the HCR for the NAP and OEAP (Ramboll, 2021b), groundwater flows into the Middle Fork through the unlithified MGU (alluvial deposits of coarser grained material encountered at the base of the Cahokia Alluvium and designated as the uppermost aquifer in the

area of the NAP and OEAP) and Lower Groundwater Unit (LGU; glacial outwash and re-worked glacial deposits of the Henry Formation in the area of the NAP and OEAP) which are the primary pathways that contaminant migration could occur in the area of the NAP and OEAP. Water level elevations collected from ND3 (a porewater well placed in the NAP) indicate the phreatic surface is above the water levels observed in the uppermost aquifer; however, the potentiometric surface of the uppermost aquifer (*i.e.*, the MGU) for July 29, 2024 (**Figure 2**) illustrate flow toward the Middle Fork with no observable radial component of flow outward along the perimeter of the NAP and OEAP (and toward the upland bluff and NEAP, both areas where the MGU does not exist and materials at similar elevations as the MGU along the perimeter of the NAP and OEAP consist of low permeability tills [with exception to bottomland areas north of the NAP]). The absence of a radial component of flow indicates the NAP and OEAP do not significantly impact regional groundwater flow direction toward the Middle Fork. As indicated by groundwater potentiometric surfaces, groundwater flows from beneath the NAP and OEAP toward the Middle Fork through the MGU, not toward the NEAP.

Groundwater flow in the LGU beneath the bluff and Company Lake appears to reflect the topography, flowing from the VPP toward the NAP, OEAP and Middle Fork to the north, and toward Company Lake to the south, which results in localized groundwater divides (**Figure 3**). Company Lake is not downgradient of the NAP and OEAP. Neither the MGU nor the LGU are present in the upland area immediately southeast of the OEAP or in the area of the NEAP. Low permeability tills of the UCU and LCU occur at similar elevations as the MGU and LGU in the upland area immediately southeast of the OEAP between the OEAP and NEAP areas creating a localized groundwater flow divide. Consequently, groundwater does not flow through the low permeability till units between the OEAP area to the NEAP area, but instead preferentially flows along a direct path to the Middle Fork through the MGU and LGU. Thus, the NAP and OEAP areas are hydraulically isolated from the NEAP in the shallow, unlithified soils overlying the bedrock.

2.3.2 Regional Bedrock Geology

Regional investigations of the Illinois Basin have identified bedrock (specifically brines within the bedrock formations) as a source of chloride in groundwater (Kelley et al., 2012; Panno et al., 2018). Studies by Cartwright (1970) and Siegel (1989) indicate that groundwater migrates toward the center of the Illinois Basin and discharges upward through overlying confining units. The "Saline groundwater and brines can be brought near or to the land surface by natural conditions, such as migrating up prominent fractures and/or faults in bedrock, or by anthropogenic activities, such as exploration for and exploitation of petroleum. The mixing of upward-migrating saline groundwater with fresh groundwater from shallow aquifers can make groundwater from private wells undrinkable and can present a very expensive problem for municipalities" (Panno and Hackley, 2010; provided in **Appendix A-4**). Illinois State Geological Survey (ISGS) reporting includes 31 chloride results from available water samples (including some samples from VPP) which range from 2.1 to 30,269 milligrams per liter (mg/L) with mean value of 1,689 mg/L and median of 13 mg/L (ISGS, 2002). The report also concludes that water from the wells completed in shale contained higher concentrations of aluminum, barium, bromide, boron, chloride, fluoride, iron, lithium, potassium, sodium, and strontium. Tritium and carbon-14 (^{14}C) age dating has demonstrated that groundwater from the bedrock is significantly older than that from the shallow Quaternary deposits (Kelron, 2003; ISGS, 2002).

2.4 Groundwater and NEAP Monitoring

The monitoring system for the NEAP was proposed in the Groundwater Monitoring Plan (Ramboll, 2021c) and consists of monitoring wells installed in the UU, UCU, and BCU, including background monitoring wells 10 and 22, located west of the NEAP, and compliance monitoring wells 16A, 16B, 35S, 35D, 70S, 70D, 71S and 71D (**Figure 1**). NED1 (installed in CCR) is used to collect porewater samples and monitor water levels within the NEAP.

In the Final Human and Ecological Risk Assessment of Coal Combustion Residuals (USEPA, 2014), the conceptual model for risks of impounded CCR concludes that "chemical constituents can be released from SIs through the leaching of soluble constituents into the water that comes in contact with the CCRs and percolation of the resulting leachate into the subsurface soil and ground water" (USEPA, 2014). This USEPA risk assessment uses data from "impoundment porewater", defined as water "collected from the interstitial water between waste particles in SIs as it occurs in the field," to characterize CCR impoundment source chemical concentrations. The cited reason for using porewater data, as opposed to total composition CCR data or leach test data (both of which were available in the compiled database), is because porewater concentrations "best reflect leachate as it is released into underlying soils." In the 2024 update to the risk assessment in support of the 2024 Final Rule – Legacy CCR Surface Impoundments and CCR Management Units, USEPA confirms that "it was most appropriate to use porewater data to model leakage from surface impoundments" (USEPA, 2024). Consistent with USEPA practice, this analysis considers CCR source water collected from porewater wells screened near the base of ash within the unit as the primary CCR source term for the purpose of alternative source evaluation.

2.5 Data Reporting and Data Quality

All groundwater and NEAP porewater data used in the following analyses collected during the second quarter (Q2) of 2023 or later were submitted quarterly to IEPA in accordance with 35 I.A.C. § 845.610(b)(3)(D) (Ramboll, 2023b; Ramboll, 2024b; Ramboll, 2024d; Ramboll, 2024e; Ramboll, 2024g; Ramboll, 2024h) and are incorporated by reference in this ASD. Analytical and quality assurance/quality control (QA/QC) results for groundwater and NEAP porewater data collected prior to Q2 2023 and porewater data from the NAP and OEAP are provided separately as Electronic Data Deliverables transmitted electronically to IEPA. Solid phase data is attached and referenced in **Appendix E**. All samples and data were collected in accordance with the Multi-Site Sampling and Analysis Plan (Ramboll 2022a) and Multi-Site Quality Assurance Project Plan (Ramboll 2022b). Data presented in documents referenced in this ASD are considered incorporated by reference and may be found in **Appendix A** or at publicly accessible internet addresses provided in the References section (**Section 5**).

3. LINES OF EVIDENCE THAT POTENTIAL GROUNDWATER PROTECTION STANDARD EXCEEDANCES ARE NOT RELATED TO THE NEAP, OEAP, OR NAP AND ARE ATTRIBUTABLE TO NATURAL VARIATION

In accordance with 35 I.A.C. § 845.650(e), the following LOEs demonstrate that natural variation in groundwater quality due to groundwater interactions with the bedrock caused the elevated lithium and chloride detected at compliance groundwater monitoring well 71D and the NEAP, OEAP, and NAP did not contribute to the potential exceedances.

1. The ionic composition of bedrock groundwater is different than the ionic composition of NEAP, OEAP, and NAP porewater and consistent with published observations for Pennsylvanian bedrock.
2. Concentrations of chloride in the NEAP, OEAP, and NAP porewater are lower than those observed in groundwater from compliance well 71D.
3. A bedrock solids and geochemical evaluation identified naturally occurring shales as the source of elevated lithium and chloride concentrations at compliance well 71D.
4. Bedrock groundwater is only slightly connected or completely isolated from the groundwater in the Quaternary deposits based on isotopic analysis, observed hydraulic conditions, and hydraulic conductivity of associated hydrostratigraphic units.

These LOEs are described and supported below.

3.1 LOE #1: The Ionic Composition of Bedrock Groundwater is Different Than the Ionic Composition of NEAP, OEAP, and NAP Porewater and Consistent with Published Observations for Pennsylvanian Bedrock

Piper diagrams graphically represent ionic composition of aqueous solutions. A Piper diagram displays the position of water samples with respect to their major cation and anion content on the two lower triangular portions of the diagram, providing the information which, when combined on the central, diamond-shaped portion of the diagram, identify composition categories or groupings (hydrochemical facies). **Figure A** on the following page is a Piper diagram that displays the ionic composition of samples collected from the bedrock background and bedrock compliance wells associated with the NEAP (sampled July 29 to August 1, 2024), porewater sampling location associated with the NAP (sampled July 30, 2024), porewater sampling location associated with the NEAP (sampled February 21, 2024; porewater well NED1, located within the NEAP, could not be accessed for sampling July 29 to August 1, 2024), and porewater sampling location associated with the OEAP (sampled July 30, 2024). **Section 2.5** identifies the previous submittals to IEPA containing laboratory reports with analysis results for the major ions that comprise the representation of ionic composition in **Figure A**, or the location of these results if not previously submitted.

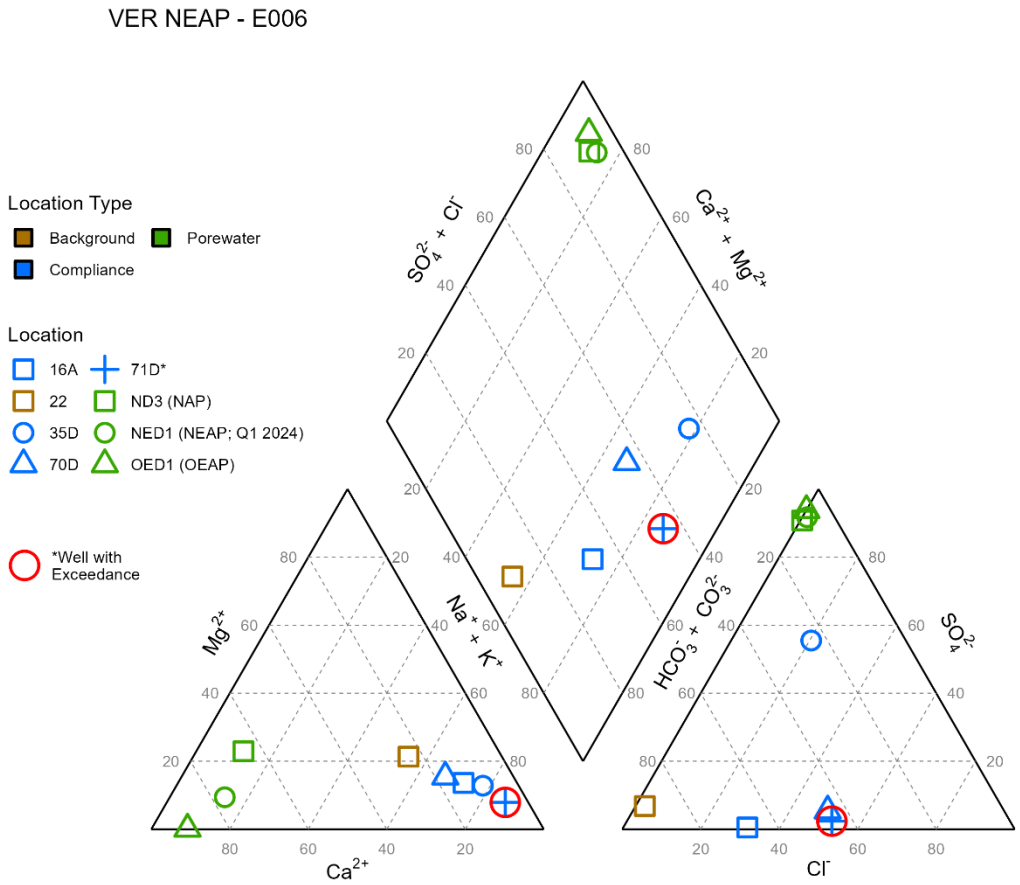

Figure A. Piper Diagram. Shows ionic composition of bedrock groundwater (July 29 to August 1, 2024), porewater associated with the NAP (July 30, 2024), porewater associated with the NEAP (February 21, 2024), and porewater associated with the OEAP (July 30, 2024)

It is evident from the piper diagram (**Figure A**) that porewater from the NEAP (green circle symbol), OEAP (green triangle symbol), and NAP (green square symbol) are primarily in the calcium-sulfate hydrochemical facies, while the bedrock groundwater from potential exceedance well 71D near the NEAP (blue plus sign inside red circle) is in the sodium-chloride hydrochemical facies. The background BCU sample (brown square symbol) is in the sodium-bicarbonate hydrochemical facies. The background BCU sample is collected from well 22, which is screened from 556 to 576 feet[1], and well 71D is screened at lower elevations, 537 to 547 feet (Ramboll, 2021a). Groundwater from deeper in Pennsylvanian aquifers tends to be more dominant in chloride, and groundwater can change from a sodium-bicarbonate to a sodium-chloride facies over small changes in depth (Lloyd and Lyke, 1995). Therefore, the compliance groundwater sample has a different ionic composition than NEAP, OEAP, and NAP porewater and a composition relative to background that is consistent with expected changes due to screen depth, indicating that NEAP, OEAP, and NAP porewater is not the source of CCR constituents detected in 71D and that the groundwater signature at 71D is consistent with influence from the bedrock alternative source.

[1] All elevations in this report are referenced to North American Vertical Datum 1988 (NAVD88) unless otherwise noted.

3.2 LOE #2: Concentrations of Chloride in the NEAP, OEAP, and NAP Porewater are Lower than Those Observed in Groundwater from Compliance Well 71D

A box plot of chloride concentrations in compliance monitoring well 71D and NEAP, OEAP, and NAP porewater wells NED1, OED1, and ND3, respectively, is provided in **Figure B** on the following page. The chloride data ranges are April 2021 to August 2024 for 71D; April 2021 to October 2024 for NED1; and June 2021 to July 2024 for OED1 and ND3. **Section 2.5** identifies the previous submittals to IEPA containing laboratory reports with chloride analysis results that are presented in **Figure B**, or the location of these results if not previously submitted.

Chloride concentrations are significantly lower in the NEAP, OEAP, and NAP porewater samples such that they do not overlap at all with the concentrations observed in compliance groundwater samples collected from well 71D. The maximum concentration of chloride detected in NEAP, OEAP, and NAP porewater (44 mg/L, 5 mg/L, and 10 mg/L, respectively) is lower than the minimum concentration of chloride in 71D (170 mg/L). In addition, the median concentration of chloride in well 71D (670 mg/L) is 37, 223, and 89 times greater than the median concentration of chloride (18 mg/L, 3 mg/L, and 7.5 mg/L) in NEAP, OEAP, and NAP porewater, respectively. Therefore, the porewater from the NEAP, OEAP, and NAP cannot be the source of the elevated chloride concentrations observed in 71D.

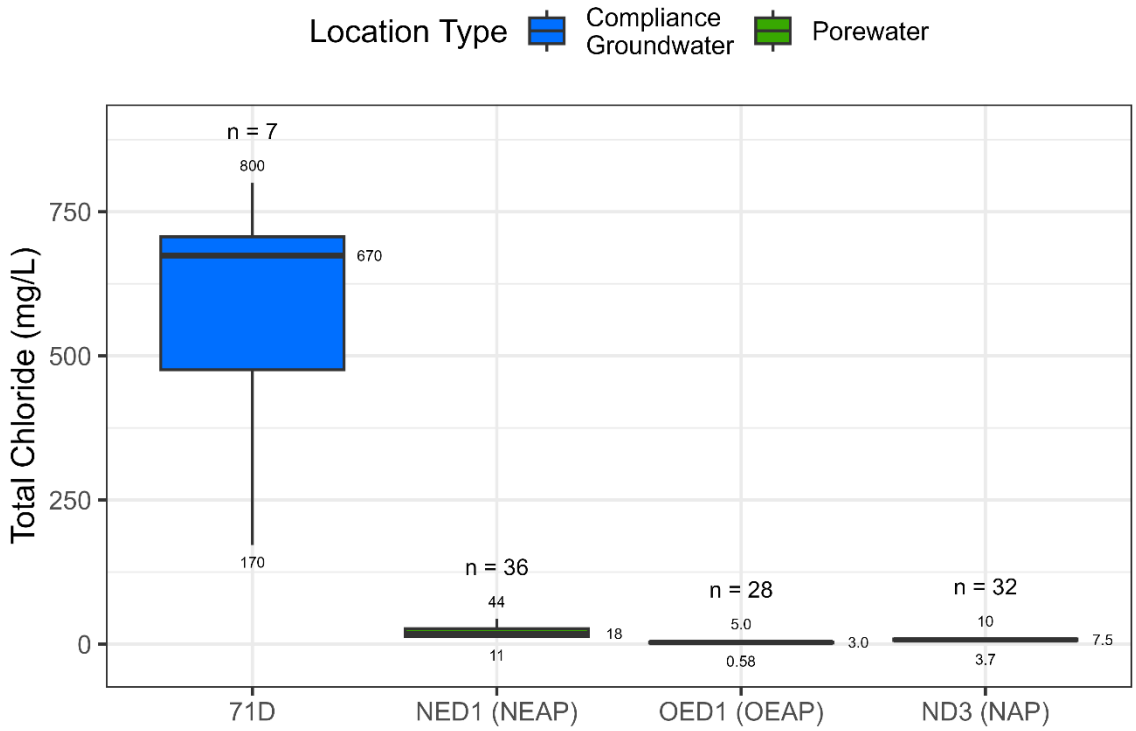

Figure B. Chloride Box Plot. The sample size (n), maximum, median, and minimum values are noted.

3.3 LOE #3: A Bedrock Solids and Geochemical Evaluation Identified Naturally Occurring Shales as the Source of Elevated Lithium and Chloride Concentrations at Compliance Well 71D

Appendix D presents an evaluation of site-specific solid phase compositions, geochemical conditions through multivariate statistical analyses, and literature review of Pennsylvanian-aged shale bedrock groundwaters that identifies naturally occurring lithium and chloride associated with shales as the alternative source of these constituents and related elevated lithium and chloride concentrations in the groundwater at 71D based on the following observations:

- Sequential extraction procedure (SEP) analyses demonstrated that much of the lithium in the solid phase is associated with the fractions which correlate to primary minerals such as micas and clay minerals, as well as the fractions associated with sulfides and oxide minerals.
- Geochemical conditions in the groundwater support desorption or dissolution of the sulfide and iron oxide mineral phases that host lithium.
- Natural weathering processes can mobilize lithium and chloride to groundwater from the micas and clay minerals in the bedrock.
- Mineralogy of bedrock samples collected from the site consists of considerable quantities of clay and mica materials that retain dissolved ions (*i.e.,* lithium and chloride) from marine water trapped in the pore space at the time of deposition of these materials.
- Groundwater chloride concentrations observed in Pennsylvanian-age shale bedrock aquifers are comparable to or higher than those observed at well 71D.

- Principal component analysis (PCA) shows that BCU well groundwater is distinct from NEAP, OEAP, and NAP porewater.

3.4 LOE #4: Bedrock Groundwater is Only Slightly Connected or Completely Isolated from the Groundwater in the Quaternary Deposits Based on Isotopic Analysis, Observed Hydraulic Conditions, and Hydraulic Conductivity of Associated Hydrostratigraphic Units

In 2002, ISGS and DMG collected groundwater samples from eight monitoring wells and tested the samples for ^{14}C and hydrogen-3 (tritium) (ISGS, 2002). Six of the monitoring wells (25, 26, 27, 28, 29, and 30) were located adjacent to the NEAP (Figure 7, **Appendix E**). Wells 26 and 28 had well screens that intersected Quaternary deposits of the UU and the remaining wells were screened in shallow shale bedrock (BCU) (**Table 2, Appendix A-3**). Results of the testing are presented in Figure 7 included in **Appendix F,** and in Table 11 of the ISGS report (2002) included below as **Table B**.

Table B. Isotopic Data from ISGS Sampled Wells (Table 11 from ISGS, 2002)

Table 11. Isotopic data for ISGS sampled wells

Parameter	Units	Well Number							
		1349	25531	KELRON 25	KELRON 26	KELRON 27	KELRON 28	KELRON 29	KELRON 30
^{14}C	RYBP	2,180	21,160	13,920	210	19,400	modern	34,610	20,850
	% modern carbon	76	7.2	18	97	8.9	102	1.4	7.5
Tritium	TU	7.8	<0.43	<0.43	5.3	<0.43	5.8	<0.52	<0.43

^{14}C = carbon-14
RYBP = Radiocarbon Years Before Present
TU = tritium units

Tritium is generated in the atmosphere and decays in the isolated subsurface. Water with tritium concentrations greater than 5 TU is considered to be recent, while water with nondetectable tritium concentrations is considered to be greater than 50 years old (ISGS, 2002). Groundwater collected from shallow Quaternary deposits is recent (TU > 5), while groundwater from the shallow bedrock is older (no tritium detected). The tritium results are consistent with the ^{14}C results, which indicate that the shallow bedrock wells contain an inorganic carbon signature substantially older than that from wells screened in the Quaternary deposits. Groundwater collected from wells screened in shallow bedrock in the vicinity of the NEAP (wells 25, 27, 29, and 30) had estimated ages ranging from 13,920 to 34,610 years based on ^{14}C age dating. This is in contrast to groundwater collected from wells 26 and 28 (screened in the Quaternary deposits) which had estimated ages of less than 210 years. These results indicated to ISGS that the wells that "draw water from the bedrock are either only slightly connected to or completely isolated from the local groundwater flow system [overlying Quaternary deposits]" (ISGS, 2002).

More recent observations of site conditions support the ISGS conclusion (2002), including the following described in further detail below:

- The lack of groundwater elevation response in BCU downgradient wells to precipitation and short-term changes in Middle Fork River stage
- Mostly upward vertical hydraulic gradients in the BCU (and observed artesian conditions in the BCU)
- Differences in vertical hydraulic conductivities between UU and BCU units

Groundwater elevation in the alluvial deposits (UU) typically conforms to ground surface topography and fluctuates in response to changes in river stage and variations in precipitation (Kelron, 2003). Data available from pressure transducers installed in the NEAP monitoring wells screened in the UU indicate relatively quick responses (increases and decreases in a period of one month) to precipitation and changes in river stage as illustrated in the hydrograph for wells 70S and 71S (**Appendix B**; note transducer data for other NEAP monitoring wells screened in the UU are not available as these wells are frequently dry). Transducer data available from NEAP monitoring wells screened in the BCU did not indicate a response to precipitation and changes in river stage like those in NEAP monitoring wells screened in the UU, as illustrated in the hydrograph for wells 22, 70D, and 71D (**Appendix B**; note transducer data is not available for BCU wells 16A and 35D). The lack of increases and decreases in the hydrographs for the BCU wells support a lack of hydraulic connection to the local groundwater flow system in the UU.

The pattern of progressively slow steady increase of water levels in BCU wells 70D and 71D between sampling events as illustrated in the hydrographs (**Appendix B**) also indicates that groundwater elevations in these wells do not reach static equilibrium following sampling events when groundwater levels were drawn down during purging and sampling as a result of the low permeability of the shale. Downgradient shallow UU wells 16B (nested with BCU well 16A) and 35S (nested with BCU well 35D) are frequently dry, and downgradient BCU groundwater level readings from wells 70D (nested with UU well 70S) and 71D (nested with UU well 71S) do not represent static groundwater elevations as previously described; therefore, the following discussion on vertical hydraulic gradient downgradient of the NEAP focuses on data collected by Kelron (2003) as recent data is not sufficient to evaluate vertical hydraulic gradients.

Further, as presented by Kelron (2003), groundwater in the shale (BCU) is at the end of its flow path as it migrates upward into the overlying alluvium (UU) and directly into the Middle Fork in some locations, as illustrated in the cross-section in Figure 28 from Kelron, 2003 and provided in **Appendix E**, preventing the downward migration into the shale of water in contact with CCR materials contained within the NEAP. In 2002, upward vertical gradients were observed between the shale and alluvial deposits at all of the nested wells within the bottomlands of the Middle Fork during at least part of the monitoring period, with the exception of nested wells 23/24 (these evaluations included alluvial deposit and shale wells nests 13B/13A, 16B/16A, 23/24, 26/27, and 28/29). The greatest upward gradients were observed between shallow shale well 13A and nested deep shale well 32. Deep shale well 32 was also reported to be flowing under artesian conditions during the investigation completed for the 2003 Report. Note that well 35D (installed in March 2017) replaced well 13A, where the greatest upward gradients within the bedrock were observed and reported in the Kelron 2003 report; it is expected that vertical gradients are upward at well nest 35S/35D under normal conditions (static conditions). According to the Kelron 2003 report, high hydraulic heads and artesian groundwater flow conditions were also observed when the coal seam and overlying fractured shale in close proximity to the mined areas were intercepted at exploratory borings B201 and B202 (boring locations shown in Figure 7 of **Appendix E**). Nested wells 16B/16A experienced upward vertical gradients in only one of the

eight groundwater level monitoring events in 2002 and the overall eight-month average vertical gradient was downward. As reported in the HCR (Ramboll, 2021a), groundwater elevations measured at BCU well 16A in 2021 ranged from 568.28 to 571.32 feet, which were consistently greater than the elevation of the top of bedrock at location 16A (approximately 566 feet National Geodetic Vertical Datum of 1929 [NGVD]) indicating the presence of upward gradients in the bedrock (nested well 16B was dry in eight monitoring events from March to August 2021, so vertical gradients could not be calculated). The upward vertical gradients discussed in Kelron, 2003 and the 2021 HCR (Ramboll, 2021a) support that BCU groundwater is hydraulically isolated from the overlying local groundwater flow system in the UU downgradient of the NEAP; groundwater does not flow from the UU downward into the BCU downgradient of the NEAP.

As described in the 2021 HCR (Ramboll, 2021a), the UU and the BCU are distinct water-bearing units based on stratigraphic relationships and hydrogeologic characteristics as described in **Section 2.3**. Field hydraulic conductivity tests indicated that the horizontal hydraulic conductivity for the UU ranged from 7.4×10^{-4} to 1.1×10^{0} centimeters per second (cm/s), with a geometric mean of 1.1×10^{-2} cm/s (Ramboll, 2021a). Based on field hydraulic conductivity testing, the horizontal hydraulic conductivity for the BCU ranged from 1.1×10^{-6} to 2.3×10^{-5} cm/s, with a geometric mean of 7.1×10^{-6} cm/s (Ramboll, 2021a). Wells 70D and 71D were installed in 2021 in the BCU, where the hydraulic conductivity of the BCU is relatively low with a geometric mean of 7.1×10^{-6} cm/s. As described previously, water levels at wells 70D and 71D did not equilibrate to static water levels following installation and initial well development in 2021 as a result of the low permeability of the shale. Two samples were collected from the UU at two locations (70S and 71S) in the vicinity of the NEAP as part of the 2021 field investigation and the resulting vertical hydraulic conductivities for the samples ranged from 5.2×10^{-4} to 1.3×10^{-3} cm/s (Ramboll, 2021a). The vertical hydraulic conductivity calculated from tests performed in the laboratory on one shale core ranged from 1×10^{-8} to 5×10^{-8} cm/s (Kelron, 2003). The geometric mean of the field hydraulic conductivity tests completed in 2021 and referenced above were four orders of magnitude lower in the BCU (7.1×10^{-6} cm/s) when compared to the UU (1.1×10^{-2} cm/s). The laboratory vertical hydraulic conductivity tests were a minimum of four orders of magnitude lower in the BCU (1×10^{-8} to 5×10^{-8} cm/s) when compared to the UU (5.2×10^{-4} to 1.3×10^{-3} cm/s). The significant difference in both horizontal and vertical hydraulic conductivities between the BCU and overlying UU hydrostratigraphic units, as well as the primarily upward vertical gradients identified downgradient of the NEAP, indicate the preferred flow path of groundwater in the UU would be laterally east and discharging into the Middle Fork rather than vertically down into the low permeability BCU, further supporting that groundwater in the BCU is hydraulically isolated from and not influenced by the local groundwater flow system in the UU.

In addition to the spatial location of the wells tested for ^{14}C and tritium relative to the NEAP, the elevations of the well screens and lithology of the age dated wells overlap with the well screen elevation and lithology of well 71D, which contains the potential lithium and chloride exceedances (**Table C** on the following page), with the exception of MW30, which is screened at a lower elevation than all of the other wells.

Table C. Summary of Bedrock Well Screen Elevations and Lithology

Well ID	Screen Elevation (feet)	Lithology
MW71D – exceedance well (Ramboll, 2021a)	547 to 537	shale bedrock
MW25 (Kelron, 2003)	560 to 540	shale bedrock
MW27 (Kelron, 2003)	557 to 537	shale bedrock
MW29 (Kelron, 2003)	558 to 538	shale bedrock
MW30 (Kelron, 2003)	519 to 499	shale bedrock

This data demonstrates that bedrock groundwater in the vicinity of the NEAP is only slightly connected or completely isolated from the groundwater in the quaternary deposits and the NEAP is not the source of the elevated lithium and chloride concentrations at well 71D.

4. CONCLUSIONS

Based on these four LOEs, it has been demonstrated that natural variation in groundwater quality due to groundwater interactions with the bedrock caused the elevated lithium and chloride detected in well 71D and the NEAP, OEAP, and NAP did not contribute to the potential exceedances.

1. The ionic composition of bedrock groundwater is different than the ionic composition of NEAP, OEAP, and NAP porewater and consistent with published observations for Pennsylvanian bedrock.
2. Concentrations of chloride in the NEAP, OEAP, and NAP porewater are lower than those observed in groundwater from compliance well 71D.
3. A bedrock solids and geochemical evaluation identified naturally occurring shales as the source of elevated lithium and chloride concentrations at compliance well 71D.
4. Bedrock groundwater is only slightly connected or completely isolated from the groundwater in the Quaternary deposits based on isotopic analysis, observed hydraulic conditions, and hydraulic conductivity of associated hydrostratigraphic units.

This information serves as the written ASD prepared in accordance with 35 I.A.C. § 845.650(e). Based on the facts and evidence included and referenced herein, a source other than the VER NEAP (natural variation in groundwater quality due to groundwater interactions with bedrock) caused the elevated lithium and chloride concentrations observed at well 71D and the VER NEAP did not contribute to the potential exceedances.

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FIGURES

- COMPLIANCE MONITORING WELL
- BACKGROUND MONITORING WELL
- PORE WATER WELL
- MONITORING WELL
- GROUNDWATER ELEVATION CONTOUR (5-FT CONTOUR INTERVAL, NAVD88)
- INFERRED GROUNDWATER ELEVATION CONTOUR
- GROUNDWATER FLOW DIRECTION
- REGULATED UNIT (SUBJECT UNIT)
- SITE FEATURE
- PROPERTY BOUNDARY

NOTES:
1. ELEVATIONS IN PARENTHESES WERE NOT USED FOR CONTOURING.
2. ELEVATION CONTOURS SHOWN IN FEET, NORTH AMERICAN VERTICAL DATUM OF 1988 (NAVD88).

0 150 300
Feet

POTENTIOMETRIC SURFACE MAP JULY 29, 2024

ALTERNATIVE SOURCE DEMONSTRATION
NEW EAST ASH POND
VERMILION POWER PLANT
OAKWOOD, ILLINOIS

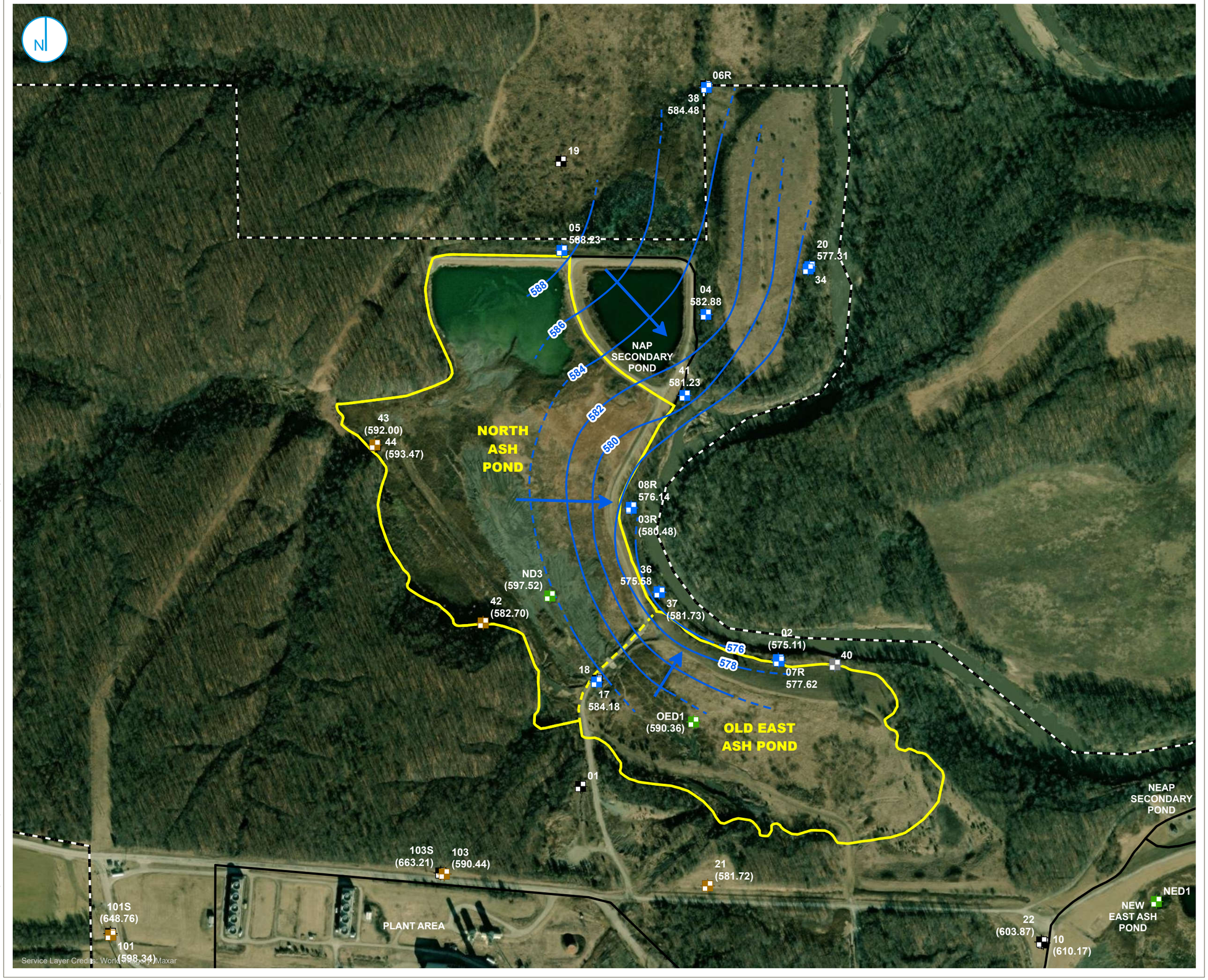
FIGURE 1

RAMBOLL AMERICAS
ENGINEERING SOLUTIONS, INC.

RAMBOLL

Y:\Mapping\Projects\222286\MXD\Alt_Source_Dem\Vermilion\NEAP_912\E006\ASD_E006.aprx\Figure 1: VER 912 NEAP Pot Surface 20240729

PROJECT: 169000XXXX | DATED: 12/9/2024 | DESIGNER: GALARNMC



COMPLIANCE MONITORING WELL
BACKGROUND MONITORING WELL
PORE WATER WELL
MONITORING WELL
CLOSED MONITORING WELL
GROUNDWATER ELEVATION CONTOUR (2-FT CONTOUR INTERVAL, NAVD88)
INFERRED GROUNDWATER ELEVATION CONTOUR
GROUNDWATER FLOW DIRECTION
REGULATED UNIT (SUBJECT UNIT)
SITE FEATURE
PROPERTY BOUNDARY

NOTES:
1. ELEVATIONS IN PARENTHESES WERE NOT USED FOR CONTOURING.
2. ELEVATION CONTOURS SHOWN IN FEET, NORTH AMERICAN VERTICAL DATUM OF 1988 (NAVD88).
3. COMPLIANCE MONITORING WELL 40 WAS ABANDONED DUE TO CONSTRUCTION ACTIVITY FOR THE GROUNDWATER EXTRACTION TRENCH.

0 200 400
Feet

POTENTIOMETRIC SURFACE MAP JULY 29, 2024

ALTERNATIVE SOURCE DEMONSTRATION
NEW EAST ASH POND
VERMILION POWER PLANT
OAKWOOD, ILLINOIS

FIGURE 2

RAMBOLL AMERICAS
ENGINEERING SOLUTIONS, INC.

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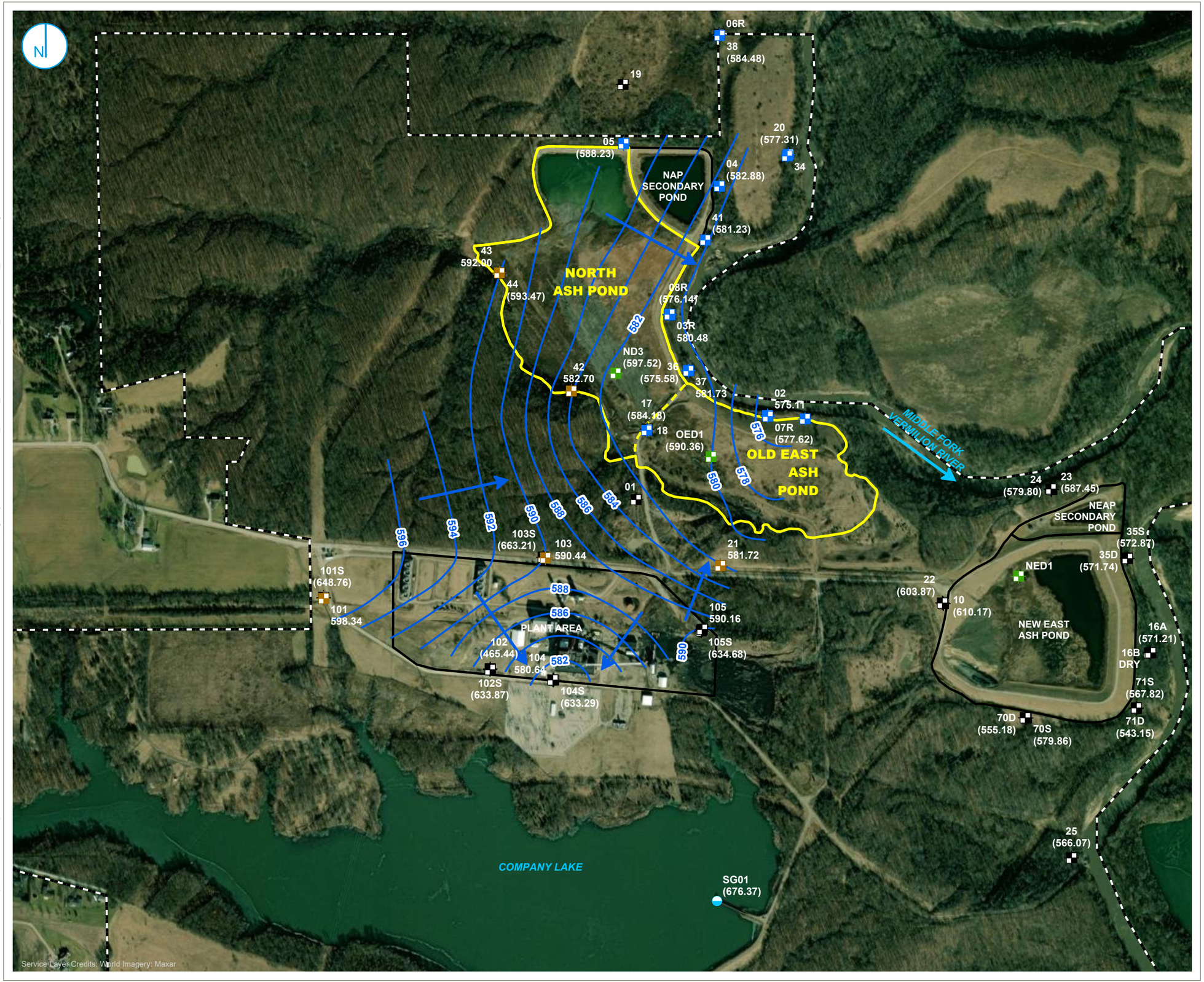
Y:\Mapping\Projects\2212285\MXD\Alt_Source_Dem\Vermilion\NEAP_912\E006ASD_E006.aprx\Figure 2: VER 910 911 NAPS OEAP Pot Surface 20240729



- COMPLIANCE MONITORING WELL
- BACKGROUND MONITORING WELL
- PORE WATER WELL
- STAFF GAGE, RIVER
- MONITORING WELL
- GROUNDWATER ELEVATION CONTOUR (2-FT CONTOUR INTERVAL, NAVD88)
- GROUNDWATER FLOW DIRECTION
- REGULATED UNIT (SUBJECT UNIT)
- SITE FEATURE
- PROPERTY BOUNDARY

NOTES:
1. ELEVATIONS IN PARENTHESES WERE NOT USED FOR CONTOURING.
2. ELEVATION CONTOURS SHOWN IN FEET, NORTH AMERICAN VERTICAL DATUM OF 1988 (NAVD88).

0 300 600
Feet

POTENTIAL MIGRATION PATHWAY LOWER GROUNDWATER UNIT POTENTIOMETRIC SURFACE MAP JULY 29, 2024

ALTERNATIVE SOURCE DEMONSTRATION
NEW EAST ASH POND
VERMILION POWER PLANT
OAKWOOD, ILLINOIS

FIGURE 3

RAMBOLL AMERICAS
ENGINEERING SOLUTIONS, INC.

RAMBOLL

Y:\Mapping\Projects\22285MXD\Alt_Source_Dem\Vermilion\NEAP_912E006\ASD_E006.aprx\Figure 3. VER 910 911 NAPS OEAP PMP Pot Surface 20240729
PROJECT: 169000XXXX | DATED: 12/9/2024 | DESIGNER: GALARNMC

APPENDICES

APPENDIX A
Referenced Documents

APPENDIX A-1
Illinois Environmental Protection Agency (IEPA) 2023, 2024a, and 2024b

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY
1021 NORTH GRAND AVENUE EAST, P.O. BOX 19276, SPRINGFIELD, ILLINOIS 62794-9276 · (217) 782-3397
JB PRITZKER, GOVERNOR **JOHN J. KIM**, DIRECTOR
217-782-1020

December 28, 2023

Dianna Tickner
Dynegy Midwest Generation, LLC
1500 Eastport Plaza Drive
Collinsville, Illinois 62234

Re: Vermilion Power Plant East Power Plant New East Ash Pond; W1838000002-4
Alternate Source Demonstration (ASD) Submittal

Dear Mrs. Tickner:

The purpose of this correspondence is to notify you that the Illinois Environmental Protection Agency (Illinois EPA) does not concur with the Vermilion New East Ash Pond System Alternative Source Demonstration (ASD) dated December 1, 2023. The Illinois EPA does not concur due to the following data gaps:

- Characterization that the draw water from the bedrock is completely isolated from local groundwater flow system.
- No assessment of the interaction between bedrock groundwater and the old east pond. Based on Fig.1 shows to be upgradient of the New East Ash Pond.
- Lack of analysis of the leachable metals from the CCR in the New East Ash Pond.

If you have any questions, please contact: **Justin Bierwagen** Illinois EPA, Bureau of Water, Groundwater Section DPWS #13, P.O. Box 19276, Springfield, Illinois 62794-9276. If you have any questions concerning the investigation described above, please call 217-782-1020.

Sincerely,

Michael Summers, P.G.
Manager, Groundwater Section
Division of Public Water Supplies
Bureau of Water

cc: Justin Bierwagen
Lynn Dunaway
Keegan MacDonna
Records 06M

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY
1021 NORTH GRAND AVENUE EAST, P.O. BOX 19276, SPRINGFIELD, ILLINOIS 62794-9276 · (217) 782-3397
JB PRITZKER, GOVERNOR **JOHN J. KIM**, DIRECTOR

217-782-1020

June 5, 2024

Dianna Tickner
Dynegy Midwest Generation, LLC
1500 Eastport Plaza Drive
Collinsville, Illinois 62234

Re: Vermilion Power Plant East Power Plant New East Ash Pond; W1838000002-4
Alternate Source Demonstration (ASD) Submittal

Dear Mrs. Tickner:

The purpose of this correspondence is to notify you that the Illinois Environmental Protection Agency (Illinois EPA) does not concur with the Vermilion New East Ash Pond System Alternative Source Demonstration (ASD) dated May 8, 2024.

The Illinois EPA does not concur due to the following data gaps:

- No assessment of the interaction between bedrock groundwater and the old east pond. Based on Fig.1 shows to be upgradient of the New East Ash Pond. The Agency is unable to review for fate and transport or related concepts without source characterization of total CCR solids.
- Lack of analysis of the leachable metals from the Coal Combustion Residuals in the New East Ash Pond. Source characterization of the CCR at New East Ash Pond must include total solids sampling in accordance with the waste characterization and/or fate and transport characterization required in 35 Ill. Adm. Code 845 and analyzed in accordance with SW846.

If you have any questions, please contact: **Justin Bierwagen** Illinois EPA, Bureau of Water, Groundwater Section DPWS #13, P.O. Box 19276, Springfield, Illinois 62794-9276. If you have any questions concerning the investigation described above, please call 217-782-1020.

Sincerely,

Darin LeCrone
Permit Section Manager
Division of Water Pollution Control
Bureau of Water

cc: Justin Bierwagen
Lauren Hunt

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY
1021 NORTH GRAND AVENUE EAST, P.O. BOX 19276, SPRINGFIELD, ILLINOIS 62794-9276 · (217) 782-3397
JB PRITZKER, GOVERNOR **JAMES JENNINGS**, INTERIM DIRECTOR

217-782-1020

August 22, 2024

Dianna Tickner
Dynegy Midwest Generation, LLC
1500 Eastport Plaza Drive
Collinsville, Illinois 62234

Re: Vermilion Power Plant East Power Plant New East Ash Pond; W1838000002-4
Alternate Source Demonstration (ASD) Submittal

Dear Mrs. Tickner:

The purpose of this correspondence is to notify you that the Illinois Environmental Protection Agency (Illinois EPA) does not concur with the Vermilion New East Ash Pond System Alternative Source Demonstration (ASD) dated July 24, 2024.

The Illinois EPA does not concur due to the following data gap:

- Lack of analysis of Chloride from the Coal Combustion Residuals in the New East Ash Pond. Source characterization of the CCR at New East Ash Pond must include total solids leachate [synthetic precipitation leaching procedure (SPLP)] sampling in accordance with the waste characterization and/or fate and transport characterization required in 35 Ill. Adm. Code 845 and analyzed in accordance with SW846.

If you have any questions, please contact: **Justin Bierwagen** Illinois EPA, Bureau of Water, Groundwater Section DPWS #13, P.O. Box 19276, Springfield, Illinois 62794-9276. If you have any questions concerning the investigation described above, please call 217-782-1020.

Sincerely,

Darin LeCrone
Permit Section Manager
Division of Water Pollution Control
Bureau of Water

cc: Justin Bierwagen
Lauren Hunt
Keegan MacDonna
Records 06M

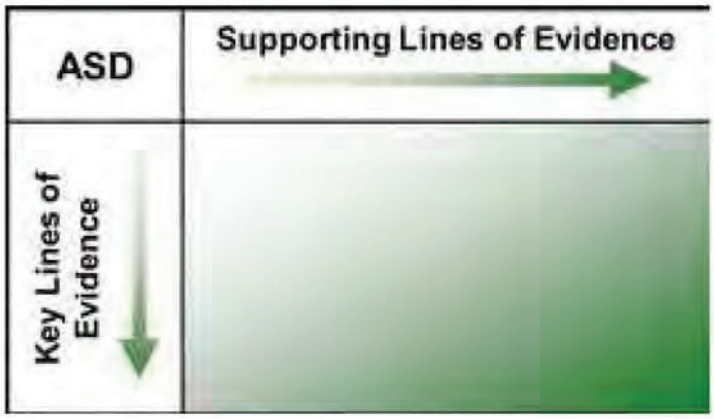
APPENDIX A-2
Electric Power Research Institute (EPRI), 2017. Guidelines for Development of Alternative Source Demonstrations at Coal Combustion Residual Sites. EPRI, Palo Alto, CA. 3002010920

Electronic Filing: Received, Clerk's Office 07/01/2024

EPRI | ELECTRIC POWER RESEARCH INSTITUTE

2017 TECHNICAL REPORT

Guidelines for Development of Alternative Source Demonstrations at Coal Combustion Residual Sites



Guidelines for Development of Alternative Source Demonstrations at Coal Combustion Residual Sites

3002010920

Final Report, October 2017

EPRI Project Manager
B. Hensel

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Natural Resource Technology, an OBG Company

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ACKNOWLEDGMENTS

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This report describes research sponsored by EPRI.

This publication is a corporate document that should be cited in the literature in the following manner:

Guidelines for Development of Alternative Source Demonstrations at Coal Combustion Residual Sites. EPRI, Palo Alto, CA: 2017. 3002010920.

ABSTRACT

EPRI's guidance for alternative source demonstrations (ASDs) was developed to provide environmental managers at electric utilities with a list of alternative sources to check as well as a standardized, defensible approach for building and documenting an ASD when there are exceedances of one or more benchmarks established within a groundwater monitoring program. This guidance is designed for statistical benchmarks, in specific, statistically significant increases (SSIs) or statistically significant levels (SSLs) for groundwater monitoring under the federal Coal Combustion Residuals (CCR) rule and/or state regulations, but the guidance also applies to exceedances of other types of benchmarks such as groundwater quality standards.

The guidance provides information to help identify when a cause other than a release from the facility is the likely source of an SSI during detection monitoring or an SSL during assessment monitoring along with a checklist-based framework for developing a defensible ASD. The guidance covers ASDs developed in response to sampling causes, laboratory causes, statistical evaluation causes, natural variation, and alternative anthropogenic sources, with emphasis on development of an ASD when an SSI, SSL, or other exceedance is due to natural variation or an alternative anthropogenic source.

Keywords

Alternative source demonstration (ASD)
CCR Rule
Coal combustion residuals
Groundwater monitoring
Statistically significant increase (SSI)
Statistically significant level (SSL)

Deliverable Number: 3002010920

Product Type: Technical Report

Product Title: Guidelines for Development of Alternative Source Demonstrations at Coal Combustion Residual Sites

PRIMARY AUDIENCE: Electric utility environmental managers interpreting and responding to groundwater data collected under the Coal Combustion Residuals (CCR) rule and/or state rules

SECONDARY AUDIENCE: Consultants working for electric utilities with responsibility for responding to potential exceedances of benchmarks or criteria established for utility groundwater monitoring programs

KEY RESEARCH QUESTION

Groundwater monitoring programs developed for compliance with the federal CCR rule, and some state rules, use statistical analysis to determine whether or not individual results represent exceedances, which are often termed statistically significant increases (SSIs) over background in detection monitoring or statistically significant levels (SSLs) relative to a groundwater protection standard in assessment monitoring. However, the statistical methods are subject to false positive results, where a value that is not a true exceedance is flagged as such. Furthermore, there are literally dozens of causes related to sampling, laboratory analysis, natural variation, and other anthropogenic sources that can trigger an exceedance that is not due to a release from the monitored unit. When an exceedance is triggered due to a cause other than a release from the facility, federal and state regulations allow for an alternative source demonstration (ASD). At present, however, there are no criteria for how to develop and document an ASD.

RESEARCH OVERVIEW

This research provides guidance for identifying when an ASD is needed, evaluation techniques that can be used to support the demonstration, and a standardized checklist-driven approach for documenting a defensible ASD. The guidance is based on experience developing ASDs in states that have long used statistical analysis to determine compliance with groundwater quality benchmarks and is tailored for application in CCR monitoring programs.

KEY FINDINGS

- Potential sampling, laboratory, and statistical causes that can trigger an exceedance that is not due to a release from the CCR facility are described in Section 2. Checklist 1 outlines a methodology for demonstrating these causes.
- Natural variation can trigger an exceedance if there are changes in mineralogy along a groundwater flow path, changes in pH and/or redox over time or along a flow path, changes in groundwater elevation over time, and/or changes in groundwater flow direction over time (Section 4).
- Potential anthropogenic sources at a power plant that can trigger an exceedance at one or more monitoring locations include, but are not limited to, spills of petroleum or other materials, road salt, leakage of runoff from coal management areas, overspray of leachate used for dust control, accumulation of blowing dust near monitoring wells, leakage from leachate conveyance pipelines or tanks, and releases from other CCR units (Section 5).

- Potential off-site anthropogenic sources include, but are not limited to, agricultural activities, road salt, coal mining, brines associated with oil and gas production, leaking underground pipes, pumping-induced brackish water, septic systems, and industrial or municipal waste management (Section 5).
- An ASD due to natural variation or an off-site or on-site anthropogenic source will be strongest if multiple lines of evidence are developed. Key lines of evidence include a lack of exceedances and a lack of increasing trends for primary indicators of the CCR, leachate concentrations for the affected constituent that are lower than concentrations observed in groundwater, major ion chemistry in the affected monitoring well that does not represent mixing of leachate with background groundwater, tritium age-dating showing that the groundwater is older than the CCR unit, and isotopic data showing that the groundwater at the affected monitoring well is not a mixture of background groundwater and leachate (Section 6).

WHY THIS MATTERS

False identification of an SSI can trigger assessment monitoring, and false identification of an SSL can trigger corrective action, either of which can increase the cost and manpower resources needed for groundwater compliance at CCR sites. An ASD can be used to demonstrate that these incremental increases in resource allotment are not necessary if the statistical exceedance is not due to a release from the facility. ASDs may be reviewed by state regulators and the public, and this guidance provides a standardized, checklist-driven approach for documenting a strong ASD.

HOW TO APPLY RESULTS

Users of this guidance can begin by reviewing Sections 2, 4, and 5 to determine whether or not an ASD is appropriate, and if so, the potential alternative causes that may explain the ASD. Section 3 describes evaluation techniques that can be used to support the ASD. The user can then use the checklists described in Section 6 and provided at the end of the document in Appendix B to build the ASD.

LEARNING AND ENGAGEMENT OPPORTUNITIES

- Statistical analysis used in CCR groundwater monitoring programs is described in *Groundwater Monitoring Guidance for the Coal Combustion Residuals Rule*. EPRI, Palo Alto, CA: November 2015. 3002006287.
- Techniques for evaluating groundwater quality data are described in *Groundwater Quality Signatures for Assessing Potential Impacts from Coal Combustion Product Leachate*. EPRI, Palo Alto, CA: October 2012. 1017923.
- Methodologies for application and evaluation of isotopic analysis are provided in *Application of Isotopic Methods to Coal Combustion Residual Groundwater Quality Investigations*. EPRI, Palo Alto, CA: December 2017. 3002010911.

EPRI CONTACT: Bruce Hensel, Principal Technical Leader, bhensel@epri.com

PROGRAM: Coal Combustion Products – Environmental Issues, P49

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ACRONYMS AND ABBREVIATIONS

ASD	Alternative Source Demonstration
CCR	Coal Combustion Residual
CCR Rule	Coal Combustion Residuals Rule (40 CFR 257 Subpart D)
CFR	Code of Federal Regulations
EPRI	Electric Power Research Institute
FR	Federal Register
GWPS	Groundwater Protection Standard
LCL	Lower Confidence Limit
MCL	Maximum Contaminant Level
MDL	Method Detection Limit
ORP	Oxidation Reduction Potential
PQL	Practical Quantitation Level
RL	Reporting Level
UCL	Upper Confidence Level
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
SSI	Statistically Significant Increase
SSL	Statistically Significant Level
TDS	Total Dissolved Solids
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey

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1
INTRODUCTION

Scope of Guidance

This guidance for alternative source demonstrations (ASDs) was developed to provide environmental managers at electric utilities with a list of alternative sources to check, and a standardized, defensible approach for building and documenting an ASD when there are exceedances of one or more benchmarks established within a groundwater monitoring program. The guidance is designed for statistical benchmarks, specifically statistically significant increases (SSIs) or statistically significant levels (SSLs) for groundwater monitoring under the Coal Combustion Residuals Rule (CCR Rule)[1] and/or state regulations, but the guidance is also applicable to exceedances of other types of benchmarks such as groundwater quality standards.[2]

The guidance provides information to help identify when a cause other than a release from the facility is the likely cause of an SSI during detection monitoring or an SSL during assessment monitoring, and a framework for developing a defensible ASD.

As provided for in the CCR Rule,[3] an alternative source demonstration can have a variety of causes:

- Sampling causes (ASD Type I)
- Laboratory causes (ASD Type II)
- Statistical evaluation causes (ASD Type III)
- Natural variation not accounted for in the basic detection monitoring or assessment monitoring statistics (ASD Type IV)
- Potential alternative sources (ASD Type V)
  - Anthropogenic impacts
  - Natural sources

Potential alternative sources, both anthropogenic and due to natural environmental influences, are the main focus of this report.

The scope of this document does not include guidance for performing a site investigation or establishing a groundwater monitoring system. Readers can refer to EPRI (2015) and a variety of other documents, many of which are listed in EPRI (2015), for such information.

[1] 40 CFR 257 Subpart D; published in 80 FR 21302-21501, April 17, 2015.

[2] The remainder of this document will primarily reference exceedances of SSIs or SSLs even though the methodology applies to exceedances of all types of benchmarks.

[3] 40 CFR 257.94(e)(2) for detection monitoring; 40 CFR 257.95(g)(3)(ii) for assessment monitoring.

2
TYPES OF ALTERNATIVE SOURCES

As stated in the CCR Rule at 40 CFR 257.94(e)(2), "The owner or operator may demonstrate that a source other than the CCR unit caused the statistically significant increase over background levels for a constituent or that the statistically significant increase resulted from error in sampling, analysis, statistical evaluation, or natural variation in groundwater quality. The owner or operator must complete the written demonstration within 90 days of detecting a statistically significant increase over background levels to include obtaining a certification from a qualified professional engineer verifying the accuracy of the information in the report." This section describes the five types of ASDs, provides example causes, and presents examples for how those causes might be identified.

Potential causes or investigation paths associated with each of the alternative source categories identified in the CCR Rule are listed in Table 2-1 and are discussed below. Anthropogenic sources are further discussed in Section 5, and natural variation is discussed in Section 4.

Table 2-1
ASD Types and Causes

Sampling Causes (ASD Type I)	Laboratory Causes (ASD Type II)	Statistical Evaluation Causes (ASD Type III)	Natural Variation (ASD Type IV)	Alternative Sources (ASD Type V - Natural and Anthropogenic)
• Sample mislabeling • Contamination • Change in technique • Excessive suspended solids or turbidity • Other sampling anomalies	• Analytical method • Calibration • Analytical technique • Contamination • Interference • Recording • Dilution errors • Digestion methods	• Lack of statistical independence • Outliers • Trends • Non-detect processing • False positives • New background data	• Geology • Precipitation • Seasonality • Water level • Changes in pH and/or ORP • Biological activity • Time of travel	• See Tables 2-2 and 2-3

Sampling Causes (ASD Type I)

- Sample mislabeling: One form of sample mislabeling is sample switching. Sample switching can be identified by sudden changes in concentration for the same constituent at two monitoring wells (Figure 2-1). Multiple constituents will be affected when this occurs, although it would only be evident for constituents with large differences in concentration

between the two monitoring wells. The multiple constituents will come from the same type of sample bottle (e.g., metals, IC analysis) if only one sample bottle is switched, and can come from multiple bottles if all bottles for two samples are switched. If analysis results suddenly differ from normal for a particular well, look for similar anomalies at other wells for patterns that could indicate swapped identification.

Another form of mislabeling can occur if the sample is taken from a different monitoring well than listed on the label (e.g., MW-01b instead of MW-01a), when the other monitoring well is not in the sampling program. In this case, only one monitoring well will show an anomaly for multiple constituents. This anomaly should affect all sampled constituents, although it will only be evident for constituents where concentration is different in the sampled well, relative to the well that should have been sampled. This case is more difficult to identify and demonstrate than the case of the switched sample. If all concentrations in a resample return to previous levels, then it is a possible explanation.

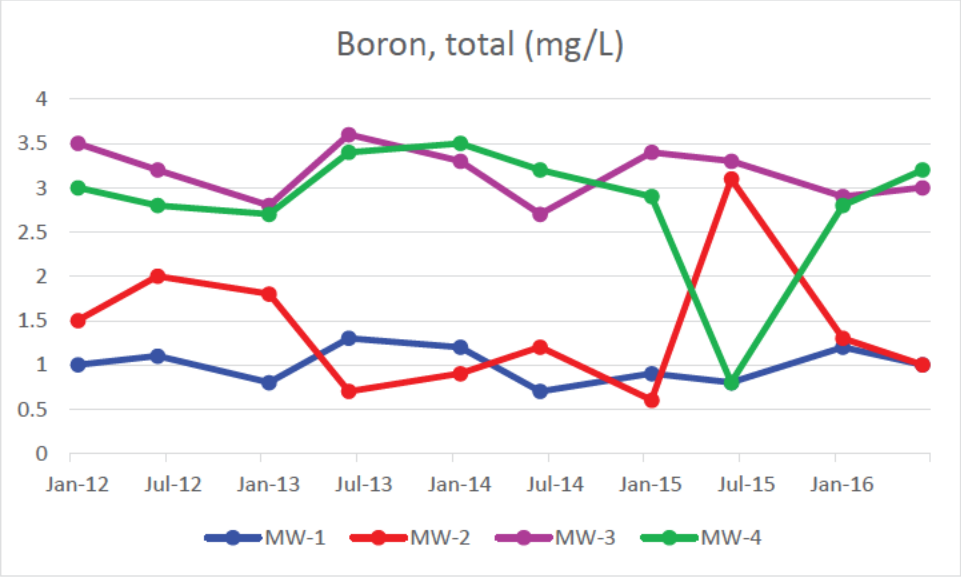

Figure 2-1
Time series plot showing potential sample mislabeling (switching)

- Contamination: If non-dedicated sampling devices are used to collect samples, contamination from the sampling equipment could potentially cause unrepresentative, elevated concentrations that could trigger an SSI/SSL. This type of sampling error is more likely to affect trace elements such as those found in Appendix IV of the CCR Rule than higher concentration elements such as those listed in Appendix III of the CCR Rule. An equipment blank (also called a rinsate blank) is a field quality control sample consisting of the rinsate from equipment used to collect the sample. Check the equipment blank analytical results to assess the potential for cross contamination, which will be evident by elevated concentration in the equipment blank. A field blank is a sample of deionized water from the laboratory that is opened in the field to assess the potential for field contamination. Field blanks are not always used for groundwater sampling at CCR sites. If field blank analytical results are available, check to assess the potential for field contamination unrelated to the sampling equipment.

- Sampling technique: A change in sampling technique, whether planned or due to an error, can have an influence on resulting concentrations if it affects the amount of sediment, as measured by turbidity, in the sample. See the next bullet for turbidity effects.
- Turbidity: Sudden increases in total dissolved solids and/or trace element concentrations can sometimes be associated with an increase in suspended solids/turbidity in a sample, relative to previous samples. Because the CCR Rule requires collection and analysis of unfiltered samples, elements comprising or attached to the particulate matter that causes turbidity are digested and analyzed along with the dissolved elements in the sample. Therefore, a turbid sample can yield higher concentrations for the elements that make up or are attached to the particulate matter. Evaluate the sampling technique used and the field analytical results, particularly the turbidity value if available, to assure that low-flow sampling procedures were properly followed. If the field analytical results do not indicate that stabilization of the field parameters (pH, temperature, specific conductance, dissolved oxygen, redox potential, and turbidity) was achieved, then sampling technique may be a defensible cause for an SSI/SSL. Some facilities establish sampling protocols that include collection of replicate filtered samples whenever a sample location has a turbidity greater than 10 to 20 NTU to allow comparison of analytical results between filtered and unfiltered samples. If filtered results are available, and are considerably lower than the unfiltered results, then turbidity resulting from differences in sampling technique, a screen failure in the monitoring well, or a need for redevelopment may be defensible alternative causes.
- Sampling anomalies: Review field documents (chain of custody form, calibration logs for field equipment, field notes, and field data) to see if any issues were encountered during the sampling event that could potentially affect the sample integrity. Potential anomalies may include improper bottles or preservation, inadequate calibration of field instruments, failure to achieve stabilized field parameters prior to sampling, use of non-dedicated or improperly cleaned equipment, improper labeling, etc.

Laboratory Causes (ASD Type II)

There are opportunities for potential contamination or errors associated with laboratory procedures, equipment decontamination and calibration, and sample handling and analysis. In addition to the analytical results, laboratory reports include documentation of methods and data qualifier flags to indicate potential issues that may affect the accuracy of results. The following are common data qualifiers for inorganic constituents sanctioned by USEPA:

- U = Reading was less than the method detection limit (MDL).
- J = Reading was less than the contract required quantitation limit but greater than or equal to the MDL.
- B = Analyte was found in the method blank as well as in the sample. Indicates possible/probable blank contamination.
- E = Reported value is estimated due to the presence of an interference. Look for comments.
- N = Spiked sample recovery not within control limits.
- * = Duplicate analysis not within control limits.
- D = The reported value is from a dilution.

The B, E, N, *, and D flags all indicate potential for laboratory errors that may have triggered an SSI/SSL, and warrant a closer look at the results to determine if the reported results may be invalid and if resampling and/or an ASD should be considered.

Potential errors associated with laboratory handling and analysis include:

- Calibration: Use of poorly or inadequately calibrated instruments may cause elevated analytical results that are not representative of the water quality at the sampling location. If results for a particular analyte in multiple samples, particularly if all were analyzed on the same day (laboratories typically recalibrate their instrumentation daily), are higher than the norm, then poor calibration of analytical equipment may be a potential cause. Consider reviewing instrument calibration records to see if poor calibration is a defensible alternative source for the SSI or SSL.
- Contamination: One or more samples may be contaminated by improperly cleaned and/or prepared sample bottles, analytical equipment, calibration standards, reagents, or preservatives. This type of error is more likely to be evident for trace elements such as those found in Appendix IV of the CCR Rule than for higher concentration constituents such as those listed in Appendix III of the CCR Rule. If sample contamination is suspected, evaluate the analytical results for trip blanks (if available) and method blanks. Trip blanks are sample bottles filled with laboratory-prepared deionized water that accompany the samples to and from the field, without being opened. If trip blank results show detection of analytes, it is possible that the sample bottles may not have been properly cleaned or the deionized water may have been contaminated. Method blanks are analyte-free laboratory quality control samples subjected to the entire analytical process used to demonstrate that the analytical system did not introduce contamination. The method blank results should be below the method reporting limits. If they are not, then the analytical process may have introduced contamination. Look for "B" data qualifiers to determine if the analytes were detected in the method blank.
- Digestion Methods: Use of more aggressive digestion methods using hydrofluoric acid for total digestion rather than concentrated nitric and/or hydrochloric acids for "total recoverable metals" may result in higher trace element concentration results compared to results using "total recoverable metals" methods. USEPA requires digestion consistent with "total recoverable metals" methods under the CCR Rule. If more aggressive digestion methods were used, reanalysis (if there is any remaining undigested sample) or resampling is warranted to determine if the SSI/SSL result persists when total recoverable digestion methods are used.
- Dilution Corrections: If dilutions were necessary to overcome matrix interferences, then review analytical results to ensure that the analytical results were properly corrected and that the resulting detection levels are low enough to detect increases over background levels. Look for the "D" data qualifiers to determine if dilutions were used. If a sample result is suddenly higher (especially if it is close to an order of magnitude higher) than the norm at a sample location and dilution was used, it is possible that the sample results were not corrected for the dilution ratio (Figure 2-2). Use of dilution ratios typically increases the MDL. If the sample results are non-detect but the MDL is higher than the norm, erroneous statistical identification of increasing trends may occur, depending on how non-detects are handled in the statistical analysis.

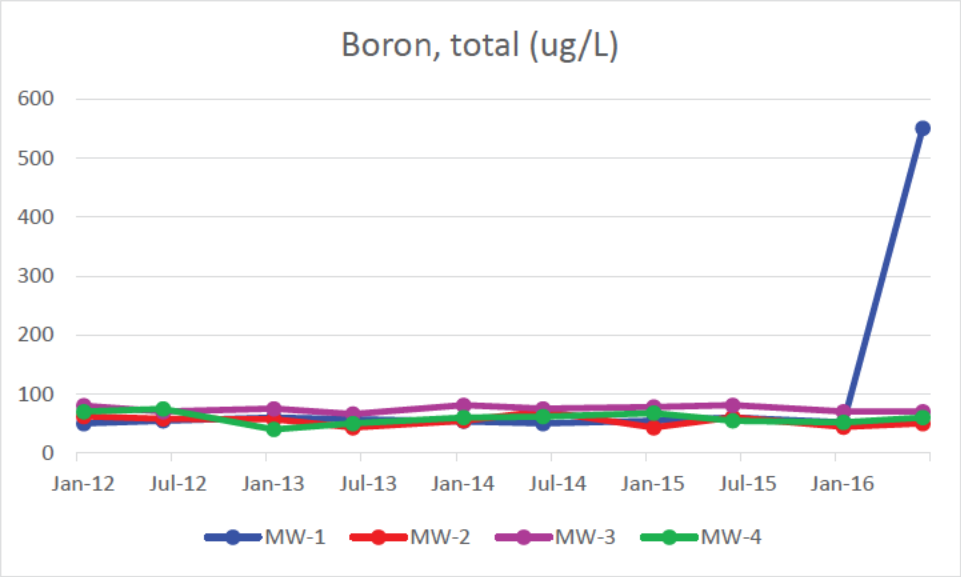

Figure 2-2
Time series plot showing potential dilution error

- Interference: Elevated analytical results may occur due to interference from other constituents present in the sample. If the laboratory identified interferences, the analytical report should include "E" data qualifiers. If interference was a problem, consider reanalyzing if there is sufficient remaining sample, and/or resampling and analyzing using methods that are less sensitive to interference from constituents of concern.
- Methods: Use of inappropriate methods or methods with reporting levels (RLs) or practical quantitation levels (PQLs) that are higher than background or maximum contaminant levels (MCLs) can result in erroneous analytical results or use of elevated non-detect values that can result in erroneous statistical determination of increasing trends. If use of inappropriate methods is suspected, verify that the methods used match those specified in the sampling and analysis plan, and are appropriate for the objectives of the groundwater monitoring program. Table 3-1 of EPRI (2015) shows methods, typical MDL and PQL capabilities, potential for interferences, and relative costs of test options for the CCR Rule Appendix III and Appendix IV constituents. This information can be very helpful in selecting and verifying that appropriate analytical methods were used.
- Technique: Poor analytical technique or use of poorly calibrated instruments (lack of quality control) can result in erroneous sample results. Check the laboratory report for data qualifiers ("B", "E", "N", "*") indicating that quality control may have been a problem.
- Transcription: Improper recording of results or mixing up results between samples can cause erroneous identification of SSI or SSL trends. If analytical results for two sampling locations are suddenly out of the norm, it's possible that the analytical results were transcribed to the wrong sampling locations. If a single location is suddenly out of the norm by an order of magnitude or more, it is possible that a transcription error such as inconsistency in units may have occurred.

Statistical Evaluation Causes (ASD Type III)

A primary challenge in statistical analysis is maintaining adequate statistical power while minimizing the false positive rate. While a detailed discussion of statistical methods and associated false positive rates is beyond the scope of this text, it is important to be aware that false positives can occur and are inherent in the statistical methods used for evaluation of groundwater quality data. See EPRI (2015) for guidance on statistical methods and recommendations for statistical approach under detection monitoring, assessment monitoring, and corrective action monitoring.

The following types of statistical errors could potentially falsely identify an SSI/SSL:

- Lack of statistical independence: The statistical comparison tests to determine if an SSI/SSL has occurred assume that the results are statistically independent. If samples are collected from the same well before the groundwater can flow through the well and be replaced with a fresh sample, then the samples are not physically independent and the comparison is not valid. As stated in the USEPA Unified Guidance (USEPA, 2009), the aquifer may "exhibit pockets or sub-zones of higher or lower concentration, perhaps due to location-specific differences in natural geochemistry or the dynamics of contaminant plume behavior over time." Generally, lack of statistical independence may be of concern if the groundwater velocity is less than 5-10 ft/yr. This type of statistical error is more likely to trigger an SSI during detection monitoring if a resampling protocol is included in the statistical plan, because the resample is collected more quickly after the original sample than the next regularly scheduled sample, and is therefore more likely to lack independence. This can be avoided by factoring groundwater flow rates into the timeframe calculation for resampling in a statistical analysis plan. Lack of independence is less likely to trigger an SSL during assessment monitoring due to the multiple sample design inherent with confidence intervals that are used in assessment monitoring statistics.
- Outliers: An outlier is a result that falls outside the typical range of values due to causes *other than* natural variability or a true change in concentration, and as such is not representative of groundwater quality. An analytical result that is suddenly much higher or lower than historical values represents a potential outlier, and there are graphical and statistical methods to identify such values. An SSI/SSL could be the result of an outlier due to transcription or typographical error, contamination, analytical interference, or other cause described under ASD Types I and II. Potential outliers need to be evaluated by reviewing sampling and laboratory documentation, and sometimes professional judgement needs to be applied to determine a) if the result is valid and should be included in the statistical analysis, b) if the result is due to an error and should be replaced with a corrected value, or c) if the value should be flagged and maintained in the database but not used in statistical calculations. If an outlier is confirmed, recalculation of the comparison to background or groundwater protection standard (GWPS) without the outlier can be performed to determine if the SSI or SSL determination was dependent on the outlier.
- False positives: A false positive is not an error per se; however, by statistical design, false positives can be expected to trigger a certain number of SSIs or SSLs under any statistical analysis plan. A false positive, also referred to as a Type I error, occurs when an SSI/SSL is falsely determined for a constituent at a compliance monitoring well relative to background groundwater quality (for SSIs) or a GWPS (for SSLs). The USEPA Unified Guidance

(USEPA, 2009) recommends that a statistical program be designed so that the site-wide false positive rate (SWFPR), which is the potential for one or more false positives on a site-wide scale, be 10% or less per year (5% per semi-annual sample event). See EPRI (2015) for a detailed discussion of statistical options and recommendations for balancing statistical power with false positive rates. Proving a false positive for an ASD may be challenging, and may require a weight of evidence approach as described in Section 6.

- Non-detect processing: Method detection limits change over time, although usually downward, or can suddenly increase by a factor of 10 or more when a laboratory dilution is used. If there is a dilution, or if MDLs increase (Figure 2-3), then an SSI could result if MDLs are used in statistical analyses. Potential for this type of statistical cause can be minimized by using set reporting limits for non-detect results and by using the double quantification rule when all background results are lower than the reporting limit.

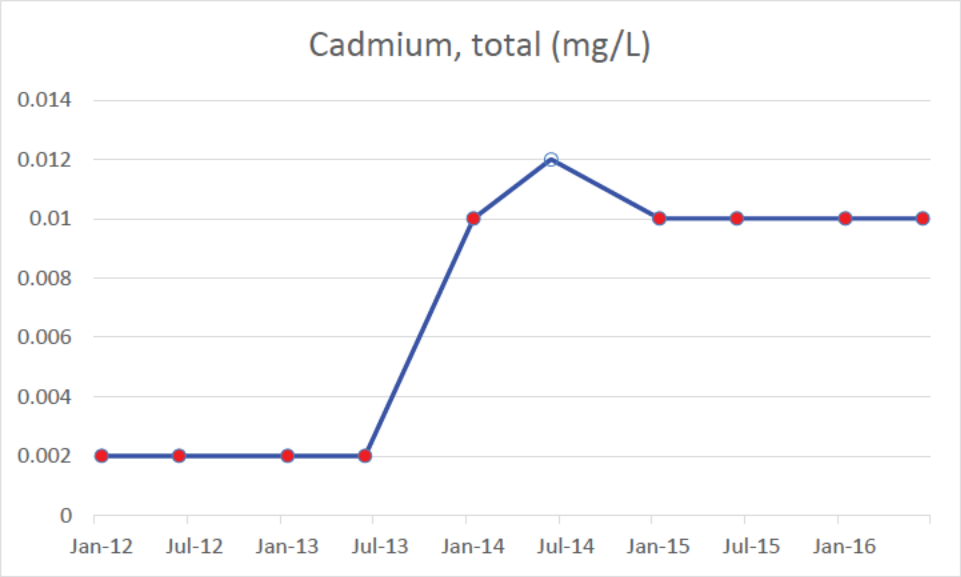

Figure 2-3
Time series plot of showing increasing trend associated with changing detection limits. Red markers indicate sample results below the minimum detection level associated with each respective sampling event.

Background Data: In the initial stages of detection monitoring, if there are numerous SSIs in the absence of a suspected release from the facility (e.g., a new lined landfill), then it is possible that background groundwater is not representative of downgradient groundwater due to spatial or temporal variability. The Unified Guidance (USEPA, 2009) states that a "high quality background dataset is the single most important key to a successful statistical groundwater monitoring program" and recommends a minimum of at least 8 to 10 independent samples for the initial background dataset before running most statistical tests.

Later on, apparent SSIs or SSLs can be triggered when new background data are added to an existing background dataset if that addition results in a change in statistical analysis method. This is particularly relevant if new data changes the distribution of the background dataset from parametric to non-parametric (Figure 2-4), because most non-parametric tests used in

groundwater analysis use the highest value as the upper limit (for detection monitoring) or GWPS (for assessment monitoring), and have a higher false-positive rate than their parametric counterparts.

Refer to Chapter 5 of the Unified Guidance (USEPA, 2009) for a thorough discussion of establishing background, reviewing and updating background, and effects of spatial and temporal variability on background.

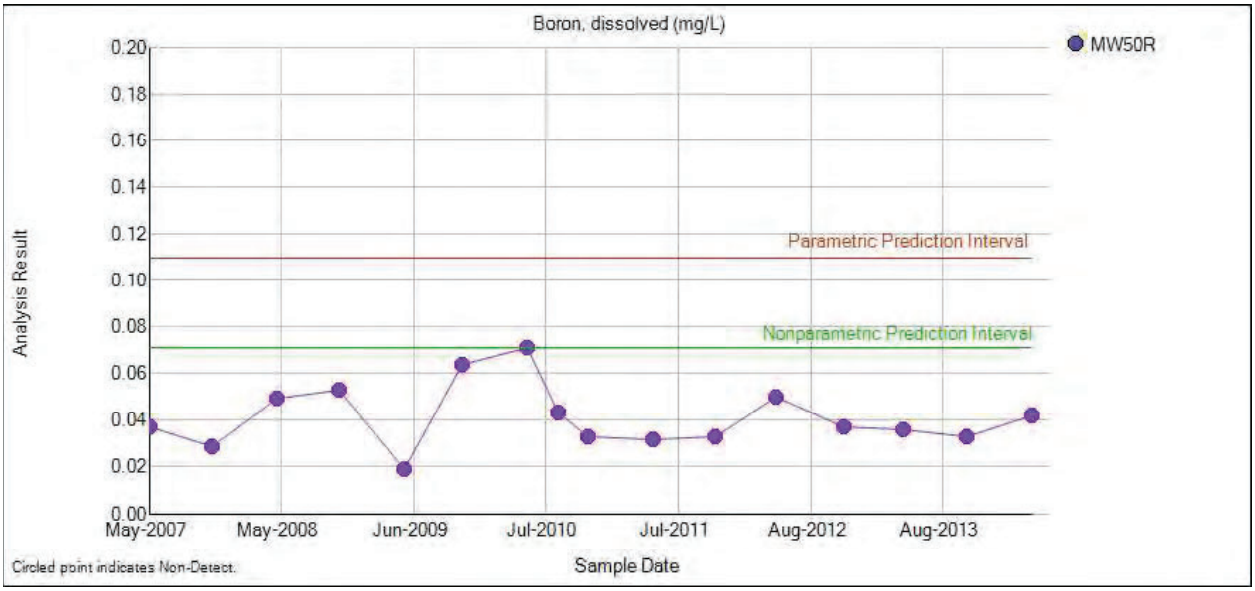

Figure 2-4
Background dataset illustrating the difference between a parametric and non-parametric upper prediction interval

Natural Variation (ASD Type IV)

Natural variation is recognized as a potential alternative cause of SSIs and SSLs under the CCR Rule. This category encompasses variability due to geologic influences such as dissolution of geomedia and natural ion exchange, changes in groundwater quality related to precipitation, seasonal changes in groundwater level or flow direction such as groundwater recharge and discharge fluctuations near surface water bodies, changing water levels in monitoring wells, time-of-travel for monitoring wells to detect upgradient changes, and influences related to changes in pH, oxidation reduction potential, and biological activity. These interactions and how they may affect groundwater quality are discussed in more detail in Section 4.

Alternative Sources (ASD Type V)

Sources for constituents dissolved in groundwater may come from both natural and anthropogenic sources. Natural sources include constituents present in groundwater from dissolution of minerals from the geomedia the groundwater has passed through. Anthropogenic sources can be complex and are too numerous to completely categorize, as many of them are likely to have source-specific signatures.

Table 2-2 provides information on natural and anthropogenic occurrence and typical behavior in groundwater for Appendix III and IV constituents as well as other constituents that may be helpful for identification of potential alternative sources. This table also identifies the relevance of the constituent as a CCR indicator for coal ash and FGD gypsum leachate.[4]

Table 2-3 provides an overview of common constituents that may be present in groundwater from a variety of anthropogenic sources. This information is intended to stimulate thought regarding constituents that *may be* present in groundwater, absent a release from the CCR site, if one of these activities is upgradient and has experienced its own release. Table 2-3 is not definitive; the information may be incomplete or not representative of actual anthropogenic sources near a particular site under evaluation. Site-specific investigation of nearby activities and history can be performed to verify groundwater impacts if an anthropogenic alternative source is suspected.[4]

A more detailed discussion of common groundwater impacts and contaminants associated with some of the more likely alternative sources is provided in Section 5.

[4] Tables 2-2 and 2-3 are also provided in Appendix A for easy reference with the ASD checklists.

Table 2-2
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix III Detection Monitoring Constituents								
Boron	Key Indicator	Yes if unwashed	17 / 35 / 82 ug/L	No	Very mobile	Boron-containing rocks (especially marine shales and clays), seawater, volcanic and geothermal activities, mined in arid regions of the United States (and other countries)	Fly ash leachate, may also be present in FGD leachate; sewage sludge, boron-containing fertilizers or herbicides, manufacture of glass, fiberglass, ceramics, soaps, detergents, bleach, fire retardants, and lubricants; used in control rods of nuclear reactors, and to produce a green color in pyrotechnics and flames; also used in the aerospace industry	Micronutrient for plants but may be toxic to some plant species in high concentrations. Boron deficiencies are more common than toxicities. Mobile in most hydrogeological environments, particularly sandy materials. Sorption to clay reaches a maximum in the pH range of 8-10.
Calcium	No	Yes	21 / 43 / 70 mg/L	CEC	Slightly mobile	Calcium carbonate rocks, limestone, calcium clay; fifth most common element in Earth's crust	Water softening wastes, soil acidity neutralization (lime additions to soil), calcium road salt, deicing, agriculture, cement and concrete, drying agents	Calcium carbonate is one of the most common calcium minerals. The concentration in groundwater may be limited by the solubility of calcium carbonate or calcium sulfate (gypsum). May be sorbed by ion exchange in soil and sediments but tends to be a reversible reaction.

Table 2-2 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix III Detection Monitoring Constituents								
Chloride	No	Yes if unwashed	3.1 / 8.6 / 23 mg/L	No	Very mobile	Salt water and brackish water sources; chloride anion is the most abundant element (other than hydrogen and oxygen) in Earth's oceans	Road salt, deicing, water softening wastes, sewage, septic effluent, livestock waste, oil-field brines, salt water intrusion (oil and gas well production), industrial emissions, incinerator ash, landfill leachate, aerospace industry, automobile industry, soaps and detergents, drying agents, flame retardants, flocculants, pharmaceutical and medical waste	
Fluoride	Yes for some coal ash	Yes for some FGD gypsum	<0.1 / 0.2 / 0.4 mg/L	No	Mobile	Natural weathering of fluoride-containing minerals	Steel, brick, and aluminum manufacturing; waste incineration, municipal water treatment	Occurs as fluoride anion at pH > 3, hydrofluoric acid at pH < 3. Can be sorbed by amorphous aluminum and iron oxides under strongly acidic conditions.
pH	No	No	6.9 / 7.3 / 7.6 SU	- -	- -	Oxidation/weathering of naturally occurring pyritic soils due to well installation or other excavation may cause low pH	Low pH: Oxidation/weathering of pyrite in coal or coal ash, leaking batteries High pH: Certain coal ash leachates may have high pH; cement and concrete manufacturing and use, soaps and detergents	Fly ash leachate pH may be acidic or basic depending on coal type. Bituminous coals tend to produce more acidic leachate, especially if comanaged with pyritic mill rejects, and subbituminous coals tend to produce more basic leachate. Important due to impact of pH on leachability of many trace elements.

Table 2-2 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix III Detection Monitoring Constituents								
Sulfate	Yes for most coal ash	Key Indicator	4.7 / 14 / 36 mg/L	No	Very mobile	Sulfur is the 14th most abundant element in the Earth's crust; oxidation/ weathering of naturally occurring pyritic soils (such as iron sulfide)	Fly ash and FGD leachate, lead acid batteries, algaecides, gypsum mines, wood pulp production (paper mills), textile mills, tanneries, coal pyrite oxidation/weathering from mining or storage, industrial emissions and effluents, soaps and detergents, drying agents, flocculants, petroleum refining	Sulfate may precipitate with calcium, barium, and strontium. Not usually sorbed due to negative charge, but can be sorbed under acidic conditions by soils and sediments containing iron, aluminum, and manganese oxides with positive charges. May precipitate from solution as sulfides under strongly reducing conditions.
Total Dissolved Solids (TDS)	No	No	146 / 254 / 381 mg/L	- -	- -	TDS is largely based on concentration of major ions in groundwater (Ca, Mg, Na, K, carbonates, Cl, SO_4)		Refer to primary components.

Table 2-2 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix IV Assessment Monitoring Constituents								
Antimony	No	No	<1 ug/L	No	Very mobile		Flameproof retardants, batteries, lead shot; metal and glass manufacturing	Usually soluble but may be sorbed by iron, aluminum and manganese oxides under acidic conditions (EPRI, 1987).
Arsenic	No	No	0.23 / 0.79 / 3.0 ug/L	Yes, pH and redox	Variable	May be present in sulfide minerals and in organic forms; concentrations can be naturally higher than typical under reduced conditions or if sulfide minerals are oxidized	Wood preservatives (chromated copper arsenate), feed additives, pharmaceuticals, electronic devices, metallurgical applications, metal mining and smelting, cemeteries; pesticides/herbicides/ insecticides (prior to 1960)	Arsenic occurs in the 5+ oxidation state as arsenate (AsO_4^{3-}) under relatively neutral pH and oxidized conditions, and as 3+ arsenite (AsO_3^{3-}) under reduced conditions. Arsenic fate and transport is complex due to sensitivity to pH and redox. Sorption usually increases with decreasing pH.
Barium	No	No	24 / 54 / 120 ug/L	Yes	Mobile	Weathering of sedimentary rocks	Well drilling mud or fluid, mining; manufacture of glass, paint, and rubber	Usually present as relatively insoluble barium sulfate in fly ash. Most barium compounds have limited solubility. Sorbed by clay, soils, and sediment.
Beryllium	No	No	<1 ug/L	Yes, pH	Immobile	Relatively scarce in Earth's crust	Electronic and electrical components, telecommunications and computer components, defense applications	Strong tendency to sorb at neutral to alkaline pH. Sorption may be reduced in the presence of humic acids.

Table 2-2 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix IV Assessment Monitoring Constituents								
Cadmium	No	No	<1 ug/L	Yes, pH	Slightly mobile	Minor component in Earth's crust, occurs in zinc minerals	Batteries, waste incineration, sewage sludge disposal, paint pigments, phosphate fertilizers, automobiles, electroplating and metal fabricating	Can be sorbed by clay, soil, and sediment at pH less than 8, but sorption decreases at low pH.
Chromium	No	No	0.68 / 1.2 / 3.0 ug/L	Yes, pH and redox	Variable	Primarily occurs as Cr(III) in soils and rocks	Electroplating, leather tanning, wood pulp production (paper mills), metal ore refining, wood preservatives, steel manufacturing, automobiles, electroplating and metal fabricating, paint and coatings	The solubility of Cr(III) generally increases at pH levels <6.5 and >11. Cr(III) is the predominant dissolved species under reducing to mildly oxidizing conditions. Cr(IV) is more soluble than Cr(III) at neutral to alkaline pH. Cr(VI) is soluble at alkaline pH and mildly to strongly oxidizing conditions.
Cobalt	No	No	0.063 / 0.17 / 0.48 ug/L	Yes	Variable	Relatively scarce in Earth's crust; usually occurs in combination with arsenic and sulfur in nature	Rechargeable battery electrodes, radial tires, drying agents, catalysts, paint pigments, medical wastes, automobiles	May be sorbed by mineral oxides (e.g., Fe and Mn), crystalline materials such as aluminosilicate, and natural organic substances in soil.
Lead	No	No	0.018 / 0.070 / 0.27 ug/L	Yes pH	Variable	Rare in Earth's crust	Smelting and mining, batteries, waste incineration, leaded gasoline (before 1996), lead-containing paint, glass manufacturing, ammunition, firing ranges, plumbing, automobiles	Sorption usually increases with pH.

Table 2-2 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix IV Assessment Monitoring Constituents								
Lithium	Yes for some coal ash	No	2.0 / 6.0 / 18 ug/L	No	Mobile	Rare in Earth's crust, dissolution of lithium-containing minerals	Glass and ceramics production, lubricants, greases, batteries, salt water intrusion	Reacts with sulfate ions to form lithium sulfate anion.
Mercury	No	No	NR	No	Slightly mobile	Occurs as HgS in nature; can be converted to methylated forms by anaerobic microbes	Waste incineration, mercury mining, metal recycling, fungicides, fluorescent lamps, batteries, thermometers/ thermostats/switches (electronic equipment), automobiles	Can be sorbed by iron, magnesium, silicon oxides, and organic matter.
Molybdenum	Yes for some coal ash	No	0.32 / 1.0 / 3.3 ug/L	No	Very mobile	Usually combined with sulfur or oxygen in natural minerals	Steel production, catalysts, lubricants, pigments, fertilizers, animal feed	Micronutrient for plants and animals; may be in fertilizers or animal feed. Peak sorption at pH <5 and limited sorption above pH 8. Phosphate and other oxyanions will depress sorption.

Table 2-2 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix IV Assessment Monitoring Constituents								
Radium 226 + 228	No	No	NR / 0.28 / 1.2 pCi/L	Yes, CEC	No data	Natural decay product of uranium and thorium ores	Uranium mines, nuclear power, nuclear fuel and weapons manufacturing, uranium in coal	Radium decays to radon gas, so it is prevalent in locations where radon gas is a concern.
Selenium	No	No	0.12 / 0.34 / 1.0 ug/L	Yes, pH and redox	Variable	Usually occurs with silver, copper, lead, and nickel sulfide minerals; may exist in a variety of organic compounds	Metal mining and milling, industrial waste water, sewage effluent, waste incineration, saline agricultural waste waters	May exist as selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), elemental selenium (Se^0), and selenide (Se^{2-}) in groundwater (shown in order from most to least oxic species). Since anionic selenium is the dominant form in groundwater, sorption typically is not significant. However, selenite can be sorbed by iron and aluminum oxides.
Thallium	No	No	<1 ug/L	Yes, redox	Mobile	Occurs in combinations with oxygen, sulfur, and halogens	Glass and electronic industries, iron and steel production, cement factories	May be immobilized under reducing conditions.

Table 2-2 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
Other Constituents								
Aluminum	No	No	0.98 / 3.0 / 4.9 ug/L	Yes, pH	Slightly mobile	Most abundant metal in Earth's crust; weathering of aluminosilicate minerals	Mining and industrial emissions and effluents; most abundant metal in coal ash, cement and concrete, drying agents, well drilling, flocculants, abrasives, aluminum manufacturing	Most soluble in water under acidic and alkaline solutions, essentially insoluble in near neutral water. May be sorbed by soils, sediments, and organic matter.
Bromide	Possible for certain coal ash	Yes if unwashed	0.02 / 0.04 / 0.09 mg/L	No	Mobile	Brackish groundwater and sea water, relatively rare in Earth's crust	CCR fly ash and emission control wastes, particularly if bromide compounds were used to facilitate mercury capture; drinking water disinfection, flame retardants	
Copper	No	No	0.47 / 1.0 / 3.0 ug/L	Yes, pH and redox	Variable	Relatively common in Earth's crust	Manufacture of bronzes, brass, electrical conductors, and ammunition; sewage sludge wastes, municipal solid wastes, copper-containing fertilizers, cemeteries, electronics, plumbing, wood preservatives, automobiles, electroplating and metal fabricating	Solubility may be controlled by solubility of copper hydroxide. May sorb to organic matter, clay, aluminum, manganese, and iron oxides.
Iron	No	No	0.81 / 7.9 / 93 ug/L	Yes, pH and redox	Variable	Commonly has high concentration in groundwater under reduced conditions; Weathering of iron-containing minerals (dissolution of iron oxides under reducing conditions), 4th most common element in Earth's crust	Industrial emissions, pyrite oxidation/acid mine drainage from coal mining or storage, flocculants	Iron oxides my dissolve and become mobile under reducing conditions. Occurs as ferrous (+2) and ferric (+3) iron. Ferric iron can be sorbed by silica, clay, and iron and manganese oxides.

Table 2-2 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
Other Constituents								
Magnesium	No	No	4.4 / 11 / 23 mg/L	CEC	Slightly mobile	Eighth most abundant element in the Earth's crust, abundant in sea water; dissolution of magnesium carbonates and clay minerals	Aluminum fabrication and welding (alloying agent), flares and pyrotechnics, fire retardants, heat-resistant bricks, animal feed, fertilizers, drying agents	Solubility may be limited under alkaline conditions. May be removed from solution by ion exchange in soils and sediments via reversible reactions.
Manganese	No	No	0.85 / 7.0 / 84 ug/L	Yes, pH and redox	Variable	Commonly has high concentration in groundwater under reduced conditions; 13th most abundant element in the Earth's crust	Production of steel and aluminum alloys, glass production, use as an additive in gasoline	
Nickel	No	No	0.35 / 1.1 / 2.5 ug/L	No	Variable	Commonly combined with iron or sulfur	Manufacture of steels, other metal alloys, and electronic applications; automobiles, electroplating and metal fabricating, petroleum	Sorbs to iron and manganese oxides, and clay to a lesser extent.
Nitrogen	No	No	0.07 / 0.55 / 2.4 (NO_3 as N) mg/L	Nitrification/ denitrifi-cation, redox	Very mobile as NO_3	In nature, nitrogen is converted from one redox state to another by abiotic reactions and microbial catalysis in oxic conditions: $NH_4OH \rightarrow NO_2 \rightarrow NO_3$; under reducing conditions: $NO_3 \rightarrow NO_2 \rightarrow N_2$	Fertilizers, livestock wastes, wastewater treatment plants, sewage and septic effluent, rubber manufacturing; ammonia sources include CCRs from sources using SNCR or SCR technology, coke production, flame retardants	NO_2 and NO_3 are not significantly sorbed by most soils, sediments, or clays, but NH_4OH is.

Table 2-2 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
Other Constituents								
Phosphate	No	No	<0.01 / 0.02 / 0.04 mg/L	Yes, pH	Variable	Phosphorus is the 11th most abundant element in the Earth's crust	Fertilizers, wastewater treatment plants, sewage and septic effluents, industrial effluents, soaps and detergents, flame retardants	Can be sorbed by iron, aluminum, and manganese oxides, and by clay under acidic conditions.
Potassium	Yes for some coal ash	No	0.9 / 1.7 / 3.5 mg/L	CEC	Mobile	7th most abundant element in the Earth's crust; Weathering of potassium-containing minerals	Water treatment, fertilizers, sea water intrusion, soaps and detergents, drying agents	May be removed from groundwater by reversible ion exchange with soils and sediments.
Silicon	No	No	12 / 19 / 31 mg/L	Yes	Very mobile	2nd most abundant element in the Earth's crust; usually in the form of SiO_2	Glass, ceramics, abrasives, electronic devices, metal alloying, water filtration, insulation, cement, concrete, paper, rubber, lubricants, flocculants	Can be sorbed by iron and aluminum oxides, and by clay minerals.
Silver	No	No	<1 ug/L	Yes, pH	Variable		Textile plant wastewater, photographic materials, sewage sludge, medical wastes, electronics, electroplating and metal fabricating	Can be sorbed by soils but affected by pH, clay content, particle size, organic content, and free iron and manganese oxide content.
Sodium	Yes for some coal ash	No	5.2 / 11 / 29 mg/L	CEC	Mobile	6th most abundant element in Earth's crust; brackish groundwater and surface water, sea water, weathering of sodium-containing minerals	Road salt, deicing, septic effluent, sodium hydroxide water treatment wastes, water softening, salt water intrusion (gas and oil well production), sewage and septic effluent, soaps and detergents, drying agents	Most sodium compounds are soluble but may be sorbed by reversible ion exchange in soils or sediments.

Table 2-2 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
Other Constituents								
Strontium	No	No	100 / 270 / 680 ug/L	Yes	Slightly mobile		Glass and ceramics production, pyrotechnics, phosphate fertilizers	Reacts with sulfate ions to form $SrSO_4^0$.
Vanadium	No	No	0.30 / 1.4 / 11 ug/L	Yes, pH and redox	Variable		Crude oil, oil shale, tar sands, phosphate fertilizers, wastes from steel production, petroleum	Can be sorbed by iron, aluminum, and manganese oxides; sorption decreases as pH increases.
Zinc	No	No	1.6 / 4.8 / 18 ug/L	Yes, pH	Variable		Fertilizers, protective coatings to reduce corrosion of metal surfaces, dry-cell batteries, castings, automobiles, lubricating oils and greases, plumbing/piping, electroplating and metal fabricating	Sorption increases with increasing pH but is also affected by clay content, particle size, organic content, and iron, aluminum, and manganese oxide content.

Notes:

1. Based on EPRI (2012). "No" indicates that the constituent it is not considered an indicator due to low concentration in CCR leachate relative to typical background, low mobility, and/or potential for reactivity.

2. Concentration ranges in ug/L from USGS (2011), Table 4; concentration ranges in mg/L or SU from USGS (2008), Tables 2 and 6; radium 226+228 from Szabo et. al (2012) supplemental table S-3; NR indicates that the concentration was not reported in any of these three documents.

3. Reactivity and mobility, while separate geochemical processes, are often interrelated. Reactivity descriptions in this table refer to chemical reactions, primarily precipitation and dissolution, that can change the concentration or mobility of the element in solution under typical aquifer conditions. Yes indicates that the constituent is subject to precipitation, coprecipitation, and/or dissolution reactions. In addition, pH and redox are indicated if they have a strong influence on the environments under which reactions occur and/or mobility. CEC is listed for constituents that are subject to cation exchange.

4. The mobility classification is based on the classification system of van Loon and Duffy (2000). See Table 2-2 of EPRI (2012) for corresponding K_d values.

5. Refer to Appendix B in EPRI (2012) for brief summaries of geochemical factors affecting reactivity and sorption. Detailed information can be found for selected constituents in the following EPRI reports:

- Arsenic
  1015550 | Chemical Constituents in Coal Combustion Product Leachate: Arsenic | Profile | 2008
  1021212 | Arsenic in Coal Combustion Products | Tech Brief | 2010
- Beryllium
  1012583 | Chemical Constituents in Coal Combustion Product Leachate: Beryllium | Profile | 2006
- Boron
  1005258 | Chemical Constituents in Coal Combustion Product Leachate: Boron | Profile | 2005
  1023737 | Boron in Coal Combustion Products | Tech Brief | 2012
- Chromium
  1022143 | Chromium in Coal Combustion Products | Tech Brief | 2011
- Lithium
  In Prep | Chemical Constituents in Coal Combustion Products: Lithium | Profile | 2018
- Molybdenum
  1021815 | Chemical Constituents in Coal Combustion Products: Molybdenum | Profile | 2011
  In Prep | Molybdenum in Coal Combustion Products | Tech Brief | 2017
- Selenium
  3002001237 | Chemical Constituents in Coal Combustion Product Leachate: Selenium | Profile | 2013
  3002003761 | Selenium in Coal Combustion Products | Tech Brief | 2014
- Thallium
  1016801 | Chemical Constituents in Coal Combustion Product Leachate: Thallium | Profile | 2008
  3002001155 | Thallium in Coal Combustion Products | Tech Brief | 2013

Table 2-3
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Abrasives	**Silicon, aluminum**
Acid mine drainage	**Low pH, sulfate, iron**, dissolved solids, metals (aluminum, cadmium, calcium, chromium, cobalt, copper, magnesium, manganese, nickel, zinc, and others); can travel along mine shafts and tunnels and show up in unexpected locations (sometimes across aquifers) (notes 1, 26, 51, 54)
Aerospace industry	**Boron, perchlorate, chloride, cyanide, cadmium**, beryllium, solvents (trichloroethane, methylene chloride, trichloroethylene, toluene, methylethylketone), metals, oils (notes 2, 3, 4, 5, 51)
Aging infrastructure (leaking sewage, urban runoff)	Nitrate, phosphorus, sodium, chloride, organic substances, bacteria, pesticides, miscellaneous chemicals, cadmium, copper, iron, lead, selenium, zinc, and other elements (note 6)
Agriculture - animal feed lots	**Nitrates, ammonia, other nitrogen compounds, phosphorus/phosphate, chloride, arsenic, magnesium, molybdenum, selenium** and other elements, organic substances, bacteria/viruses (notes 7, 22, 51, 52, 54)
Agriculture - fertilization	**Nitrates, ammonia, other nitrogen compounds, phosphorus/phosphate, boron, cadmium, calcium**, chloride, cobalt, **copper**, cyanide, **magnesium, molybdenum, potassium, selenium, strontium, vanadium, zinc**, and other elements (notes 7, 22, 51, 52, 54)
Agriculture - irrigation	**Nitrates, ammonia, other nitrogen compounds, phosphorus/phosphate,** arsenic, boron, cadmium, calcium, chloride, cobalt, copper, cyanide, magnesium, mercury, molybdenum, potassium, **selenium**, sodium, sulfate, and other elements (notes 7, 8, 9, 22, 52)
Agriculture - lime addition	**Calcium** (note 22)
Agriculture - pesticides, herbicides, and insecticides	Aldicarb, Aldrin, alachlor, atrazine, carbofuran, chlordane, dacthal, DDT, dieldrin, bibromo-chloropropane, 1,2-dichloropropane, dinoseb, endrin, endosulfan, ethylene dibromide, heptachlor, hexachlorobenzene, lindane, mirex, PCBs, prometon, simazine, toxaphene, trifluralin; **arsenic** (prior to 1960), chloride, **mercury, boron, sulfate** (notes 10, 51, 52, 54)
Airport runways	**Sodium, potassium**, acetate, formate, urea (note 11)
Aluminum manufacturing	**Aluminum, fluoride, sodium**, magnesium, manganese, perfluorocarbons, polycyclic aromatic hydrocarbons (notes 12, 13)
Ammunition, firearms	**Lead, antimony, copper,** other heavy metals, nitrate, perchlorate, potassium, sulfur/sulfate, chloride (notes 14, 15, 22)
Asphalt plants	Oils, greases, PAHs, other hydrocarbons (note 16)
Automobile production	**Chloride, sulfate, phosphate,** oil and grease, solvents, ethylene glycol. Potential for heavy metals: aluminum (auto bodies), **cadmium** (tires and batteries), **cobalt** (radial tires), **chromium** (brakes, coolants, engine parts), **copper** (brake linings), iron (auto bodies), **lead** (batteries, lube oil and grease, bearings, brakes), **mercury** (batteries), **nickel** (lube oil, brakes), **zinc** (tires, fuel oil, lubricants) (notes 17, 18, 22)
Automobile repair shops	Gasoline, diesel fuel, oil, degreasing solvents (toluene, xylene, chlorinated solvents, MEK), ethylene glycol, lead, sulfate (notes 19, 44)

Table 2-3 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Batteries	**Sulfate, lead, antimony, cadmium, cobalt, lithium, mercury, zinc, low pH** (notes 22, 51)
Bleach manufacturing	**Boron** (bleaches containing sodium perborate) (notes 20, 31)
Brick manufacturing	**Aluminum, silicon, iron**, calcium, **fluoride**, **magnesium,** chromium (notes 21, 22, 52)
Catalysts	Aluminum, chromium, **cobalt**, copper, iron, **molybdenum**, titanium, tungsten, vanadium, zinc, and other metals (depends on catalyst manufactured or used) (note 22)
CCR - ash	**Boron, sulfate**, molybdenum, lithium, bromide, potassium, sodium, fluoride, selenium; may contain ammonia (nitrogen) if SCR or SNCR technology was used at the power plant (note 22)
CCR - FGD gypsum	**Sulfate**, fluoride, calcium, boron, bromide, chloride, selenium (note 22)
CCR - FGD fixated sludge	**Boron, sulfate**, calcium, chloride, molybdenum, lithium, bromide, potassium, sodium, fluoride, selenium (note 22)
Cemeteries	**Formaldehyde, copper, arsenic,** mercury, pesticides, fertilizers, weed killers (note 23)
Cement and concrete manufacturing and use	**High pH, aluminum, calcium, silicon, thallium,** chromium and other elements (notes 22, 24, 51)
Ceramics production	Oxides of carbon, **silicon, boron**, and nitrogen; may include aluminum, antimony, barium, copper, fluoride, iron, **lithium**, **strontium**, and other elements (notes 21, 22, 51)
Coal mining	**Sulfate, low pH, iron**, dissolved solids, trace elements (aluminum, beryllium, cadmium, chromium, cobalt, copper, lead, magnesium, manganese, mercury, nickel, selenium, **uranium (decays into radium 226+228)**, zinc and others); Oxidation of pyrite in coal can form sulfuric acid. The low pH increases solubility of many metals. (notes 1, 26, 51, 54)
Coatings	VOCs, solvents (halogenated solvents and non-halogenated solvents such as acetone, cresols, cresylic acid, nitrobenzene, benzene, toluene, xylene, methyl ethyl ketone, methylene chloride, etc.); trace elements may include barium, cadmium, **chromium**, cobalt, lead, mercury, molybdenum, nickel, titanium, and **zinc** (note 27)
Coke production (from coal)	**Phenols, ammonia (nitrogen), polycyclic aromatic hydrocarbons, cyanide**, benzene, naphthalene, anthracene, cresols, metals (see metals in "coal piles or coal waste piles") (note 28)
Computer and telecommunications components (electronics)	Trace elements may include aluminum, arsenic, barium, **beryllium**, cadmium, chromium, cobalt, **copper**, gallium, **gold**, iron, **lead**, manganese, mercury, palladium, platinum, selenium, **silver**, and zinc; solvents may include benzene, xylene (dimethylbenzene), trichloroethane, tetrachloroethane, ethylene glycol, methyl cellosolve; **silicon** (notes 29, 30, 32)

Table 2-3 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Defense applications	**Beryllium** (note 22)
Detergent or soap manufacturing	**Sodium, potassium, sulfates and sulfonates, high pH, phosphate, chloride, boron**, phenol, aluminosilicate, sodium citrate, nitrilotriacetate, alcohol ethoxylates, fats, oil and grease, lead, hexane, methyl alcohol, trichloroethane, perchloroethylene, benzene, toluene (notes 22, 34, 35)
Deicing	**Sodium, chloride, calcium**, magnesium, urea (notes 44, 51)
Drying agents	**Aluminum, calcium, sodium, potassium, magnesium, sulfate, chloride,** cobalt, lithium, phosphorus, silicon and/or other substances (notes 22, 36, 37)
Electronic equipment manufacturing and disposal	**Copper, silver, gold, palladium, arsenic, beryllium, copper, mercury, nickel,** selenium, **silicon, thallium** and other trace elements, chloride, fluoride, solvents (benzene, xylene, 1,1,1-trichloroethane, tetrachloroethane, methanol), ethylene glycol, hydrogen chloride, hydrogen fluoride (notes 22, 29, 30, 33, 51)
Electroplating and metal fabricating	**Cadmium, chromium, copper, nickel, silver**, sodium, tin, **zinc**, spent solvents, paints, spent acidic and alkaline solutions, cyanide, waste oils (notes 17, 22, 44, 51, 52, 56)
Explosives manufacturing and testing	**Nitroglycerin and nitro-aromatic compounds**, nitrate, perchlorate, ammonia, lithium, sodium, potassium, sulfur/sulfate, aluminum, chloride, **lead**, antimony, **copper**, nickel, silver (notes 38, 39, 40, 51)
Fertilizers	See Agriculture - fertilization
Fiberglass manufacturing	Aluminum, silicon, calcium, magnesium, **boron**, polyester or epoxy resin, styrene, solvents, volatile organic compounds, formaldehyde, urea, phenol, vinyl acetate (notes 31, 41)
Firearms, ammunition	See Ammunition, firearms
Firing ranges	**Lead**, antimony (notes 14, 22)
Fireworks manufacturing or use	Aluminum, antimony, arsenic, barium, **boron**, chloride, copper, **lead**, **magnesium**, nitrate, perchlorate, potassium, sulfur/sulfate, **strontium** (notes 31, 38, 39, 40, 51)
Flame retardant manufacturing or use	**Bromine, phosphate, nitrogen/nitrate, chloride, antimony, boron, magnesium**, polybrominated diphenyl ethers (PBDEs), PCBs (notes 22, 42, 43, 51)
Flocculants	**Sulfate, chloride, aluminum, iron**, ammonium, calcium, silica, polyamines (note 45)
Fluorescent lamps/bulbs	**Mercury**, PCBs in ballasts (note 47)
Fracking	See Oil and gas wells / production

Table 2-3 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Fungicides	See Pesticides
Furniture (wood stripping and refinishing)	Methylene chloride, methanol, isopropyl alcohol, acetone, perchloroethylene, toluene, acidic and alkaline solutions, metals, other solvents, petroleum distillates, resins, halogenated hydrocarbons, glycol ether (note 44)
Gasoline stations	**Benzene, ethylbenzene, toluene, xylene, MTBE**, ethylene dichloride, naphthalene, other organic compounds, lead (prior to 1996), **manganese**; trichloroethylene, perchloroethylene, methylene chloride, carbon tetrachloride, oils, ethylene glycol, hydraulic fluid, detergents, and acids (notes 22, 49, 51, 52)
Glass manufacturing	**Silicon**, antimony, **barium, boron, lead**, iron, **lithium, manganese**, nickel, potassium, **strontium, thallium**, tin, zinc, fluoride (notes 22, 31, 50, 51)
Industrial emissions	**Chloride, sulfate, iron,** wide variety of other elements and chemical substances (notes 22, 51, 54)
Irrigation	See Agriculture – irrigation
Junk and scrap yards	Used oil, gasoline, antifreeze, lead, sulfuric acid, agricultural chemicals/pesticides/other chemicals, metals (note 44)
Lamp manufacturing and disposal	**Mercury**, bromide, chloride, fluoride, iodide, PCBs, sodium (notes 22, 47)
Landfills - industrial	Wide range of trace metals, acids, **chloride**, sulfate, organic substances and pesticides (notes 51, 53, 54)
Landfills - municipal	Salts (sodium, calcium, magnesium, **chloride**, etc.), metals (iron, copper, zinc, other heavy metals), nitrate, organic compounds, solvents, pesticides (notes 22, 51, 54)
Laundry - dry cleaning	**Perchloroethylene (tetrachloroethylene)**, camphor oil, turpentine spirits, benzene, kerosene, white gasoline, petroleum solvents (petroleum naphtha), chloroform, carbon tetrachloride, trichloroethylene, 1,1,2-trichlorotrifluoroethane, glycol ethers, 1,1,1-trichloroethane, decamethylcyclopentasiloxane, n-propyl bromide, liquid carbon dioxide, fluorocarbon-113, antimony, cadmium, copper, lead, sulfate, zinc (notes 20, 31, 44, 52)
Leather tanning	**Chromium, cyanide, tannins,** chlorinated phenols including PCB, azodyes, cadmium, cobalt, copper, antimony, barium, lead, selenium, mercury, zinc, arsenic, nickel, formaldehyde, pesticides, salts, lime, acids, sodium sulfide, hydrogen sulfide, sulfate (notes 22, 55, 56)
Lubricants and greases	**Zinc**, polyaromatic hydrocarbons, arsenic, **boron**, cadmium, lead, **lithium, molybdenum**, PCBs, **silicon**, and other elements (note 22)
Medical supplies or wastes	Chloride, formaldehyde, **arsenic**, cadmium, **cobalt**, lead, mercury, **silver**, other heavy metals, radioactive waste, infectious or pathological waste, dioxins and furans from incineration; Also see Pharmaceutical industry (notes 22, 51, 57, 58, 59, 62)

Table 2-3 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Metal manufacturing - smelting	**Aluminum**, **antimony**, **arsenic**, beryllium, cadmium, **chromium**, **copper**, cyanide, iron, **lead**, **magnesium** (aluminum manufacturing), **manganese** (steel and aluminum manufacturing), mercury, **molybdenum** (steel manufacturing), **nickel** (steel and other metal manufacturing), **selenium**, silver, **thallium** (iron and steel manufacturing), zinc and other elements, **fluoride** (steel and aluminum manufacturing), **silicon**, **vanadium** (steel manufacturing), **zinc** (notes 22, 44, 51, 52)
Metal mining	Aluminum, antimony, **arsenic**, beryllium, cadmium, **chromium**, **copper**, **cyanide**, iron, **lead**, **manganese**, **mercury**, **nickel**, **selenium**, silicon, silver, thallium, tungsten, zinc and other elements (notes 22, 51, 52, 54, 56)
Metal plating	Spent solvents, paints, spent acidic and alkaline solutions, waste oils, heavy metal sludges, metal dust, chromium, copper, nickel, selenium, **zinc** and other elements (notes 22, 44, 51, 52)
Metal recycling	Iron, copper, **mercury**, nickel, zinc, and other elements (note 22)
Mining - unspecified	Depends on contents of ore; may include aluminum, antimony, arsenic, beryllium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, **sulfate** (gypsum mines), thallium, zinc, other minerals, hydraulic oils; **radium 226+228 (uranium mines)** (notes 22, 51)
Natural gas pipelines	**Methane**, **PCBs** (notes 60, 61)
Nuclear power	**Tritium**, **strontium 90**, **radium 226+228**, boron, beryllium (notes 31, 51, 54)
Oil and gas wells / production	Produced water may contain high **TDS**, **chloride**, **sodium**, sulfate, barium, boron, bromide, iodide, lithium, potassium, radionuclides, **vanadium** and other minerals, methane, volatile organic compounds (notes 52, 60, 63)
Ore refining / smelting	Aluminum, antimony, arsenic, beryllium, cadmium, chromium, copper, cyanide, iron, lead, manganese, mercury, nickel, selenium, silver, thallium, zinc and other elements (notes 22, 44, 51)
Paint and pigment manufacturing	VOCs, solvents (halogenated solvents, non-halogenated solvents such as acetone, cresols, cresylic acid, nitrobenzene, benzene, toluene, xylene, methyl ethyl ketone, methylene chloride, etc.); metals may include **barium**, **cadmium**, **cobalt**, **chromium**, **lead**, mercury, **molybdenum**, titanium, and zinc (notes 22, 44, 51, 52, 64)
Paper and pulp manufacturing	Organic and inorganic compounds including lignin, cellulose, phenols, mercaptans, **chromium**, nitrates, phosphates, **silicon**, **sulfides/sulfates**, chlorinated compounds including chloroform and dioxin (notes 22, 65)
Petroleum facilities and refining	Benzene, ethylene, toluene, xylene, methane, other organic compounds, hydrogen sulfide, **sulfate**, **nickel**, **vanadium** and other elements; some refineries use deep-injection wells to dispose of highly contaminated wastewater that could potentially contaminate groundwater (note 51)
Pharmaceutical industry	Wide variety of organic solvents; **arsenic**, **cobalt**, ammonia, chloride, cobalt, **silver** and other elements; Also see Medical supplies or wastes (notes 22, 51, 57, 62)
Photographic materials/photography	**Silver**, sodium, potassium (notes 22, 51)

Table 2-3 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Pigments	See Paint and pigment manufacturing
Plastic manufacturing	Cadmium, cyanide, benzene, vinyl hydrochloride, phthalates, trichloroethane, acetone, methylene chloride, methyl ethyl ketone, styrene, toluene, trichloroethane, sulfate, methanol, ethylene oxide, volatile organic compounds, sodium, caustic, nickel, lead, cadmium, mercury (notes 51, 66)
Plumbing	**Copper, lead, zinc** (note 51)
Road salting	**Chloride, sodium, calcium**, other salts (notes 22, 44)
Rubber manufacturing	**Ammonia, amines**, acetic acid, **barium**, cobalt, formic acid, sodium, **silicon**, sulfite/sulfate, organics, nitrogen compounds (notes 22, 69)
Salt or brackish water intrusion (from well drilling)	**High TDS, chloride**, boron, bromide, calcium, **lithium**, magnesium, **potassium, sodium**, sulfate, and other minerals (notes 22, 51, 54)
Salvage and junk yards	Grease, oil, solvents, lead and acid from batteries, metals (notes 44, 54)
Semiconductor manufacturing	Copper, silver, gold, palladium, arsenic, beryllium, copper, mercury, nickel, selenium, silicon, thallium and other elements, chloride, fluoride, solvents (benzene, xylene, 1,1,1-trichloroethane, tetrachloroethane, methanol), ethylene glycol, hydrogen chloride, hydrogen fluoride (notes 22, 29, 30, 33, 51)
Septic effluent	**Nitrate, phosphorus, chloride, sodium**, organic substances, bacteria and viruses, detergents, oils, heavy metals including cadmium, copper, lead, **selenium**, salts, septic tank cleaners such as trichloroethane or methylene chloride, and a wide variety of other chemicals (notes 22, 51, 52, 53)
Sewage	**Nitrate, phosphorus, chloride, sodium**, organic substances, bacteria and viruses, detergents, oils, **boron, cadmium, copper**, lead, **selenium, silver**, salts, and a wide variety of other chemicals (notes 22, 51, 52)
Soap or detergent manufacturing or use	See Detergent and soap manufacturing
Soil acidity neutralization	**Calcium**
Steel (including stainless) and iron manufacturing	Iron, chromium, manganese, nickel, ammonia, cyanide, chloride, copper, fluoride, molybdenum, sulfate, tin, thallium, zinc, hydraulic oils
Textiles	Polyvinyl chloride, chlorine bleach, benzidine, toluidine, cyanide, formaldehyde, hydrocarbons, ammonia, nitrate, organic solvents, chloride, sodium, fluoride, silicon, **sulfate**, phosphate, boron, bromide, chromium, copper, aluminum, antimony, potassium, aluminum, **silver**, titanium, zinc, copper, insecticides (notes 22, 51, 56, 67, 68)
Thermometers, thermostats, switches	**Mercury** (note 51)

Table 2-3 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Underground storage tanks (USTs leaking petroleum products such as gasoline)	Benzene, toluene, xylene, other organic compounds (notes 49, 51, 53)
Urban runoff	Oils, heavy metals, salts, copper, zinc, and other chemicals (notes 6, 18, 54)
Waste incineration	**Chloride, cadmium**, chromium, **fluoride, lead, mercury**, selenium, dioxins and furans (note 22)
Water treatment - flocculants	See Flocculants (note 45)
Water treatment - industrial effluents	Wide variety of metals, aluminum, **chloride, phosphate, potassium, sulfate**, nitrate, **selenium, silicon, sodium**, organics depending on industry (notes 22, 46)
Water treatment - municipal supply	Bromide, **chlorine, fluoride** (notes 22, 51)
Water treatment - treated sewage effluent	May contain **nitrates and other nitrogen compounds, phosphates, sodium, chloride, selenium, silicon**, and a variety of other elements (notes 22, 51, 52)
Water treatment - water softening	**Sodium, chloride, calcium**, magnesium, iron, other salts and metals (note 22)
Water treatment - cooling water	Chromium, zinc (notes 51, 52)
Well drilling (mud or fluid)	Constituents of bentonite clay and the natural geomedia including **aluminum, barium**, calcium, potassium, sodium and other minerals (note 22)
Wood preservatives and treatments	**Pentachlorophenol (PCP), creosote, copper, chromium, arsenic** (chromated copper arsenic, ammoniacal copper arsenate) (notes 22, 44, 48, 51)

* Bold indicates likely key indicators; list will vary by site-specific source; list may be incomplete or may not accurately represent a particular source.

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3
ASD EVALUATION TECHNIQUES

Primary Indicators for Coal Combustion Residual Leachate

A key line of evidence in any ASD will be whether or not there is an SSI/SSL for one or more primary CCR leachate indicator constituents. For ASD purposes, a primary indicator is:

- a constituent that typically has high concentration in leachate, relative to background, such that it is expected to have elevated concentration in the event of a release, *and*
- is not reactive, and has high mobility in groundwater such that it is expected to be at the leading edge of the plume, meaning that it will have elevated concentrations relative to background across the entire area of the plume.

Boron (B) and sulfate (SO_4) are primary indicators for coal ash leachate (EPRI 2012). The association of both boron and sulfate with CCP leachate was established during the late 1970s (EPRI 1979, Cherkauer 1980). Based on the EPRI CPInfo database, boron concentrations in fly ash leachate range between 1.1 and 109 mg/L with an average concentration of 8.3 mg/L; sulfate concentrations range from 89 to 6,070 mg/L with an average concentration of 1,370 mg/L (EPRI 2012). For FGD gypsum, sulfate is a primary indicator constituent. Sulfate concentrations for FGD leachate range from 437 to 1,549 mg/L with average concentrations around 1,300 mg/L (EPRI 2012).

There may be other primary indicators for a given CCR site depending on a variety of factors (Table 3-1). For example, molybdenum may be a primary indicator for landfilled fly ash derived from bituminous coal, and boron, bromide, and chloride may be primary indicator constituents for unwashed FGD gypsum. When determining primary indicator constituents, the optimal approach is to start with field-measured leachate concentrations. If field data are not available, published sources provide an alternative source of data. EPRI (2016) provides landfill leachate data ranges for a variety of CCRs and source coals.

Table 3-1
Potential Indicator Constituents for Coal Ash and FGD Gypsum

Potential Indicators for Coal Ash		Potential Indicators for FGD Gypsum	
Constituent	**Advantages and Caveats**	**Constituent**	**Advantages and Caveats**
Boron	Typically present in leachate, non-reactive and mobile in common hydrogeologic environments, and not a common anthropogenic contaminant.	Sulfate	High concentrations expected in both washed and unwashed FGD gypsum (EPRI, 2011). Commonly analyzed. Very mobile in all hydrogeologic environments. Less useful in strongly reducing environments where sulfate can be reduced to hydrogen sulfide gas.
Molybdenum	Most useful for dry-managed coal ash. May be less mobile than boron in some hydrogeologic environments. Concentrations may be too low in impoundment leachate to be useful if background groundwater has detectable concentrations.	Fluoride	Assure that leachate concentration is higher than background, particularly for washed gypsum. Mobile in common hydrogeologic environments, although precipitation as CaF_2 is possible.
Lithium	Useful for coal ash management sites where the power plant burned bituminous coal. Leachate concentrations are typically low in coal ash derived from subbituminous and lignite coal (EPRI, 2006).	Calcium	High concentrations expected in both washed and unwashed FGD gypsum (EPRI, 2011). Understanding of carbonate chemistry necessary to assure that precipitation or dissolution does not affect downgradient concentrations.
Sulfate	Commonly analyzed and very mobile in all hydrogeologic environments. Concentration in impoundment leachate may in some cases be too low relative to background to be useful. Less useful in strongly reducing environments where sulfate can be reduced to hydrogen sulfide gas.	Boron	Mobile indicator constituent for unwashed FGD gypsum. Concentrations for washed gypsum may be too low to be useful (EPRI, 2011).
Bromide	May have high concentration in coal ash leachate at power plants where brominated powdered activated carbon (Br-PAC) or calcium bromide is used for mercury control. Leachate concentrations for coal ash generated absent use of these technologies may be too low to be useful. Mobile and non-reactive in typical groundwater environments.	Bromide	Mobile indicator constituent for unwashed FGD gypsum, especially if Br-PAC or CaBr used for mercury controls. Concentrations for washed gypsum may be too low to be useful (EPRI, 2011).

Table 3-1 (continued)
Potential Indicator Constituents for Coal Ash and FGD Gypsum

Potential Indicators for Coal Ash		Potential Indicators for FGD Gypsum	
Constituent	**Advantages and Caveats**	**Constituent**	**Advantages and Caveats**
Potassium	Commonly analyzed, although may be less mobile than boron and sulfate. Assure that leachate concentration is higher than background and that there are no anthropogenic sources such as agricultural fields where potassium may be applied in fertilizers.	Chloride	Mobile indicator constituent for unwashed FGD gypsum. Concentrations may be very high if transport water is recirculated. Concentrations for washed gypsum may be too low to be useful (EPRI, 2011).
Sodium	Useful for coal ash management sites where the power plant injects trona or sodium bicarbonate, or burned subbituminous coal. Absent dry sorbent injection, leachate concentrations are considerably lower in coal ash derived from bituminous coal, particularly at impoundments (EPRI, 2006). Assure that leachate concentration is higher than background and that there are no anthropogenic sources such as agricultural fields, or major highways in northern climates where sodium may be applied as road salts.		
Fluoride	Mobile and non-reactive in common hydrogeologic environments. Assure that leachate concentration is higher than background.		
Source: EPRI, 2012			

Site-Specific Leachate Analysis

Collection of site-specific field leachate data is useful for ASDs because it identifies 1) whether or not particular constituents that can cause an exceedance have higher concentration in leachate than in background groundwater, and 2) the leachate signature or fingerprint.

Where possible, leachate samples from landfills and impoundments can be collected using leachate wells, lysimeters, and/or leachate collection systems. These collection methods are preferred because the samples collected are representative of interstitial porewater. Because leachate characteristics will change with coal types and sources as well as changes in emission control technology, it is important to collect leachate samples representative of the spectrum of CCR materials placed into the CCR unit. Samples of pond water, sluice water, and runoff water are less useful than porewater samples for groundwater fingerprint analysis because their chemistry is affected by the composition of the source water used for sluicing as well as the leachate. Laboratory samples do not always represent actual leaching conditions (pH, redox, and liquid-to-solid ratio) and therefore, are less representative of actual field leachate composition than field samples. They are also more likely to provide only a snapshot of leachate chemistry based on the coal type and technologies used at the time of generation.

Water Quality Analyses for an ASD

The constituents included in a groundwater monitoring plan may not provide all data needed to evaluate certain lines of evidence for an ASD. The list below will typically provide the information needed for all except specialized lines of evidence.[5] Some of these constituents may already be part of the monitoring plan, while others may represent extra or special analyses.

- The constituents listed in Table 3-1, depending on the CCR managed in the site, in order to identify primary indicators for the leachate. All of these could be analyzed in leachate samples, and those with elevated concentration could be analyzed in groundwater samples.
- Major ion concentrations (alkalinity, chloride, sulfate, calcium, magnesium, potassium, and sodium) in leachate and groundwater. These concentrations can be used to evaluate whether downgradient groundwater chemistry remains representative of background groundwater chemistry. Major ion chemistry can also be used to evaluate natural variability due to seasonal changes or other causes.
- Field turbidity in groundwater is an indicator of the presence of suspended solids that may contribute to elevated concentrations of constituents monitored in unfiltered samples under the CCR Rule.
- pH in leachate and groundwater because it provides information on chemical reactions and mobility in groundwater.
- Dissolved oxygen (DO), oxidation reduction potential (ORP), and iron and manganese in groundwater are all indicators of redox conditions. Changes in redox can affect the chemical state and solubility of sulfate in addition to trace elements including arsenic and selenium. For example, under strongly reduced conditions, sulfate can be reduced to form hydrogen sulfide or it can precipitate as iron sulfide, arsenic reduces to the more mobile arsenite species, and selenium reduces to the low-mobility selenite species.

Water Quality Signatures

Natural surface water and groundwater may contain literally thousands of other substances (USGS, 2003). In fact, water is often referred to as the universal solvent because it dissolves more substances than any other solvent. Sources of these dissolved constituents or solutes include dust and gases collected as precipitation falls to the earth, dissolution of minerals in the soil and rocks, infiltration of contaminants from anthropogenic sources, etc. Groundwater monitored at a CCR unit for compliance with the CCR Rule is a compilation of the history of all sources of water comingling at that particular monitoring well. Different sources may contribute some of the same solutes, making source identification challenging. The identification and use of water quality "signatures" can be used as a tool for deciphering the similarity between potential sources and the water quality at a specific monitoring point.

EPRI (2012) describes three tiers of investigation for evaluation of water quality signatures to determine if elevated concentrations represent a release from a CCR facility. Conversely, these

[5] Specialized lines of evidence include geochemical modeling, isotopic signatures, and tritium age dating. Refer to EPRI (2017).

tools can also be used to evaluate whether or not sources other than CCR are contributing to groundwater quality degradation. The three tiers defined by EPRI (2012) are:

- Tier I: Trend Analysis and Statistics
- Tier II: Advanced Geochemical Evaluation Methods
- Tier III: Isotopic Analyses

This section provides guidance for interpretation of results using these evaluation techniques for an ASD.

Tier I Evaluation

By requiring determination of statistically significant increases/levels, the CCR Rule essentially requires Tier I statistical analysis under detection monitoring and under assessment monitoring. Many of the indicator constituents listed in Table 3-1 are included in constituent lists for these monitoring programs, including the primary constituents boron and sulfate. As discussed next, if there is an SSI/SSL without a corresponding increase in a primary indicator constituent (boron and usually sulfate[6] for coal ash), then this is a key line of evidence for an alternative source demonstration.

As previously introduced, an ideal primary indicator is a constituent that has concentrations in leachate greater than concentrations in background/upgradient groundwater, is mobile, and is relatively non-reactive in the hydrogeologic environment. Boron and sulfate are the most common primary indicators for coal ash leachate (EPRI, 2012). This is the first line of evidence to investigate for an ASD. If a constituent other than boron and/or sulfate is identified as an SSI/SSL but boron and/or sulfate are not also identified as elevated over background, it is unlikely that leakage from the CCR unit is the source of the SSI/SSL. This relationship holds for other potential indicators identified in Table 3-1, such as fluoride and sodium, if they have elevated concentration in site leachate relative to background.

If the site-specific leachate signature has not been determined, the potential indicators identified for fly ash and FGD gypsum in Table 3-1 can be considered. All of these potential indicators are naturally occurring and may be present in background groundwater. If any of these potential indicators are elevated over background but boron and/or sulfate are not, that provides a line of evidence for an ASD. Conversely, if any of these constituents have been identified as an SSI/SSL in addition to boron and sulfate, then temporal trends can be compared to determine if the constituents are trending together in the same direction. The more this "fingerprint" matches, the more strongly the monitoring results point to a release from the CCR unit. The trends in Figure 3-1 for boron, lithium, and sulfate indicate that lithium concentrations tend to rise and fall with boron and sulfate concentrations indicating that lithium may be an additional indicator parameter for a release from this site.

[6] Sulfate concentration increases may not be evident if groundwater is strongly reduced.

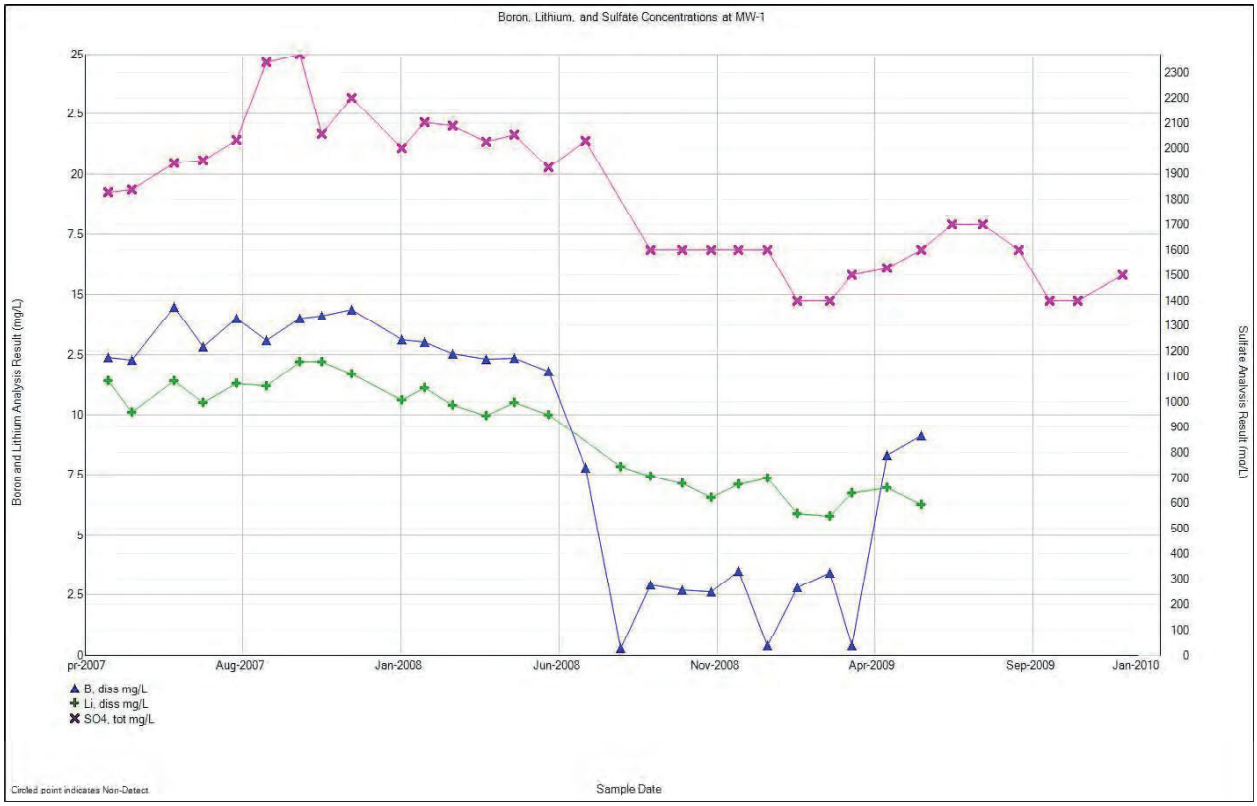


Figure 3-1
Time series plot showing potential correlation for lithium with boron and sulfate concentration changes indicating that lithium may be an indicator parameter for this site.

Scatter plots are another useful technique for identifying or refuting indicator parameters and identifying the presence of alternative sources. This technique plots one constituent on the X axis against another constituent on the Y axis. It can be used to show the relationship between two constituents. If the pattern of dots slopes from the lower left to the upper right portion of the graph, the two constituents are positively related (as one increases the other also increases). In this case, they are both likely related to the same source. If the pattern of dots slopes from the upper left to the lower right portion of the graph, the two constituents are negatively related and not from the same source. Figure 3-2 shows that arsenic and boron are not positively related. Therefore, even though the elevated boron concentrations suggest that a release has occurred, the lack of correlation suggests that the highest arsenic concentrations have a different source than the boron, which becomes a line of evidence in an ASD *specific to the arsenic*.

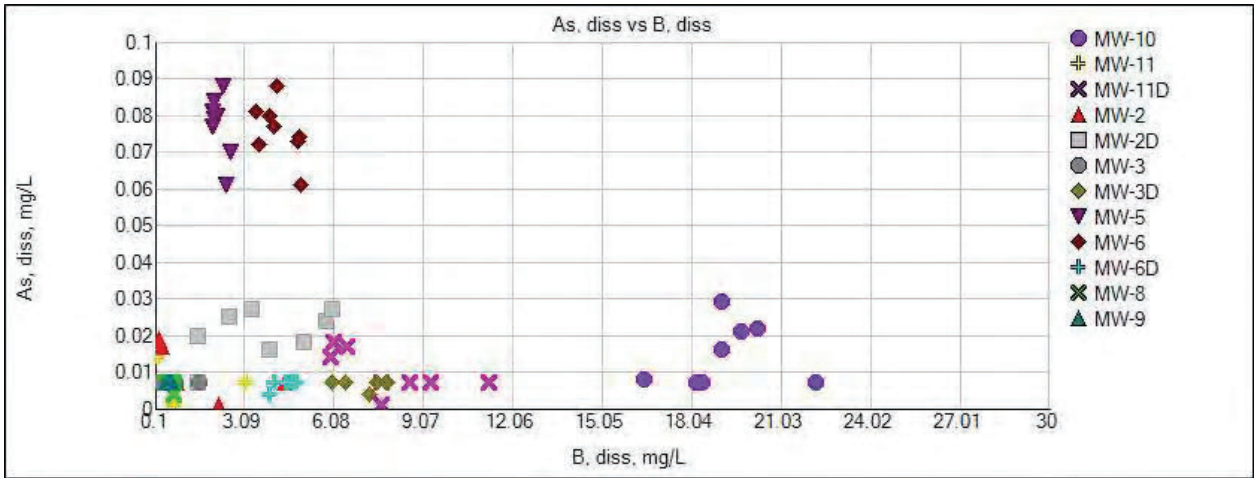


Figure 3-2
Scatter plot of arsenic versus boron, showing no correlation

Tier II Evaluation – Advanced Geochemical Evaluation Methods

Analysis of indicator constituents may not provide the lines of evidence needed for a strong ASD. More sophisticated methods may be needed at sites that have high concentrations of naturally occurring indicator constituents, multiple CCR sources, or upgradient sources of indicator constituents not related to the monitored unit, or where groundwater is brackish or saline. Furthermore, as groundwater travels through the environment, the composition may change due to geochemical interactions such as pH and ORP changes, influences from microbial activity, mixing with recharging surface water or other aquifers, or contamination from a variety of other anthropogenic or natural sources. The methods described below are useful for evaluating and visualizing the differences in water chemistry between upgradient and downgradient sampling locations.

Five Tier II methods were recommended in EPRI (2012) for multi-parameter comparison of water chemistry at multiple locations:

1. Ion ratios
2. Piper diagrams
3. Durov diagrams
4. Stiff diagrams
5. Fingerprint Analysis of Leachate Contaminants (FALCON)

This section adds a geochemical modeling and multivariate statistics to the EPRI (2012) list.

Ion Ratios and FALCON

The ion ratio method is the simplest approach from the list above and, unlike items 2 through 5, does not require analytical data for all major cations (calcium, magnesium, sodium, and potassium) and anions (chloride, sulfate, carbonate and bicarbonate or total alkalinity). Ion ratios are calculated by dividing the concentration of one constituent (usually the higher concentration constituent) by the concentration of another constituent from the same sample. Any units may be

used as long as the units are the same, because the ratio calculation is dimensionless. Ion ratios can be used to identify different source waters, or to determine that an additional source water is being added along a flow path. The method is based on the premise that if two constituents with similar mobility are released to groundwater, they will travel in groundwater at the same relative concentration or ratio unless they are mixed with water from other sources that have significantly different ratios of the same constituents. In other words, if leachate is released, then the relative concentration (ion ratio) in downgradient wells should be similar to the relative concentration in the leachate even if the concentration is diluted due to mixing with background groundwater. EPRI 2012 recommends that mobile, non-reactive constituents such as boron, chloride, lithium, molybdenum, and sulfate are the best candidates for this approach.

Table 3-2 illustrates the use of ion ratios as a line of evidence that downgradient well MW-3 is not impacted by ash leachate. In this example, MW-3 has higher sulfate concentrations than the two background wells, indicating that it may be impacted by CCR leachate. Boron concentrations at MW-3 are similar to upgradient well MW-1, whereas boron was not detected at upgradient well MW-2. Field leachate data indicate that chloride may be a CCR leachate indicator for this site in addition to boron and sulfate. Ion ratios for sulfate/chloride and boron/chloride were calculated and are provided in the chart (note that the boron/chloride ratios were multiplied by 1000 for enhanced visual representation). Since boron, sulfate, and chloride are all non-reactive in groundwater, ion ratios (boron/chloride and sulfate/chloride) representative of the leachate should remain consistent as leachate disperses and is diluted in groundwater unless there is another source of these constituents. In this case, the ion ratios at MW-3 are more representative of those at background wells MW-1 and MW-2, providing a line of evidence that CCR leachate is not the source of these constituents at MW-3.

Table 3-2
Use of Ion Ratios to Show that Groundwater Concentrations Are Not Caused by a CCR Release

		Background Wells		Downgradient Well	Field Leachate Concentration
Constituent	**Units**	**MW-1**	**MW-2**	**MW-3**	**LH-1**
B, tot	mg/L	0.02	<0.01	0.02	29
Cl, tot	mg/L	15	8	34	2,500
SO4, tot	mg/L	33	31	130	3,294
SO4/Cl Ratio		2.2	3.9	3.8	1.3
B/Cl Ratio	*1000	1.3	1.2	0.59	12

Ion ratios are also the basis of the Fingerprint Analysis of Leachate Contaminants (FALCON) method that was developed by the U.S. EPA. The FALCON method is more robust than simple ion ratios because it utilizes multiple constituents including all major cations and anions, as well as selected indicator constituents representative of the leachate signature. Regression analysis is used to mathematically represent the correlation between monitoring well, leachate, and background well signatures. EPRI (2012) provides a step-by-step procedure for the application of FALCON.

Piper, Durov, and Stiff Diagrams

Piper, Durov, and Stiff diagrams use graphical methods to group groundwater data to evaluate major ion chemistry. For an ASD, these methods are used to determine whether or not downgradient groundwater quality is a mixture of background groundwater and leachate. Interpretation of these plots can be subjective due to variation in the quality of various water groups. However, with Piper and Durov diagrams, a mixture is evident when downgradient groundwater quality plots at a point between leachate and background groundwater quality, and little or no mixing is determined if downgradient points plot with background, or at a point that is not between background and leachate. For a Stiff diagram, mixing is determined if the downgradient point evolves along a flow path to look less like background and more like leachate, where little or no mixing can be concluded if the shape of the downgradient point remains similar to background. These methods can also be used to evaluate whether or not an alternative source is affecting downgradient groundwater quality.

Common to each method is the necessity to conduct chemical analyses of the leachate and groundwater samples that include major cations and anions. Major cations present in natural water sources are calcium, magnesium, sodium, and potassium. Major anions are chloride, sulfate, bicarbonate, and carbonate. Bicarbonate and carbonate can be analyzed and reported together as total alkalinity. Prior to using graphical analysis for evaluation of major ion chemistry, it is good practice to calculate the charge balance in the sample. If the charge balance is not within an acceptable criterion (typically ±10%), it indicates that analytical results may be missing significant constituents, or there may be errors in the reported results. EPRI (2012) provides the equation and describes how to calculate and interpret the charge balance error for a water sample.

A Piper diagram is a graphical technique used to classify types of groundwater. It consists of two ternary plots (one for cations, and one for anions) linked to a diamond plot that is a combination of cations and anions. The Piper diagram below (Figure 3-3) shows an example where mixing is evident between leachate and groundwater, as denoted by the yellow-shaded area; however, the lysimeter chemistry does not indicate mixing of groundwater and leachate (primarily based on the cation triangle).

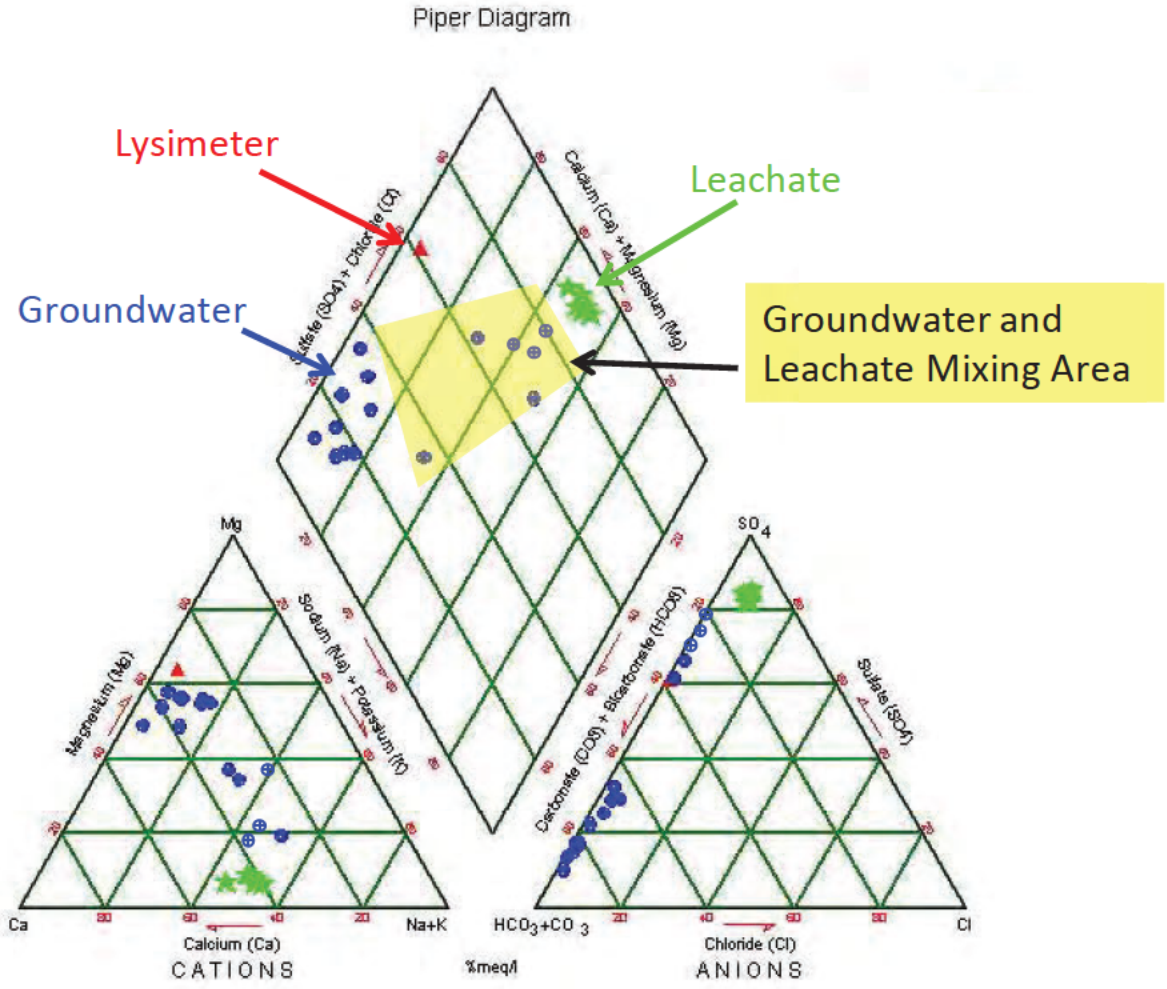


Figure 3-3
Example Piper diagram (from EPRI, 2012)

A Durov diagram is a combination of two ternary plots attached to a square-shaped plot. It displays data similar to a Piper diagram in different format. An example is provided in Figure 3-4. This diagram shows that bituminous coal ash leachate can be characterized as calcium-magnesium-sulfate water type, leachate from subbituminous coal ash can be characterized as sodium-calcium-sulfate water type, and background groundwater in this illustration can be characterized as calcium-magnesium-bicarbonate type.

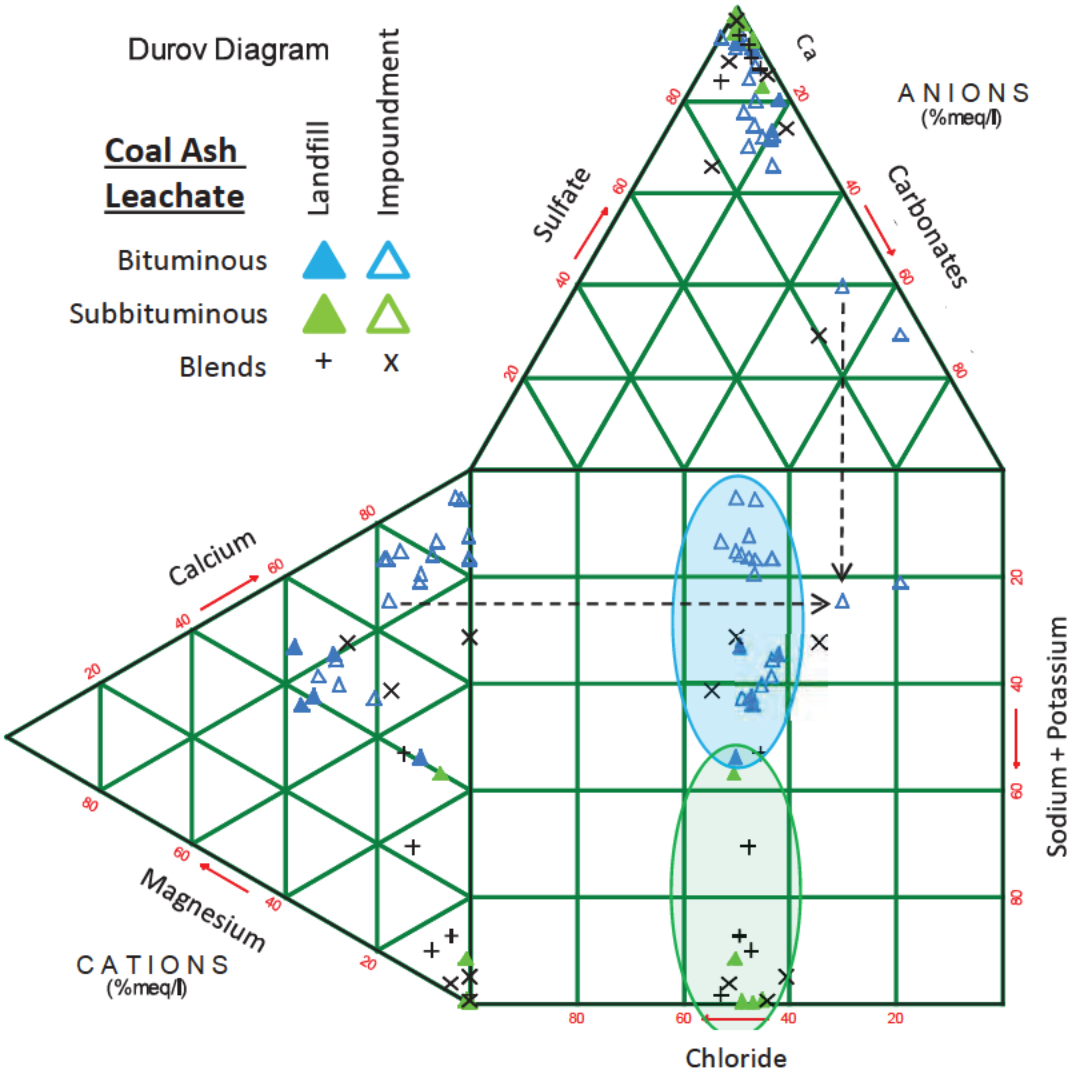


Figure 3-4
Durov diagram showing coal ash leachate derived from bituminous coal compared to subbituminous-lignite coal (From EPRI, 2012)

A Stiff diagram (Figure 3-5) is a multi-sided figure that compares the major cations in solution with the major anions. The resulting polygon can be placed in cross-sections or maps to show how the composition of the groundwater changes spatially.

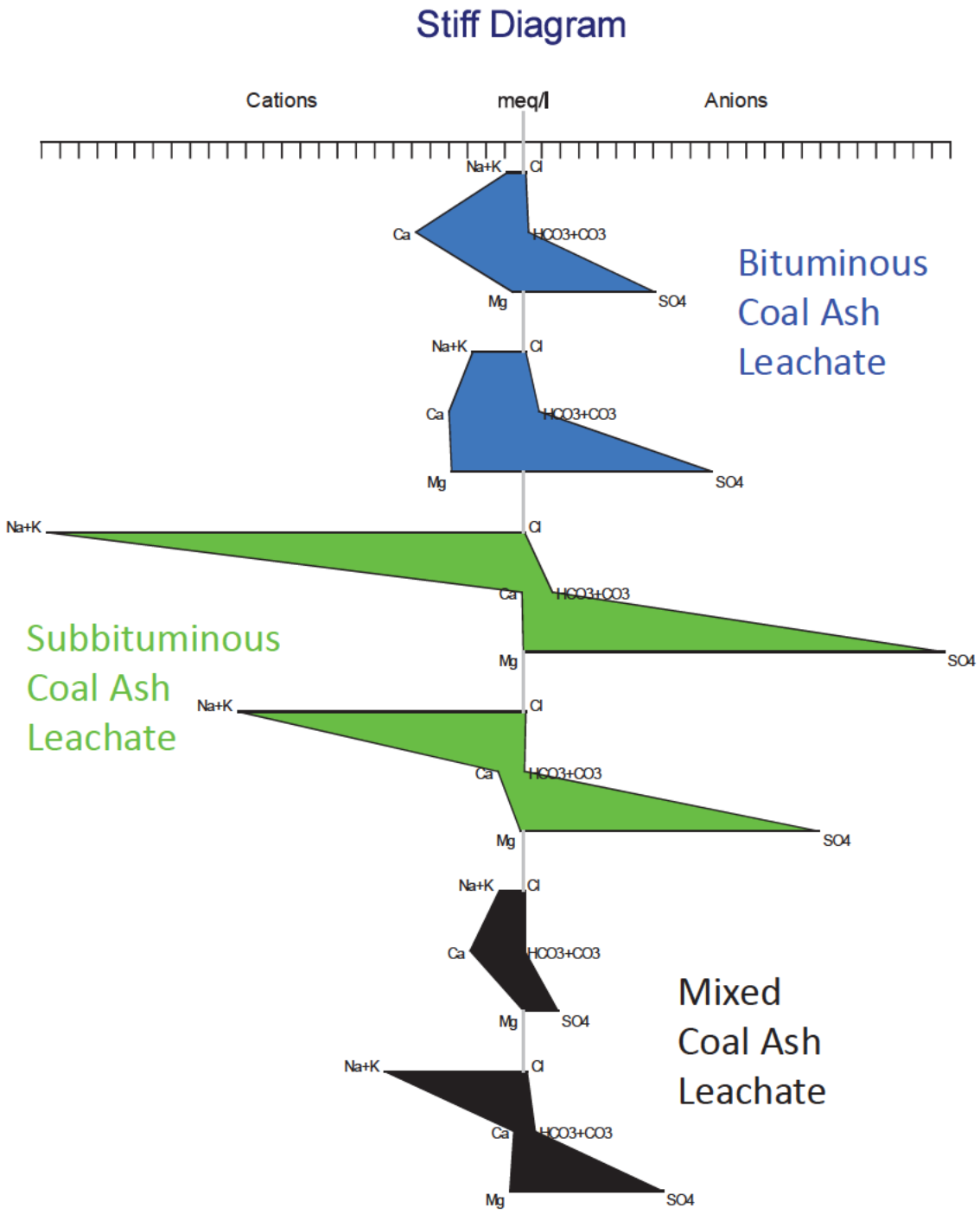


Figure 3-5
Stiff diagram showing six coal ash leachate samples (From EPRI, 2012)

Geochemical Modeling

Geochemical modeling is an additional Tier II geochemical method that can be used to evaluate the mobility of leachate or groundwater constituents based on chemical equilibrium and to potentially differentiate sources of groundwater contamination. Computer-assisted geochemical modeling has been used for many years to investigate the chemical equilibria of laboratory

extracts and field groundwater-leachate samples. EPRI (2017) discusses use of geochemical modeling to evaluate whether or not observed concentrations in a downgradient monitoring well can be a result of a groundwater flow path that includes mixing with CCR leachate.

Geochemical modeling can be used to identify the solid mineral phases that are controlling the solubility of dissolved cations and anions. Modeling can be used to identify whether dissolved constituents are thermodynamically favored to precipitate or remain in solution. Kinetic modeling attempts to identify the rate of chemical reactions. Such information is potentially useful for predicting the fate of dissolved constituents in a timeframe beyond the monitoring period. Kinetic modeling, however, may require additional information about the chemical and physical characteristics of the geomedia of the area under study.

Use of geochemical computer models requires entry of chemical characterization data for the groundwater sample(s) being evaluated. Analytical data, such as total sulfate or boron, are entered into the model, which will estimate the concentrations of several ionic forms (speciation) of each parameter. The model then calculates the degree of saturation of the liquid sample for hundreds of solid mineral phases. For example, if the liquid sample appears to be supersaturated with respect to a specific mineral, then that mineral is thermodynamically poised to precipitate from solution. Chemical precipitation may limit the movement of CCR constituents off-site.

The data required for chemical modeling are more extensive than those typically collected during a groundwater monitoring program. Most geochemical models require data for pH, ORP, alkalinity, and all the major anions and cations to ensure that the liquid sample is electrically balanced. In addition, solids data are often collected and used in the model to enhance confidence in results.

Multivariate Statistics

Multivariate statistics encompasses statistical analysis methods for evaluating more than two variables simultaneously and to determine how those variables relate to each other. Multivariate statistical techniques can be paired with geochemical modeling to determine the main sources of groundwater impacts in an aquifer, whether from a CCR leachate source, a naturally occurring source, or an anthropogenic source. Hydrogeological factors can also be co-evaluated with water quality data, including isotopic data from Tier III evaluations, using multivariate statistical methods. Although multivariate statistics is a powerful analysis tool for evaluating more complex datasets, it requires robust datasets, an experienced statistician, and a conceptual understanding of the input variables and their potential correlations. Computer software to perform multivariate statistical analysis relevant to environmental data is readily available.

Multivariate statistical methods utilized in the environmental field are typically correlation analysis, principal components analysis (PCA), and cluster analysis (CA). However, there are numerous other statistical methods available. Detailed explanations of the various multivariate methods available for statistical analysis are found in the following references:

- Anderson, T.W., 2003. An Introduction to Multivariate Statistical Analysis, Third Edition, John Wiley and Sons, Inc.
- Johnson, T.W. and D.W. Wichern, 2007. Applied Multivariate Statistical Analysis, Sixth Edition, Pearson Prentice Hall.

The scientific objectives identified by Johnson and Wichern (2007) for which multivariate statistics might be used include the following:

- **Data reduction or structural simplification**. To represent the information or conceptual model as simply as possible to aid in interpretation.
- **Sorting and grouping**. Groups of similar objects or variables are created based upon measured characteristics.
- **Investigation of dependence among variables**. Relationships between variables are evaluated to determine which variables might be independent and what two or more variables are dependent. From that information, the investigator might determine how the variables are related or what factor or feature they are related to.
- **Prediction**. Predicting the values of one or more variables based on observations of other variables. This is not a typical objective for an ASD evaluation.
- **Hypothesis construction and testing**. Testing of statistical hypotheses about multivariate populations to validate assumptions or reinforce other lines of evidence.

A brief description of a few of the more commonly used multivariate statistical methods pertinent to evaluation of groundwater and hydrogeologic data during an ASD is provided here, with the caveat that there are numerous other methods available.

Correlation Analysis can be performed on multiple variables, such as water quality constituents, to determine how much the variance of each constituent can be explained by the relationship with other constituents. Table 3-3 shows the Pearson product moment correlation matrix between pairs of variables measured in groundwater in background monitoring wells at a site. The correlation coefficients range between -1 and 1 and measure the strength of the linear relationship between the variables. The number of pairs of data values used to compute each coefficient was 60 (6 observations of each chemical parameter in groundwater per well for 10 wells). In the case of this dataset, correlations greater than 0.50 or less than -0.50 indicate statistically significant non-zero correlations at the 95 percent confidence level. Positive numbers indicate that the parameters are directly proportional, and negative numbers indicate that the parameters are inversely proportional. Bold-face numbers within highlighted boxes in the sample table indicate a high level of correlation between two parameters. Typically, correlation coefficients are rated as “high”, “medium”, and “low” (or “strong”, “moderate”, and “weak”) for values > 0.75, 0.75 to 0.50, and 0.50 to 0.30, respectively.

Table 3-3
Example Correlation Analysis Table

	Boron	Barium	Calcium	Chloride	Iron	Potassium	Lithium	Magnesium	Manganese	Sodium	Sulfate	TDS
Boron		0.13	-0.20	0.65	-0.02	0.25	0.47	-0.10	-0.04	0.63	-0.19	0.61
Barium			-0.11	0.77	**0.87**	0.38	0.28	-0.04	-0.16	0.73	-0.23	0.72
Calcium				-0.30	0.06	0.18	0.01	**0.98**	**0.81**	-0.34	**0.86**	0.00
Chloride					0.55	0.32	0.48	-0.17	-0.23	**0.94**	-0.37	**0.88**
Iron						0.40	0.31	0.11	0.10	0.58	0.06	0.62
Potassium							0.67	0.15	0.07	0.37	0.06	0.42
Lithium								0.05	0.08	0.45	-0.08	0.47
Magnesium									**0.86**	-0.21	**0.86**	0.14
Manganese										-0.18	**0.91**	0.15
Sodium											-0.29	**0.93**
Sulfate												0.01
TDS												

Principal Components Analysis (PCA) is used to reduce data to a small number of significant factors (i.e., components) for analyzing relationships among variables. PCA can be performed to evaluate the spatial variations of groundwater quality data and determine possible sources of specific contaminants. An analysis of principal components may reveal relationships between variables that were not readily apparent or suspected (Johnson and Wichern, 2007), or may assist in removing variables from an analysis that have no bearing on the objectives of an investigation. PCA analysis may serve as an intermediate step to determining what factors to focus on in an investigation and to assist in developing multiple lines of evidence in an ASD.

Cluster Analysis (CA) is a descriptive statistical analysis method used to identify groupings (i.e., clusters) of samples or other variables. CA is used to reveal the latent structure within a data set and is an exploratory tool only. For example, the data from a site can be analyzed using cluster analysis to demonstrate the following:

- Groupings of samples from wells into clusters based on water quality as defined by the major cations and anions
- Groupings of samples from wells into clusters based on water quality of minor and trace elements
- Groupings of wells into clusters based on selected water quality parameters and/or hydrogeologic variables

CA analysis results can be presented in several ways. To visually interpret how the data have been categorized, a graphical depiction of the clusters can be shown with a dendrogram. The dendrogram is a linkage tree that first links those samples or parameters that have the greatest similarity. Each subsequent linkage (or cluster) is less similar than earlier linkages. The greater the distance on the y-axis between linkages, the lower the significance between the linked samples or variables. In the example dendrogram displayed below (Figure 3-6), the first clusters of trace elements in groundwater upgradient from a CCR unit are between barium and iron, and the next cluster is aluminum and lithium. The correlation coefficient {R} calculated for barium and iron is strong at R = 0.87. The R value for aluminum and lithium is moderate at 0.63. Next, barium-iron is clustered with strontium (R = 0.54 and 0.56, respectively) and aluminum-lithium

is clustered with boron (R = -0.02 and 0.47, respectively). Manganese concentrations in groundwater at the study site are very poorly correlated with all the other minor/trace elements, and there is no cluster formed with any other parameters.

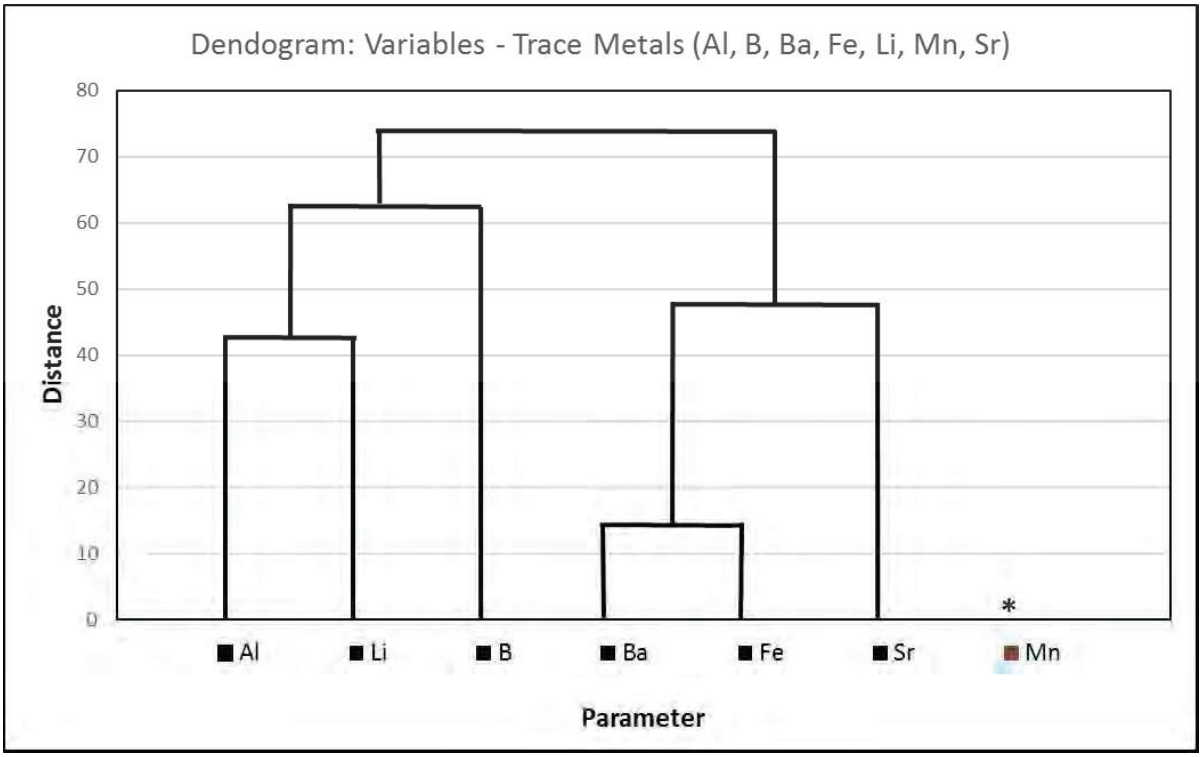


Figure 3-6
Example Cluster analysis dendrogram

Tier III Evaluation – Isotopic Analyses

Tier III uses isotopic analyses as a method to determine a groundwater signature. As described in EPRI (2017), isotopes have the same number of protons, but each form has a different number of neutrons. Because of this difference in atomic mass (neutrons plus protons), the isotopes will react differently with geomedia as they migrate in groundwater. These differences can be expressed as isotopic ratios, and can be used as diagnostic tools.

The application of isotopes as groundwater signatures is a relatively new technique, but boron isotopes are particularly relevant to CCR. Boron-11 is heavier than boron-10, and the heavier isotope is preferentially precipitated or sorbed from solution. Changes in the ratio of these two isotopes can yield information about the source of boron in the groundwater. Available data suggest that CCR leachate is often isotopically light, while groundwater may be isotopically heavy. Other isotopes that may be useful include strontium, oxygen, and hydrogen. EPRI (2012 and 2017) provides a comprehensive review on the use of boron and selected other isotopes as groundwater signatures.

Another form of isotopic analysis is tritium age dating. As discussed in EPRI (2017), tritium has a relatively short half-life of 12.3 years. Furthermore, there was an accumulation of tritium in the atmosphere in the early 1960s due to atmospheric atomic bomb testing. These two observations

enable use of tritium data to determine whether or not groundwater recharged prior to atmospheric testing of atomic bombs (i.e., prior to the 1960s) or since that time. If a CCR site was built during or after the 1960s, but the groundwater does not have detectable levels of tritium (meaning it recharged prior to the 1960s), that provides a line of evidence that an SSI/SSL is not due to a release from that site because the leachate from such a site would have detectable levels of tritium that should be evident in the downgradient groundwater.[7]

Hydrogeologic Scenario Evaluation

Hydrogeologic scenario evaluation is another line of evidence that can be used in an ASD. The premise is that if a mobile and non-reactive constituent is released to groundwater, it will travel in groundwater with a predictable concentration profile unless mixed with water from other sources that have significantly different concentrations of the same constituent. Following the ion ratio approach discussed above, the downgradient concentration of the mobile, non-reactive constituent of concern should be proportional to the mixing ratio of the relative volumes and concentrations of all sources combined and collected at the downgradient monitoring point.

Figure 3-7 presents a variety of hydrogeologic scenarios comparing leachate concentration of a mobile, non-reactive constituent to the concentrations observed in upgradient and downgradient wells. Groundwater flow directions are also considered to point out that some downgradient monitoring wells may be in a side-gradient or partial intercept path rather than in the direct path of the monitored upgradient groundwater. Each column in Figure 3-7 presents two to three hydrogeologic scenarios as follows:

- Column 1 – Scenarios providing a line of evidence that a CCR facility is the source of an SSI/SSL.
- Column 2 – Scenarios providing a line of evidence that both a CCR facility and a possible alternative source are the source of an SSI/SSL.
- Column 3 – Scenarios providing a line of evidence that an alternative source is causing an SSI/SSL.

The basis for these scenarios is fairly straightforward:[8]

- If leachate concentration is less than background, leachate cannot cause downgradient concentrations to be higher than background, and an alternative source is indicated.
- If downgradient concentrations are greater than leachate concentrations, an alternative source (natural or anthropogenic) must be present.

These scenarios, particularly those shown in columns 2 and 3 of Figure 3-7, demonstrate the benefit of multiple upgradient monitoring wells. This benefit is also realized for intrawell statistical programs if there is any potential for naturally occurring or anthropogenic changes in groundwater quality upgradient of the monitored unit.

[7] This line of evidence may not be valid in the case of a pond where "old" groundwater, for example from a deep aquifer, was used for sluice water.

[8] Assuming that leachate and background concentrations are well-characterized.

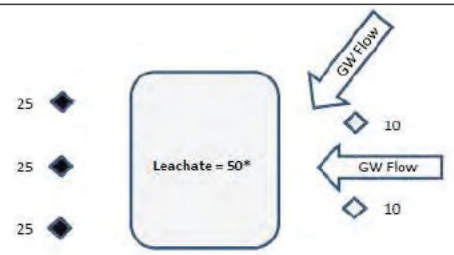
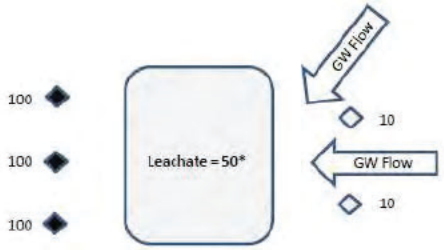
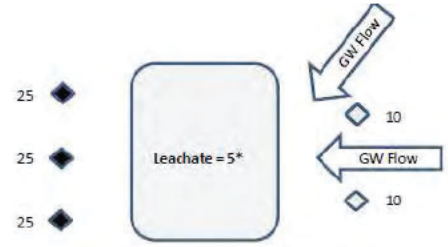
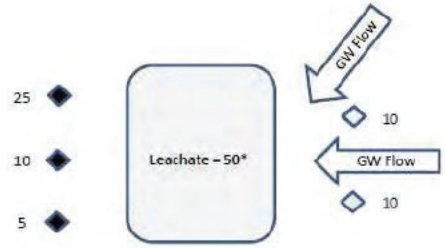
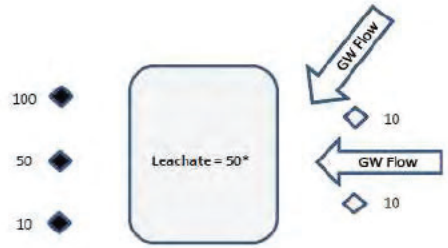
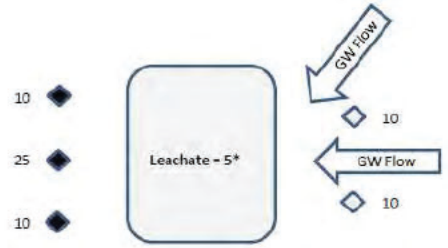
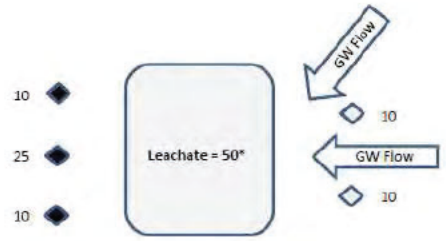
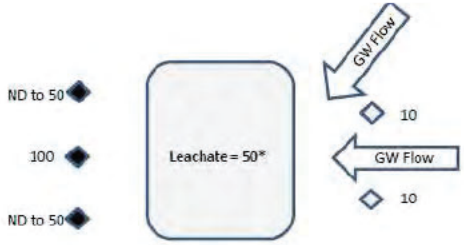
Line of Evidence for:			
	CCR Leachate Release	**Possible CCR Leachate Release + Possible Alternative Source**	**Alternative Source Release**
	Column 1	**Column 2**	**Column 3**
Row a			
Row b			
Row c			
	1. Leachate concentration is higher than upgradient/background. 2. One or more downgradient concentrations are higher than upgradient/background but lower or equal to leachate concentration.	1. Leachate concentration is higher than upgradient/background. 2. One or more downgradient concentrations are higher than the leachate concentration.	1. Leachate concentration is less than upgradient/background.

Figure 3-7
Example hydrogeologic lines of evidence

Time-of-Travel Evaluation

Time-of-travel for a mobile and non-reactive source constituent to a downgradient monitoring well can also be considered as a potential line of evidence for connecting a source to an elevated result at a downgradient monitoring location. It takes time for a source constituent to travel downward to reach the aquifer and then travel within the aquifer to the downgradient monitoring location. For example, if groundwater velocity is 50 ft/year, assuming minimal dispersion, it would take about two years for a release to reach a monitoring well 100 feet from the waste boundary *if* the release occurred at the waste boundary, and *assuming* a relatively thin unsaturated zone. It would take more than two years if the release occurred toward the center of the facility as opposed to the waste boundary of a lined facility, or if there was a thick unsaturated zone. Since the permeability of different geological media such as sand, gravel, clay, silt, and fractured bedrock can vary considerably, time-of-travel evaluation requires knowledge of site and regional hydrogeology. If this information is available, it can be used to identify or discredit potential sources. Horizontal groundwater flow velocity through a uniform (homogeneous) water-bearing unit with no preferential flow direction (i.e., anisotropic), is calculated as follows:

$$V = K i / n_e$$

V = Groundwater Velocity
K = Hydraulic Conductivity
i = Hydraulic Gradient (unitless value)
n_e = Effective Porosity

Simple analytical models such as MYGRT (EPRI, 2005), or more advanced fate and transport models, can also be used for this evaluation. Models can account for dispersivity, which is not accounted for in the equation above.

4
NATURAL VARIATION

Natural variation encompasses natural variation in background levels and variability due to geologic influences such as dissolution of geomedia and natural ion exchange, changes in groundwater quality and/or flow related to precipitation such as changing water levels in monitoring wells, groundwater recharge and discharge fluctuations near surface water bodies, and time-of-travel for monitoring wells to detect upgradient changes, as well as influences related to changes in pH, oxidation reduction potential, and biological activity. These interactions, and how they may affect groundwater quality, are discussed below.

Changes in Mineralogy Along a Groundwater Flow Path

The mineralogy of soils and rocks near the monitored CCR unit can affect the natural chemistry of groundwater. For example:

- Geomedia such as limestones and certain sand units that are rich in carbonates can add calcium to the groundwater.
- Geomedia with little carbonates lack buffering capability that can enable changes in chemistry if low-pH recharge from precipitation reduces the overall pH of the aquifer along the flow path.
- Geomedia that contain reactive clay minerals can alter the chemical composition of groundwater by dissolution-precipitation reactions, and by either removing (by sorption) or adding (by desorption) solutes along the flow path.

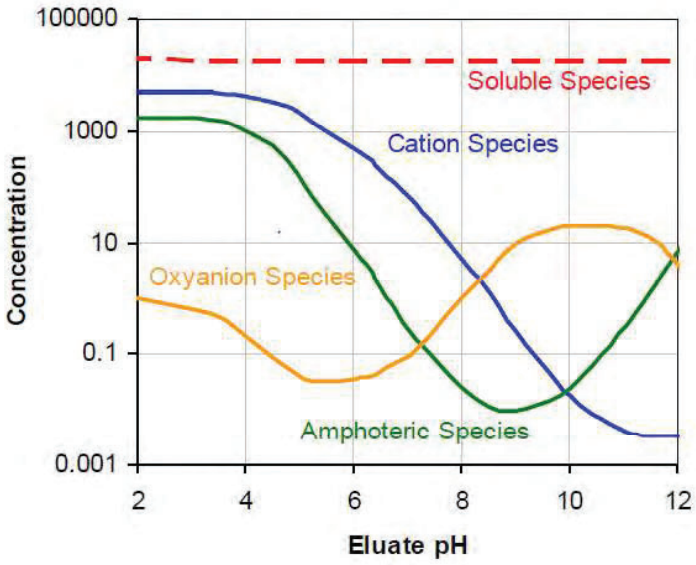
The extent of the reactions can be pH-dependent, which may depend on changes in mineralogy. These examples underscore the importance of placing background monitoring wells in the same geomedia as compliance monitoring wells. If background and compliance wells are in different geomedia,[9] then SSIs/SSLs due to this natural variation and unrelated to a release from the facility are possible, and even likely. An ASD in this case would highlight the mineralogical differences between the geomedia and constituents expected to be affected.

Changes in pH Along a Flow Path or over Time

If pH is different between background and compliance wells, and/or changes over time, it can cause chemical changes capable of triggering an SSI/SSL. Examples of concentration changes that can occur due to a change in pH are illustrated in Figure 4-1 and the text that follows. For the purposes of an ASD, if there is an SSI/SSL at a monitoring well where pH is different from

[9] It is not always possible to screen background wells in the same geomedia as compliance wells. In these cases, intrawell statistical analysis can avoid this form of natural variation; however, intrawell analysis may not be an option in certain detection monitoring plans if monitoring wells have already been affected by a release.

or has changed from background (SSI) or baseline (SSL), and the constituent with the SSI/SSL is sensitive to changes in pH, then the pH difference can be a line of evidence in an ASD.



Soluble Species: Sodium, potassium, chloride, boron, sulfate. Solubility is high and not dependent on pH.
Cation Species: Iron. Solubility is high at low pH and decreases with increasing pH.
Oxyanion Species: Arsenic, selenium, molybdenum. Solubility is characterized by pH dependent curves. Solubility is typically at a minimum at near neutral to slightly acidic pH range and at a maximum at near neutral to slightly alkaline pH.
Amphoteric Species: Aluminum, lead, copper. Solubility curve is similar to the cation species curve, but with a distinct low solubility range with higher solubility at lower and higher pH ranges.

Figure 4-1
Typical solubility behavior of various constituents as pH changes (EPRI, 2007)

Soluble species such as sodium, potassium, chloride, boron, and sulfate tend to have relatively high solubility that is not affected by changes in pH. Cation species such as iron usually have higher solubility at low pH and minimum solubility at high pH.

Oxyanion species include elements such as arsenic, selenium, and molybdenum that react with oxygen or hydroxide to form anions. The solubility of oxyanion species varies with pH and often ORP because their chemical form changes as these two variables change. For example, the specific form of arsenic in solution depends on both pH and ORP. Under highly alkaline conditions (pH > 11), the dominant form of arsenic is AsO_4^{3-}. In relatively acidic groundwater (pH < 7), the dominant form is $H_2AsO_4^-$ under oxidized conditions, and $As(OH)_3$ under reduced conditions. The solubility curves of oxyanions characteristically have minimum solubility at near neutral to slightly acidic pH and maximum solubility at slightly alkaline pH.

Amphoteric species such as aluminum, lead, and copper have solubility curves similar to the cation species; however, they typically exhibit a range of minimum solubility, with higher solubility at lower and higher pH ranges.

Changes in Redox

Similar to a change in pH, a change in the redox state of the groundwater can have a significant impact on the concentration of some constituents in groundwater. If there is an SSI/SSL at a monitoring well where there is indication that redox is different from or has changed from background (SSI) or baseline (SSL), and the constituent with the SSI/SSL is sensitive to changes in redox, then the redox change can be a line of evidence in an ASD (Figure 4-2).

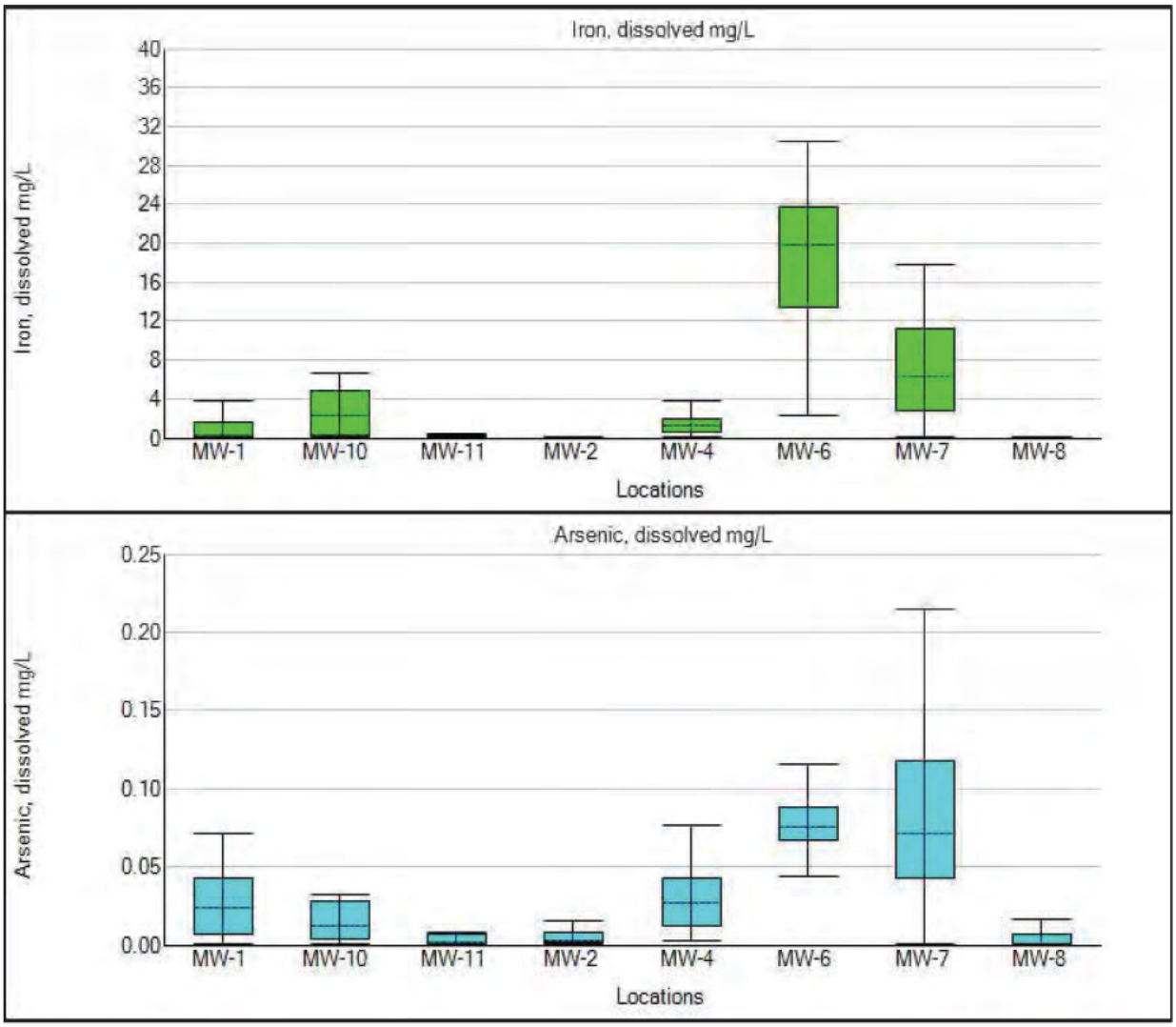


Figure 4-2
Example ASD line of evidence where elevated arsenic concentrations occur in monitoring wells with elevated iron, indicative of reduced conditions

The term redox refers to reduction-oxidation. Oxidation is the loss of electrons or an increase in the oxidation state of an ion or molecule. Reduction is the gain of electrons or a decrease in the oxidation state of an ion or molecule. In a more practical sense, the redox potential of groundwater reflects the dissolved oxygen content. Oxic water has higher levels of oxygen—if an element has multiple oxidation states in groundwater, then the species with a higher electrical charge will be prevalent in an oxic environment. Reduced groundwater typically has low dissolved oxygen content—the species with a lower electrical charge will be prevalent in a reduced environment. Redox potential, Eh, ORP, and pE are all measures of redox state. In addition, concentrations of iron and manganese can be used as indicators of redox state in groundwater because these constituents tend to have low concentration in oxic groundwater and high concentration in reduced groundwater.

Examples of redox-sensitive constituents include, but are not limited to the following:

- Naturally occurring sulfide minerals in reduced soils may form soluble sulfate if exposed to oxygen—which can occur when a monitoring well is installed, resulting in a naturally occurring increase in sulfate concentration in that monitoring well. Conversely, under strongly reducing conditions, sulfur in groundwater can convert from sulfate to hydrogen sulfide gas, with a corresponding reduction in sulfate concentration.
- Under oxidized conditions, arsenic in groundwater occurs in the 5+ oxidation state as arsenate (AsO_4^{3-}), but under reducing conditions it occurs in the 3+ oxidation state as arsenite (AsO_3^{3-}) and is more soluble and mobile. It is not uncommon to see naturally occurring arsenic in reduced groundwater. Conversely, if arsenic-containing sulfide minerals are present in an aquifer under reduced conditions, introduction of oxygen, for example by installing a monitoring well, can result in release of arsenic to groundwater in the vicinity of the monitoring well.
- The solubility and speciation of selenium in groundwater is dependent on the pH and ORP of the solution. In highly oxidized solutions, selenium exists as highly mobile selenate. Over a relatively large range in pH and ORP, selenium occurs in the selenite forms as $HSeO_3^-$ and SeO_3^{2-}. Under oxygen-poor conditions, the concentration of selenium in groundwater (as HSe^-) may be controlled by the solubility of ferroselite ($FeSe_2$). Because anionic selenium is the dominant form of the element in groundwater, sorption may not be significant by many types of geologic media.
- Boron, molybdenum, lithium, and cobalt concentrations are not significantly impacted by the range of redox commonly observed in groundwater.

Influence of Biological Activity

The potential for biologically mediated chemical reactions should not be overlooked. Some of the redox reactions described above, particularly release of naturally occurring arsenic, can be biologically mediated. For example, when pyrite (ferrous sulfide) deposits (commonly present in coal) are exposed to air by mining operations, oxidation and release of ferric iron, sulfate, and sulfuric acid can be accelerated by bacteria that thrive in a low-pH sulfuric acid environment, accelerating the reaction and increasing the release of sulfuric acid and other minerals present in the geomedia that are more soluble in low pH and/or oxidizing environments, such as arsenic. Another example of natural microbial redox activity in geomedia is oxidation of ammonia nitrogen to nitrate and/or nitrite compounds. As discussed in Section 5, the presence of ammonia, nitrate, or nitrite in CCR monitoring wells is typically related to agricultural activities; however, it may also be due to leaching of ammonia compounds deposited on fly ash or FGD solids due to the use of ammonia in selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) emission control technology for reduction of nitrogen oxide emissions.

Changes in Groundwater Elevation at Compliance Wells

In some cases, groundwater can be naturally stratified, for example if shallow groundwater is oxic and deeper groundwater is reduced. Stratification may also occur near groundwater discharge points where upwelling of deep groundwater, which may have higher dissolved solids content than shallow groundwater, may be occurring. Stratification is also common near oceans

where saltwater wedges form beneath fresh water due to the higher density of seawater. When there is a natural stratification of groundwater quality, changes in groundwater elevation can trigger a naturally occurring SSI/SSL if the deeper water rises and intersects the monitoring well screen.

Such changes in groundwater elevation can be due to precipitation/recharge events, or changes in elevation at nearby groundwater discharge points such as rivers (which can also affect flow direction as described next). Changing groundwater elevation can be a line of evidence for an ASD if there is evidence that the groundwater is naturally stratified. A hydrograph showing a change in groundwater elevation (up or down) that corresponds with the SSI/SSL may be useful in supporting this cause.

Changes in Groundwater Flow Direction at Compliance Wells

Groundwater flow direction naturally exhibits variability. For many sites, this variability may not be significant; however for some sites, flow direction can vary by as much as 180 degrees. Inland locations may have relatively narrow ranges of variability, such that groundwater flow is usually in one broad direction. Sites along rivers can exhibit very large ranges of variability, including complete flow reversals, that are dependent on river stage. Much of this variability will be accounted for during the background monitoring period. However, if the background monitoring was performed during a period of little variation, or if there is an extreme hydrologic event such as a 100-year (or larger) flood, then groundwater flow can change in a way that was not accounted for during the background monitoring period, and if there is aerial variability in groundwater chemistry, then this change in flow direction can trigger an SSI/SSL due to natural variation in groundwater flow direction.

If groundwater flow direction at the time of, or prior to, sampling for an SSI/SSL is different than flow directions that occurred during the background monitoring period, then that is a line of evidence for a naturally occurring ASD. Groundwater flow direction is not typically monitored between sampling events, so a change in flow direction prior to a sampling event may need to be demonstrated based on indirect evidence such as river hydrographs showing that a particular river stage was not representative of the background monitoring period.

Another ASD consideration with changes in groundwater flow direction is detection of an alternative anthropogenic source that had not previously been detected. While the cause of the SSI/SSL in this case is not natural variation, the detection of the alternative source is due to natural variation.

Time-of-Travel Consideration for Natural Variation

As noted in Section 3, there will be a time lag between the time that a change in concentration affects background groundwater and when that same change is detected in downgradient groundwater. Just as it takes time for somebody to walk from point A to point B, it takes time for water to travel through geomedia. Methods for calculating that time lag are presented at the end of Section 3.

If a change in concentration is noted at an upgradient monitoring location, and a similar change at a downgradient well triggers an SSI/SSL at a later date, then a line of evidence for an ASD can be developed if it can be demonstrated that the detected constituents are the same as detected in

the upgradient well, and the time lag is consistent with groundwater velocity between the upgradient and downgradient locations.

This line of evidence applies to both natural variability and upgradient anthropogenic sources. A natural variability example would be a case where pH changes in groundwater chemistry affect upgradient locations before downgradient locations.

5
ANTHROPOGENIC IMPACTS TO GROUNDWATER

When considering alternative sources that may be contributing to an SSI/SSL, it is important to investigate the site and surrounding area for current and historical land uses. Mapping descriptions and locations of current and historical land uses near the CCR unit, along with groundwater flow direction and locations of surface water bodies, can narrow the list of likely alternative anthropogenic sources and identify constituents to look for that may point to an alternative source (Figure 5-1).

If the CCR unit is on or near a power plant, note the past and current locations of coal piles, impoundments, landfills, underground and aboveground oil storage tanks, known oil and chemical spill areas, CCR transport routes (i.e., haul roads and sluice lines) and processing areas, and areas where ash or other fill material has been used as structural fill. This information may help identify on-site activities that may be contributing to an SSI/SSL.

Understanding the area surrounding the CCR unit can guide the ASD investigation, because the groundwater signature often reflects the combined local land uses. Land uses and/or features that may be near coal-fired power plants are discussed below. Tables A-3 and A-4 in Appendix A list activities that can affect the groundwater concentrations of constituents monitored at CCR management facilities by constituent and by activity, respectively.[10]

[10] Tables A-3 and A-4 are also presented in Section 2 as Tables 2-2 and 2-3.

Figure 5-1
Examples of anthropogenic activities near a CCR unit with potential to affect groundwater quality in one or more monitoring wells, depending on the direction and variability of groundwater flow.

Power Plant Land Use and Operations

Power plant operations including other CCR impoundments and landfills, as well as historical land uses, can be reviewed as potential alternative sources, depending on their location relative to groundwater flow at the CCR unit with the SSI/SSL and the water quality signature. Areas to evaluate during the ASD include areas of coal or coal ash spillage, coal piles and coal pile runoff conveyance structures, underground storage tanks, underground piping, locations of past chemical spills, and other CCR management facilities.

Preparation of subgrades to achieve favorable power plant building conditions may have required low areas to be filled with structural fill. Historical requirements for fill material were not as strict as current standards for leachability and therefore, materials such as fly ash, bottom ash, construction debris, demolition debris, dredge spoils, and/or incinerator residue may have been used as fill material, particularly at older power plant sites. If these types of materials are present, they may contribute leachate to groundwater from random, non-point source locations. If historical fill practices are a potential concern, consider researching fill locations and material types and quality by reviewing historical fill maps and aerial photographs, reviewing historical fill records with sampling data and/or fill material descriptions, reviewing information available on neighboring properties, and interviewing knowledgeable persons and neighbors.

Historical ash management practices may have included on-site use of fly ash and/or bottom ash for fill, road base, berm construction, and other structural applications. Ash may also have been piled in various areas for dewatering or temporary storage or transfer to trucks. Former ash ponds and/or landfills may have been covered and closed on-site, or may have a residual contribution to groundwater contamination.

Current or past ash handling practices may also have allowed for dispersion of ash and subsequent accumulation in plant sumps, storm water swales and ponds, and other low-lying areas. In particular, wind-blown ash may accumulate in ditches, or leachate sprayed for dust control on an active landfill face may be blown off the lined area where it can infiltrate. Such conditions can contribute to localized, elevated groundwater concentrations with ash leachate signatures. It is important to be aware of these activities and their locations because their presence can result in SSIs/SSLs, but from sources other than a release from the liner/base of the monitored CCR unit.

Contaminants from underground storage tank (UST) leaks, aboveground tank and transformer leaks, underground oil piping leaks, or oil and/or chemical spills may also cause groundwater impacts, the extent of which depends on the severity and duration of the leak or spill. Oil-based contamination primarily involves organic constituents; however, trace elements may also be of concern. For example, biological activity associated with a petroleum plume may result in biologically mediated arsenic release from minerals in the aquifer. Therefore, it is important to be aware of site history as it relates to major oil and chemical spills, and UST and underground piping leaks in case these issues may potentially be impacting CCR monitoring.

If an on-site anthropogenic source is suspected, consider testing for additional analytes such as organics (to diagnose oil-related contamination), and/or all major ions to enable use of Tier II geochemical analysis to help determine similarity and source of groundwater collected at the monitoring wells. Other constituents such as aluminum, iron, and manganese may also be helpful in fingerprinting potential alternative power-plant-related groundwater impacts. Perhaps most

importantly, knowledge of site history can be very helpful in determining whether or not alternative plant-related sources are positioned upgradient of wells where an SSI/SSL was determined.

Agricultural Activities

If the CCR unit is located in an area with upgradient farmlands or livestock, then groundwater impacts associated with these agricultural activities can be evaluated for an ASD. Agricultural impacts to groundwater are possible due to its prevalence and the use of irrigation water, fertilizers, and pesticides to support optimal plant growth. The most common constituents of concern include nitrogen compounds (nitrate, nitrite, and ammonium) and phosphorus compounds associated with fertilizers, runoff from animal feedlots, and the use of manure for crop fertilization; however, other inorganic constituents may also come from agricultural sources (refer to Table A-4).

Relatively high levels of nitrate, nitrite, and/or ammonium ions in groundwater are indicators of agricultural impacts. Consider analyzing for these constituents, particularly in upgradient wells, if groundwater degradation from surrounding agriculture is possible.

If the power plant that produced the CCR utilizes SCR or SNCR technology, ammonia compounds may have adsorbed onto the ash (usually as ammonium bisulfate or ammonium sulfate) and may subsequently be released to groundwater as ammonium ions. Biological activity may convert the ammonium ions into nitrate and/or nitrite. Nitrogen compounds also may occur naturally in soil due to fixation by bacteria in the root nodules of legume plants, such as soybeans and alfalfa. Therefore, when considering a potential alternative source demonstration related to nitrogen compounds, consider agricultural activities surrounding the CCR management unit, the potential for natural occurrence associated with legumes, and the processes used to produce the CCR. It may be difficult to distinguish between naturally occurring nitrates/nitrites and those present due to leaching from fertilizers, animal wastes, or ammoniated CCR. However, phosphorus is not a common constituent of CCR, so the presence of elevated concentrations of phosphorus in groundwater typically points towards agricultural sources.

In addition to nitrogen and phosphorus, agricultural activities may also contribute trace elements, salts, herbicides, pesticides, and pathogens to the groundwater. Because herbicides, pesticides, and pathogens are not monitored under the CCR Rule, they are not discussed in more detail here, but if they are known to be present, their presence indicates a source other than CCR.

Salts and trace elements may leach into groundwater as a result of agriculture, particularly in arid western regions of the United States that rely heavily on irrigation to support agricultural activity (Carter, 1980). This is particularly a concern if the native soils originated from marine mud and sediments that may contain elevated concentrations of arsenic, boron, calcium, chloride, magnesium, mercury, molybdenum, nitrate, potassium, selenium, sodium, and sulfate, and/or if the irrigation water is salty.[11] Selenium is a common constituent of concern in these environments (Fio et al., 1991). Use of salty irrigation water can result in salt deposition and the

[11] http://www.waterboards.ca.gov/waterrights/water_issues/programs/bay_delta/docs/cmnt081712/cwin/cwinappendix_a.pdf

need for increased irrigation to flush salts from the root zone of the crops, resulting in increased leaching of these salts and trace elements to the receiving groundwater. Distinguishing between agricultural sources and CCR sources may be challenging in this situation. Evaluation of nitrogen and phosphorus compounds and/or use of Tier 2 geochemical methods can be used to try to distinguish between sources. Another evaluation option in this case is analysis for boron isotopes.

Road Salting

Use of salt or salt spray for road deicing can affect groundwater quality near roads in northern climates (Kelly et al., 2009). Common types of salt used for road deicing include sodium chloride, calcium chloride, magnesium chloride, and potassium chloride. High chloride concentrations in groundwater observed during detection monitoring may be due to road salting rather than a release from the monitored facility.

Leaking Underground Pipes

In large urban areas, liquid waste including household and commercial sewage, storm water runoff, and industrial wastewater, is transported to treatment facilities in underground pipes. Under certain conditions (i.e., leaks and outward flow) this underground infrastructure may serve as conduits to transport contaminants from their original source to other areas that may be difficult to connect with the source. If the groundwater quality signature indicates an anthropogenic source, but does not resemble CCR, and no other anthropogenic source is apparent, then it may be worthwhile to investigate whether or not leakage from underground pipes is a potential alternative source.

Gasoline (Gas) Stations

Leaking underground storage tanks (LUSTs) at gas stations containing gasoline, diesel, kerosene or oil are a common source of groundwater contamination. As of March 2012, over 504,000 leaks had been recorded from federally regulated LUSTs in the United States.[12] The associated groundwater contaminants include benzene, toluene, ethylbenzene, xylene, lead, MTBE (a gasoline additive), ethylene dichloride, and naphthalene. If the gas station included a service shop, other compounds that may be released include trichloroethylene, perchloroethylene, methylene chloride, carbon tetrachloride, oils, ethylene glycol, motor oil, hydraulic fluid, detergents, and acidic solutions. These compounds are not present in CCR leachate, so their presence in groundwater indicates a source other than CCR leachate.

Septic Systems

Septic systems are potential sources of nitrate, phosphorus, chloride, organic substances, bacteria and viruses, detergents, oils, salts, septic tank cleaners such as trichloroethane or methylene chloride, and a wide variety of other chemicals.[13] These systems rely on the capacity of the native soils to attenuate, and naturally occurring microbes to digest, elements and compounds

[12] http://earthrepair.ca/resources/scenarios/gas-stations/

[13] http://infohouse.p2ric.org/ref/01/00065.htm

contained in the sewage. If improperly located, designed, constructed, or maintained these systems may fail or inadequately treat the effluent. If spaced too closely due to residential population density, these systems may exceed the capacity of the local soil to assimilate the chemical loads. High concentrations of chloride, nitrate, phosphorus, and/or sodium provide a line of evidence for an ASD for monitoring wells downgradient of areas where septic systems are used.

Mineral and Oil Extraction

Mining (Non-Coal)

Leaching from slag piles and other mining-related activities can result in groundwater quality impacts. If the background monitoring does not fully characterize these impacts, then SSIs/SSLs are possible. The water quality signatures from mining sources are highly variable depending on the substance being mined and the composition of the local soils, but common constituents include phosphates, sulfates, fluorides, and trace elements. Furthermore, if pyrite (FeS_2) was exposed to oxygen and water from the mining process, the drainage may be acidic (low pH) and have high iron and sulfate concentrations, as discussed next.

Major ion chemistry may provide a line of evidence for an ASD in this case if groundwater at the monitoring well(s) with an SSI/SSL plots in a region of the Piper diagram that is not between leachate and background groundwater. Isotopic analysis may be also considered, although unless an isotopic signature is available for the suspected mining source, it would only demonstrate that the CCR is or is not the source of an SSI/SSL. As with all potential upgradient sources, a stronger line of evidence would be installation of an intermediate monitoring well if it is possible to install such a well downgradient of the suspected mining-related source *and* upgradient or side gradient of the CCR units.

Coal Mining

The coal mining process exposes underground coal, as well as stock piles of coal and coal refuse, to oxygen and moisture, which results in oxidation of the pyrite (iron and other sulfides). The resultant leachate has high concentrations of iron and is acidic due to high concentrations of sulfuric acid. As the acidic leachate moves through the natural environment, it breaks down clay, and silicate and carbonate minerals releasing silica, aluminum, calcium, magnesium, and manganese. Concentrations of trace elements including chromium, cobalt, copper, nickel, and zinc may also increase above background levels (USEPA, 1980). The solubility of most of these elements is higher under acidic conditions. If limestone is present near the mining site, the acidic water may be neutralized by the calcium carbonate alkalinity of the limestone, and the concentrations of these elements may decrease. If the soil does not have this inherent alkalinity, the acidic water, known as acid mine drainage, may migrate from the mine site as contaminated groundwater or surface water. Mine-impacted groundwater may travel to deeper or more distant aquifers along fractures, seams, mining tunnels, and other subsurface conduits, sometimes making it difficult to trace the source.

Building an ASD where coal mining impacts are the suspected source of an SSI/SSL may require multiple lines of evidence because the water quality signatures may be only slightly different from that of groundwater mixed with CCR leachate. An obvious line of evidence for an ASD

would be the presence of a coal mine in an upgradient position. Other lines of evidence may include pH differences if the CCR leachate is alkaline, since the coal mining leachate would be expected to be acidic; absolute concentrations if it can be demonstrated that groundwater has higher concentrations for some constituents than CCR leachate; and Tier II data comparison techniques such as geochemical modeling, multivariate statistics, and/or FALCON. Isotopic analysis would need to look at more than boron and strontium, since the coal may have similar isotopic ratios, and could also include hydrogen and oxygen isotopes to build an isotopic signature.

Oil and Gas Production

Hundreds of thousands of wells have been drilled in the United States for oil and gas exploration, production, and brine disposal. Brines with high concentrations of dissolved solids are extracted with oil and gas and separated from the oil and gas at the land surface. The brines, called produced water, are stored in tanks or surface impoundments until they are disposed, often by reinjecting back into the subsurface oil and gas formation. Mechanisms for brine release include leaks from tanks, impoundments (which are usually lined but were not always lined in the past) and piping. Oil field brines may also be released to groundwater if there is a leak in the casing of an injection well. In addition, abandoned oil and gas wells can act as direct conduits for vertical oil field brine migration if the seal is incomplete or has failed. Vertical migration via abandoned oil and gas wells can occur either up or down, depending on a variety of factors. Pressure-induced upwelling of brine from depth to shallow aquifers is most relevant for ASD purposes.

Multiple lines of evidence may be available for an ASD where impacts from oil field brines are suspected. Oil field brines can have elevated boron, chloride, and other constituent concentrations. The first line of evidence would be confirmation that oil and gas production occurred in the area of the CCR unit—such areas are commonly mapped by state geological surveys. Another line of evidence is major ion chemistry, because brines have high chloride concentrations while coal ash leachate has high sulfate concentration. Brines can have much higher total dissolved solids (TDS) than CCR leachate, and depending on the level of dilution in groundwater, absolute concentrations of constituents such as barium may be higher in the monitoring well than in the CCR leachate. Ion ratios may also yield a considerably different signature than CCR leachate (Figure 5-2).

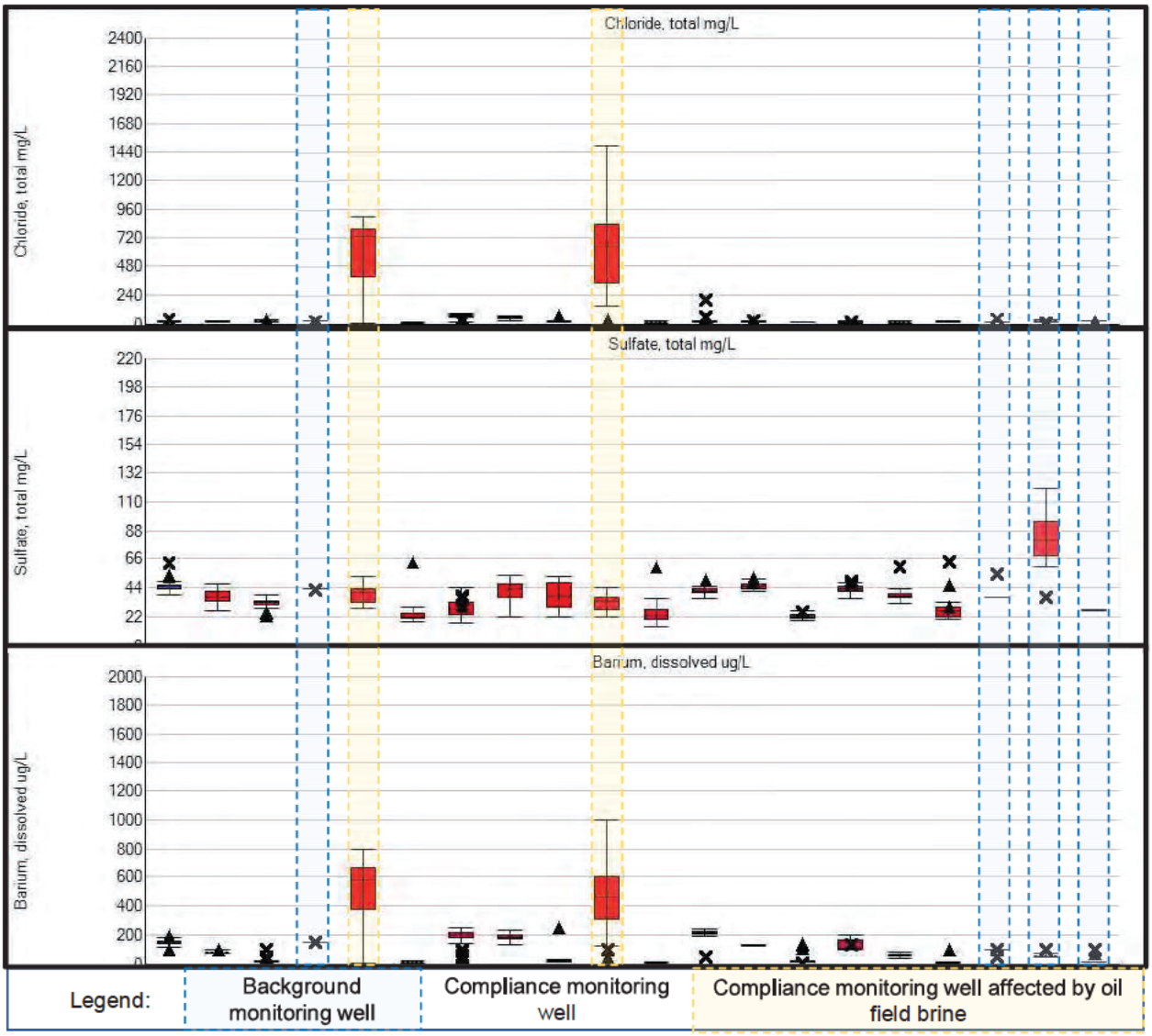


Figure 5-2
Box-whisker plots showing relatively high chloride and barium, and low sulfate concentrations, in brine-impacted groundwater monitored at a CCR management facility

Induced Salt Water Intrusion into Freshwater Aquifers

The water quality in shallow freshwater aquifers can be degraded by upwelling of deeper, naturally salty groundwater caused by heavy pumpage for anthropogenic activities such as mine dewatering, irrigation, or drinking water supplies if there is an underlying source of salt water. Salt water sources include seawater wedges and brackish groundwater that occurs naturally at depth in many areas of the United States.

Lines of evidence for an ASD based on induced pumping are similar to the lines of evidence when oil and gas brines are suspected as the cause of an SSI/SSL. First, there must be evidence for seawater or brackish water underlying the area where an SSI/SSL is observed. Additional lines of evidence can include major ion chemistry, because brackish groundwater and seawater have high chloride concentrations, while coal ash leachate has high sulfate concentration.

Brackish groundwater and seawater can also have higher TDS than CCR leachate, and depending on the level of dilution in groundwater, absolute concentrations of constituents such as barium may be higher in the monitoring well than in the CCR leachate. Ion ratios may also yield a considerably different signature than CCR leachate. Isotopic analysis could also be considered if other lines of evidence do not build a strong ASD, because boron in seawater and brines tends to be isotopically heavy ($\delta^{11}B > 0$), and boron in CCR leachate tends to be isotopically light ($\delta^{11}B < 0$) (Figure 5-3).

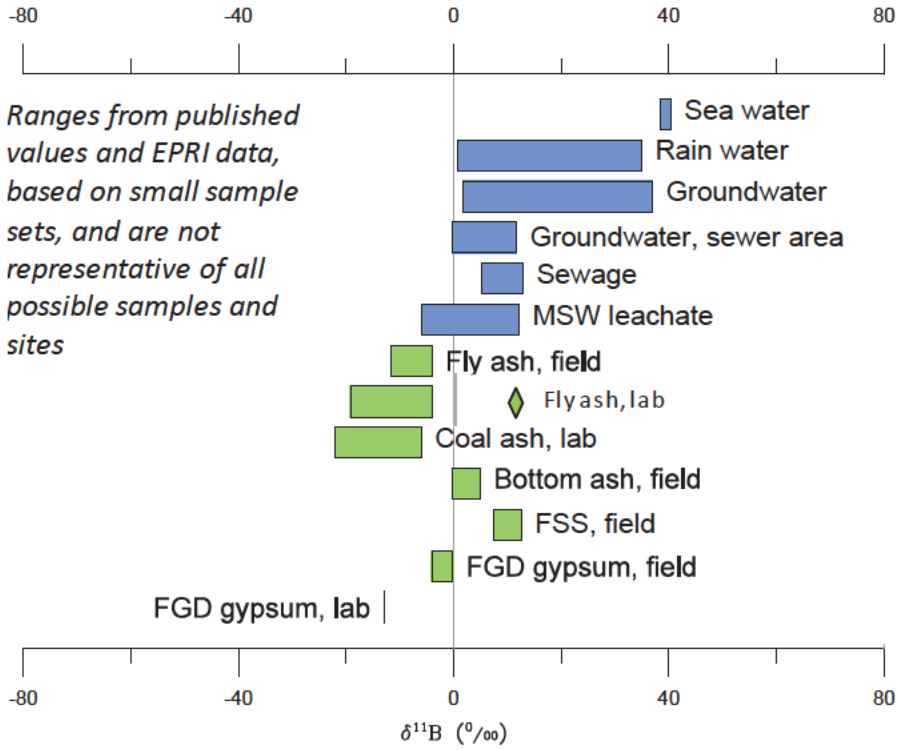


Figure 5-3
Boron isotope ranges, expressed as $\delta^{11}B$, based on EPRI (2012)

Industrial Land Use and Activities

Industrial activities produce liquid and solid waste containing a variety of inorganic constituents, organic compounds, acids, and chemicals that is too variable to cover in detail in this report. Environmental regulations now require treatment and proper disposal to prevent or minimize the risk of contamination to land and water resources, but this has not always been the case. Historical dumping, land application, seepage from unlined or poorly lined impoundments and landfills, and discharge of untreated or poorly treated waste may have contaminated the environment near areas with present or historical industrial activity.

If industrial impacts other than CCP leachate are suspected, the first line of evidence is to identify current and historical industrial activities and land use in the vicinity and upgradient of the monitored CCR unit. Identification of the types of industrial uses can help identify likely contaminants associated with these industrial activities. If these "industrial signatures" can be identified in the CCR program wells, they can be used as lines of evidence supporting an ASD.

Waste Disposal – Municipal and Industrial Landfills

State and federal regulations mandate liners and leachate collections for current landfills. However, prior to enactment and promulgation of implementing rules, waste disposal was often managed in open pits with minimal or no barriers to migration of leachate into groundwater. In the event of a release from a current or legacy solid waste landfill, potential constituents in the leachate include sodium and chloride, nitrate, organic compounds, and trace elements.

If a solid waste landfill is a suspected cause of an SSI/SSL, it may be possible to obtain leachate data from the agency that regulates the facility for use in a water quality signature evaluation. Groundwater monitoring data may also be available from the same agency, which could be used to document whether or not the solid waste landfill monitoring wells had elevated concentrations of the constituent(s) with an SSI/SSL. This assumes that the constituent is monitored at the solid waste landfill, because CCR indicators such as boron, lithium, and molybdenum are not always monitored at non-CCR sites. Otherwise, lines of evidence for an ASD can include major ion chemistry, ion ratio analysis, and perhaps isotopic analysis.

6
PREPARATION OF AN ALTERNATIVE SOURCE DEMONSTRATON

Overview

A combination of tables and checklists have been developed to guide development of an ASD. The following assumptions are inherent with this process:

- There has been an SSI, an SSL, or an exceedance of a groundwater quality standard or benchmark.[14]
- The SSI/SSL is not due to a release from the CCR unit. Note that in some situations, ASDs may apply to all SSI/SSLs at a site, for example at a lined landfill where background groundwater monitoring does not fully characterize the variability possible in groundwater quality. In other situations, ASDs may apply to some, but not all, SSIs/SSLs at a CCR unit, as may be the case for an unlined impoundment where boron and sulfate concentrations in downgradient groundwater may be elevated due to a release, while other constituents in groundwater may be due to naturally occurring or anthropogenic sources.
- ASDs based on sampling (ASD I), laboratory (ASD II), or statistical (ASD III) causes do not require a weight of evidence approach, provided that the cause is documented, or otherwise verified and defensible.
- For natural variation (ASD IV) or alternative sources (ASD V), it is assumed that there are sufficient data to build a weight of evidence case that the SSI/SSL is not due to a release from the CCR unit. If such data are not available, then the ASD process may identify additional data collection that could be used to build a stronger ASD.

The first step in an ASD is to determine if ASD Types I, II, or III explain the SSI/SSL. If not, then a weight of evidence approach is used for ASD Types IV and V. The weight of evidence approach outlined here is dependent on two types of lines of evidence (Figure 6-1):

- Key lines of evidence are based on relationships that must be observed in order for an SSI/SSL to be due to a release from a CCR unit. If these relationships are not observed, then they are critical to establishing an ASD. It is difficult to build a strong ASD without any key lines of evidence. It may be possible to build an ASD with a single key line of evidence, but the ASD will be stronger with additional key or supporting lines of evidence.
- Supporting lines of evidence provide additional information that supports the ASD. Supporting lines of evidence are generally not sufficient to build an ASD unless there is at least one key line of evidence, although it may be possible if there are many supporting lines of evidence.

[14] Throughout this document, and continuing into this chapter, this is referred to as an SSI/SSL.

		Supporting Lines of Evidence		
		None	**Few**	**Many**
Key Lines of Evidence	**None**	No ASD	Weak ASD	ASD possible
	One	Weak ASD	ASD possible	**Strong ASD**
	Multiple	ASD possible	**Strong ASD**	**Strong ASD**

Figure 6-1
Use of key and supporting lines of evidence for ASD Types IV and V

Reference tables for the ASD process are included in the text of this report, and are also provided in Appendix A for simplified reference. The ASD checklists are provided in Appendix B. Table 6-1 summarizes potential causes to consider under each of the ASD types.

Table 6-1
Potential Causes for an SSI/SSL

Sampling Causes (ASD Type I)	Laboratory Causes (ASD Type II)	Statistical Evaluation Causes (ASD Type III)	Natural Variation (ASD Type IV)	Alternative Sources (ASD Type V - Natural and Anthropogenic)
• Sample mislabeling • Contamination • Change in technique • Excessive suspended solids or turbidity • Other sampling anomalies	• Analytical method • Calibration • Analytical technique • Contamination • Interference • Recording • Dilution errors • Digestion methods	• Lack of statistical independence • Outliers • Trends • Non-detect Processing • False positives • New background data	• Geology • Precipitation • Seasonality • Water level • Changes in pH and/or ORP • Biological activity • Time of travel	• See Appendix A, Tables A-3 and A-4

ASD Evaluation Checklists

Checklist 1: ASD Types I, II, and III

The evaluation process starts with ASD Checklist 1 (Appendix B). This checklist is based on the discussion in Section 2 and lists potential sampling, laboratory, and statistical causes for an SSI/SSL. In some cases, the data record may contain sufficient information to document an ASD, but in some cases resampling may be required. If there is documentation, or a resample to demonstrate one of these types of ASD, or if there is irrefutable evidence that one of these ASDs

caused the SSI/SSL, then a weight of evidence approach is not needed. Examples of documentation and evidence include, but are not limited to:

- Laboratory reports showing qualifier flags, uncorrected dilution calculations, contamination in blanks, poor spike recovery, or other anomalies
- Field sampling notes describing difficulties or anomalies encountered while sampling
- High turbidity values in the unfiltered sample, accompanied by filtered sample showing low concentration
- Resample results showing low concentrations
- Graphs clearly showing reversed results (see Figure 2-1), or concentration spikes by a factor of 10 or more (see Figure 2-2)
- Graphs and calculations showing that new background data have triggered a change in background normality, while downgradient concentrations have not increased

If the ASD is not documented, and other evidence is not irrefutable, or if there is insufficient time for resampling, then ASD Checklist 2 could be used to build a weight of evidence approach that the SSI/SSL is not due to a release from the site.

Checklist 2: ASD Types IV and V Lines of Evidence Associated with the CCR Unit

Checklist 2 can be used to guide the evaluation of lines of evidence associated with the CCR unit. The checklist provides a template for recording answers to questions related to primary indicator constituents, secondary indicator constituents, other chemical evaluation techniques, and hydrogeological evaluation. The answers to each question can be recorded in columns that organize the evidence pointing to a release from the CCR Unit (Column A), evidence pointing to a natural or anthropogenic alternative source (Column B), or unknown or indeterminate evidence (Column C). Note that all key lines of evidence are contained in Checklist 2.

If most answers fall into Column B, and particularly if the line of evidence is identified as "key," then weight of evidence is developed that an alternative cause explains the SSI/SSL. Checklist 3 can then be used to guide further evaluation of alternative causes.

Checklist 3: ASD Types IV and V Lines of Evidence Associated with Alternative Natural and Anthropogenic Sources

Checklist 3 is designed to develop lines of evidence to identify alternative source(s) for an SSI/SSL. There are no key lines of evidence on Checklist 3. Rather, it provides for a methodical approach to documenting alternative sources if evaluation using Checklist 2 indicates that an ASD is likely.

ASD Reporting

An ASD requires both defensible lines of evidence and a well-organized presentation of the lines of evidence that clearly lead to the conclusion that the SSI/SSL is not due to a release from the monitored CCR facility. The following format, modified from one developed by Southern Company (2016), provides a viable approach for ASD documentation. Other formats may be equally effective.

Introduction and summary of the SSI/SSL

An example of language that could be used for introducing the SSI/SSL is: "Review of the statistical analysis indicates that the concentrations of the parameters were within the [specify statistical test used] limits for each constituent at each monitoring well except for the following statistically significant increases/levels (SSIs/SSLs): [List each well with SSI/SSL constituents and identify all constituents at each well location that were identified to have SSI or SSL trends.]

Cite the ASD language included in the CCR Rule (or state rule is applicable) using explicit language

For example: "40 CFR 257.94(e)(2) allows the owner or operator 90 days from the date of determination to demonstrate that a source other than the CCR unit caused the SSI or that the apparent SSI was from a source other than the CCR unit or resulted from errors in sampling, analysis, statistical evaluation, or natural variation in groundwater quality. Pursuant to 40 CFR 257.94(e)(2), the following text is provided as a demonstration that the listed SSIs are due to [identify the cause(s) applicable to the site-specific case]."

Present the ASD checklists

Identify all lines of evidence, and supporting data as needed, that the release is not from the CCR unit and is explained by alternative causes. Identify whether each line of evidence is key or supporting, and why. Also group and explain the evidence by well if multiple constituents have SSI trends at the same well(s). If the same constituent has SSI trends at multiple wells, explain how this is relevant to the ASD being presented. Include supporting data such as the checklists, maps, trend charts, geological factors, hydrogeological factors, and any geochemical data analysis tools used that support the conclusions.

Clearly state the conclusion and provide a closing statement

Example language for the closing statement if the ASD is for SSIs during detection monitoring: "The preceding information serves as the ASD prepared in accordance with 40 CFR 257.94(e)(2) and supports the position that the SSIs during [the monitoring period] are not due to a release from the CCR unit. Therefore, no further action (i.e., assessment monitoring) is warranted and [name the CCR unit] will remain in detection monitoring."

Certification by a PE (for ASDs developed under the CCR Rule)

An ASD developed under the CCR Rule requires certification by a Professional Engineer (PE). Including the PE early in the evaluation process can improve this individual's confidence in supporting the conclusions. Keep in mind that the PE may request time to review the data and the ASD report, and factor this time into schedules so that ASD compliance dates can be achieved (the demonstration must be completed and posted to the owner's CCR website within 90 days from the determination that an SSI or SSL has occurred under the CCR Rule). If the PE requires approval by a Professional Geologist (PG), ensure that a PG is also involved early in the evaluation. It may also be beneficial to develop a certification statement that passes management and legal approval.

7
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A
ASD REFERENCE TABLES

Table A-1
Potential Indicator Constituents for Coal Ash and FGD Gypsum

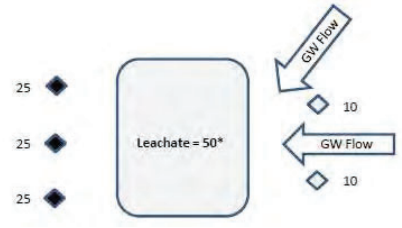
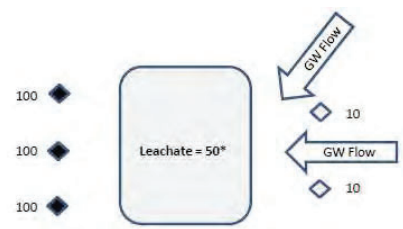
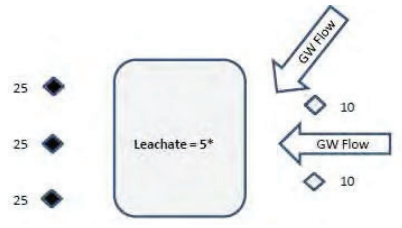
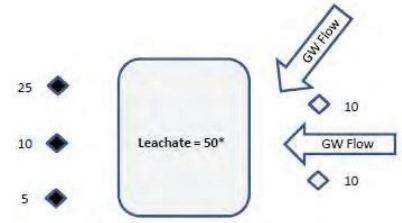
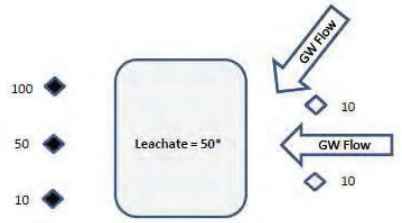
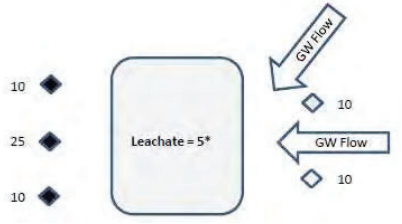
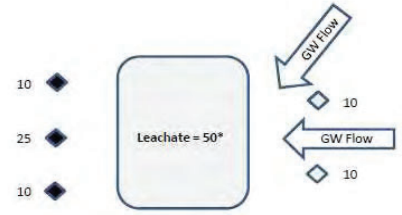
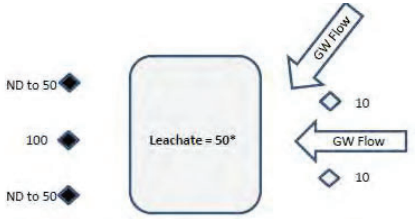
Potential Indicators for Coal Ash		Potential Indicators for FGD Gypsum	
Constituent	**Advantages and Caveats**	**Constituent**	**Advantages and Caveats**
Boron	Typically present in leachate, non-reactive and mobile in common hydrogeologic environments, and not a common anthropogenic contaminant.	Sulfate	High concentrations expected in both washed and unwashed FGD gypsum (EPRI, 2011). Commonly analyzed. Very mobile in all hydrogeologic environments. Less useful in strongly reducing environments where sulfate can be reduced to hydrogen sulfide gas.
Molybdenum	Most useful for dry-managed coal ash. May be less mobile than boron in some hydrogeologic environments. Concentrations may be too low in impoundment leachate to be useful if background groundwater has detectable concentrations.	Fluoride	Assure that leachate concentration is higher than background, particularly for washed gypsum. Mobile in common hydrogeologic environments, although precipitation as CaF_2 is possible.
Lithium	Useful for coal ash management sites where the power plant burned bituminous coal. Leachate concentrations are typically low in coal ash derived from subbituminous and lignite coal (EPRI, 2006).	Calcium	High concentrations expected in both washed and unwashed FGD gypsum (EPRI, 2011). Understanding of carbonate chemistry necessary to assure that precipitation or dissolution does not affect downgradient concentrations.
Sulfate	Commonly analyzed and very mobile in all hydrogeologic environments. Concentration in impoundment leachate may in some cases be too low relative to background to be useful. Less useful in strongly reducing environments where sulfate can be reduced to hydrogen sulfide gas.	Boron	Mobile indicator constituent for unwashed FGD gypsum. Concentrations for washed gypsum may be too low to be useful (EPRI, 2011).

Table A-1 (continued)
Potential Indicator Constituents for Coal Ash and FGD Gypsum

Potential Indicators for Coal Ash		Potential Indicators for FGD Gypsum	
Constituent	**Advantages and Caveats**	**Constituent**	**Advantages and Caveats**
Bromide	May have high concentration in coal ash leachate at power plants where brominated powdered activated carbon (Br-PAC) or calcium bromide is used for mercury control. Leachate concentrations for coal ash generated absent use of these technologies may be too low to be useful. Mobile and non-reactive in typical groundwater environments.	Bromide	Mobile indicator constituent for unwashed FGD gypsum, especially if Br-PAC or CaBr used for mercury controls. Concentrations for washed gypsum may be too low to be useful (EPRI, 2011).
Potassium	Commonly analyzed, although may be less mobile than boron and sulfate. Assure that leachate concentration is higher than background and that there are no anthropogenic sources such as agricultural fields where potassium may be applied in fertilizers.	Chloride	Mobile indicator constituent for unwashed FGD gypsum. Concentrations may be very high if transport water is recirculated. Concentrations for washed gypsum may be too low to be useful (EPRI, 2011).
Sodium	Useful for coal ash management sites where the power plant injects trona or sodium bicarbonate, or burned subbituminous coal. Absent dry sorbent injection, leachate concentrations are considerably lower in coal ash derived from bituminous coal, particularly at impoundments (EPRI, 2006). Assure that leachate concentration is higher than background and that there are no anthropogenic sources such as agricultural fields, or major highways in northern climates where sodium may be applied as road salts.		
Fluoride	Mobile and non-reactive in common hydrogeologic environments. Assure that leachate concentration is higher than background.		
Source: EPRI, 2012			

Note: This table is also presented in the body of the report as Table 3-1.

Table A-2
Hydrogeologic Scenarios

	Line of Evidence for:		
	CCR Leachate Release	**Possible CCR Leachate Release + Possible Alternative Source**	**Alternative Source Release**
	Column 1	**Column 2**	**Column 3**
Row a			
Row b			
Row c			
	1. Leachate concentration is higher than upgradient/background. 2. One or more downgradient concentrations are higher than upgradient/background but lower or equal to leachate concentration.	1. Leachate concentration is higher than upgradient/background. 2. One or more downgradient concentrations are higher than the leachate concentration.	1. Leachate concentration is less than upgradient/background.

This table is also presented in the body of the report as Figure 3-7.

Table A-3
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix III Detection Monitoring Constituents								
Boron	Key Indicator	Yes if unwashed	17 / 35 / 82 ug/L	No	Very mobile	Boron-containing rocks (especially marine shales and clays), seawater, volcanic and geothermal activities, mined in arid regions of the United States (and other countries)	Fly ash leachate, may also be present in FGD leachate; sewage sludge, boron-containing fertilizers or herbicides, manufacture of glass, fiberglass, ceramics, soaps, detergents, bleach, fire retardants, and lubricants; used in control rods of nuclear reactors, and to produce a green color in pyrotechnics and flames; also used in the aerospace industry	Micronutrient for plants but may be toxic to some plant species in high concentrations. Boron deficiencies are more common than toxicities. Mobile in most hydrogeological environments, particularly sandy materials. Sorption to clay reaches a maximum in the pH range of 8-10.
Calcium	No	Yes	21 / 43 / 70 mg/L	CEC	Slightly mobile	Calcium carbonate rocks, limestone, calcium clay; fifth most common element in Earth's crust	Water softening wastes, soil acidity neutralization (lime additions to soil), calcium road salt, deicing, agriculture, cement and concrete, drying agents	Calcium carbonate is one of the most common calcium minerals. The concentration in groundwater may be limited by the solubility of calcium carbonate or calcium sulfate (gypsum). May be sorbed by ion exchange in soil and sediments but tends to be a reversible reaction.

Table A-3 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix III Detection Monitoring Constituents								
Chloride	No	Yes if unwashed	3.1 / 8.6 / 23 mg/L	No	Very mobile	Salt water and brackish water sources; chloride anion is the most abundant element (other than hydrogen and oxygen) in Earth's oceans	Road salt, deicing, water softening wastes, sewage, septic effluent, livestock waste, oil-field brines, salt water intrusion (oil and gas well production), industrial emissions, incinerator ash, landfill leachate, aerospace industry, automobile industry, soaps and detergents, drying agents, flame retardants, flocculants, pharmaceutical and medical waste	
Fluoride	Yes for some coal ash	Yes for some FGD gypsum	<0.1 / 0.2 / 0.4 mg/L	No	Mobile	Natural weathering of fluoride-containing minerals	Steel, brick, and aluminum manufacturing; waste incineration, municipal water treatment	Occurs as fluoride anion at pH > 3, hydrofluoric acid at pH < 3. Can be sorbed by amorphous aluminum and iron oxides under strongly acidic conditions.
pH	No	No	6.9 / 7.3 / 7.6 SU	- -	- -	Oxidation/weathering of naturally occurring pyritic soils due to well installation or other excavation may cause low pH	Low pH: Oxidation/weathering of pyrite in coal or coal ash, leaking batteries High pH: Certain coal ash leachates may have high pH; cement and concrete manufacturing and use, soaps and detergents	Fly ash leachate pH may be acidic or basic depending on coal type. Bituminous coals tend to produce more acidic leachate, especially if comanaged with pyritic mill rejects, and subbituminous coals tend to produce more basic leachate. Important due to impact of pH on leachability of many trace elements.

Table A-3 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix III Detection Monitoring Constituents								
Sulfate	Yes for most coal ash	Key Indicator	4.7 / 14 / 36 mg/L	No	Very mobile	Sulfur is the 14th most abundant element in the Earth's crust; oxidation/weathering of naturally occurring pyritic soils (such as iron sulfide)	Fly ash and FGD leachate, lead acid batteries, algaecides, gypsum mines, wood pulp production (paper mills), textile mills, tanneries, coal pyrite oxidation/weathering from mining or storage, industrial emissions and effluents, soaps and detergents, drying agents, flocculants, petroleum refining	Sulfate may precipitate with calcium, barium, and strontium. Not usually sorbed due to negative charge, but can be sorbed under acidic conditions by soils and sediments containing iron, aluminum, and manganese oxides with positive charges. May precipitate from solution as sulfides under strongly reducing conditions.
Total Dissolved Solids (TDS)	No	No	146 / 254 / 381 mg/L	- -	- -	TDS is largely based on concentration of major ions in groundwater (Ca, Mg, Na, K, carbonates, Cl, SO_4)		Refer to primary components.

Table A-3 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix IV Assessment Monitoring Constituents								
Antimony	No	No	<1 ug/L	No	Very mobile		Flameproof retardants, batteries, lead shot; metal and glass manufacturing	Usually soluble but may be sorbed by iron, aluminum and manganese oxides under acidic conditions (EPRI, 1987).
Arsenic	No	No	0.23 / 0.79 / 3.0 ug/L	Yes, pH and redox	Variable	May be present in sulfide minerals and in organic forms; concentrations can be naturally higher than typical under reduced conditions or if sulfide minerals are oxidized	Wood preservatives (chromated copper arsenate), feed additives, pharmaceuticals, electronic devices, metallurgical applications, metal mining and smelting, cemeteries; pesticides/herbicides/ insecticides (prior to 1960)	Arsenic occurs in the 5+ oxidation state as arsenate (AsO_4^{3-}) under relatively neutral pH and oxidized conditions, and as 3+ arsenite (AsO_3^{3-}) under reduced conditions. Arsenic fate and transport is complex due to sensitivity to pH and redox. Sorption usually increases with decreasing pH.
Barium	No	No	24 / 54 / 120 ug/L	Yes	Mobile	Weathering of sedimentary rocks	Well drilling mud or fluid, mining; manufacture of glass, paint, and rubber	Usually present as relatively insoluble barium sulfate in fly ash. Most barium compounds have limited solubility. Sorbed by clay, soils, and sediment.
Beryllium	No	No	<1 ug/L	Yes, pH	Immobile	Relatively scarce in Earth's crust	Electronic and electrical components, telecommunications and computer components, defense applications	Strong tendency to sorb at neutral to alkaline pH. Sorption may be reduced in the presence of humic acids.

Table A-3 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix IV Assessment Monitoring Constituents								
Cadmium	No	No	<1 ug/L	Yes, pH	Slightly mobile	Minor component in Earth's crust, occurs in zinc minerals	Batteries, waste incineration, sewage sludge disposal, paint pigments, phosphate fertilizers, automobiles, electroplating and metal fabricating	Can be sorbed by clay, soil, and sediment at pH less than 8, but sorption decreases at low pH.
Chromium	No	No	0.68 / 1.2 / 3.0 ug/L	Yes, pH and redox	Variable	Primarily occurs as Cr(III) in soils and rocks	Electroplating, leather tanning, wood pulp production (paper mills), metal ore refining, wood preservatives, steel manufacturing, automobiles, electroplating and metal fabricating, paint and coatings	The solubility of Cr(III) generally increases at pH levels <6.5 and >11. Cr(III) is the predominant dissolved species under reducing to mildly oxidizing conditions. Cr(IV) is more soluble than Cr(III) at neutral to alkaline pH. Cr(VI) is soluble at alkaline pH and mildly to strongly oxidizing conditions.
Cobalt	No	No	0.063 / 0.17 / 0.48 ug/L	Yes	Variable	Relatively scarce in Earth's crust; usually occurs in combination with arsenic and sulfur in nature	Rechargeable battery electrodes, radial tires, drying agents, catalysts, paint pigments, medical wastes, automobiles	May be sorbed by mineral oxides (e.g., Fe and Mn), crystalline materials such as aluminosilicate, and natural organic substances in soil.
Lead	No	No	0.018 / 0.070 / 0.27 ug/L	Yes pH	Variable	Rare in Earth's crust	Smelting and mining, batteries, waste incineration, leaded gasoline (before 1996), lead-containing paint, glass manufacturing, ammunition, firing ranges, plumbing, automobiles	Sorption usually increases with pH.

Table A-3 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix IV Assessment Monitoring Constituents								
Lithium	Yes for some coal ash	No	2.0 / 6.0 / 18 ug/L	No	Mobile	Rare in Earth's crust, dissolution of lithium-containing minerals	Glass and ceramics production, lubricants, greases, batteries, salt water intrusion	Reacts with sulfate ions to form lithium sulfate anion.
Mercury	No	No	NR	No	Slightly mobile	Occurs as HgS in nature; can be converted to methylated forms by anaerobic microbes	Waste incineration, mercury mining, metal recycling, fungicides, fluorescent lamps, batteries, thermometers/ thermostats/switches (electronic equipment), automobiles	Can be sorbed by iron, magnesium, silicon oxides, and organic matter.
Molybdenum	Yes for some coal ash	No	0.32 / 1.0 / 3.3 ug/L	No	Very mobile	Usually combined with sulfur or oxygen in natural minerals	Steel production, catalysts, lubricants, pigments, fertilizers, animal feed	Micronutrient for plants and animals; may be in fertilizers or animal feed. Peak sorption at pH <5 and limited sorption above pH 8. Phosphate and other oxyanions will depress sorption.

Table A-3 continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
CCR Rule Appendix IV Assessment Monitoring Constituents								
Radium 226 + 228	No	No	NR / 0.28 / 1.2 pCi/L	Yes, CEC	No data	Natural decay product of uranium and thorium ores	Uranium mines, nuclear power, nuclear fuel and weapons manufacturing, uranium in coal	Radium decays to radon gas, so it is prevalent in locations where radon gas is a concern.
Selenium	No	No	0.12 / 0.34 / 1.0 ug/L	Yes, pH and redox	Variable	Usually occurs with silver, copper, lead, and nickel sulfide minerals; may exist in a variety of organic compounds	Metal mining and milling, industrial waste water, sewage effluent, waste incineration, saline agricultural waste waters	May exist as selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), elemental selenium (Se^0), and selenide (Se^{2-}) in groundwater (shown in order from most to least oxic species). Since anionic selenium is the dominant form in groundwater, sorption typically is not significant. However, selenite can be sorbed by iron and aluminum oxides.
Thallium	No	No	<1 ug/L	Yes, redox	Mobile	Occurs in combinations with oxygen, sulfur, and halogens	Glass and electronic industries, iron and steel production, cement factories	May be immobilized under reducing conditions.

Table A-3 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
Other Constituents								
Aluminum	No	No	0.98 / 3.0 / 4.9 ug/L	Yes, pH	Slightly mobile	Most abundant metal in Earth's crust; weathering of aluminosilicate minerals	Mining and industrial emissions and effluents; most abundant metal in coal ash, cement and concrete, drying agents, well drilling, flocculants, abrasives, aluminum manufacturing	Most soluble in water under acidic and alkaline solutions, essentially insoluble in near neutral water. May be sorbed by soils, sediments, and organic matter.
Bromide	Possible for certain coal ash	Yes if unwashed	0.02 / 0.04 / 0.09 mg/L	No	Mobile	Brackish groundwater and sea water, relatively rare in Earth's crust	CCR fly ash and emission control wastes, particularly if bromide compounds were used to facilitate mercury capture; drinking water disinfection, flame retardants	
Copper	No	No	0.47 / 1.0 / 3.0 ug/L	Yes, pH and redox	Variable	Relatively common in Earth's crust	Manufacture of bronzes, brass, electrical conductors, and ammunition; sewage sludge wastes, municipal solid wastes, copper-containing fertilizers, cemeteries, electronics, plumbing, wood preservatives, automobiles, electroplating and metal fabricating	Solubility may be controlled by solubility of copper hydroxide. May sorb to organic matter, clay, aluminum, manganese, and iron oxides.
Iron	No	No	0.81 / 7.9 / 93 ug/L	Yes, pH and redox	Variable	Commonly has high concentration in groundwater under reduced conditions; Weathering of iron-containing minerals (dissolution of iron oxides under reducing conditions), 4th most common element in Earth's crust	Industrial emissions, pyrite oxidation/acid mine drainage from coal mining or storage, flocculants	Iron oxides my dissolve and become mobile under reducing conditions. Occurs as ferrous (+2) and ferric (+3) iron. Ferric iron can be sorbed by silica, clay, and iron and manganese oxides.

Table A-3 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
Other Constituents								
Magnesium	No	No	4.4 / 11 / 23 mg/L	CEC	Slightly mobile	Eighth most abundant element in the Earth's crust, abundant in sea water; dissolution of magnesium carbonates and clay minerals	Aluminum fabrication and welding (alloying agent), flares and pyrotechnics, fire retardants, heat-resistant bricks, animal feed, fertilizers, drying agents	Solubility may be limited under alkaline conditions. May be removed from solution by ion exchange in soils and sediments via reversible reactions.
Manganese	No	No	0.85 / 7.0 / 84 ug/L	Yes, pH and redox	Variable	Commonly has high concentration in groundwater under reduced conditions; 13th most abundant element in the Earth's crust	Production of steel and aluminum alloys, glass production, use as an additive in gasoline	
Nickel	No	No	0.35 / 1.1 / 2.5 ug/L	No	Variable	Commonly combined with iron or sulfur	Manufacture of steels, other metal alloys, and electronic applications; automobiles, electroplating and metal fabricating, petroleum	Sorbs to iron and manganese oxides, and clay to a lesser extent.
Nitrogen	No	No	0.07 / 0.55 / 2.4 (NO_3 as N) mg/L	Nitrification/ denitrifi-cation, redox	Very mobile as NO_3	In nature, nitrogen is converted from one redox state to another by abiotic reactions and microbial catalysis in oxic conditions: $NH_4OH \rightarrow NO_2 \rightarrow NO_3$; under reducing conditions: $NO_3 \rightarrow NO_2 \rightarrow N_2$	Fertilizers, livestock wastes, wastewater treatment plants, sewage and septic effluent, rubber manufacturing; ammonia sources include CCRs from sources using SNCR or SCR technology, coke production, flame retardants	NO_2 and NO_3 are not significantly sorbed by most soils, sediments, or clays, but NH_4OH is.

Table A-3 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
Other Constituents								
Phosphate	No	No	<0.01 / 0.02 / 0.04 mg/L	Yes, pH	Variable	Phosphorus is the 11th most abundant element in the Earth's crust	Fertilizers, wastewater treatment plants, sewage and septic effluents, industrial effluents, soaps and detergents, flame retardants	Can be sorbed by iron, aluminum, and manganese oxides, and by clay under acidic conditions.
Potassium	Yes for some coal ash	No	0.9 / 1.7 / 3.5 mg/L	CEC	Mobile	7th most abundant element in the Earth's crust; Weathering of potassium-containing minerals	Water treatment, fertilizers, sea water intrusion, soaps and detergents, drying agents	May be removed from groundwater by reversible ion exchange with soils and sediments.
Silicon	No	No	12 / 19 / 31 mg/L	Yes	Very mobile	2nd most abundant element in the Earth's crust; usually in the form of SiO_2	Glass, ceramics, abrasives, electronic devices, metal alloying, water filtration, insulation, cement, concrete, paper, rubber, lubricants, flocculants	Can be sorbed by iron and aluminum oxides, and by clay minerals.
Silver	No	No	<1 ug/L	Yes, pH	Variable		Textile plant wastewater, photographic materials, sewage sludge, medical wastes, electronics, electroplating and metal fabricating	Can be sorbed by soils but affected by pH, clay content, particle size, organic content, and free iron and manganese oxide content.
Sodium	Yes for some coal ash	No	5.2 / 11 / 29 mg/L	CEC	Mobile	6th most abundant element in Earth's crust; brackish groundwater and surface water, sea water, weathering of sodium-containing minerals	Road salt, deicing, septic effluent, sodium hydroxide water treatment wastes, water softening, salt water intrusion (gas and oil well production), sewage and septic effluent, soaps and detergents, drying agents	Most sodium compounds are soluble but may be sorbed by reversible ion exchange in soils or sediments.

Table A-3 (continued)
Potential Alternative Sources by Constituent

Constituent Name	Coal Ash Indicator? (note 1)	FGD Gypsum Indicator? (note 1)	Typical U.S. Groundwater Concentration at 25th / 50th / 75th Percentile (note 2)	Reactivity (note 3)	Mobility (note 4)	Natural Prevalence and Naturally Occurring Causes for Presence in Groundwater	Potential Anthropogenic Sources	Comments (note 5)
Other Constituents								
Strontium	No	No	100 / 270 / 680 ug/L	Yes	Slightly mobile		Glass and ceramics production, pyrotechnics, phosphate fertilizers	Reacts with sulfate ions to form $SrSO_4^0$.
Vanadium	No	No	0.30 / 1.4 / 11 ug/L	Yes, pH and redox	Variable		Crude oil, oil shale, tar sands, phosphate fertilizers, wastes from steel production, petroleum	Can be sorbed by iron, aluminum, and manganese oxides; sorption decreases as pH increases.
Zinc	No	No	1.6 / 4.8 / 18 ug/L	Yes, pH	Variable		Fertilizers, protective coatings to reduce corrosion of metal surfaces, dry-cell batteries, castings, automobiles, lubricating oils and greases, plumbing/piping, electroplating and metal fabricating	Sorption increases with increasing pH but is also affected by clay content, particle size, organic content, and iron, aluminum, and manganese oxide content.

Notes:

1. Based on EPRI (2012). "No" indicates that the constituent it is not considered an indicator due to low concentration in CCR leachate relative to typical background, low mobility, and/or potential for reactivity.

2. Concentration ranges in ug/L from USGS (2011), Table 4; concentration ranges in mg/L or SU from USGS (2008), Tables 2 and 6; radium 226+228 from Szabo et. al (2012) supplemental table S-3; NR indicates that the concentration was not reported in any of these three documents.

3. Reactivity and mobility, while separate geochemical processes, are often interrelated. Reactivity descriptions in this table refer to chemical reactions, primarily precipitation and dissolution, that can change the concentration or mobility of the element in solution under typical aquifer conditions. Yes indicates that the constituent is subject to precipitation, coprecipitation, and/or dissolution reactions. In addition, pH and redox are indicated if they have a strong influence on the environments under which reactions occur and/or mobility. CEC is listed for constituents that are subject to cation exchange.

4. The mobility classification is based on the classification system of van Loon and Duffy (2000). See Table 2-2 of EPRI (2012) for corresponding K_d values.

5. Refer to Appendix B in EPRI (2012) for brief summaries of geochemical factors affecting reactivity and sorption. Detailed information can be found for selected constituents in the following EPRI reports:

- Arsenic
  1015550 | Chemical Constituents in Coal Combustion Product Leachate: Arsenic | Profile | 2008
  1021212 | Arsenic in Coal Combustion Products | Tech Brief | 2010
- Beryllium
  1012583 | Chemical Constituents in Coal Combustion Product Leachate: Beryllium | Profile | 2006
- Boron
  1005258 | Chemical Constituents in Coal Combustion Product Leachate: Boron | Profile | 2005
  1023737 | Boron in Coal Combustion Products | Tech Brief | 2012
- Chromium
  1022143 | Chromium in Coal Combustion Products | Tech Brief | 2011
- Lithium
  In Prep | Chemical Constituents in Coal Combustion Products: Lithium | Profile | 2018
- Molybdenum
  1021815 | Chemical Constituents in Coal Combustion Products: Molybdenum | Profile | 2011
  In Prep | Molybdenum in Coal Combustion Products | Tech Brief | 2017
- Selenium
  3002001237 | Chemical Constituents in Coal Combustion Product Leachate: Selenium | Profile | 2013
  3002003761 | Selenium in Coal Combustion Products | Tech Brief | 2014
- Thallium
  1016801 | Chemical Constituents in Coal Combustion Product Leachate: Thallium | Profile | 2008
  3002001155 | Thallium in Coal Combustion Products | Tech Brief | 2013

Table A-4
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Abrasives	**Silicon, aluminum**
Acid mine drainage	**Low pH, sulfate, iron**, dissolved solids, metals (aluminum, cadmium, calcium, chromium, cobalt, copper, magnesium, manganese, nickel, zinc, and others); can travel along mine shafts and tunnels and show up in unexpected locations (sometimes across aquifers) (notes 1, 26, 51, 54)
Aerospace industry	**Boron, perchlorate, chloride, cyanide, cadmium**, beryllium, solvents (trichloroethane, methylene chloride, trichloroethylene, toluene, methylethylketone), metals, oils (notes 2, 3, 4, 5, 51)
Aging infrastructure (leaking sewage, urban runoff)	Nitrate, phosphorus, sodium, chloride, organic substances, bacteria, pesticides, miscellaneous chemicals, cadmium, copper, iron, lead, selenium, zinc, and other elements (note 6)
Agriculture - animal feed lots	**Nitrates, ammonia, other nitrogen compounds, phosphorus/phosphate, chloride, arsenic, magnesium, molybdenum, selenium** and other elements, organic substances, bacteria/viruses (notes 7, 22, 51, 52, 54)
Agriculture - fertilization	**Nitrates, ammonia, other nitrogen compounds, phosphorus/phosphate, boron, cadmium, calcium**, chloride, cobalt, **copper**, cyanide, **magnesium, molybdenum, potassium, selenium, strontium, vanadium, zinc**, and other elements (notes 7, 22, 51, 52, 54)
Agriculture - irrigation	**Nitrates, ammonia, other nitrogen compounds, phosphorus/phosphate,** arsenic, boron, cadmium, calcium, chloride, cobalt, copper, cyanide, magnesium, mercury, molybdenum, potassium, **selenium**, sodium, sulfate, and other elements (notes 7, 8, 9, 22, 52)
Agriculture - lime addition	**Calcium** (note 22)
Agriculture - pesticides, herbicides, and insecticides	Aldicarb, Aldrin, alachlor, atrazine, carbofuran, chlordane, dacthal, DDT, dieldrin, bibromo-chloropropane, 1,2-dichloropropane, dinoseb, endrin, endosulfan, ethylene dibromide, heptachlor, hexachlorobenzene, lindane, mirex, PCBs, prometon, simazine, toxaphene, trifluralin; **arsenic** (prior to 1960), chloride, **mercury, boron, sulfate** (notes 10, 51, 52, 54)
Airport runways	**Sodium, potassium**, acetate, formate, urea (note 11)
Aluminum manufacturing	**Aluminum, fluoride, sodium**, magnesium, manganese, perfluorocarbons, polycyclic aromatic hydrocarbons (notes 12, 13)
Ammunition, firearms	**Lead, antimony, copper,** other heavy metals, nitrate, perchlorate, potassium, sulfur/sulfate, chloride (notes 14, 15, 22)
Asphalt plants	Oils, greases, PAHs, other hydrocarbons (note 16)
Automobile production	**Chloride, sulfate, phosphate,** oil and grease, solvents, ethylene glycol. Potential for heavy metals: aluminum (auto bodies), **cadmium** (tires and batteries), **cobalt** (radial tires), **chromium** (brakes, coolants, engine parts), **copper** (brake linings), iron (auto bodies), **lead** (batteries, lube oil and grease, bearings, brakes), **mercury** (batteries), **nickel** (lube oil, brakes), **zinc** (tires, fuel oil, lubricants) (notes 17, 18, 22)
Automobile repair shops	Gasoline, diesel fuel, oil, degreasing solvents (toluene, xylene, chlorinated solvents, MEK), ethylene glycol, lead, sulfate (notes 19, 44)

Table A-4 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Batteries	**Sulfate, lead, antimony, cadmium, cobalt, lithium, mercury, zinc, low pH** (notes 22, 51)
Bleach manufacturing	**Boron** (bleaches containing sodium perborate) (notes 20, 31)
Brick manufacturing	**Aluminum, silicon, iron**, calcium, **fluoride, magnesium,** chromium (notes 21, 22, 52)
Catalysts	Aluminum, chromium, **cobalt**, copper, iron, **molybdenum**, titanium, tungsten, vanadium, zinc, and other metals (depends on catalyst manufactured or used) (note 22)
CCR - ash	**Boron, sulfate**, molybdenum, lithium, bromide, potassium, sodium, fluoride, selenium; may contain ammonia (nitrogen) if SCR or SNCR technology was used at the power plant (note 22)
CCR - FGD gypsum	**Sulfate**, fluoride, calcium, boron, bromide, chloride, selenium (note 22)
CCR - FGD fixated sludge	**Boron, sulfate**, calcium, chloride, molybdenum, lithium, bromide, potassium, sodium, fluoride, selenium (note 22)
Cemeteries	**Formaldehyde, copper, arsenic,** mercury, pesticides, fertilizers, weed killers (note 23)
Cement and concrete manufacturing and use	**High pH, aluminum, calcium, silicon, thallium,** chromium and other elements (notes 22, 24, 51)
Ceramics production	Oxides of carbon, **silicon, boron**, and nitrogen; may include aluminum, antimony, barium, copper, fluoride, iron, **lithium, strontium**, and other elements (notes 21, 22, 51)
Coal mining	**Sulfate, low pH, iron**, dissolved solids, trace elements (aluminum, beryllium, cadmium, chromium, cobalt, copper, lead, magnesium, manganese, mercury, nickel, selenium, **uranium (decays into radium 226+228)**, zinc and others); Oxidation of pyrite in coal can form sulfuric acid. The low pH increases solubility of many metals. (notes 1, 26, 51, 54)
Coatings	VOCs, solvents (halogenated solvents and non-halogenated solvents such as acetone, cresols, cresylic acid, nitrobenzene, benzene, toluene, xylene, methyl ethyl ketone, methylene chloride, etc.); trace elements may include barium, cadmium, **chromium**, cobalt, lead, mercury, molybdenum, nickel, titanium, and **zinc** (note 27)
Coke production (from coal)	**Phenols, ammonia (nitrogen), polycyclic aromatic hydrocarbons, cyanide**, benzene, naphthalene, anthracene, cresols, metals (see metals in "coal piles or coal waste piles") (note 28)
Computer and telecommunications components (electronics)	Trace elements may include aluminum, arsenic, barium, **beryllium**, cadmium, chromium, cobalt, **copper**, gallium, **gold**, iron, **lead**, manganese, mercury, palladium, platinum, selenium, **silver**, and zinc; solvents may include benzene, xylene (dimethylbenzene), trichloroethane, tetrachloroethane, ethylene glycol, methyl cellosolve; **silicon** (notes 29, 30, 32)

Table A-4 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Defense applications	**Beryllium** (note 22)
Detergent or soap manufacturing	**Sodium, potassium, sulfates and sulfonates, high pH, phosphate, chloride, boron**, phenol, aluminosilicate, sodium citrate, nitrilotriacetate, alcohol ethoxylates, fats, oil and grease, lead, hexane, methyl alcohol, trichloroethane, perchloroethylene, benzene, toluene (notes 22, 34, 35)
Deicing	**Sodium, chloride, calcium**, magnesium, urea (notes 44, 51)
Drying agents	**Aluminum, calcium, sodium, potassium, magnesium, sulfate, chloride,** cobalt, lithium, phosphorus, silicon and/or other substances (notes 22, 36, 37)
Electronic equipment manufacturing and disposal	**Copper, silver, gold, palladium, arsenic, beryllium, copper, mercury, nickel,** selenium, **silicon, thallium** and other trace elements, chloride, fluoride, solvents (benzene, xylene, 1,1,1-trichloroethane, tetrachloroethane, methanol), ethylene glycol, hydrogen chloride, hydrogen fluoride (notes 22, 29, 30, 33, 51)
Electroplating and metal fabricating	**Cadmium, chromium, copper, nickel, silver**, sodium, tin, **zinc**, spent solvents, paints, spent acidic and alkaline solutions, cyanide, waste oils (notes 17, 22, 44, 51, 52, 56)
Explosives manufacturing and testing	**Nitroglycerin and nitro-aromatic compounds**, nitrate, perchlorate, ammonia, lithium, sodium, potassium, sulfur/sulfate, aluminum, chloride, **lead**, antimony, **copper**, nickel, silver (notes 38, 39, 40, 51)
Fertilizers	See Agriculture - fertilization
Fiberglass manufacturing	Aluminum, silicon, calcium, magnesium, **boron**, polyester or epoxy resin, styrene, solvents, volatile organic compounds, formaldehyde, urea, phenol, vinyl acetate (notes 31, 41)
Firearms, ammunition	See Ammunition, firearms
Firing ranges	**Lead**, antimony (notes 14, 22)
Fireworks manufacturing or use	Aluminum, antimony, arsenic, barium, **boron**, chloride, copper, **lead**, **magnesium**, nitrate, perchlorate, potassium, sulfur/sulfate, **strontium** (notes 31, 38, 39, 40, 51)
Flame retardant manufacturing or use	**Bromine, phosphate, nitrogen/nitrate, chloride, antimony, boron, magnesium**, polybrominated diphenyl ethers (PBDEs), PCBs (notes 22, 42, 43, 51)
Flocculants	**Sulfate, chloride, aluminum, iron**, ammonium, calcium, silica, polyamines (note 45)
Fluorescent lamps/bulbs	**Mercury**, PCBs in ballasts (note 47)
Fracking	See Oil and gas wells / production

Table A-4 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Fungicides	See Pesticides
Furniture (wood stripping and refinishing)	Methylene chloride, methanol, isopropyl alcohol, acetone, perchloroethylene, toluene, acidic and alkaline solutions, metals, other solvents, petroleum distillates, resins, halogenated hydrocarbons, glycol ether (note 44)
Gasoline stations	**Benzene, ethylbenzene, toluene, xylene, MTBE**, ethylene dichloride, naphthalene, other organic compounds, lead (prior to 1996), **manganese**; trichloroethylene, perchloroethylene, methylene chloride, carbon tetrachloride, oils, ethylene glycol, hydraulic fluid, detergents, and acids (notes 22, 49, 51, 52)
Glass manufacturing	**Silicon**, antimony, **barium, boron, lead**, iron, **lithium, manganese**, nickel, potassium, **strontium, thallium**, tin, zinc, fluoride (notes 22, 31, 50, 51)
Industrial emissions	**Chloride, sulfate, iron,** wide variety of other elements and chemical substances (notes 22, 51, 54)
Irrigation	See Agriculture – irrigation
Junk and scrap yards	Used oil, gasoline, antifreeze, lead, sulfuric acid, agricultural chemicals/pesticides/other chemicals, metals (note 44)
Lamp manufacturing and disposal	**Mercury**, bromide, chloride, fluoride, iodide, PCBs, sodium (notes 22, 47)
Landfills - industrial	Wide range of trace metals, acids, **chloride**, sulfate, organic substances and pesticides (notes 51, 53, 54)
Landfills - municipal	Salts (sodium, calcium, magnesium, **chloride**, etc.), metals (iron, copper, zinc, other heavy metals), nitrate, organic compounds, solvents, pesticides (notes 22, 51, 54)
Laundry - dry cleaning	**Perchloroethylene (tetrachloroethylene)**, camphor oil, turpentine spirits, benzene, kerosene, white gasoline, petroleum solvents (petroleum naphtha), chloroform, carbon tetrachloride, trichloroethylene, 1,1,2-trichlorotrifluoroethane, glycol ethers, 1,1,1-trichloroethane, decamethylcyclopentasiloxane, n-propyl bromide, liquid carbon dioxide, fluorocarbon-113, antimony, cadmium, copper, lead, sulfate, zinc (notes 20, 31, 44, 52)
Leather tanning	**Chromium, cyanide, tannins**, chlorinated phenols including PCB, azodyes, cadmium, cobalt, copper, antimony, barium, lead, selenium, mercury, zinc, arsenic, nickel, formaldehyde, pesticides, salts, lime, acids, sodium sulfide, hydrogen sulfide, sulfate (notes 22, 55, 56)
Lubricants and greases	**Zinc**, polyaromatic hydrocarbons, arsenic, **boron**, cadmium, lead, **lithium, molybdenum**, PCBs, **silicon**, and other elements (note 22)
Medical supplies or wastes	Chloride, formaldehyde, **arsenic**, cadmium, **cobalt**, lead, mercury, **silver**, other heavy metals, radioactive waste, infectious or pathological waste, dioxins and furans from incineration; Also see Pharmaceutical industry (notes 22, 51, 57, 58, 59, 62)

Table A-4 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Metal manufacturing - smelting	**Aluminum**, **antimony**, **arsenic**, beryllium, cadmium, **chromium**, **copper**, cyanide, iron, **lead**, **magnesium** (aluminum manufacturing), **manganese** (steel and aluminum manufacturing), mercury, **molybdenum** (steel manufacturing), **nickel** (steel and other metal manufacturing), **selenium**, silver, **thallium** (iron and steel manufacturing), zinc and other elements, **fluoride** (steel and aluminum manufacturing), **silicon**, **vanadium** (steel manufacturing), **zinc** (notes 22, 44, 51, 52)
Metal mining	Aluminum, antimony, **arsenic**, beryllium, cadmium, **chromium**, **copper**, **cyanide**, iron, **lead**, **manganese**, **mercury**, **nickel**, **selenium**, silicon, silver, thallium, tungsten, zinc and other elements (notes 22, 51, 52, 54, 56)
Metal plating	Spent solvents, paints, spent acidic and alkaline solutions, waste oils, heavy metal sludges, metal dust, chromium, copper, nickel, selenium, **zinc** and other elements (notes 22, 44, 51, 52)
Metal recycling	Iron, copper, **mercury**, nickel, zinc, and other elements (note 22)
Mining - unspecified	Depends on contents of ore; may include aluminum, antimony, arsenic, beryllium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, **sulfate** (gypsum mines), thallium, zinc, other minerals, hydraulic oils; **radium 226+228 (uranium mines)** (notes 22, 51)
Natural gas pipelines	**Methane**, **PCBs** (notes 60, 61)
Nuclear power	**Tritium**, **strontium 90**, **radium 226+228**, boron, beryllium (notes 31, 51, 54)
Oil and gas wells / production	Produced water may contain high **TDS**, **chloride**, **sodium**, sulfate, barium, boron, bromide, iodide, lithium, potassium, radionuclides, **vanadium** and other minerals, methane, volatile organic compounds (notes 52, 60, 63)
Ore refining / smelting	Aluminum, antimony, arsenic, beryllium, cadmium, chromium, copper, cyanide, iron, lead, manganese, mercury, nickel, selenium, silver, thallium, zinc and other elements (notes 22, 44, 51)
Paint and pigment manufacturing	VOCs, solvents (halogenated solvents, non-halogenated solvents such as acetone, cresols, cresylic acid, nitrobenzene, benzene, toluene, xylene, methyl ethyl ketone, methylene chloride, etc.); metals may include **barium**, **cadmium**, **cobalt**, **chromium**, **lead**, mercury, **molybdenum**, titanium, and zinc (notes 22, 44, 51, 52, 64)
Paper and pulp manufacturing	Organic and inorganic compounds including lignin, cellulose, phenols, mercaptans, **chromium**, nitrates, phosphates, **silicon**, **sulfides/sulfates**, chlorinated compounds including chloroform and dioxin (notes 22, 65)
Petroleum facilities and refining	Benzene, ethylene, toluene, xylene, methane, other organic compounds, hydrogen sulfide, **sulfate**, **nickel**, **vanadium** and other elements; some refineries use deep-injection wells to dispose of highly contaminated wastewater that could potentially contaminate groundwater (note 51)
Pharmaceutical industry	Wide variety of organic solvents; **arsenic**, **cobalt**, ammonia, chloride, cobalt, **silver** and other elements; Also see Medical supplies or wastes (notes 22, 51, 57, 62)
Photographic materials/photography	**Silver**, sodium, potassium (notes 22, 51)

Table A-4 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Pigments	See Paint and pigment manufacturing
Plastic manufacturing	Cadmium, cyanide, benzene, vinyl hydrochloride, phthalates, trichloroethane, acetone, methylene chloride, methyl ethyl ketone, styrene, toluene, trichloroethane, sulfate, methanol, ethylene oxide, volatile organic compounds, sodium, caustic, nickel, lead, cadmium, mercury (notes 51, 66)
Plumbing	**Copper, lead, zinc** (note 51)
Road salting	**Chloride, sodium, calcium**, other salts (notes 22, 44)
Rubber manufacturing	**Ammonia, amines**, acetic acid, **barium**, cobalt, formic acid, sodium, **silicon**, sulfite/sulfate, organics, nitrogen compounds (notes 22, 69)
Salt or brackish water intrusion (from well drilling)	**High TDS, chloride**, boron, bromide, calcium, **lithium**, magnesium, **potassium, sodium**, sulfate, and other minerals (notes 22, 51, 54)
Salvage and junk yards	Grease, oil, solvents, lead and acid from batteries, metals (notes 44, 54)
Semiconductor manufacturing	Copper, silver, gold, palladium, arsenic, beryllium, copper, mercury, nickel, selenium, silicon, thallium and other elements, chloride, fluoride, solvents (benzene, xylene, 1,1,1-trichloroethane, tetrachloroethane, methanol), ethylene glycol, hydrogen chloride, hydrogen fluoride (notes 22, 29, 30, 33, 51)
Septic effluent	**Nitrate, phosphorus, chloride, sodium**, organic substances, bacteria and viruses, detergents, oils, heavy metals including cadmium, copper, lead, **selenium**, salts, septic tank cleaners such as trichloroethane or methylene chloride, and a wide variety of other chemicals (notes 22, 51, 52, 53)
Sewage	**Nitrate, phosphorus, chloride, sodium**, organic substances, bacteria and viruses, detergents, oils, **boron, cadmium, copper**, lead, **selenium, silver**, salts, and a wide variety of other chemicals (notes 22, 51, 52)
Soap or detergent manufacturing or use	See Detergent and soap manufacturing
Soil acidity neutralization	**Calcium**
Steel (including stainless) and iron manufacturing	Iron, chromium, manganese, nickel, ammonia, cyanide, chloride, copper, fluoride, molybdenum, sulfate, tin, thallium, zinc, hydraulic oils
Textiles	Polyvinyl chloride, chlorine bleach, benzidine, toluidine, cyanide, formaldehyde, hydrocarbons, ammonia, nitrate, organic solvents, chloride, sodium, fluoride, silicon, **sulfate**, phosphate, boron, bromide, chromium, copper, aluminum, antimony, potassium, aluminum, **silver**, titanium, zinc, copper, insecticides (notes 22, 51, 56, 67, 68)
Thermometers, thermostats, switches	**Mercury** (note 51)

Table A-4 (continued)
Constituents Potentially Associated with Alternative Anthropogenic Sources

Potential Source	Constituents That May Be released to Groundwater*
Underground storage tanks (USTs leaking petroleum products such as gasoline)	Benzene, toluene, xylene, other organic compounds (notes 49, 51, 53)
Urban runoff	Oils, heavy metals, salts, copper, zinc, and other chemicals (notes 6, 18, 54)
Waste incineration	**Chloride, cadmium**, chromium, **fluoride, lead, mercury**, selenium, dioxins and furans (note 22)
Water treatment - flocculants	See Flocculants (note 45)
Water treatment - industrial effluents	Wide variety of metals, aluminum, **chloride**, **phosphate**, **potassium, sulfate**, nitrate, **selenium, silicon**, **sodium**, organics depending on industry (notes 22, 46)
Water treatment - municipal supply	Bromide, **chlorine, fluoride** (notes 22, 51)
Water treatment - treated sewage effluent	May contain **nitrates and other nitrogen compounds, phosphates, sodium, chloride**, **selenium, silicon**, and a variety of other elements (notes 22, 51, 52)
Water treatment - water softening	**Sodium, chloride**, **calcium**, magnesium, iron, other salts and metals (note 22)
Water treatment - cooling water	Chromium, zinc (notes 51, 52)
Well drilling (mud or fluid)	Constituents of bentonite clay and the natural geomedia including **aluminum, barium**, calcium, potassium, sodium and other minerals (note 22)
Wood preservatives and treatments	**Pentachlorophenol (PCP), creosote**, **copper, chromium, arsenic** (chromated copper arsenic, ammoniacal copper arsenate) (notes 22, 44, 48, 51)

* Bold indicates likely key indicators; list will vary by site-specific source; list may be incomplete or may not accurately represent a particular source.

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B
ASD CHECKLISTS

		Supporting Lines of Evidence		
		None	**Few**	**Many**
Key Lines of Evidence	**None**	No ASD	Weak ASD	ASD possible
	One	Weak ASD	ASD possible	**Strong ASD**
	Multiple	ASD possible	**Strong ASD**	**Strong ASD**

Figure B-1
Use of key and supporting lines of evidence for ASD Types IV and V

ASD Checklist 1: Sampling, Laboratory, or Statistical Causes

ASD Type	Potential Cause	Identify and Comment on Applicability of Potential Cause
Sampling Causes (ASD Type I)	Sample mislabeling	
	Contamination	
	Sampling technique	
	Turbidity	
	Sampling anomalies	
Laboratory Causes (ASD Type II)	Calibration	
	Contamination	
	Digestion methods	
	Dilution corrections	
	Interference	
	Analytical methods	
	Laboratory technique / qualifier flags	
	Transcription error(s)	
Statistical Evaluation Causes (ASD Type III)	Lack of statistical independence	
	Outliers	
	False positives	
	Non-detect processing	
	Background data / change in normality	

ASD Types I, II, and III do not require a weight of evidence approach. Refer to Section 2 for descriptions of potential causes.

ASD Checklist 2: Lines of Evidence Associated with the CCR Unit

		Column A	Column B	Column C				
	Line of Evidence (LOE)	**Points to release from the CCR unit if:**	**Points to alternative source if:**	**LOE is not applicable if:[1]**	**LOE Type[2]**	**Applies to[3]**	**Weight of Evidence Determination / Basis**	**Alternative Source Demonstration Approach**
	Primary CCR Indicators							
1a	If the CCR unit contains fly ash, is there an SSI/SSL for boron and sulfate?	Yes	No	ND	Key	Monitoring Point	The primary indicators for CCR leachate typically have high concentration in the leachate, are mobile, and are not reactive in groundwater, such that any groundwater affected by a leachate release will have elevated concentration for the indicator constituent. Boron and sulfate are primary indicators for coal ash leachate. Sulfate is a primary indicator for FGD gypsum leachate. Other potential indicators are identified in Table A-1. Leachate analysis can confirm site-specific primary indicators by identifying constituents present in leachate in concentrations higher than background. An SSI/SSL is unlikely to be due to release from the facility if the leachate concentration is not higher than background.	Demonstrate using graphical and statistical analysis. Special leachate sampling may be needed if not already routinely sampled.
1b	If the CCR unit contains FGD gypsum (only) is there an SSI/SSL for sulfate?	Yes	No	ND	Key	Monitoring Point		
1c	Are there other constituents in the groundwater that represent primary indicators? List the applicable constituents.	Yes	No	ND	Supporting	Monitoring Point		
1d	Is there an SSI/SSL for any of the other primary indicators?	Yes	No	ND	Key if No	Monitoring Point		
1e	Is the *leachate* concentration for any of the primary indicators (including boron and sulfate) with an SSI/SSL statistically higher than background? List the applicable constituents.	Yes	No	ND	Key if No	Constituent		
1f	Are concentrations for the primary indicators increasing?	Yes	No	ND	Supporting	Monitoring Point		
	Secondary Indicators							
2a	Are there other SSI(s) or SSL(s) of Appendix III or IV parameters? (These are potential secondary indicators. List the applicable constituents.)	Yes	No	ND	Supporting	Monitoring Point	Secondary CCR indicators are defined by high concentration in the CCR leachate, but they may be less mobile or more reactive in the environment, or they may be relatively common in groundwater due to natural or anthropogenic causes. Leachate analysis is used to determine site-specific secondary indicators. An SSI/SSL is not likely to be due to release from the facility if the leachate concentration is not higher than background. This line of evidence is secondary to LOE 1. If LOE 1 points to an alternative source, then the alternative sources may also explain SSI/SSLs for secondary indicators.	Demonstrate using graphical and statistical analysis. Special leachate sampling may be needed if not already routinely sampled.
2b	Are the constituents identified in 2a present *in leachate* in concentrations statistically higher than background?	Yes	No	ND	Key if No	Constituent		
2c	Are concentrations for any of the secondary indicators increasing? List the applicable constituents.	Yes	No	ND	Supporting	Monitoring Point		

		Column A	Column B	Column C				
	Line of Evidence (LOE)	**Points to release from the CCR unit if:**	**Points to alternative source if:**	**LOE is not applicable if:[1]**	**LOE Type[2]**	**Applies to[3]**	**Weight of Evidence Determination / Basis**	**Alternative Source Demonstration Approach**
	Other Chemistry							
3a	Are organic constituents present in concentrations statistically higher than background? If "yes," mark column B. (May not be relevant if the CCR unit is not a monofill.)	Not applicable	Yes	No	Supporting	Monitoring Point	Organic compounds are combusted in the power plant boiler. EPRI data [1987, 2016] has shown that organic compounds typically have non-detectable concentrations in CCR leachate. The presence of organic constituents in groundwater indicates that an alternative source has affected groundwater quality at that monitoring point, although it does not rule out the CCR unit as a source for inorganic constituents. Biologically mediated reactions within organic plumes can result in natural release from soil of redox-sensitive constituents such as arsenic.	Special analyses for organic compounds may be needed if there is reason to suspect that organic compounds are present in the groundwater. Demonstrate using graphical and statistical analysis.
3b	Is major ion chemistry similar to leachate?	Yes	No	ND	Key	Monitoring Point	If the SSI/SSL is due to a release from the facility, then the major ion chemistry of the groundwater sample should be a mixture of leachate and background groundwater.	Special sampling for all eight major ions may be necessary if not routinely analyzed as part of the groundwater monitoring program. This demonstration can be performed using Piper diagrams, Stiff charts, and ion ratios (see Section 3; Tier II analysis is also described in EPRI 2012).
3c	Does major ion chemistry suggest a mixture of leachate and background groundwater?	Yes	No	ND				
3d	Does tritium age dating indicate that the groundwater was recharged after the facility was first used?	Not applicable	No	Yes	Key if No	Monitoring Point	Tritium can be used to determine if groundwater recharged prior to atomic testing in the 1950s. The CCR unit is unlikely to be the cause of an SSI/SSL if groundwater is older than the unit.	Special analysis for tritium is required, refer to EPRI (2017) for more on this method.
3e	Does isotopic analysis show evidence of mixing with CCR leachate?	Yes	No	ND	Key	Monitoring Point	The CCR unit is unlikely to be the cause of an SSI/SSL if isotope ratios show no evidence of mixing between leachate and background groundwater.	Special analyses required for isotope testing, refer to EPRI (2017).

		Column A	Column B	Column C				
	Line of Evidence (LOE)	**Points to release from the CCR unit if:**	**Points to alternative source if:**	**LOE is not applicable if:[1]**	**LOE Type[2]**	**Applies to[3]**	**Weight of Evidence Determination / Basis**	**Alternative Source Demonstration Approach**
	Hydrogeology							
4a	Is the monitoring well with an SSI/SSL downgradient from CCR unit at any point during year?	Yes	No	ND	Key if No	Monitoring Point	The monitoring well must be downgradient for the SSI/SSL to be attributed to the CCR unit.	Demonstrate using maps or calculated vectors for groundwater flow direction.
4b	Review the Hydrogeological vs Leachate Scenario Table (Table A-2) and identify the most representative scenario for each SSI or SSL case. List cases and scenario numbers.	(Check here for cases indicating a possible CCR release.) (Scenario types from Table A-2, column 1 or 2)	(Check here for cases indicating a possible alternative source.) (Scenario types from Table A-2, column 2 or 3)	ND	Key	Monitoring Point	CCR Leachate Release (Table A-2, column 1 scenarios) - If the CCR unit is the only source and the leachate concentration is higher than background, the downgradient well concentration should be equal to or less than the leachate concentration due to mixing with groundwater. CCR Leachate Release and/or Alternative Source (Table A-2, column 2 scenarios) - If the leachate concentration is higher than background and a downgradient concentration is higher than the leachate concentration, both leachate and an alternative source may be contributing to downgradient concentrations. Alternative Source Release (Table A-2, column 3 scenarios) - If the leachate concentration is less than background, the leachate cannot cause downgradient concentrations to be higher than background, and an alternative source is indicated.	This LOE requires site-specific knowledge of leachate concentrations. Demonstrate by comparing site-specific flow and concentration maps to Table A-2.
4c	Is the CCR unit immediately underlain by clay, shale, or other geologic media with low hydraulic conductivity?	No	Yes	ND	Supporting	Unit	Clay and shale can provide a physical barrier to migration from a CCR unit; however, CCR indicator concentrations, particularly boron, can be naturally elevated in these formations.	Cross-sections developed from boring logs
4d	Is the monitoring point distant from the facility AND does the constituent with an SSI/SSL have low mobility in groundwater given the hydrogeologic environment at the monitoring location (see Table A-3)?	No	Yes	ND	Supporting	Case	The CCR unit is less likely to be the source of the SSI/SSL if the constituent has low mobility and is monitored at a distant point.	Groundwater modeling, accounting for sorption, can be used to determine whether or not migration to the monitoring location is possible.
4e	Are the background monitoring wells screened in the same hydrostratigraphic unit, and along the same groundwater flow path, as the monitoring location with the SSI?	Yes	No	ND	Supporting	Monitoring Point	If the background and downgradient wells are not along the same flow path and/or are not screened in the same hydrostratigraphic unit, the SSI/SSL may indicate a natural difference between formations or flow paths, rather than an anthropogenic release.	The site conceptual model, based on groundwater flow and hydrogeology, provides data that can be used for this determination. Geochemical modeling can be used to evaluate the naturally occurring geochemistry expected for different hydrostratigraphic units, and whether or not the observed evolution in groundwater quality is consistent with what is known about the geochemistry of each hydrostratigraphic unit.

		Column A	Column B	Column C				
	Line of Evidence (LOE)	**Points to release from the CCR unit if:**	**Points to alternative source if:**	**LOE is not applicable if:[1]**	**LOE Type[2]**	**Applies to[3]**	**Weight of Evidence Determination / Basis**	**Alternative Source Demonstration Approach**
	CCR Unit Design							
5a	Does the entire footprint of the monitored CCR unit have a liner?	No	Yes	ND	Supporting	Unit	The presence of a liner reduces the potential (relative to an unlined unit) for a release from the CCR unit, particularly if it is not underlain by a natural barrier material.	Review design documentation. The response to this question would be no if any portion of the monitored CCR unit is unlined.
5b	If the facility is lined, is it a composite liner?	No	Yes	ND	Supporting	Unit	A composite liner, consisting of a geosynthetic barrier material over clay, further reduces the potential for a release (relative to a clay liner) from a CCR unit.	Review design documentation. The response to this question would be no if any portion of the monitored CCR unit does not have a composite liner.
5c	Does the entire footprint of the CCR unit have a leachate collection system?	No	Yes	ND	Supporting	Unit	A leachate collection system further reduces the potential (relative to a unit with liner and no leachate collection) of a release from a CCR unit.	Review design documentation. The response to this question would be no if any portion of the monitored CCR unit does not have leachate collection.
5d	If the CCR unit is unlined, is it known to have or is it likely to have groundwater intersecting the CCR?	Yes	No	ND	Supporting	Unit	This LOE is indeterminate for active impoundments. This LOE is indeterminate for CCR units with engineered or natural liners. For cases that are not indeterminate, an intersecting water table increases the potential for a release to groundwater, relative to a facility where groundwater is below the CCR.	Water table elevation contours and engineering drawings can be compared to project whether or not the water table intersects the CCR. If engineering drawings are not available, and the facility is unlined, then borings can be performed to gauge CCR depth. Spring seepage into a CCR unit would be counted as intersecting groundwater.

Table Notes:

1. ND (not determined) indicates that this line of evidence was not tested or there are insufficient data to make a determination.
2. Line of Evidence (LOE) Types:
   Key lines of evidence are based on relationships that must be observed in order for an SSI/SSL to be due to a release from a CCR unit. If these relationships are not observed, then they are critical to establishing an ASD. It is difficult to build a strong ASD without any key lines of evidence. It may be possible to build an ASD with a single key line of evidence, but the ASD will be stronger with additional key or supporting lines of evidence.
   Supporting lines of evidence provide additional information that supports the ASD. Supporting lines of evidence are generally not sufficient to build an ASD unless there is at least one key line of evidence, although it may be possible if there are many supporting lines of evidence.
3. This LOE applies to:
   Constituent: An SSI/SSL for that constituent at any monitoring point
   Monitoring Point: All SSIs/SSLs at a specific monitoring point
   Case: An SSI/SSL for a specific constituent at a specific monitoring point
   Unit: All SSIs/SSLs at the monitored unit

ASD Checklist 3: Lines of Evidence Associated with Alternative Natural and Anthropogenic Sources

		Column A	Column B	Column C				
	Line of Evidence (LOE)	***Does not* point to alternative source if:**	**Points to alternative source if:**	**LOE is not applicable if:[1]**	**LOE Type[2]**	**Applies to[3]**	**Weight of Evidence Determination / Basis**	**Alternative Source Demonstration Approach**
General								
6a	Are there any known alternative sources for any of the constituents of concern on-site or off-site?	No	Yes	ND	Supporting	Unit	Identification of an alternative source for one or more constituents with an SSI/SSL, in an upgradient location, establishes potential for an ASD.	Consider answering the questions below first to help identify possibilities, and then come back to this set of questions. Refer to Tables A-3 and A-4 for common anthropogenic sources for various constituents in groundwater. List and draw locations with reference to the CCR unit on a map.
6b	Are any current or former potential alternative sources upgradient of the monitoring location?	No	Yes	ND	Supporting	Monitoring Point		
6c	Do monitoring locations between a potential upgradient source and CCR unit have concentrations at SSI/SSL levels?	No	Yes	ND	Supporting	Constituent	If a constituent has high concentration in groundwater, relative to background, both upgradient and downgradient from a CCR unit, then an alternative source is possible, regardless of whether or not the responses to 6a and 6b are yes. If the upgradient concentration is similar to or higher than the downgradient concentration, then an alternative source is likely.	Demonstrate using statistical and graphical methods.
On-Site Alternative Source								
7a	Is the monitoring point downgradient of or near a coal pile, or coal pile runoff, or coal pile leachate management area?	No	Yes	ND	Supporting	Monitoring Point	If yes, the coal pile may be a potential alternative source if it is unlined.	Use Tier II analysis to test for differences in leachate and groundwater signatures. May require special sample from coal pile runoff ditch or collection pond.
7b	Are there former coal mines, mine spoil, or conveyers near the CCR unit or upgradient from the facility?	No	Yes	ND	Supporting	Unit	If yes, these may be alternative sources.	pH may be lower, and concentrations of iron, manganese, and trace elements may be higher in groundwater impacted by a coal mine relative to CCR leachate.
7c	Does the site have other CCR units that are upgradient or side gradient of the affected monitoring location?	No	Yes	ND	Supporting	Monitoring Point	If yes, the other CCR units may be alternative sources, particularly if they are unlined impoundments or landfills.	For this case CCR indicator constituents should have an SSI/SSL or increasing trend at the monitoring location. If water quality signatures are not different, then intermediate monitoring points may be needed.
7d	Is the CCR unit built on top of a former CCR disposal area (i.e., has a lined impoundment been built on top of a former unlined impoundment, or has a lined landfill been built on top of a portion of an unlined impoundment)?	No	Yes	ND	Supporting	Unit	If yes, groundwater quality may be affected by leachate from the underlying CCR.	For this case CCR indicator constituents should have an SSI/SSL or increasing trend at the monitoring location. If the overfill CCR unit is lined and concentrations of CCR leachate indicators are decreasing, an ASD may be possible showing that the groundwater impacts are due to the former CCR disposal activities. The water quality signature and isotope ratios for a legacy site may be different than those for the overfill unit if there has been a coal switch.

		Column A	Column B	Column C				
	Line of Evidence (LOE)	***Does not* point to alternative source if:**	**Points to alternative source if:**	**LOE is not applicable if:[1]**	**LOE Type[2]**	**Applies to[3]**	**Weight of Evidence Determination / Basis**	**Alternative Source Demonstration Approach**
On-Site Alternative Source (continued)								
7e	Do the CCR unit or adjacent units have an active underdrain piping system or groundwater pumping system, or are there any groundwater pumping activities nearby, that could have localized influence on groundwater flow and quality?	No	Yes	ND	Supporting	Unit	If yes, consider potential effects on localized groundwater flow directions and quality.	Groundwater with CCR constituents can be pulled toward another CCR unit with an underdrain system or if CCR units are within the radius of influence of on-site production wells. For example, elevated CCR constituents from an unlined fly ash pond (e.g., boron) can occur in adjacent gypsum pond downgradient wells due to localized groundwater flow.
7f	Is there evidence that water used for dust suppression on uncovered CCR or coal piles flowed off the footprint of the liner or runoff containment system near the monitoring point?	No	Yes	ND	Supporting	Monitoring Point	Runoff water from dust control can contain many of the same constituents as CCR leachate. If wind or other issues cause a spray irrigation system to deposit leachate beyond the landfill boundary, then an SSI/SSL with a CCR leachate signature can result. These are examples of an ASD where management of the unit is responsible for the SSI/SSL, but the SSI/SSL is not due to a direct release of leachate to groundwater from the unit. A change in management can mitigate this SSI/SSL source.	Identify the source of dust suppression water (coal pile runoff water, leachate, reused water from other sources). Document, using photos or other evidence, potential pathways off the liner or beyond the runoff containment system. For these cases, CCR indicator constituents should have an SSI/SSL or increasing trend at the monitoring location. Concentrations should decrease after management improvements are implemented.
7g	Is leachate or sluice water used for dust control close to the monitoring location?	No	Yes	ND	Supporting	Monitoring Point		
7h	Is the monitoring point downgradient of or near a CCR handling area (silo, storage area, dewatering bin, sump, truck loading/unloading or washing area, etc.) or haul road?	No	Yes	ND	Supporting	Monitoring Point	These are examples of an ASD where CCR handling associated with the unit is responsible for the SSI/SSL, but the SSI/SSL is not due to a direct release of leachate to groundwater from the unit. Revisions to handling practices, or repairs to handling structures, can mitigate this SSI/SSL source.	Engineering investigation of CCR and leachate handling structures may be required to demonstrate these alternative sources. Documentation of spillage or leaks (by material type, source, and location) will support this ASD. For these cases, CCR indicator constituents should have an SSI/SSL or increasing trend at the monitoring location. This ASD is particularly effective if concentrations begin to decrease after the alternative source is mitigated (allowing for lag time due to slow-moving groundwater).
7i	Is the monitoring point downgradient of or near sluice water lines, handling equipment, or storage areas?	No	Yes	ND	Supporting	Monitoring Point		
7j	Is the monitoring point downgradient of or close to a leachate collection pipeline or leachate storage structure?	No	Yes	ND	Supporting	Monitoring Point		
7k	Have there been any documented spills of CCR or leachate or sluice water in upgradient or nearby locations?	No	Yes	ND	Supporting	Monitoring Point		
7l	Were CCRs ever drained or stockpiled in unlined areas and/or without run-off/leachate control in upgradient or nearby areas?	No	Yes	ND	Supporting	Monitoring Point		

		Column A	Column B	Column C				
	Line of Evidence (LOE)	***Does not* point to alternative source if:**	**Points to alternative source if:**	**LOE is not applicable if:[1]**	**LOE Type[2]**	**Applies to[3]**	**Weight of Evidence Determination / Basis**	**Alternative Source Demonstration Approach**
On-Site Alternative Source (continued)								
7m	Is there any history of on-site or upgradient oil or chemical spills or leaking underground storage tanks?	No	Yes	ND	Supporting	Monitoring Point	If yes, groundwater may be impacted by oil or chemical spills.	Documentation of spillage or leaks (by material type, source, and location) will support this ASD. For this case, look for constituents that are higher than background that are not primary indicators of the site-specific CCR leachate signature.
7n	Does a significant amount of road salting occur on-site? (also see 9b)	No	Yes	ND	Supporting	Monitoring Point	If yes, concentrations for chloride and other major ions (depending on the type of salt; see Table A-4) may have an SSI/SSL.	If yes, look for notably elevated concentrations of the cations and anions comprising the salts used. If these are elevated, then an ASD related to road salting may be possible.
7o	Are fertilizers being used on-site for cap vegetation or other uses?	No	Yes	ND	Supporting	Monitoring Point	Consider if groundwater impacts include nitrates or phosphates, or if the fertilizers include calcium, sulfate, or other minerals that are monitored under the CCR program.	Documentation of on-site use of fertilizers will help support this ASD.
7p	Is there any history of on-site or upgradient ash utilization (structural fill, landfill, road base, berm construction, soil stabilization, etc.)?	No	Yes	ND	Supporting	Monitoring Point	If yes, these may be on-site alternative sources.	Documentation of historical site structural fill activities, source information, and analytical data will help support this ASD.
7q	Was the power plant site subgrade prepared with CCR, dredge spoils, incinerator residue, construction debris, industrial waste, or non-native soils?	No	Yes	ND	Supporting	Monitoring Point		
Natural Variation								
8a	Are background wells screened in the same geomedia as the monitoring point?	Yes	No	ND	Supporting	Monitoring Point	If no, then one or more SSI/SSL may be a result of naturally occurring differences in groundwater quality.	Geochemical modeling can be used to evaluate whether or not observed concentrations are consistent with the geomedia.
8b	Is the aquifer comprised of poorly buffered media such as sand and gravel?	No	Yes	ND	Supporting	Unit	If yes, then pH may be evolving if the pH or precipitation water is different than the groundwater, which can cause desorption or dissolution of pH-sensitive constituents.	Investigate long-term data records for evidence of pH changes. Refer to Table A-3 to determine if this case applies to the constituent with an SSI/SSL. Geochemical modeling may be considered to fully document this effect.
8c	Is the pH at the monitoring point similar to the background pH?	Yes	No	ND	Supporting	Monitoring Point	If no, then background is not fully representative of downgradient groundwater. Concentrations may evolve over the groundwater flow path.	Refer to Table 3 to determine if this case applies to the constituent with an SSI/SSL Geochemical modeling may be considered to fully document this effect

		Column A	Column B	Column C				
	Line of Evidence (LOE)	***Does not* point to alternative source if:**	**Points to alternative source if:**	**LOE is not applicable if:[1]**	**LOE Type[2]**	**Applies to[3]**	**Weight of Evidence Determination / Basis**	**Alternative Source Demonstration Approach**
Natural Variation (continued)								
8d	Is the monitoring point near a river?	No	Yes	ND	Supporting	Monitoring Point	If yes, then there may be changes in flow direction and/or groundwater elevations in response to changes in river stage that could result in monitoring different groundwater than during the background monitoring period. A yes response here also signifies potential for a redox change from oxic in upgradient areas where groundwater recharges, to reduced near the river where groundwater discharges.	Time-series plots can be used to see if there are correlations between river stage and concentration. Concentration distribution maps can be used to investigate effects of changes in flow direction. Check redox indicators to look for changes in redox.
8e	Is the constituent chemically reactive in groundwater, such that dissolution or desorption is possible (see Table A-3)?	No	Yes	ND	Supporting	Constituent	Reactive constituents can exhibit naturally occurring concentration changes if pH or redox conditions change along the flow path.	Refer to Table A-3 to determine if this case applies to the constituent with an SSI/SSL. Geochemical modeling can be used to test whether or not a change in geochemical conditions is causing a naturally occurring evolution of the groundwater.
8f	Is there a difference in redox indicators between background and compliance monitoring data?	No	Yes	ND	Supporting	Monitoring Point	This can affect redox-sensitive constituents, and can cause an SSI/SSL if the different redox environment only occurs at downgradient monitoring locations.	Compare background and compliance redox indicators to determine if this case applies. Refer to Table A-3 to determine if this case applies to the constituent with an SSI/SSL. Geochemical modeling may be considered to fully document this effect.
8g	Has there been a recent flood, recharge event, or dry period that caused groundwater elevation to rise or fall to elevations higher or lower than observed during the background monitoring period?	No	Yes	ND	Supporting	Unit	If yes, then there may be changes in groundwater elevation that could result in monitoring different groundwater than during the background monitoring period.	Time-series plots can be used to see if there are correlations between river stage and concentration.
8h	Does the aquifer contain saline water at depth?	No	Yes	ND	Supporting	Unit	If yes, monitoring wells close to the ocean, or that are deeper than background, may have higher concentrations of indicators for brine than background groundwater. Implementation of, or an increase in, groundwater withdrawals near the monitoring point could cause upwelling that would be a change over time.	The water quality signature for seawater and brines should be different than leachate, as described in Section 4.
8i	Was the direction of groundwater flow prior to or during the sample event different than observed during the background prior?	No	Yes	ND	Supporting	Monitoring Point	If yes, then the changes in flow direction could result in monitoring different groundwater than during the background monitoring period.	Concentration distribution maps can be used to investigate effects of changes in flow direction.

		Column A	Column B	Column C				
	Line of Evidence (LOE)	***Does not* point to alternative source if:**	**Points to alternative source if:**	**LOE is not applicable if:[1]**	**LOE Type[2]**	**Applies to[3]**	**Weight of Evidence Determination / Basis**	**Alternative Source Demonstration Approach**
Off-Site Anthropogenic								
9a	Are there former coal mines, mine spoil, or conveyers near the CCR unit or upgradient from the facility (also consider under "On-site")?	No	Yes	ND	Supporting	Unit	If yes, these may be alternative sources.	pH may be lower, and concentrations of iron, manganese, and trace elements may be higher, in groundwater impacted by a coal mine relative to CCR leachate.
9b	Does a significant amount of road salting occur off-site?	No	Yes	ND	Supporting	Unit	If yes, concentrations for chloride and other major ions (depending on the type of salt; see Table A-4) may have an SSI/SSL.	If yes, look for notably elevated concentrations of the cations and anions comprising the salts used. If these are elevated, then an ASD related to road salting may be possible.
9c	Does the surrounding land use include agriculture (crops)?	No	Yes	ND	Supporting	Unit	If yes, then concentrations of nitrates and other agricultural constituents (see Table A-4) may be elevated.	Use graphical or statistical analysis to demonstrate presence of agricultural indicators. This ASD is most effective if agricultural indicators are present in upgradient or intermediate monitoring points.
9d	Does the surrounding land use include agriculture (animal)?	No	Yes	ND	Supporting	Unit		
9e	Are there current or former underground or aboveground storage tanks that have had a release? (Consider gas stations and surrounding industrial activities.)	No	Yes	ND	Supporting	Unit	If yes, these may be alternative sources.	Identification of locations of underground and aboveground storage tanks, along with documented leak history (if known), will help support this ASD. Include locations of gas stations.
9f	Are there, or were there, oil and gas production wells in the vicinity of the site?	No	Yes	ND	Supporting	Unit	If yes, look for evidence of salt water intrusion, seepage of drilling fluid or additive chemicals, and organics.	Document locations of oil and gas wells.
9g	Are there existing or historical commercial and/or industrial sources of impacts, such as metal manufacturing, mining, landfills, Superfund or brownfield sites, wood treatment, etc.?	No	Yes	ND	Supporting	Unit	First determine if surrounding land use includes current or former industrial or commercial activity and identify types and locations. Then look for evidence of potential impacts to groundwater. Tables A-3 and A-4 provide information on potential impacts to groundwater related to common anthropogenic activities.	Review historical aerial photos, Sanborn maps, and available GIS data showing changing landscape and property use since the late 19th century. USGS topographic maps can be used to evaluate drainage patterns and topographic changes as well as locations of mines, quarries, and landfills. Review local, state, and federal information available through online databases or Freedom of Information Act requests related to brownfield sites and NPL listings. The local fire department and county health department may be good sources of information.
9h	Could any potential anthropogenic sources be causing changes to groundwater chemistry that would result in release of the constituent of concern through changes to pH, redox, etc.?	No	Yes	ND	Supporting	Unit	As noted, a change in pH or redox along a flow path or over time can cause concentrations for pH or redox-sensitive constituents to change.	Review field data to determine if a pH or redox change has occurred. Document the source of the pH or redox change. Refer to Table A-3 to verify that the SSI/SSL is for a constituent that is pH or redox-sensitive.
	Time-of-Travel Analysis							
10	Has groundwater flowing beneath potential sources had enough time to migrate to the affected monitoring well location?	No	Yes	ND	Supporting	Monitoring Point	Constituents must have time to travel downward to the aquifer and travel with the aquifer to the monitoring point. Sources must also be in upgradient or side gradient locations.	Use groundwater velocity calculation or simple analytical model to determine if there has been sufficient time for transport to the monitoring point.

Table Notes:

1. ND (not determined) indicates that this line of evidence was not tested or there are insufficient data to make a determination.
2. Line of Evidence (LOE) Types:
   Key lines of evidence are based on relationships that must be observed in order for an SSI/SSL to be due to a release from a CCR unit. If these relationships are not observed, then they are critical to establishing an ASD. It is difficult to build a strong ASD without any key lines of evidence. It may be possible to build an ASD with a single key line of evidence, but the ASD will be stronger with additional key or supporting lines of evidence.

Supporting lines of evidence provide additional information that supports the ASD. Supporting lines of evidence are generally not sufficient to build an ASD unless there is at least one key line of evidence, although it may be possible if there are many supporting lines of evidence.

3. This LOE applies to:
   Constituent: An SSI/SSL for that constituent at any monitoring point
   Monitoring Point: All SSIs/SSLs at a specific monitoring point
   Case: An SSI/SSL for a specific constituent at a specific monitoring point
   Unit: All SSIs/SSLs at the monitored unit

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APPENDIX A-3
Kelron Environmental (Kelron), 2003. Regional and Local Hydrogeology and Geochemistry, Vermilion Power Plant, Illinois. Dynegy Midwest Generation, LLC, November 2003

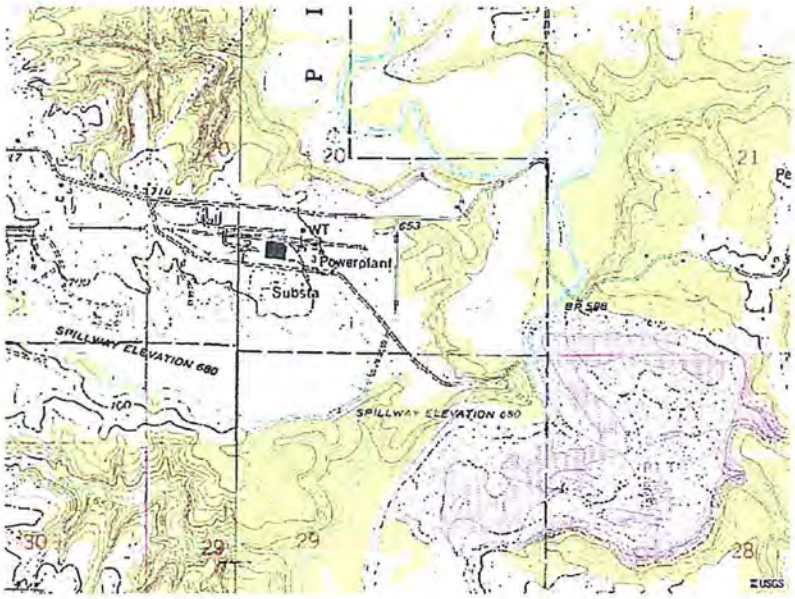
REGIONAL AND LOCAL HYDROGEOLOGY AND GEOCHEMISTRY VERMILION POWER PLANT, ILLINOIS

VOLUME 1 OF 2

November 30, 2003

Prepared for:

Dynegy Midwest Generation, Inc.
Decatur, Illinois



KELRON ENVIRONMENTAL
CHAMPAIGN, ILLINOIS

REGIONAL AND LOCAL HYDROGEOLOGY AND GEOCHEMISTRY VERMILION POWER PLANT, ILLINOIS

VOLUME 1 OF 2

November 30, 2003

Prepared for:

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EXECUTIVE SUMMARY

Background and Objectives

The East Ash Pond System (East Ash Pond) of the Vermilion Power Plant is owned and operated by Dynegy Midwest Generation, Inc. (DMG). The Vermilion Power Plant is located in Vermilion County, Illinois. Following a hydrogeologic investigation by Mathes Geotechnical Services, Inc. in 1987, the primary and secondary cells of the East Ash Pond were constructed in 1989. A planned expansion of the primary cell of the East Ash Pond beginning in 2002 prompted DMG to authorize in October 2001 a comprehensive regional and local hydrogeologic and geochemical investigation. Secondary objectives of the study were:

- To determine if the East Ash Pond was causing any changes to groundwater quality in the alluvial deposits or underlying bedrock;
- To assess the impacts of nearby coal mines on the hydrology and groundwater quality; and,
- To determine the appropriate groundwater classification for the East Ash Pond.

Due to the large scope of work involved and the need to establish the background geochemistry both in the vicinity of the study site (see Figures 1, 2, 3) and within the larger region, the Illinois State Geological Survey (ISGS) was contracted by Kelron Environmental (Kelron) to provide technical assistance in determining the background geochemistry of the bedrock deposits in the vicinity of the study site. The results of the ISGS investigation have been incorporated into this report.

Investigation Methods

In order to characterize both the geology and groundwater quality in the vicinity of the study site, a total of 40 borings and 16 monitoring wells were utilized. Groundwater and surface-water quality data were collected monthly over a six-month period for 19 inorganic parameters and four field parameters. In addition, as part of their separate study the ISGS collected groundwater samples from both DMG wells and private wells for inorganic and isotopic (tritium and Carbon-14) chemical analysis.

Other data collection activities employed during the study included:

- field permeability testing and analysis of the geologic materials by Kelron;
- seismic investigation of bedrock and coal mines near the East Ash Pond by URS Corp.;
- downhole geophysical logging of borings by the ISGS; and,
- laboratory analysis of rock-core samples by the ISGS.

The field and laboratory data collected during 2001 and 2002 were used to create a variety of products, including topographic maps, geologic maps, potentiometric surface maps, geologic cross-sections, hydrographs, and geochemical tables and figures.

Results

Geology

The deposits covering the bedrock in the study site are derived from recent river deposition (alluvial sediments) in the river valleys and glacial drift deposits occurring below the alluvial sediments and in the upland areas. Thickness of these deposits in the region range from zero thickness along portions of the Middle Fork of the Vermilion River (Middle Fork) where bedrock is exposed, to over 200 feet in the upland areas. The unlithified alluvial and glacial deposits in the vicinity of the East Ash Pond and within the floodplain generally range in thickness from 10 to 25 feet.

Rocks of Pennsylvanian age form the bedrock surface in the region surrounding the site. The Danville area is located on the northeast flank of the Illinois basin. Regionally, the Pennsylvanian bedrock consists of mainly shale with thin limestone, sandstone, and coal beds. The upper 75 feet of bedrock at the study site typically consists of the Shelburn Formation, which is composed of non-marine and marine, silty and micaceous shales. The Shelburn Formation contains a major coal seam mined in the region, the Danville Coal, also called the No. 7 Coal.

The top of the Danville Coal, or the void remaining where the coal was removed through mining, was intercepted at depths of 80 to 102.5 feet on the floodplain adjacent to the East Ash Pond. The thickness of the coal seam ranged from four to seven feet with an average thickness of 5.4 feet.

Hydrogeology

Groundwater within the alluvial and, where present, the glacial (till) deposits within the floodplain generally conforms to the ground surface topography. Groundwater elevations in the glacial and alluvial deposits demonstrate that groundwater elevations in the unlithified materials are higher than those in the adjacent Middle Fork through much of the year. The groundwater surface in the alluvial deposits fluctuates in response to changes in river stage and variations in precipitation. The groundwater surface is not affected by water levels in the East Ash Pond, which has been hydraulically isolated from both the shale and alluvial deposits by soil/bentonite slurry walls and a compacted clay core. Changes in pond elevation do not result in any corresponding changes in the shallow groundwater levels.

Groundwater elevations in the bedrock shale are highest in the topographically highest areas to the west and east of the Middle Fork of the Vermilion River. The lowest groundwater elevations occur at wells located adjacent to the Middle Fork. **Flow lines derived from the potentiometric surface maps indicate that the Middle Fork of the Vermilion in this area is a zone of discharge for the shale. The occurrence of the Middle Fork in this area as a regional discharge zone for the shallow bedrock is supported by the upward vertical hydraulic gradients measured within the shale. The shale outcrops along the banks of the Middle Fork and groundwater moving**

upward through the shale discharges into both the alluvium and directly into the Middle Fork.

The coal mines in the vicinity of the East Ash Pond System have been shown to have significant collapse features where the overlying shale has collapsed or partially collapsed downward into the void or mined coal seam. The collapse of the shale into the void translates upward through the shale, resulting in fracturing and in some cases surface subsidence.

Groundwater Chemistry

Based on the groundwater and surface water quality data collected in 2002, the affects of the East Ash Pond on groundwater quality are either negligible or not present. Groundwater quality data for most major ions and trace constituents is similar to background groundwater quality. In cases where elevated concentrations of a parameter were found to occur in groundwater near the East Ash Pond there were also elevated concentrations in background wells screened within coal deposits or in the proximity of abandoned coal mines.

Trace metal concentrations in groundwater were compared to East Ash Pond water samples and there was no commonality between the two water types. The deficiency of trace metals such as molybdenum, selenium, and vanadium in groundwater within both the alluvial deposits and the Pennsylvanian age bedrock at both background and East Ash Pond wells, as compared to their ubiquitous presence within waters of the East Ash Pond, suggests that **based on trace water quality data there is no impact to unlithified or bedrock groundwater quality by the East Ash Pond.**

The results of the isotopic analyses of groundwater samples from the background bedrock wells by the ISGS resulted in Carbon-14 ages ranging from 13,000 to 35,000 RYBP (radiocarbon years before present). In support of the Carbon-14 results, tritium concentrations for the same set of bedrock groundwater samples were all below detection limits ranging from 0.43 to 0.52 TU (tritium units). Water with non-detectable tritium concentrations is considered to be greater than 50 years old (Mehnert and Dreher, 2002).

The isotopic and other geochemical data from background monitoring wells supports the hydrogeologic conceptualization that **the Middle Fork of the Vermilion River is a regional discharge area for the bedrock.** Groundwater within the bedrock is at the end of its flow path and has upward hydraulic gradients, high dissolved mineral content, and is thousands of years older than recent groundwater in the overlying unlithified deposits.

Groundwater Classification

No groundwater parameters measured in the unlithified (i.e., alluvium and till) deposits of the study site exceeded Class I or II groundwater standards during March through August 2002. However, background well MW28 (see Figures 7, 8) exceeded the sulfate and TDS standards of 400 and 1,200 mg/L, respectively, during January and February 2002. Three bedrock monitoring wells at the East Ash Pond and four background wells

regularly exceeded standards for at least one of the parameters of chloride, sulfate, and TDS.

The occurrence of parameters within the bedrock at sufficiently high concentrations to exceed groundwater standards can be attributed to three sources: natural geochemistry; natural geochemistry associated with coal deposits; and, anthropogenic (man-made) affects on geochemistry associated with former coal mines and mine spoil. Similarly, high concentrations of inorganic parameters within the unlithified deposits can be attributed to natural geochemistry and the impacts of former coal mines and mine spoil.

Based on the hydrogeology and geochemistry established for the vicinity of the East Ash Pond and surrounding region, and given the influence of former coal mines documented at the study site on the geochemistry of groundwater, it appears that the groundwater designation is Class IV – Other Groundwater, in accordance with Section 620.201 of Part 620 (IAC Title 35, Subtitle F, Chapter I). Class IV groundwater is defined as groundwater within a previously mined area that cannot meet the standards of Class I or II groundwater.

1.0 INTRODUCTION

1.1 PURPOSE

The East Ash Pond System (East Ash Pond) of the Vermilion Power Plant, which is owned and operated by Dynegy Midwest Generation, Inc. (DMG), is located in Vermilion County, Illinois (Figures 1, 2, 3). Following a hydrogeologic investigation by Mathes Geotechnical Services, Inc. (Mathes) in 1987, the primary and secondary cells of the East Ash Pond were constructed in 1989. A planned expansion of the primary cell of the East Ash Pond beginning in 2002 prompted DMG to authorize in October 2001 a comprehensive regional and local hydrogeologic and geochemical investigation by Kelron Environmental (Kelron). The secondary purpose of the investigation was to determine if the East Ash Pond was impacting groundwater quality in the surficial and underlying bedrock deposits.

1.2 APPROACH

In order to characterize both the regional and local groundwater quality, the existing groundwater data collected from five monitoring wells from the earlier Mathes investigation had to be supplemented with new data from an expanded network of downgradient and background wells. Eleven new monitoring wells were installed to expand the existing network from 5 to 16 wells (Figures 7, 8). The larger network of wells and new boring data were used to re-define and expand upon the earlier hydrogeologic conceptualization by Mathes. In addition, the new groundwater quality data were combined with surface-water quality data collected from the East Ash Pond and the Middle Fork of the Vermilion River to determine potential interactions between natural and man-made surface water bodies with the shallow and deeper groundwater systems.

Due to the large scope of work involved and the need to establish the background geochemistry both in the vicinity of the study site and within the larger region, the Illinois State Geological Survey (ISGS) was contracted by Kelron to conduct an independent research investigation. The ISGS research and approach is discussed in the following section.

1.2.1 Illinois State Geological Survey Research

Kelron Environmental contracted with the ISGS to provide technical assistance in determining the background geochemistry of the bedrock deposits in the vicinity of the study site. As part of their independent study of background geochemistry, the ISGS performed the following tasks.

- Literature search, including unpublished data sources, for information pertaining to groundwater geochemistry of shale and coal. The search focused on the groundwater quality of Pennsylvanian-age shale and coal in Illinois and the Midwest. Unpublished data sources included the ISGS and Illinois State Water Survey (ISWS) databases.

- Reviewed geologic data from bedrock cores obtained during drilling of monitoring wells by Kelron and also reviewed geophysical logs recorded by the ISGS scientists.
- Reviewed and incorporated groundwater chemistry data for samples collected from background monitoring wells by Kelron and Dynegy.
- Provided advice on the list of analytes for groundwater sampling of monitoring wells by Kelron.
- Analyzed rock samples from bedrock cores for mineralogy.
- Collected groundwater samples from four private wells, two in the vicinity of the study site, and analyzed samples for anions, cations, pH, and alkalinity.
- Collected groundwater samples from two private wells and analyzed for the isotopes tritium [^{3}H] and Carbon-14 [^{14}C].
- Collected groundwater samples from six background monitoring wells installed by Kelron and analyzed for anions, cations, pH, alkalinity, and selected isotopes (^{3}H and ^{14}C).
- Prepared a final report that included pertinent literature and data on the geochemistry of shale and coal, discussion of the geochemistry of shallow bedrock groundwater in background wells based on the data collected as part of the study, and conclusions on the geochemistry of shallow bedrock groundwater in background wells in the region surrounding Dynegy's Vermilion Power Plant.

The results of the ISGS study have been incorporated into this report. The full ISGS study report is included as Appendix A.

1.3 SITE DESCRIPTION

The East Ash Pond is located in Vermilion County, primarily in the east half of the northeast quarter of the southeast quarter of Section 20, Township 20 North, Range 12 West (Figure 1). The entire study site, encompassing both the East Ash Pond and background wells, is located in the east half of Section 20 and the west half of Section 21. The Middle Fork of the Vermilion River (Middle Fork) borders the East Ash Pond along its north and east edges. The East Ash Pond lies in the flood plain of the Middle Fork and is bordered by bluffs to the west.

A topographic map (Figure 2) and aerial photograph (Figure 3) show the topographic and natural features in the vicinity of the East Ash Pond. The V-shaped lake in the lower right hand corner of the aerial photograph is a remnant of strip mining activity southeast of the East Ash Pond on the east side of the Middle Fork.

1.4 SITE HISTORY

1.4.1 Previous Investigations

A hydrogeological investigation was performed by Mathes in 1987 in the vicinity of the current East Ash Pond. The purpose of the 1987 study was to obtain sufficient

information concerning subsurface conditions at the site to make recommendations concerning location and construction of a new ash pond system for the Vermilion Power Plant.

Information from the 1987 Mathes investigation was incorporated into the current study. In addition, several monitoring wells from the Mathes study, which were not destroyed during construction of the East Ash Pond in 1989, were incorporated into the current investigation.

1.4.2 East Ash Pond Construction and Expansion

The East Ash Pond consists of two cells: an 11-acre primary (main) pond and a 0.8-acre secondary (polishing) pond. Ash in the main pond settles out of the sluice water, is decanted to the secondary pond, and then discharged to the Middle Fork in accordance with the effluent limits and monitoring requirements of an NPDES permit.

The original primary and secondary cells of the East Ash Pond System were constructed in 1989. The entire East Ash Pond was built directly overtop a thick shale formation which is greater than 80 feet thick in the vicinity of the ash ponds. The alluvial deposits overlying the shale formation were excavated so that the shale surface was exposed. The earthen berms on the north, east, and south sides of the primary cell are "keyed" into the underlying shale formation with two four-foot thick soil/bentonite slurry walls. Bentonite is an absorbent aluminum silicate clay formed from volcanic ash. These walls extend approximately 8 feet down into the shale and approximately 12 feet above the shale surface into the clay-core center of the earthen berms (see Figure 4). A natural earthen bluff composed of low permeability native clays forms the west side of the primary cell. The maximum permeability of the soil/bentonite slurry wall was specified not to exceed $1x10^{-8}$ cm/s.

The earthen berms built on top of the soil/bentonite slurry walls are approximately 18 feet tall, 80 to 120 feet wide at the base, and 15 feet wide at the top. The outside portion of the berms is constructed of locally excavated sand and clay. The center of these berms is constructed with a compacted clay core ranging in thickness from 15 feet at the top to 30 feet near the base. The permeability of the clay core is approximately 10^{-7} cm/s.

The new berms constructed to expand the capacity of the primary cell of the East Ash Pond System in 2002 raised the height of the original berms by approximately 20 feet. The new berms are constructed with 8-foot clay liners keyed into the underlying clay core. The 8-foot clay liners are on the wetted-side of the berm surrounding the expanded ash pond. The clay liners are placed within berms constructed of local clay and silty clay materials. The permeabilities of these materials are within the same specification range as for the original ash pond. A natural earthen bluff wall forms the west side of the enlarged primary cell.

The secondary pond is not being expanded or modified as part of the East Ash Pond System expansion.

1.4.3 Coal Mines

The vicinity of the Vermilion Power Plant has seen extensive coal-mining activity from 1893 to 1970. Two coal mines, called the Crawford Mine (ISGS Mine Index No. 3889) and Fletcher's Middlefork Mine (ISGS Mine Index No. 3888), are located beneath the East Ash Pond and vicinity (Figure 5). Based on data and maps obtained from the ISGS, the former entrances to the two coal mines beneath the site are located just north of the secondary cell of the East Ash Pond (Mine 3889) and 600 hundred feet southwest of the primary cell (Mine 3888) (ISGS, 1996). Information pertaining to both these mines and other mines in the vicinity of the Site are provided in Appendix B.

The entrance to the Crawford Mine was field located. It is a slope shaft mine with the main coal seam (the Danville, or No. 7 Coal) located between the depths of 80 and 92 feet below land surface (BLS). The average thickness of the main coal seam is approximately 5 ½ feet. Several borings were advanced in order to locate both this mine and the Middlefork Mine. The procedures and data gathered during the coal-mine investigation, in addition to the subsequent geophysical investigation, are discussed later in the report. The Middlefork Mine operated between 1939 and 1949 using the room-and-pillar method, whereby the coal is removed in 'rooms' with 'pillars' of coal left in place to support the roof. During the course of the investigation of this mine both mined and un-mined areas were intercepted during exploratory borings. Mined areas were identified based on the drill bit dropping through voids where the coal had been removed. In addition to locating the mined interval, the slope shaft descending to the coal seam was intercepted near the mine entrance at a depth of 28 to 37 feet BLS.

The exact entrance to Middlefork Mine was not located, although based on mine tailings, topography, and historic records it is somewhere between the north end of the secondary cell and the Middle Fork of the Vermilion River. This mine is a vertical shaft mine with the main seam of the Danville Coal located between the depths of 102 and 115 feet BLS. The average thickness of the seam in this area is estimated at five to six feet. This mine operated between 1905 and 1919 using the room-and-pillar method. Three borings were advanced to locate this mine and two of them intercepted mined-out coal seams, one of which had collapsed. The coal mine collapse and subsidence at the Middlefork Mine caused some fracturing of the overlying shale and also changed the groundwater hydraulics in the vicinity of the mine. The potential effect of the coal mine on the groundwater hydrology is discussed in Section 5.

Other mines, both shaft and strip, are located south and southeast of the Crawford and Middlefork mines discussed above (Appendix B). Some of these mines are located within or adjoining the property of the Vermilion Power Plant. The Danville Coal has been extensively mined using both subsurface and strip methods in the vicinity of the Site. To varying degrees, these mining activities have altered the natural topography, hydrology, surface water chemistry, and groundwater chemistry that existed in the area before mining began.

A geophysical study was conducted by URS Corp. in early 2002 to further investigate and locate the coal mines in the vicinity of the East Ash Pond. The results of this investigation are presented in Section 4.2.1.2.

2.0 STUDY METHODS AND PROCEDURES

The objective of the investigation was to conduct a full hydrogeologic and groundwater geochemical characterization in the vicinity of the East Ash Pond of the Vermilion Power Plant and compare the investigation results to the regional background hydrogeology and geochemistry. Secondary objectives of the study were:

- To determine if the East Ash Pond was causing any changes to groundwater quality in the alluvial deposits or underlying bedrock;
- To assess the impacts of nearby coal mines on the hydrology and groundwater quality; and,
- To determine the appropriate groundwater classification for the site.

Data collected from the previous investigation at the site (Mathes, 1987) and quarterly groundwater quality data collected since 1994 were incorporated into the study. The methods used to conduct the study and procedures used for obtaining the necessary geologic, hydrologic, and chemical data are presented in this section.

2.1 METHODS

2.1.1 Previous Data

As mentioned earlier, the prior investigation by Mathes (1987) was incorporated into the study, both as background data for developing an initial conceptual understanding of the hydrogeology and for inclusion of pertinent hydrogeologic data directly into the current investigation. Five wells installed by Mathes in 1987 that were not destroyed by the subsequent construction of the East Ash Pond were incorporated into the study. These five wells include the alluvial wells MW13B and MW16B, which were nested with the shale bedrock wells MW13A and MW16A, respectively, and the till well MW10 (Figures 6, 7, 8). In addition to the existing wells, the Mathes study provided borehole geologic data and hydraulic conductivity data.

Supplementing the geologic data available for the site, inorganic groundwater quality data and water-level data were available for the five monitoring wells for the period of 1994 to the present. Quarterly groundwater monitoring for selected inorganic parameters was instituted beginning in 1994.

Site topographic maps, as-built diagrams of the East Ash Pond, and aerial photographs were used to develop base maps, locate wells, and develop geologic cross-sections.

2.1.2 Geologic Data

The geology presented in this report is primarily based on the geotechnical and monitoring well borings listed in Table 1 and summarized below.

- Nine borings drilled by Mathes (1987) as part of a hydrogeologic investigation for construction of the East Ash Pond.

- Eleven borings drilled in 2001 as part of the current investigation. Four borings were drilled at locations near the East Ash Pond and seven were placed at locations to the south, east, and north.
- Twelve borings drilled in 2001 for geotechnical characterization for expansion of the East Ash Pond; and,
- Eight exploratory borings drilled in 2002 for locating and characterizing the coal mines in the vicinity of the East Ash Pond.

Detailed geologic logs are provided for all of the borings in Appendix C.

Other information incorporated into the study for characterizing the geology was provided by the ISGS. The ISGS performed downhole geophysical logging of three of the deepest borings, logged three bedrock cores, and provided geologic logs and well construction data for a one-mile radius around the study site. The ISGS also provided information for coal mines and coal seams in the vicinity of the site.

In addition to the above geologic information, the results of the geophysical investigation into coal mine locations at the East Ash Pond, conducted in early 2002 by URS Corp., have also been incorporated into this report.

The assembled geologic data were used to develop the following:

- thickness maps of the unlithified deposits;
- bedrock elevation map;
- coal seam elevation map; and,
- coal mine location maps.

2.1.3 Hydrologic Data

The hydrology of the unlithified deposits and underlying bedrock presented in this report was based on the data obtained from a network of 16 monitoring wells installed at the site: five from the 1987 Mathes study and 11 installed in 2001 (Table 2 and Figure 6). Six monitoring wells are installed in the unlithified deposits, with four located near the East Ash Pond and two background wells located north of the Middle Fork (Figure 7). Ten monitoring wells are installed in the bedrock, with five installed near the East Ash Pond, four background wells located to the north and east of the Middle Fork, and one background well located south near the river pump station. Water-level measurements were made monthly for the eight months from January through August 2002 (Table 3 and Figure 8).

In addition to the hydrologic data collected from the monitoring wells, surface water measurements were obtained from the Middle Fork upriver from the East Ash Pond near nested wells MW26/MW27, downriver at MW25, and from the primary and secondary cells of the East Ash Pond. Surface water measurements of the East Ash Pond were not conducted after May 22 because the primary and secondary ponds were drained during construction activities. The last discharge from the East Ash Pond outfall to the Middle

Fork during 2002 was on May 26. Discharging from the East Ash Pond System resumed in January 2003 after construction of the enlarged primary cell was completed.

The groundwater and surface water measurements were used to develop the following:

- potentiometric surface maps;
- groundwater and surface water hydrographs showing temporal variations in water levels;
- horizontal groundwater flow directions and velocities;
- vertical hydraulic gradients between the alluvial deposits and underlying bedrock;
- hydraulic connection between groundwater in the alluvium and bedrock with surface water in the Middle Fork; and,
- impact assessment of the East Ash Pond on alluvium and bedrock groundwater levels.

2.1.4 Groundwater and Surface Water Chemical Data

The groundwater chemistry data presented in this report is based on six months (March through August 2002) of field and laboratory data collected from 16 monitoring wells. Three of the wells (MW13B, MW16B, and MW22) were typically dry or had insufficient water for groundwater sampling. In addition to the above samples, inorganic and isotopic chemistry data analyzed by the ISGS for the five background bedrock wells (MW25, MW27, MW29, MW30 and MW31) sampled in June 2002 were also incorporated into this report. The surface water chemistry data are based on five months of data collected from the East Ash Pond primary cell (January through May 2002) and six months (March through August 2002) of data collected upriver on the Middle Fork at the Higginsville Bridge. No East Ash Pond samples were collected after May 2002 because the pond was drained and no further effluents were being discharged into the impoundment during construction activities.

The chemical data presented in this report for the monitoring wells includes the field parameters temperature, pH, and conductivity and the following laboratory analytical parameters:

Alkalinity	Aluminum	Barium	Boron	Calcium
Chloride	Iron	Lithium	Magnesium	Manganese
Molybdenum	Phosphorus	Potassium	Selenium	Sodium
Strontium	Sulfate	TDS	Vanadium	

The above parameters, with the exception of the field parameters, were also analyzed in the surface water samples. However, all of the inorganic parameters in groundwater were analyzed as dissolved while those in surface water were analyzed as totals.

In addition to the samples collected and analyzed monthly from March through August 2002, the background monitoring wells MW25 through MW31 and the East Ash Pond primary cell were sampled in February 2002 for the same inorganic constituents listed above plus cadmium, chromium, and zinc. Based on this first round of sampling in February, the analytes cadmium, chromium, and zinc were dropped from the study

because they were below their respective method detection limits (1, 1, and 5 micrograms per liter [ug/L], respectively) in almost all of the samples analyzed.

2.2 TECHNICAL PROCEDURES

2.2.1 Borehole Drilling

Eleven boreholes drilled for the installation of monitoring wells were numbered sequentially from MW22 to MW32. Borehole logs are provided in Appendix C for both the current and prior studies at the Site. The eight boreholes drilled for the coal mine investigation were numbered sequentially from B201 through B208. Boreholes were drilled using a Diedrich D-120 rig equipped with hollow-stem augers and rock coring equipment. Drilling through the unlithified deposits was performed utilizing hollow-stem augers. Samples were obtained using a 24-inch long by two-inch outside diameter (O.D.) split-spoon sampler. The sampler was mechanically driven using a 140-pound hammer with a 30-inch drop. Soil samples were collected continuously in unlithified deposits less than 25 feet thick and at intervals of five to ten feet in deposits greater than 100 feet thick.

All soil samples were logged in the field for sample interval and soil recovery, stratum thickness and depth, visual soil classification by the Unified Soil Classification System [(USCS); ASTM D 2487 and 2488], moisture content and presence of water, soil stiffness, and horizontal compressive strength using a pocket penetrometer.

For those boreholes cored into the underlying bedrock, 4.5-inch O.D. steel surface casing was installed to the top of the bedrock. The outer casing was left permanently in place for all of the bedrock holes with the exception of MW25, MW30, MW31, and the coal mine boreholes. Following installation of the outer casing, continuous sampling of the bedrock was performed using an HQ-core (2.25-inch I.D.) for the monitoring well locations and NQ-core (1.88-inch I.D.) for coal mine borings. Wireline coring, which is a type of rotary drilling, was used to obtain continuous samples of consolidated (i.e., bedrock) formations. A hollow coring bit was used to cut the rock and the samples of rock were removed at designated intervals, in the case of this study every 10 feet. Clean water was used as the drilling fluid.

All core samples were logged in the field for sample interval and soil recovery, stratum thickness and depth, and visual soil classification by the USCS System. In addition, the cores obtained from boreholes MW25, MW30, and MW31 were delivered to the ISGS for more detailed classification and analysis (Appendix A).

2.2.2 Monitoring Well Installation and Development

Groundwater monitoring wells were constructed of two-inch diameter, flush-threaded (Schedule 40) polyvinyl chloride (PVC) screens and risers. Well screens were 0.010-inch slot size machine cut. Screen lengths (Table 2) were 20 feet for all of the bedrock wells except MW32, which had a 10-foot screen. Screen lengths for new wells installed in the unlithified deposits were five feet for MW26 and MW28 and 10 feet for MW23.

Following placement of the screen and riser, the annular space between the well screen and borehole wall was backfilled with well-sorted quartz sand. The sand filter was placed from the bottom of the borehole to approximately 2-feet above the top of the well screen. A minimum two-foot thick bentonite seal (bentonite chips, pellets, or grout) was placed above the sand pack. The remainder of the borehole annulus was filled to the surface with bentonite grout using a 1.25-inch ID PVC tremie pipe which was placed down the inside of the augers as they were removed from the ground. Monitoring wells were completed with steel well protectors extending approximately 2 ½ to 3 feet above ground surface and set in a cement pad. Monitoring well construction forms and diagrams are provided in Appendix C. In addition, the Well Completion Reports and Well Construction Reports required by the Illinois Environmental Protection Agency and the Illinois Department of Public Health, respectively, are provided in Appendix D.

At least 48-hours following well completion, all monitoring wells were developed to attempt to restore the natural hydraulic conductivity of the monitored formation and remove all drilling-induced sediment to provide turbidity-free groundwater samples. Development was performed using air-lift displacement and submersible pumps. The wells were developed until a minimum three to five well volumes were removed from each well. However, some of the wells installed into the shale did not produce sufficient groundwater before being pumped dry (i.e., MW25, MW31 and MW32); in those cases the wells were developed on more than one occasion in order to remove at least two to three well volumes. Water samples collected during well development were monitored for the field parameters pH, temperature, and conductivity. Development was considered complete when the field parameters had stabilized. Well development data sheets are provided in Appendix E.

2.2.3 Site Surveying

Monitoring well locations were surveyed by an Illinois Professional Land Surveyor to an accuracy of 0.1-foot horizontal and 0.01-foot vertical relative to the state planar horizontal datum NAD83 and vertical datum NAVD88 Geoid 96, respectively. Borehole locations were surveyed to a minimum accuracy of 1-foot horizontal and 0.1-foot vertical. Boring and monitoring well locations are shown in Figure 7 and elevations are provided in Table 1.

2.2.4 Water-Level Measurement Collection

Prior to collecting groundwater samples, static water depth was measured to an accuracy of 0.01 foot in each monitoring well using a Solinst-101 electronic water-level indicator. The groundwater depths were measured relative to the top of the PVC riser and subsequently subtracted from the measuring point elevation to determine the groundwater elevation within the well. In addition to groundwater elevation at all of the monitoring wells, surface water elevation measurements were obtained from the following locations:

- Middle Fork of Vermilion River adjacent to wells MW26/MW27;
- Middle Fork of Vermilion River adjacent to well MW25 at the downriver pump station;

- Primary cell of the East Ash Pond; and,
- Secondary cell (i.e., Polishing Pond) of the East Ash Pond.

Groundwater and surface water level measurements were conducted on a monthly basis from January through August 2002. The measurements were used to develop hydrographs, potentiometric surface maps, vertical gradients between formations, and evaluate hydrologic interactions between the unlithified deposits, bedrock, Middle Fork, and East Ash Pond. Water levels and elevations for the period of investigation are provided in Table 3.

2.2.5 Groundwater and Surface Water Sampling and Chemical Analyses

Water samples were collected from the background wells MW25 through MW31 and the primary cell of the East Ash Pond on a monthly basis by the DMG Environmental Laboratory beginning in January 2002. The remaining monitoring wells in the vicinity of the East Ash Pond, and upriver samples from the Middle Fork at the Higginsville Bridge, were sampled monthly beginning in March 2002. Samples from all wells and surface-water collection points were obtained within a period of one to two days each month with the exception of the March sampling event, when poor weather and equipment problems extended the sampling period to three days.

Groundwater samples were collected using a low-flow sampling technique with Well Wizard® bladder pumps and MicroPurge® equipment. The bladder pumps prevent contact between the pump drive air and the sample, and the downhole equipment is permanently dedicated to each well, preventing cross-contamination caused by transporting pumps between wells. The specification sheets for each of the bladder pumps placed in monitoring wells at the Site are provided in Appendix F. The bladder pumps were placed within the screened interval of each well so that groundwater being pumped would come from the formation pore water and minimize pumping of the overlying static water within the well casing. The only wells that did not have bladder pumps installed were MW10, MW13B, and MW16B. These three wells are typically dry or have insufficient groundwater for sampling. In those cases where there was sufficient groundwater to be sampled from these wells it was removed using dedicated bailers or a peristaltic pump.

The low-flow ground water sampling procedures followed for this study are based on the sampling protocol provided by the United States Environmental Protection Agency (USEPA) in a document authored by Puls and Barcelona (1995). This document has been incorporated into the report as Appendix G. Due to the extremely low permeability of the shale formation from which many of the groundwater samples were obtained, passive sample collection techniques were utilized. Passive sample collection was conducted at the bedrock wells by setting the pump rate at less than 0.2 Liters per minute (L/m), pumping sufficient water to clear the tubing and bladder pump of stagnant water, and collection of samples for laboratory analysis. Three sets of measurements for the field parameters of temperature, pH, and conductivity were collected and documented as follows: at the start of pumping, prior to sample collection, and at the conclusion of

sample collection. Sampling of the higher permeability wells installed within the unlithified deposits was conducted at higher flow rates of 0.2 to 0.5 L/m.

Analysis of field parameters (pH, specific conductivity, and temperature) were conducted using either a Hydrolab® Minisonde Model 4a or a Hydrolab Surveyor Model 4a water quality analyzer connected directly to the discharge tubing from the bladder pump. Samples for laboratory chemical analysis were collected using in-line filtration (0.45 micron filter size) that prevented contract with air prior to collection. Water samples were collected in new or acid-washed polypropylene bottles and subsequently stored at 4° C for transport back to the laboratory.

Surface water samples were collected from the East Ash Pond primary cell and the Middle Fork upriver by submerging the sample bottles directly into the water and, where possible, capping under water to minimize air contact. Surface water samples were collected for analysis of total inorganic parameters and were not field filtered. No field parameters were analyzed for the surface water samples.

Chemical analyses were performed by the DMG laboratory. Inorganic analyses were performed in accordance with U.S. EPA SW-846 and Standard Methods for the Examination of Water and Wastewater, 19th Edition. The following parameters and analytical methods were analyzed by DMG for the groundwater and surface water samples:

- Total Alkalinity: EPA Method 310.1 (Titremetric Method);
- Total Dissolved Solids (TDS): EPA Method 160.1 (Gravimetric Method);
- Chloride: Standard Methods, Method 4500-Cl (Potentiomeric Method);
- Sulfate: EPA Method 375.4 (Turbidimetric Method);
- Phosphorus: EPA SW-846 Method 365.2 (ascorbic-acid Colorometric Method); and,
- Boron, Manganese, Magnesium, Calcium, Potassium, Iron, Aluminum, Lithium, Molybdenum, Selenium, Strontium, Vanadium, Barium: EPA Method 200.7 (ICP).

2.2.6 Illinois State Geological Survey Sampling and Chemical Analyses

The ISGS accompanied DMG laboratory personnel on June 18, 2002 in order to obtain split samples for analysis. The ISGS returned to the study site on June 25 and 26 along with Kelron to obtain groundwater for isotope analyses. The methods by which samples were collected and analyzed by the ISGS for their background water quality study are presented in detail in the ISGS report (Appendix A).

2.2.7 Field Permeability Tests

In-situ hydraulic conductivity tests were performed on seven of the newly installed shale monitoring wells (MW24, MW25, MW27, MW29, MW30, MW 31, and MW32) and two

of the newly installed alluvial monitoring wells (MW26 and MW28) during September 2002. The monitoring wells were tested by the variable head ("slug") test method.

Most of the slug tests were conducted using three and four foot long by 1-1/4 inch diameter PVC slugs with rope and recorded using In-Situ® Troll 8000 datalogger with 15 pounds per square inch (psi) transducer. The Troll 8000 is a combination downhole transducer and datalogger. Due to the slow recharge of some of the shale monitoring wells, a few tests were conducted without the Troll 8000 by measuring water levels using the Solinst 101 electronic water-level meter and recording the measurements by hand. In some cases only rising head tests were performed and in others both rising and falling head tests were performed.

A laptop computer was used to download the data from the datalogger and analyze the data with the use of AQTESOLV™ for Windows (Version 2.5), an aquifer test analysis software package by HYDROSOLVE. All of the analytical solutions used the Bouwer-Rice method (1980). The AQTESOLV™ for Windows output is included in Appendix H.

2.2.8 Data Management

Field data were recorded on pre-printed forms including:

- Daily field reports;
- Boring logs;
- Monitoring well completion reports;
- Well development reports; and,
- Water sampling forms.

Groundwater and surface water sample data, including water levels, field parameter analyses, and laboratory chemical analyses, were entered and stored on a proprietary groundwater data management software package (MANAGES™ Version 2.7, Electric Power Research Institute). Data collected from wells MW10, MW13A/13B, and MW16A/16B beginning in 1994 were already incorporated into the database prior to the beginning of the current study.

3.0 REGIONAL GEOLOGY AND HYDROLOGY

3.1 TOPOGRAPHY

The uplands are fairly uniform in elevation. They generally occur between the elevations of 650 and 700 feet National Geodetic Vertical Datum (NGVD) in the vicinity of the study site. The lowland areas (floodplains) along the Middle Fork lie between elevations of 550 and 600 feet NGVD. The natural surface topography within the floodplain is relatively flat with drainage toward the river.

3.2 BEDROCK GEOLOGY

The Danville area is located on the northeast flank of the Illinois basin. The bedrock strata are of Pennsylvanian age and in general dip gently southwestward toward the center of the basin.

The study site lies approximately 3 miles west of the central axis of the Danville Bedrock Valley, which is oriented northwest to southeast and midway between the Middle Fork and North Fork of the Vermilion River (Selkregg and Kempton, 1958).

Regionally, the Pennsylvanian bedrock consists of mainly shale with thin limestone, sandstone, and coal beds (Selkregg and Kempton, 1958). The bedrock surface elevation in the vicinity of the study site is between 500 and 600 feet NGVD (Willman et al., 1967). The rocks were originally deposited as unlithified sediments in coastal marshes or in shallow seas that repeatedly formed in the area. The shale was originally deposited as clay, while coal was formed from plants buried in the coastal swamps. Sandstone was deposited as sand and the limestone was formed by precipitation of carbonates and by accumulation of seashells on the sea floor (Selkregg and Kempton, 1958).

After the Pennsylvanian sediments were deposited, the seas retreated and the upper part of the bedrock was deeply eroded. During the Pleistocene epoch, continental glaciers advanced from the north and overrode the eroded bedrock surface (Selkregg and Kempton, 1958), leaving the glacial deposits that mantle the area today.

The principal formations within the Pennsylvanian bedrock in the region are, from upper to lower, the Bond, Shelburn, and Carbondale Formations. In the vicinity of the Site the principal formation is the Shelburn, which contains a major coal seam mined in the region, the Danville (No. 7). The Danville coal has been mined extensively in the region both as surface (strip) mines and underground mines. The northernmost mines identified by the ISGS (ISGS, 1996) are located in the immediate vicinity of the Site (Figure 5) within Township 20 North and Range 12 West. Additional information pertaining to coal seams and mines in the vicinity of the Site is provided in Section 4.2.1.1.

Several geologic logs obtained from the ISGS files (ISGS, 2001) were for exploratory borings for coal seams in 1910 and 1911 (Appendix I). In the vicinity of the site (Sections 20 and 21), the deepest borings were to depths of 166 and 131 feet BLS with

bedrock intercepted at depths of 105 and 26 feet BLS, respectively. The formations intercepted by the two borings consisted of shale containing the following two coal seams:

- Danville (No. 7) coal at depths of 113 to 120 feet BLS and 79 to 83 feet BLS; and,
- Herrin (No. 6) coal at depths of 144 to 148 feet BLS and 110 to 114 feet BLS.

No limestone or sand layers were identified on these borings. However, further to the south in Section 28, a 1910 boring for the Big Four Railroad was progressed to 312 feet BLS. The Danville and Herrin coal seams were intercepted at depths of 72 and 96 feet BLS, respectively. Several other layers of coal, less than two feet in thickness, were intercepted. Five limestone layers ranging in thickness from one to eight feet were intercepted between 99 and 257 feet BLS. One sandstone layer was intercepted at 211 to 213 feet BLS. The entire bedrock interval cored was 247 feet, of which 220 feet was shale, 11 feet coal, 14 feet limestone, and 2 feet sandstone.

3.3 UNLITHIFIED DEPOSITS GEOLOGY

The deposits covering the bedrock in the region surrounding the study site are derived from recent river deposition (alluvial sediments) in the river valleys and glacial drift deposits occurring below the alluvial sediments and in the upland areas. The glacial and interglacial geologic events that shaped the topography seen today occurred during the Pleistocene Epoch, about two million to 12,000 years ago (ISWPTF, 1997). Thickness of these deposits in the region range from zero thickness along portions of the Middle Fork where bedrock is exposed to over 200 feet in the upland areas (Piskin and Bergstrom, 1975).

Although there were several major glaciations – pre-Illinoisan, Illinoisan, and Wisconsin – glaciers of only the last three are known to have entered the east-central Illinois region (Selkregg and Kempton, 1958). Each glaciation was followed by an interglacial period in which the climate warmed and the ice front moved back. The surficial features seen in the upland areas are part of the Gifford Moraine, which was formed during the Woodfordian Substage of the Wisconsinan Stage of glaciation (Willman and Frye, 1970).

Based on stack-unit maps of geologic materials to a depth of 15 meters (49.3 feet) prepared by Berg and Kempton (1988), the lowlands (floodplains) adjacent to the Middle Fork are characterized by the following downward sequence of unlithified deposits:

- Less than six meters (19.7 feet) of Cahokia Alluvium (i.e., alluvial sediments deposited by streams and rivers);
- Less than six meters of Henry Formation deposits of Wisconsinan age, which consist of glacial outwash dominated by sand and gravel; and,
- Less than six meters of Glasford Formation deposits of Illinoian age, which consist of silty and clayey diamictons.

Diamicton is unsorted, nonstratified sediment with a wide range of particle sizes (i.e., clay, silt, sand, gravel, cobbles, and boulders). When diamicton is due to glacial deposition it is known as till. The diamictons in the vicinity of the study site are till deposits characterized by a clay matrix containing variable percentages of silt, sand, gravel, cobbles, and boulders.

The unlithified deposits of the upland areas bordering the Middle Fork are characterized by the following downward sequence:

- Greater than six meters (19.7 feet) of Wedron Formation deposits of Wisconsinan age, which consist of silty and clayey diamictons; and
- Less than six meters of Glasford Formation silty and clayey diamictons (Berg and Kempton, 1988).

Unlithified deposits below 15 meters (49.3 feet) are not identified in the stack-unit maps, but based on published literature the Glasford Formation deposits either extend to the top of bedrock or are underlain by the Banner Formation of pre-Illinoisan age (i.e., greater than 500,000 years of age). The Banner Formation, which consists of till and intercalcated outwash where present, is draped over the bedrock surface and is generally deepest where the bedrock is deepest.

3.4 BEDROCK HYDROLOGY

The Pennsylvanian rocks generally have low porosities and permeabilities. The porosity of shale typically ranges from 1 to 20 percent (Walton, 1988). Representative horizontal field hydraulic conductivity (permeability) for shale typically ranges from $5x10^{-6}$ to $5x10^{-10}$ centimeters per second (cm/s). Representative aquitard field permeability ranges for shale, which is defined as the rate of vertical flow of water through a unit horizontal cross-sectional area of the aquitard, are $5x10^{-8}$ to $5x10^{-12}$ cm/s. In contrast to the low permeability of shale, coal deposits have horizontal permeability ranging from $5x10^{-2}$ to $5x10^{-5}$ cm/s (Walton, 1988).

The Pennsylvanian rocks in the region yield small amounts of water to wells from interconnected pores, cracks, fractures, crevices, joints, and bedding planes. Water-bearing openings are variable from place to place and are best developed near the surface in thin limestones and sandstones, when present, within the predominantly shale formation. Shallow sandstone and creviced limestone may yield small supplies in some areas, but water quality becomes poorer with increasing depth. The Pennsylvanian bedrock is not a reliable source of groundwater and the quality varies considerably. Small domestic supplies have been obtained from creviced limestone, permeable sandstone, or cracked shale and coal in the upper part of the bedrock (Selkregg and Kempton, 1958).

Water in the Pennsylvanian rocks becomes highly mineralized with increasing depth. Recharge to the Pennsylvanian rocks is derived locally from vertical leakage through the glacial drift and other unlithified materials that are in turn recharged from precipitation.

Water occurs in these rocks mainly under artesian and leaky-artesian conditions (Csallany, 1966).

3.5 UNLITHIFIED DEPOSITS HYDROLOGY

Alluvial deposits along the Middle Fork valley contain a wide variety of sediments ranging from clay to sand, gravel, and cobbles. The effective porosities for the types of sediments found in the vicinity of the study site range from 20 to 35 percent for poorly sorted sand and gravel alluvial deposits to 10 to 20 percent for the diamictons found in the upland areas (Fetter, 1980). Effective porosity, which is a measure of the pore space thorough which saturated flow can occur, typically ranges from 10 to 30 percent for poorly sorted sand and gravel deposits to 5 to 20 percent for diamictons (Walton, 1988).

Horizontal hydraulic conductivity for the alluvial deposits as measured by field tests can vary greatly depending on the percentage of fine-grained materials within those deposits. Deposits with materials ranging from sand to gravel typically have horizontal permeability ranging from 10^{-1} to 10^{-4} cm/s. Silt, clay, and mixtures of sand, silt, and clay typically have horizontal permeability ranging from 10^{-4} to 10^{-7} cm/s (USDI, 1981; Fetter, 1980).

Groundwater in the alluvial deposits discharges into the Middle Fork during most of the year with the exception of flood events, when localized flow-reversals may occur. No published information is available concerning the hydrology of the shallow deposits in the vicinity of the study site.

Permeable deposits capable of supplying sufficient groundwater for domestic use are scattered and discontinuous, with aquifers varying in permeability (Selkregg and Kempton, 1958). Water-well logs and a well location map were obtained from the ISGS during October 2001 (Appendix I; ISGS, 2001) for a four square mile area surrounding the study site. Ten water wells installed between 1967 and 1999 in upland areas were screened across permeable formations ranging in depth from 40 to 160 feet BLS. Eight of the ten wells were screened at depths greater than 100 feet BLS and had an average depth of 132 feet BLS. Groundwater was obtained primarily from sand and gravel deposits within the drift. The sand and gravel layers ranged from 3 to 13 feet in thickness. However, one well obtained groundwater from gravelly clay at 135 to 160 feet BLS and another well, drilled in 1999, was a dry hole.

4.0 STUDY SITE GEOLOGY AND HYDROLOGY

Characterization of the geology and hydrogeology at the study site is based on previous investigations conducted prior to construction of the East Ash Pond in 1989 and on new boring and monitoring well data from the current 2001-2002 investigation. Mathes Geotechnical Services, Inc. conducted a hydrogeologic investigation in a portion of the current study site (Mathes, 1987) prior to construction of the original East Ash Pond. The information used to describe the study site geology and hydrogeology is based on the borings and monitoring wells summarized in Table 1 and provided in Appendix C in addition to all of the field data collected during the course of the study in 2001 and 2002.

The two types of materials present at the study site consist of unlithified deposits (alluvium and glacial deposits) and bedrock. Each of these materials will be discussed in detail in order to establish a framework with which to understand the hydrogeology, and in later sections the geochemistry, of the site. Figure 7 shows the locations of all of the borings used in describing the geology of the site. Figure 9 shows the locations of the east-west (Figure 10) and north-south (Figure 11) geologic cross-sections through the study site.

4.1 UNLITHIFIED DEPOSITS

4.1.1 Alluvial and Glacial Geology

The cross-sections across the Site (Figures 9, 10, and 11) best demonstrate the correlation between topography and stratigraphy of the unlithified deposits. The other variable that affects the thickness and composition of the unlithified deposits is the bedrock surface topography. Glacial deposits are thickest (greater than 100 feet) where the shale bedrock decreases in elevation. The glacial materials consist primarily of low plasticity silty to sandy clays with occasional layers of silt, sand, and gravel.

The unlithified alluvial and glacial deposits in the vicinity of the East Ash Pond and within the floodplain generally range in thickness from 10 to 25 feet (Figure 12). Thickness of the alluvial deposits immediately adjacent to the Middle Fork is generally 10 to 15 feet. The unlithified deposits increase in thickness towards the uplands as the alluvial deposits pinch out and are supplanted by glacial deposits at higher topographic elevations.

Along the western portion of the study site, to the west of the East Ash Pond, the thickest glacial deposits range from 71 feet at Well MW22 to the north to 103 feet at Boring B208 to the south. North and east of the Middle Fork the thickness of the glacial deposits are 116 feet at Well MW30 and 155 feet at Well MW31, respectively.

The uppermost unlithified deposits in the floodplain consist of alluvium composed primarily of sand with occasional layers of silty clay. The sand is generally a fine to medium sand that contains silts, clays, and gravels in varying amounts. The sand in some areas may be overlain by silty to sandy clay. In places where the unlithified deposits in

the floodplain become thicker, the alluvium may be underlain by glacial deposits consisting of outwash sand and gravel or diamictons. The shallow geology at Boring MW23, located within 25 feet of the south bank of the Middle Fork, has approximately 14 feet of alluvial deposits ranging from silt to gravel overlying eight feet of glacial deposits consisting of sandy clay with gravel.

4.1.2 Alluvial and Glacial Hydrology

Groundwater elevation within the alluvial and, where present, the glacial deposits within the floodplain generally conform to the ground surface topography. Prior to construction of the East Ash Pond, groundwater elevations documented by Mathes (1987) in the alluvial deposits generally ranged from five to six feet below ground surface in most of the alluvial wells where the East Ash Pond was constructed.

The only alluvial wells remaining from the 1987 study are MW13B and MW16B, located between the East Ash Pond and the Middle Fork. Hydrographs of groundwater levels in these two wells for 2002 are provided in Figures 13 and 14. Groundwater elevations measured in Well MW13B in 2002 have ranged from dry (no groundwater) in January and July to 573.44 feet NGVD in May, which is approximately 1.9 feet above the bottom of the screen and two feet above the bedrock surface. Groundwater elevations in Well MW16B were dry (no groundwater) in January, February, May, July, and August and were approximately 570 feet NGVD in March, April and June. The bottom of the well screen and the bedrock surface are at elevations of 566.5 and 566 feet NGVD, respectively.

Figure 15 shows the relationship of groundwater-levels in the alluvial wells MW26 and MW28 versus the Middle Fork of the Vermilion River elevations during 2002. During the period of measurement in 2002 groundwater levels in both these wells were above river elevation, demonstrating the potential for shallow groundwater discharge to the Middle Fork.

Groundwater elevations in the till and alluvial deposits in January 2002 (Figure 16) and hydrographs (Figure 15) demonstrate that groundwater elevations in the unlithified materials are higher than those in the adjacent Middle Fork through much of the year. The groundwater surface in the alluvial deposits fluctuates in response to changes in river stage and variations in precipitation. Based on the groundwater levels measured in wells MW13B and MW16B during 2002 and earlier years, groundwater elevations within the alluvial deposits in the vicinity of the East Ash Pond have not been elevated since the East Ash Pond was constructed. Groundwater levels are frequently measured at or near the base of the well screens of MW13B and MW16B, suggesting that the East Ash Pond has been hydraulically isolated from both the shale and alluvial deposits by soil/bentonite slurry walls and a compacted clay core.

Groundwater-level contour maps of the unlithified deposits could not be prepared due to the limited number and distribution of shallow wells. All of the shallow wells with the exception of Well MW10, which is installed in till, are adjacent to the Middle Fork. The

presence of the East Ash Pond prevented the installation of upgradient wells within the alluvial deposits.

Groundwater gradients in the alluvial deposits prior to pond construction were determined by Mathes (1987). During the period of April to July 1987, horizontal gradients between downgradient wells MW13B and MW16B and upgradient alluvial wells ranged from 0.014 to 0.028 ft/ft and flow direction was towards the Middle Fork.

The hydraulic conductivity of the alluvium was estimated by Mathes (1987) by conducting field permeability (slug) tests. The horizontal hydraulic conductivity ranged from $1x10^{-3}$ to $7x10^{-3}$ cm/s. Field hydraulic conductivities determined during September 2002 for the alluvial deposits at monitoring wells MW26 and MW28, located on the north side of the Middle Fork across from the East Ash Pond, resulted in a computed geometric mean hydraulic conductivity of $1.5x10^{-2}$ cm/s (Table 4). The higher permeabilities calculated at wells MW26 and MW28 during 2002 relative to the lower values calculated by Mathes (1987) could be either from actual permeability differences of the alluvial deposits (i.e., coarser-grained or better sorted alluvium at MW26 and MW28 relative to the Mathes well locations) or systematic differences due to differences in analysis methods.

4.2 BEDROCK

The bedrock at the study site has been investigated using the following sources of data:

- Six borings from the 1987 Mathes hydrogeologic investigation;
- Two monitoring wells (MW13A and MW16A) remaining from the 1987 Mathes investigation;
- Eight borings and monitoring wells installed in 2001 as part of the current hydrogeologic investigation;
- Eight borings from the 2001 geotechnical investigation for expansion of the East Ash Pond;
- Eight borings from the 2002 coal mine investigation at the East Ash Pond;
- Geophysical logging of three boreholes by the Illinois State Geological Survey in 2001 (Appendix A);
- Geophysical investigation for location of coal mines by URS Corp in 2002;
- Bedrock core logs prepared by the ISGS (Appendix A); and,
- Mineralogical analyses of 19 rock samples (from three bedrock cores) by the ISGS in addition to geochemical modeling (Appendix A).

Based on the above sources of information a comprehensive evaluation of the bedrock geology and hydrology is presented below.

4.2.1 Bedrock Geology

The upper 75 feet of bedrock was cored at the study site and consists of non-marine and marine, silty and micaceous shales of the Pennsylvanian Age Shelburn Formation. The Shelburn Formation contains a major coal seam mined in the region, the Danville Coal,

also called the No. 7 Coal. Geologic logs of selected cores (from borings for Wells MW25, MW30, and MW31) were prepared by the ISGS (Appendix A). Based on these logs, the shale has been described as medium to dark gray, massive, and with blocky fracture. Some intervals have thin interbeds of light gray shale.

The shale cores at Well MW25, located to the south of the East Ash Pond, are non-marine and contain abundant carbonized plant material. The shale cores at Well MW30, a background well located at the north end of the study area, have been identified as non-marine from 116 to 135 feet BLS and marine from 135 to 144 feet BLS, with abundant fossils, including brachiopods, gastropods, and bivalves. The Danville Coal was intercepted at 145 feet BLS before the coring was discontinued at 148 feet BLS. The coal contained abundant pyrite along cleats. The shale cores at Well MW31, located at the east end of the study site, also consist of a non-marine shale overlying a fossiliferous marine shale.

The upper zone of the shale is often weathered so that it appears as a greenish-gray to bluish-gray silty clay. Determination of the interval at which weathered shale turns into an unlithified silty clay is often based on the presence of fissility.

Based on the mineralogical analyses of 19 samples from three cores (from the borings for MW29, MW30, and MW31) conducted by the ISGS (Appendix A), the shale is composed principally of clay minerals and quartz with minor amounts of potassium feldspar, plagioclase feldspar, siderite, and marcasite or pyrite. The most abundant clay minerals in the cores were illite, kaolinite, and chlorite, with minor amounts of illite/smectite mixed-layer clay.

The depth to the top of the bedrock (i.e., shale), bedrock surface elevation, and depth/elevation of the Danville Coal are provided in Table 5. Figure 12, which shows the thickness of the unlithified deposits, also provides the depth to bedrock. Generally, the top of the shale occurs within 10 to 25 feet of ground surface in the vicinity of the East Ash Pond and rapidly increases in depth toward the western upland bordering the Site. The depth to bedrock is greatest towards the east, where it exceeds 150 feet.

Another way to view the shale bedrock is by looking at a bedrock elevation map, which can also be called a bedrock topography map. Figure 17 shows that the bedrock high within the study area occurs directly west of the East Ash Pond and the higher elevations trend toward the northeast. The lowest bedrock elevations occur to the north (530 feet NGVD at Well MW30) and the east (544 feet NGVD at Well MW31). The slope of the bedrock surface between the bedrock high and the eastern low at MW31 is approximately 0.018 foot per foot (95 feet per mile), which is a relatively mild slope when compared to the greater relief of the glacially-carved Middle Fork valley.

4.2.1.1 Danville (No. 7) Coal

The Danville (No. 7) Coal is found within the Shelburn Formation (ISGS, 1996) and was intercepted at eight locations (Table 5) in the vicinity of the East Ash Pond (Borings B201 to B208) and one location to the north of the Middle Fork (Boring MW30). Most

of the borings advanced during both this and prior studies did not penetrate deep enough into the bedrock to intercept the coal seam. The top of the Danville Coal was intercepted at depths of 80 to 102.5 feet BLS on the floodplain adjacent to the East Ash Pond. Greater boring depths were required to intercept the coal seam in the upland areas. Borings B203, B208, and MW30 intercepted the coal seam at depths of 127, 152, and 144 feet BLS, respectively.

The top of the Danville Coal, or the void remaining where the coal was removed through mining, was intercepted at elevations between 496 and 509 feet NGVD. The thickness of the coal seam ranged from four to seven feet with an average thickness of 5.4 feet. Thin layers of coal interlayered with shale occurred above or below the main coal seam; these were not included in calculating the main seam thickness. The elevation of the top of the Danville Coal has been mapped on Figure 18. The Danville Coal generally decreases in elevation northward under the East Ash Pond at a gradient of 0.004 ft/ft (22 feet per mile). The coal increases in elevation from north of the East Ash Pond (493 to 496.6 feet NGVD at B201 and B202) to 501.5 feet NGVD at Well MW30 at a gradient of 0.0024 ft/ft (12.8 feet per mile).

Further information about the occurrence and mining of the Danville Coal in the vicinity of the East Ash Pond and other portions of the Vermilion Power Plant is provided in Section 1.4.3. Coal mine maps prepared by the ISGS, and other historical information pertaining to coal mining at the site is discussed. The potential effects of coal mines on subsurface geology, groundwater hydraulics, and water quality are discussed in greater detail in Sections 4.2.1.2, 4.2.2.5, and 5.2, respectively.

4.2.1.2 Geophysical Investigation of East Ash Pond

A geophysical investigation was conducted by URS Corp. in April 2002 (URS, 2002) to determine if mining occurred below the East Ash Pond, and if so to determine its lateral extent. The investigation was conducted by running five separate high-resolution seismic lines (Figure 19): three along the south, east, and north dikes (Lines A, B, and C, respectively), one calibration line (Line D) over an area of known mine voids based on test borings, and a final Line E over an area of suspected mine collapse features north of the secondary pond.

Based on the data obtained from the geophysics investigation, the findings are summarized below.

- The survey confirmed that mining occurred in the vicinity of the East Ash Pond; however, the mining appeared to be sporadic and of limited extent along the lines of seismic investigation.
- The surface depressions north of the secondary (polishing) pond (along Line E of Figure 19) are most likely mine collapse features. The largest of these features is about 100 feet across and shows 4 to 5 feet of vertical displacement. These features are pit-type collapses consistent with mining depths less than about 150 feet below grade.

- The survey detected 12 anomalies judged to be mine-related voids, collapse features, or partial collapse features along the five lines A through E. The mine-related voids are locations where the coal has been mined, leaving a void in the bedrock. The voids may eventually work to the surface resulting in settlement (surface depressions) similar to the collapse features north of the secondary pond.

4.2.2 Bedrock Hydrology

Hydrologic data have been incorporated from data collected from both the current investigation and from the previous hydrogeologic study completed in 1987 (Mathes, 1987). Both observed and predicted effects of coal mines on the hydrology of the bedrock are discussed at the conclusion of this section.

4.2.2.1 Hydraulic Conductivity

The upper zone of the shale is moderately weathered at the surface at most of the boring locations. Generally, the shale is massive with very few horizontal joints or partings. Some near vertical joints were observed near the surface, but these were typically irregular and closed.

The horizontal hydraulic conductivity of the shale was determined by Mathes (1987) from field permeability tests. Seven wells screened in the shale were tested and the computed hydraulic conductivity ranged from $4x10^{-10}$ to $1x10^{-8}$ cm/s. The geometric mean hydraulic conductivity of the shale based on the seven wells tested was $4.3x10^{-9}$ cm/s. The vertical hydraulic conductivity calculated from tests performed in the laboratory on one shale core ranged from $1x10^{-8}$ to $5x10^{-8}$ cm/s. The field and laboratory values for hydraulic conductivity of the shale all fall within the range of $5x10^{-6}$ to $5x10^{-10}$ cm/s reported by Walton (1988).

Field hydraulic conductivity tests conducted by Kelron in 2002 (Table 4) on seven monitoring wells screened within the Pennsylvanian Shale at the Site resulted in a higher estimate of permeability than Mathes (1987). The geometric mean hydraulic conductivity for all seven shale wells was $3x10^{-6}$ cm/s and the range was $1.04x10^{-4}$ to $1.45x10^{-7}$ cm/s.

The higher permeabilities calculated by Kelron during 2002 relative to the lower values calculated by Mathes (1987) could be either from actual permeability differences of the bedrock deposits or systematic differences due to differences in analysis methods.

4.2.2.2 Potentiometric Surface Maps

Potentiometric surface maps of the upper shale were prepared using groundwater-elevation data from January and May 2002 for the nine shale monitoring wells located at the study site (Figures 20 and 21). Groundwater elevations in the shale are highest in the topographically highest areas to the west and east of the Middle Fork. The lowest groundwater elevations occur at wells located adjacent to the Middle Fork. Flow lines

derived from the potentiometric surface maps indicate that the Middle Fork of the Vermilion River in this area is a zone of discharge for the shale.

Horizontal hydraulic gradients in the shallow shale range from 0.026 to 0.038 ft/ft and are towards the Middle Fork. However, the upland wells are screened at shallower (MW22) or deeper (MW30 and MW31) elevations then most of the shale wells along the Middle Fork, possibly resulting in lower or higher gradient calculations then actually exist.

The occurrence of the Middle Fork in this area as a regional discharge zone for the shallow bedrock is supported by the upward vertical hydraulic gradients measured within the shale and the upward vertical hydraulic gradients observed during various periods and at multiple locations between the shale and the alluvium. The shale outcrops along the banks of the Middle Fork in this area and groundwater moving upward through the shale discharges into both the alluvium and directly into the Middle Fork.

The east-west and north-south cross sections shown on Figures 22 and 23, respectively, show the groundwater elevations at the monitoring wells relative to the geology

4.2.2.3 Vertical Hydraulic Gradients

Vertical hydraulic gradients are a measure of the change in total head with a change in vertical distance. The vertical hydraulic gradient measures the potential for groundwater to move upward or downward. Vertical gradients were calculated using the monthly groundwater data for the five paired (nested) well sets within the shale and alluvium and at one nested set within the shale. Gradients were computed by dividing the difference in the potentiometric head in the nested wells (i.e., dh) by the difference in the midpoint of the screened elevations (i.e., dl). A positive vertical gradient indicates a downward potential for groundwater movement and a negative gradient indicates an upward potential for groundwater movement.

All of the nested wells within the floodplain of the Middle Fork, with the exception of MW23/MW24, had an upward gradient from the shale to the overlying unlithified deposits during part of the eight months of monitoring (Table 6). Two sets of nested wells, MW13A/MW13B/MW32 and MW28/MW29, had large upward gradients during the entire study period with only one exception during May.

Nested wells MW13A/MW13B/MW32, located between the East Ash Pond and the Middle Fork, had an average upward gradient of 0.043 ft/ft between the shale well MW13B and alluvial well MW13A. The average upward gradient within the shale, between wells MW32 and MW13A, was even greater at 0.585 ft/ft. The only time that the gradient was measured as downward instead of upward between the alluvium and shale (MW13A and MW13B) was during May, when a slight downward gradient of 0.003 ft/ft was measured. However, during this same time the gradient within the shale was upward at 0.588 ft/ft. Figure 24 shows the relationship between water levels in the shale and alluvial wells relative to the land surface. The upward gradient within the shale is so great that groundwater at the deepest shale well (MW32) was under flowing artesian conditions during the study.

Nested wells MW16B and MW16A, also located between the East Ash Pond and Middle Fork, had an upward gradient during one of the three months during which the alluvial well (MW16B) was not dry (Figure 25). The vertical gradient at this location was downward during the March and April measurements and upward in June.

Nested wells MW28 and MW29, located northeast of the East Ash Pond on the north side of the Middle Fork, had an average upward gradient of 0.228 ft/ft between the shale and alluvium (Figure 26). The upward gradient over the eight months study period was very consistent, ranging from 0.204 to 0.251. Similarly, nested wells MW26 and MW27, located west of MW28/MW29, had an upward gradient of 0.01 to 0.053 ft/ft during five of the eight months (Figure 26). During March, April, and May the gradient at this location was downward from the alluvium to the shale at 0.001 to 0.032 ft/ft.

The only location within the floodplain where the gradient between the unlithified deposits and the shale was downward throughout the study was at nested wells MW23 and MW24, located north of the East Ash Pond. The unlithified deposits are thicker at this location and consist of finer grained alluvial deposits overlying glacial sediments. The 8-month average downward gradient at this location was 0.018 ft/ft. This is most likely a very localized flow cell where groundwater moves downward from the unlithified deposits to the shale. However, groundwater elevations in the shale during the study were still higher then river elevations, meaning that groundwater was discharging from the shale into the river.

Unlike the lowlands along the Middle Fork where groundwater within the shale is typically discharging upward into the unlithified deposits and the river, vertical groundwater movement in the uplands to the east, west, and north is downward. Figure 27 shows groundwater levels within the diamicton and shale wells MW10 and MW22, respectively. Groundwater levels in the glacial deposits are consistently higher than those in the underlying shale.

4.2.2.4 Groundwater-Flow Direction and Velocity

In upland areas bordering the Middle Fork valley the groundwater within the glacial deposits flows downward into the shale bedrock and along the top of the shale. Groundwater within the shale moves from upland areas and discharges into the regional discharge area of the Middle Fork (Figure 28). Groundwater generally moves upward from the shale deposits into the overlying alluvial (and glacial) sediments within the Middle Fork valley. Groundwater from the shale also discharges into the Middle Fork either through the overlying alluvium or, where bedrock is exposed, directly into the river. The groundwater elevations measured in the shale monitoring wells and shown on Figure 28 support this conceptualization of groundwater movement within the Pennsylvanian bedrock.

Groundwater flow velocity within the shale bedrock, computed based on a horizontal gradient of 0.027 ft/ft, hydraulic conductivity of $3x10^{-6}$ cm/s, and an effective porosity of 0.10, was 0.26 meters per year (0.85 feet per year), or 10.2 inches per year. The

calculated velocity is based on the geometric mean hydraulic conductivity determined by Kelron in 2002.

4.2.2.5 Coal Mine Effects on Hydrology

The presence of a coal mine beneath portions of the East Ash Pond and study area has been documented based on exploratory borings, geophysics, and historic data acquired from the ISGS. The coal mine has been shown to have significant collapse features where the overlying bedrock (shale) has collapsed or partially collapsed downward into the void or mined coal seam. The collapse of the shale into the void translates upward through the shale, resulting in fracturing and in some cases surface subsidence. Both surface depressions from subsidence and fractured shale within bedrock cores were observed during coal mine investigation activities.

A hydrologic feature noted during the exploratory boring phase of the coal mine investigation was the presence of substantial hydraulic head within the coal and overlying fractured shale in proximity to mined areas. Borings B201 and B202 (Figure 18 and Appendix C), located northwest of the East Ash Pond and secondary pond, both intercepted groundwater under high hydraulic head that resulted in temporary suspension of drilling. Upon intercepting fractured shale above the coal mines during coring, the groundwater, which had accumulated within the fractured shale and underlying coal seam and voids, rose to over 30 feet above ground surface at an estimated flow volume of greater than 100 gallons per minute. The flow rate slowly subsided, but groundwater continued to flow above the ground surface for several hours following penetration of the fractured (collapsed) shale.

The high hydraulic head that developed in the coal mine and overlying shale would be expected based on the strong upward gradient measured within the shale in monitoring wells located along the Middle Fork of the Vermilion River (see Section 4.2.2.3). Since groundwater within the shallow Pennsylvanian bedrock at the study site discharges upward into the Middle Fork, the buildup of groundwater with high hydraulic head within a more permeable confined unit of coal and fractured shale would be expected.

In addition to the high hydraulic head associated with the mined area at borings B201 and B202, hydrogen sulfide gas (developed within the reducing environment of the sulfur-rich coal beds) vented at a high rate and continued to vent until the borings were sealed over 12 hours later.

A major concern at the study site is the affects of abandoned mines on the water quality of the overlying shale, alluvial deposits and the Middle Fork. Groundwater quality issues related to coal mines are discussed further in Sections 5.2.1.3 and 6.4.

5.0 WATER QUALITY

Water quality of the groundwater and surface water at the East Ash Pond and in the surrounding region has been extensively assessed during 2002. Kelron has assessed groundwater quality at background and site wells for 22 parameters. The ISGS has evaluated background groundwater quality for 40 parameters, including the carbon and hydrogen (tritium) isotopes. In addition, the ISGS evaluated the background bedrock groundwater quality for 31 samples acquired from databases from the ISGS, ISWS, IEPA, and Indiana Geological Survey.

DMG collected groundwater samples from all of the site and background wells, both in the unlithified and bedrock deposits, monthly from March through August of 2002. Various wells were also sampled during January and February 2002, but that data was not used in statistical analyses because it was only a subset of all wells used in the study, the wells were still being developed and uniform sampling equipment had not been put into all the wells.

During June 2002 the ISGS split samples with DMG at background wells MW25 through MW 30 (ISGS designation KELRON 25 to KELRON 30) for separate analysis by the ISGS laboratory. In addition to groundwater samples, surface water samples were collected by DMG from the East Ash Pond monthly from January through May of 2002 and from upriver on the Middle Fork from March through August 2002. No East Ash Pond water samples were collected after May 2002 because of construction activities associated with expansion of the East Ash Pond. All effluent discharges to the East Ash Pond were halted and the remaining water was pumped to the secondary pond for discharge to the Middle Fork, resulting in almost no standing water within the East Ash Pond. The last discharge from the East Ash Pond outfall into the Middle Fork of the Vermilion River during the study period was May 26, 2002. Discharging from the East Ash Pond System did not resume until January 2003.

Water quality analytical results for both groundwater and surface water are provided in Appendix J for analyses conducted by DMG. All analytical results for ISGS samples are included with their report in Appendix A.

5.1 GROUNDWATER QUALITY OF THE UNLITHIFIED DEPOSITS

Water quality in the unlithified deposits at the East Ash Pond was evaluated by looking at groundwater in background wells MW26 and MW28 and comparing to East Ash Pond well MW23, located north of the secondary (polishing) pond. Groundwater quality was also compared to surface water quality upgradient on the Middle Fork and in the East Ash Pond. In addition, isotopic data collected and evaluated by the ISGS are included for the background wells MW26 and MW28 (ISGS designation's KELRON 26 and KELRON 28). No water quality data were available for East Ash Pond wells MW10, MW13B, and MW16B due to the lack of water in the wells. Wells MW13B and MW16B are typically dry or have insufficient water-column depth to obtain groundwater samples.

5.1.1 Summary of Groundwater and Surface Water Quality

5.1.1.1 Major Anions and Cations

Groundwater compositions can be grouped into identifiable categories to assist in interpreting the distribution of principal types of groundwater. A hydrochemical facies diagram, also called a Piper diagram, displays the position of water samples with respect to their major cation and anions so that composition categories can be defined (Walton, 1998). Figure 29 shows the position of groundwater samples obtained in June 2002 from East Ash Pond well MW23 and background wells MW26 and MW28. Also shown on the diagram are the surface water samples from the East Ash Pond and from the Middle Fork (labeled as "Upstream River" on the diagram).

The principal anion in background wells MW26 and MW28 and in the Middle Fork sample is bicarbonate. Well MW23 has no dominant type of anion, but is dominated by both bicarbonate and sulfate. In contrast is the East Ash Pond water sample, which has sulfate as the dominant anion. The cation portion of the diagram is much more definitive in grouping the data. All three of the wells and the Middle Fork sample cluster together between calcium and magnesium while the East Ash Pond sample is clearly dominated by calcium. Based on the observed cations and anions, and looking at the upper portion of the diagram, the hydrochemical facies of the water samples can be defined as follows: wells MW26, and MW28 and the Middle Fork of the Vermilion River are calcium-magnesium and bicarbonate type waters; the East Ash Pond is a calcium-sulfate dominated water; and, MW23 falls in-between.

The above categorizations of water types based on principal anions and cations are further demonstrated by the Stiff diagrams shown on Figure 30. The Stiff diagram for the June 2002 water samples shows the similarity between all three of the wells. The higher sulfate in well MW23 relative to bicarbonate is again demonstrated, but all other cations and anions in MW23 are similar to the background wells. The East Ash Pond water is clearly dominated by the cation calcium and the anion sulfate.

The correlation between parameters in groundwater within the unlithified materials is displayed on Table 7. The cations calcium and magnesium have a high correlation of 0.84, which indicates that these parameters vary proportionately within groundwater adjacent to the Middle Fork. The bicarbonate anion has a very high correlation of 0.94 with magnesium and the sulfate anion has a very high correlation of 0.92 with calcium. TDS concentrations in the shallow groundwater are principally controlled by the cations calcium and magnesium (correlation coefficients with TDS of 0.97 and 0.89, respectively) and the anions bicarbonate and sulfate (correlation coefficients with TDS of 0.72 and 0.89, respectively).

5.1.1.2 Statistical Analyses

In order to summarize all of the water quality data generated during 2002 so that some clear observations can be made about both the major and minor ions, including trace elements, several types of tables and figures were prepared. Each of the forms of

analysis is discussed below with a summary of all the inorganic data and statistical analyses provided in Section 5.1.1.3.

Detailed Statistical Tables

A summary of groundwater quality data for the unlithified wells, East Ash Pond, and Middle Fork of the Vermilion River (Table 8) lists the mean, median, minimum, and maximum concentration for each chemical parameter. The comments under each parameter include the results of a non-parametric test called the Wilcoxon Rank-Sum Test for Comparison of Means. This statistical test, which has no distributional assumptions, was used to compare the data collected for each parameter at East Ash Pond well MW23 versus the pooled background data from wells MW26 and MW28 to determine if there was any significant difference between their means at a 95 percent confidence level. The detailed test results (Appendix K) were used to make one of three statements for each individual parameter: (1) groundwater from the East Ash Pond well MW23 comes from the same population as the background wells; (2) groundwater from the East Ash Pond well has a statistically significant lower concentration than the background wells; or, (3) groundwater from the East Ash Pond well has a statistically significant higher concentration than the background wells.

Box-and-Whisker Plots

The box-and-whisker plots in Figure 31 provide a visual representation of some of the statistical data presented on Table 8. The rectangular part of the plot extends from the lower quartile to the upper quartile, covering the center half of each sample. The center lines within each box show the sample medians and the plus signs the sample means. The whiskers extend from the box to the minimum and maximum values in each sample, except for any outside or far outside points, which are plotted separately. Outside points are points that lie more than 1.5 times the interquartile range above or below the box and are shown as small squares. Far outside points, more than 3 times the interquartile range above or below the box, are shown as small squares with plus signs through them. Far outside points may indicate outliers or a highly skewed distribution.

Cluster Analysis

Cluster analysis is a descriptive statistical method used to identify groupings (i.e., clusters) of samples or variables. Cluster analysis is used to reveal the latent structure within a data set and is an exploratory tool only. The data from the East Ash Pond study were analyzed using cluster analysis to demonstrate the following:

- grouping of samples from wells and the Middle Fork into clusters based on water quality as defined by absolute concentrations of the major cations and anions (alkalinity, calcium, chloride, potassium, magnesium, sodium, and sulfate);
- grouping of samples from wells and the Middle Fork into clusters based on water quality as defined by absolute concentrations of minor and trace metals (aluminum, boron, barium, iron, lithium, manganese, selenium, and strontium);
- grouping of major cations and anions into clusters with common characteristics; and,
- grouping of minor and trace metals into clusters with common characteristics.

The cluster analysis results can be presented in several ways. In order to visually interpret how the data have been categorized, a graphical depiction of the clusters is shown with a dendrogram. The dendrogram is a linkage tree which first links those samples or parameters that have the greatest similarity (i.e., highest correlation). Each subsequent linkage (or cluster) is less similar than earlier linkages. The greater the distance on the y-axis between linkages, the lower the significance between the linked samples or variables.

The dendrograms of major and minor/trace ions (Figure 32) both show that the first sets of clusters are within each sample location (i.e., samples from each monitoring point cluster together first since they are most similar). The next set of clusters occurs between some of the samples from background well MW26 and samples from the Middle Fork. Although the major ions do not result in any significant linkages after well MW26 and the Middle Fork are grouped together, the minor/trace metals in the water samples result in clustering of East Ash Pond well MW23 with MW26 and the Middle Fork. The final cluster, based on minor/trace metals, is the samples from background well MW28. Based on these dendrograms, the samples from well MW28 are the least similar to samples from the other locations.

The dendrograms formed by looking only at the parameters irrespective of the specific sample locations (Figure 33) used the same data as for Figure 32. The most similar major ions (i.e., the first linkages) were calcium and sulfate followed by: magnesium, alkalinity, sodium, chloride, and finally potassium. The relationship between the parameters clustered together in the dendrograms is partially quantified by the correlation coefficients listed in Table 7. The correlation coefficient between calcium and sulfate was very high at 0.92. The correlation between calcium and magnesium was 0.84 and between sulfate and magnesium was 0.97. Alkalinity had a correlation with magnesium of 0.94. The least similar parameter to the other major ions was potassium, which had a negative (i.e., inverse) correlation with magnesium of –0.69.

The dendrogram for the minor/trace metal parameters (Figure 33) has the first clusters between iron and manganese (correlation coefficient {R} = 0.82 [Table 7]) and lithium and strontium (R = 0.89). These two clusters are then clustered with selenium. Later linkages with boron, barium, and aluminum are much less significant as the similarities between parameters in all of the groundwater and Middle Fork river samples markedly decrease.

5.1.1.2 Summary of Data

All of the statistical analyses and observations listed on Table 8 and graphically presented in Figures 29 to 33 are summarized and consolidated onto Table 9 so that all of the parameters can be assessed together. Based on the Wilcoxon Rank-Sum tests presented in Table 8, the only parameters that have statistically significant greater concentrations in East Ash Pond well MW23 relative to background groundwater concentrations are boron, chloride, potassium, sodium, and sulfate. Each of these parameters will be discussed in detail below along with other trace parameters.

Boron

The box-and-whisker diagram for boron on Figure 31 shows the relative concentrations of boron in the East Ash Pond versus the background wells, well MW23, and the Middle Fork of the Vermilion River. The median boron concentration of 0.27 milligrams per liter (mg/L) in MW23 is 0.15 mg/L above background concentrations, but is 38 times lower than the 10 mg/L median concentration in the East Ash Pond samples. Figure 34a shows the trend in boron concentrations in shallow groundwater versus the river during 2002. Boron concentrations in groundwater at MW23 trend independently from wells MW26 and MW28 and the river. Boron in wells MW26 and MW28 has a parallel trend. Boron concentrations in the river generally lay between those observed in MW26 and MW28.

Boron concentrations in MW23 are due to either natural variation as a result of geologic and hydrologic differences at MW23 relative to the background wells or may be partly affected by the presence of the former coal mine, mine spoil, or the presence of the East Ash Pond. Any impact by the East Ash Pond on shallow groundwater quality is uncertain due to the similarity between groundwater quality impacts from coal ash disposal, coal mine spoil, and coal mine drainage.

Chloride

Chloride concentrations on the box-and-whisker diagram (Figure 31) are similar between the East Ash Pond well MW23 and the Middle Fork of the Vermilion River. Well MW23 has a median chloride concentration of 38.5 mg/L, which is only 9 mg/L above the median Middle Fork concentration. Chloride in MW23 is 5.2 times lower than the median East Ash Pond concentration of 200 mg/L. Chloride has a high correlation of 0.89 (Table 7) with boron based on data from both background wells and MW23. The natural correlation between boron and chloride makes it difficult to distinguish the co-variance of these parameters in groundwater versus potential impacts from the East Ash Pond water, which also has a high correlation between boron and chloride.

The trend in chloride concentrations (Figure 34b) are very different between groundwater sampled from well MW23 versus wells 26, 28, and the river. Wells 26 and 28 have similar chloride trends but are markedly different from chloride concentration changes in the Middle Fork.

The chloride concentrations observed in MW23 are most likely due to either natural variation as a result of geologic and hydrologic differences at MW23 relative to the background wells or may be partly affected by the presence of the former coal mine and mine spoil. Impact by the East Ash Pond on shallow groundwater quality is uncertain due to the similarity between groundwater quality impacts from coal ash disposal, coal mine spoil, and coal mine drainage.

Potassium

Potassium concentrations are similar between East Ash Pond wells MW23, background wells, and the Middle Fork. Median concentrations of 3.25 mg/L in MW23 are 0.9 mg/L above background. Potassium in MW23 is 7.7 times lower than the median East Ash

Pond concentration of 25 mg/L. The trend in potassium concentrations (Figure 34c) demonstrate the similarity between background wells MW26 and MW28, although concentrations in MW23 and the river also have similar trends to the background wells.

The potassium concentrations observed in MW23 are most likely due to either natural variation as a result of geologic and hydrologic differences at MW23 relative to the background wells or may be partly affected by the presence of the former coal mine or associated mine spoils. Impact by the East Ash Pond on potassium concentrations is uncertain due to the similarity between groundwater quality impacts from coal ash disposal, coal mine spoil, and coal mine drainage. However, the similarity between potassium concentration trends in well MW23 and background wells suggests that the East Ash Pond has negligible impact on shallow groundwater concentrations of potassium.

Sodium

Median sodium concentration of 19.5 mg/L in well MW23 is 2.5 mg/l above the median in the background well MW28 and 10.3 mg/L above the median concentration in the Middle Fork of the Vermilion River. Sodium in MW23 is 7.2 times lower than the median East Ash Pond concentration of 140 mg/L. Maximum observed sodium concentrations in 2002 at MW23 and the East Ash Pond were 26 and 240 mg/L, respectively. Similar to chloride trends, the trend in sodium concentrations (Figure 34d) are very different between groundwater sampled from well MW23 versus wells 26, 28, and the river.

The sodium concentrations observed in MW23 are most likely due to either natural variation as a result of geologic and hydrologic differences at MW23 relative to the background wells or may be partly affected by the presence of the former coal mine and mine spoil. Impact by the East Ash Pond on shallow groundwater quality is uncertain due to the similarity between groundwater quality impacts from coal ash disposal, coal mine spoil, and coal mine drainage.

Sulfate

Sulfate concentrations in East Ash Pond well MW23 in 2002 ranged from 280 to 380 mg/L with a median concentration of 320 mg/L. Concentrations in surface water at the East Ash Pond ranged from 440 to 1,500 mg/L with a median concentration of 780 mg/L, or approximately 2.4 times higher than observed in groundwater at MW23. Sulfate concentrations in the shallow unlithified deposits at MW23 and MW28 have a high variability, as seen by the box-and-whisker diagram for sulfate (Figure 31). Sulfate also has a very high correlation of 0.92 with calcium (Table 7) and these two parameters are within the first (most similar) cluster in the dendrogram discussed earlier (Figure 33).

Trends in sulfate concentration (Figure 34e) at well MW23 and background well MW28 are very similar. Sulfate concentrations at wells MW23 and MW28 are above those observed in background well MW26 and the river, which also trend closely together.

The concentrations observed for sulfate in well MW23 can partly be attributed to natural groundwater variations in conjunction with changes observed for calcium. Calcium in groundwater at MW23 is statistically from the same population as background groundwater concentrations and the high correlation between calcium and sulfate in groundwater suggests that the sulfate concentrations at MW23 are also partly natural. Impacts by the East Ash Pond, coal mine, or mine spoils on sulfate concentrations are uncertain.

Aluminum, Barium, Lithium, Molybdenum, Selenium, Strontium, and Vanadium
Concentrations of the trace metals aluminum, barium, lithium, molybdenum, selenium, strontium, and vanadium in the East Ash Pond during 2002 were all significantly higher than those in groundwater within the unlithified deposits (background and on-site). Lithium, molybdenum, selenium, and vanadium concentrations in all shallow groundwater samples were typically below or near their detection limits compared to significantly higher concentrations in the East Ash Pond surface water samples.

Statistically, the trace metal groundwater parameters sampled at well MW23 near the East Ash Pond are from the same population as the background groundwater (exception is barium, which has lower concentrations than background). The deficiency of all the trace metals in shallow groundwater near the East Ash Pond, as compared to their ubiquity in the surface water of the pond itself, suggests there is no impact on shallow groundwater by the East Ash Pond.

5.1.2 Exceedances of Groundwater Quality Standards

During March through August 2002 no groundwater samples collected from the unlithified deposits at the East Ash Pond or from the background monitoring wells exceeded any of the Class I or II groundwater standards (Illinois Administrative Code [IAC] Title 35, Part 620, Section 620.410 and 620.420) for inorganic parameters. However, background well MW28 did exceed the sulfate and TDS standards of 400 and 1,200 mg/L, respectively, during January and February 2002.

5.2 GROUNDWATER QUALITY OF THE BEDROCK DEPOSITS

Water quality in the bedrock was evaluated by comparing background wells to the East Ash Pond wells. Both the ISGS and Kelron investigated background groundwater quality through independent investigations. The ISGS investigated background groundwater quality of the Pennsylvanian age bedrock in two ways: literature and database search, including unpublished data sources, for information pertaining to groundwater geochemistry of shale and coal in Illinois and the Midwest; and, groundwater sampling and analysis during June 2002 using four private wells in Vermilion County and four of the site background wells (MW25, MW27, MW29, and MW30). Kelron investigated the background groundwater quality of the bedrock by utilizing the same four Site wells as the ISGS in addition to well MW31 and had the wells sampled by DMG for 6 consecutive months from March through August 2002.

Utilizing the data collected and analyzed by both the ISGS and DMG, the groundwater quality data from the background wells was grouped according to the source of the data and compared to the East Ash Pond bedrock wells (MW13A, MW16A, MW22, MW24, and MW32) using a variety of statistical and graphical methods.

5.2.1 Summary of Groundwater Quality

5.2.1.1 Major Anions and Cations

The major anions and cations of background and East Ash Pond wells are graphically displayed on the hydrochemical facies (Piper) diagram of Figure 35 and the Stiff diagrams of Figure 36. The principal cations in groundwater from the background wells are typically sodium and potassium, although a few wells have groundwater with higher concentrations of calcium and magnesium. The median value derived from the ISGS literature and database search, which is weighted heavily by groundwater samples from coal-bearing deposits, is dominated by calcium. A ternary plot of the cation data for background bedrock wells (Figure 37; modified from ISGS Figure 13, Appendix A) displays the linear nature of the data points. The ISGS (Mehnert and Dreher, 2002) hypothesized that "groundwater with greater concentrations of sodium plus potassium (Na+K, e.g., KELRON 27 or KELRON 29) migrated over a longer distance from the recharge area to the respective well than samples with lower concentrations of Na+K (e.g., well 23343). During migration, the groundwater dissolved increasingly greater amounts of sodium from the aquifer rocks and increasing amounts of calcium and magnesium were removed from the water, probably by adsorption of clay minerals in the aquifer rocks."

Cation data for groundwater sampled from the East Ash Pond wells plots along the same line as the background wells. Most of the East Ash Pond wells are dominated by sodium and potassium relative to calcium and magnesium. Conversely, surface water sampled from the East Ash Pond is dominated by calcium.

The principal anion in groundwater from background wells and East Ash Pond wells in the vicinity of the Site is chloride. The median value from the ISGS database is dominated by bicarbonate. Surface water from the East Ash Pond is also dominated by sulfate.

The correlation between parameters in groundwater sampled from background and East Ash Pond bedrock wells at the Site is displayed on Table 10. The cations calcium and magnesium have a very high correlation of 0.98, which reflects the data shown on the Piper and Stiff diagrams that calcium and magnesium have been removed from the groundwater by clay minerals in the shale during migration. Sodium and chloride, the principal cations and anions in bedrock groundwater at the Site, are also highly correlated with a coefficient of 0.94. These two parameters, as will be discussed later, account for much of the variability observed in groundwater from the bedrock. In addition, sodium and chloride have correlation coefficients of 0.88 and 0.93, respectively, with TDS. A large amount of the TDS observed in groundwater from the bedrock wells, both

background and at the East Ash Pond, is directly correlated to changes in sodium and chloride concentrations.

As observed by the ISGS (Mehnert and Dreher, 2002) for samples from bedrock wells, "sodium and chloride concentrations apparently increase at the expense of calcium, magnesium, and other high valence cations due to adsorption as groundwater moves away from recharge areas."

5.2.1.2 Statistical Analyses

Several types of tables and figures were prepared to summarize the groundwater quality data for the bedrock. Each of the forms of analysis is discussed in the following sections. A summary of all the anlyses for each of the major ions and minor ions, including trace metals, is provided in Section 5.2.1.3

Detailed Statistical Tables

A summary of groundwater quality data is presented in Table 11 for the following groupings of data:

- Background bedrock wells at the Site using all results from the 6 monthly samplings from March through August 2002: wells MW25, MW27, MW29, MW30, and MW30;
- ISGS background data for 27 wells derived from the scientific literature and state databases (see Appendix A);
- ISGS background data for 4 wells sampled and analyzed by the ISGS in Vermilion County: wells 1349, 21903, 23343, and 25531;
- East Ash Pond bedrock wells using all results from the 6 monthly samplings in 2002: MW13A, MW16A, MW22, MW24, and MW32; and,
- East Ash Pond surface water samples from the 5 monthly samplings from January to May 2002.

The statistical summary lists the mean, median, minimum, and maximum concentration for each parameter. The comments under each parameter include the results of a non-parametric test called the Wilcoxon Rank-Sum Test for Comparison of Means. This statistical test, which has no distributional assumptions, was used to compare the data collected for each parameter at each individual East Ash Pond bedrock well (MW13A, MW16A, MW22, MW24, and MW32) versus the pooled background data from the Site background wells (MW25, MW27, MW29, MW30, and MW31) to determine if there was any significant difference between their means at a 95 percent confidence level. The detailed test results (Appendix K) were used to make one of three statements for each individual parameter: (1) groundwater from the East Ash Pond well(s) comes from the same population as the background wells; (2) groundwater from the East Ash Pond well(s) has a statistically significant lower concentration than the background wells; or, (3) groundwater from the East Ash Pond well(s) has a statistically significant higher concentration than the background wells.

Box-and-Whisker Plots

The box-and-whisker plots in Figure 38 provide a visual representation of some of the statistical data presented in Table 11. The rectangular part of the plot extends from the lower quartile to the upper quartile, covering the center half of each sample. The center-lines within each box show the sample medians and the plus signs the sample means. The whiskers extend from the box to the minimum and maximum values in each sample, except for any outside or far outside points, which are plotted separately. Outside points are points that lie more than 1.5 times the interquartile range above or below the box and are shown as small squares. Far outside points, more than 3 times the interquartile range above or below the box, are shown as small squares with plus signs through them. Far outside points may indicate outliers or a highly skewed distribution.

Cluster Analysis

Cluster analysis is a descriptive statistical method used to identify groupings (i.e., clusters) of samples or variables. Cluster analysis is used to reveal the latent structure within a data set and is an exploratory tool only. The data from the East Ash Pond study was analyzed using cluster analysis to demonstrate the following:

- grouping of samples from background wells and East Ash Pond wells at the Site into clusters based on water quality as defined by the major cations and anions (alkalinity, calcium, chloride, potassium, magnesium, sodium, and sulfate);
- grouping of samples from background wells and East Ash Pond wells at the Site into clusters based on water quality as defined by minor and trace metals (aluminum, boron, barium, iron, lithium, manganese, and strontium);
- grouping of major cations and anions into clusters with common characteristics; and,
- grouping of minor and trace metals into clusters with common characteristics.

The cluster analysis results can be presented in several ways. In order to visually interpret how the data have been categorized, a graphical depiction of the clusters is shown with a dendrogram. The dendrogram is a linkage tree which first links those samples or parameters that have the greatest similarity. Each subsequent linkage (or cluster) is less similar than earlier linkages. The greater the distance on the y-axis between linkages, the lower the significance between the linked samples or variables.

The dendrogram of major ions (Figure 39 top) shows that the first sets of clusters are typically within each sample location (i.e., groundwater sample data from each monitoring point cluster together first since they are most similar). The next set of clusters occur between East Ash Pond well MW32 and background well MW30, followed by a cluster with East Ash Pond well MW13A. Wells MW13A and MW32, located immediately east of the East Ash Pond, are nested within the bedrock; well MW32 is the screened at a lower elevation than well MW13A. Another separate clustering occurs between East Ash Pond wells MW22 and MW24 with background wells MW27 and MW29, located on the other side of the Middle Fork of the Vermilion River. The clusterings of background wells with East Ash Pond wells based on major ion

composition is indicative of strong similarities between the overall groundwater composition at these locations and depths within the Pennsylvanian bedrock.

The dendrogram of minor ions and trace metals (Figure 39 bottom) has a slightly different set of clusters than that of the major ions above. The first sets of clusters following those within each sample location are between wells MW13A - MW32, MW27 - MW29, and MW22 - MW24. Wells MW13A and MW32 are the nested wells that clustered together for the major ions, but well MW30 no long clusters with these wells due to the differences in the trace element composition of the groundwater. This may be due to the presence of coal within the screened interval of well MW30. The next level of clusters occurs between all of the wells listed above: MW13A, MW32, MW27, MW29, MW22, and MW24; four of these wells are at the East Ash Pond and two (MW27 and MW29) are background wells. The next set of clusters in order of distance along the dendrogram incorporates background wells MW25 and MW31 followed by East Ash Pond well MW16A. The trace metal data from MW30 is very dissimilar from all other wells and is clustered last.

The dendrograms formed by looking only at the parameters irrespective of the specific sample locations (Figure 40 used the same data as for Figure 39. The most similar major ions (i.e., the first linkages) were calcium-magnesium and sodium-chloride followed by: calcium-magnesium and sulfate, sodium-chloride and alkalinity, and sodium-chloride-alkalinity and potassium. The relationship between the parameters clustered together in the dendrograms is partially quantified by the correlation coefficients listed in Table 10. The correlation coefficients between calcium-magnesium and sodium-chloride were very high at 0.98 and 0.94, respectively. The correlations between calcium and magnesium with sulfate were both 0.86. The correlations between sodium and chloride with alkalinity were 0.70 and 0.46, respectively.

The dendrogram for the minor/trace metal parameters (Figure 40, bottom) has the first clusters between barium and iron (correlation coefficient {R} = 0.87 [Table 10]) and aluminum and lithium (R = 0.63). Next, barium-iron is clustered with strontium (R = 0.54 and 0.56, respectively) and aluminum-lithium is clustered with boron (R= -0.02 and 0.47, respectively). Manganese concentrations in groundwater at the study site are very poorly correlated with all the other minor/trace metals and there is no cluster formed with any other parameters.

5.2.1.3 Summary of Data

All of the statistical analyses and observations listed on Table 11 and graphically presented in figures 35 to 40 are summarized on Table 12 so that all of the parameters can be assessed together. Based on the Wilcoxon Rank-Sum tests presented in Table 11, the only parameters that have statistically significant greater concentrations in any of the East Ash Pond wells relative to background groundwater quality in the bedrock are the following:

- Boron at wells MW13A and MW32;
- Calcium at well MW16A;

- Lithium at wells MW13A and MW16A;
- Magnesium at well MW16A;
- Manganese at wells MW13A and MW16A;
- Phosphorus at well MW24;
- Sodium at wells MW13A and MW32;
- Sulfate at wells MW16A, MW22, and MW24; and,
- TDS at wells MW13A and MW32.

Each of these parameters and wells listed above will be discussed in detail below. Other parameters measured in groundwater samples from the bedrock and East Ash Pond will also be discussed.

Boron

The box-and-whisker diagram for boron on Figure 38 shows the relative concentrations of boron in the East Ash Pond wells relative to background wells and the East Ash Pond. The range of boron concentrations in the Site background wells during 2002 was between 0.20 and 1.30 mg/L versus a range for the East Ash Pond wells of 0.30 to 1.60 mg/L. Median boron concentrations at East Ash Pond wells MW13A and MW32 were 1.40 and 1.50 mg/L, respectively. These median boron concentrations are approximately 7 times lower than those observed in the East Ash Pond sluice water.

Wells MW13A and MW32 are both at a location where groundwater has a large upward vertical gradient as it discharges into the alluvial deposits and the Middle Fork of the Vermilion River. The similarity of boron concentrations at this nested well location, along with the upward gradient, indicates that the occurrence of boron is either naturally occurring or may be influenced by the occurrence of past coal mining activities as discussed earlier in Section 4.2.2.5.

Calcium

Calcium concentrations in all of the East Ash Pond wells with the exception of MW16A are either equal to or below background concentrations based on the Wilcoxon Rank-Sum Test. Well MW16A has a median calcium concentration of 135 mg/L, which is above the range of values observed at the Site background wells (median values of 29.5 to 85.5 mg/L). However, the concentrations measured for calcium at well MW16A in 2002 are well above the historical median of 33 mg/L for the period of 1993 through 2001. Calcium concentrations at well MW16A have historically been similar to those at well MW13A and the Site background wells. East Ash Pond surface water samples had calcium concentrations ranging from 150 to 450 mg/L and a median concentration of 350 mg/L.

It is uncertain what factors may have resulted in higher calcium concentrations at well MW16A during 2002. However, well MW16A also had historically high concentrations of magnesium, sulfate, and TDS during 2002. Calcium and magnesium are very highly correlated (R = 0.98, Table 10) in groundwater at the Site and the higher observed

concentrations of both these parameters at only one location may be due to the affects of the former coal mine on groundwater geochemistry.

Chloride

Chloride concentrations at the East Ash Pond wells are generally below those observed at Site background wells (Figure 38). The highest chloride concentrations at the East Ash Pond are found in groundwater at nested wells MW13A and MW32, with median concentrations of 570 and 845 mg/L, respectively. These concentrations are below the median chloride concentrations of 840 and 1,200 mg/L measured in groundwater at Site background wells MW25 and MW30, respectively. It is of interest that the highest chloride concentrations occur at well MW30, which is partially screened across coal deposits, and at wells MW25, MW13A, and MW32, all of which occur near (and may be impacted by) former coal mines.

The median chloride concentration in surface water at the East Ash Pond ranged from 100 to 240 mg/L with a median value of 200 mg/L during the study period, or approximately 3 to 4 times lower than the median chloride concentrations observed at wells MW13A and MW32. Chloride in groundwater at the Site is naturally occurring at most bedrock well locations, including the elevated concentrations observed at well MW30 due to coal deposits. However, elevated concentrations observed in some bedrock wells may occur due to former coal mines located nearby.

Lithium

Although lithium concentrations in groundwater at East Ash Pond wells MW13A and MW32 were identified by the Wilcoxon Rank-Sum Test as being above site background, a closer look at the data on the box-and-whisker diagrams (Figure 38) and on Table11 show that the relative concentrations of lithium in wells MW13A and MW32 are within the range of data at Site background wells MW25 and MW30. Lithium concentrations in all of the East Ash Pond wells range from non-detect at 0.005 mg/L to 0.19 mg/L versus a range of non-detect to 0.40 mg/L in the Site background wells.

Similar to observed chloride concentrations, the lithium concentrations in groundwater at wells MW13A and MW32 are higher than other East Ash Pond wells but within the range of values observed in background wells MW25 and MW30. As discussed for chloride, the higher lithium concentration at well MW30 may be caused by the presence of coal in the screened interval. Similarly, higher lithium concentrations in wells MW13A, MW32, and MW25 may be related to the presence of former coal mines.

Lithium concentrations in the East Ash Pond ranged from non-detect to 0.30 mg/L with a median concentration of 0.27 mg/L, or approximately 3 to 14 times greater than the median concentrations observed in the East Ash Pond wells.

Magnesium

Magnesium concentrations in all of the East Ash Pond wells with the exception of MW16A are either equal to or below background concentrations based on the Wilcoxon Rank-Sum Test. Well MW16A has a median manganese concentration of 72.5 mg/L,

which is above the range of values observed at the Site background wells. However, the concentrations measured for magnesium at well MW16A in 2002 are well above the historical median of 20 mg/L for the period of 1993 through 2001. Magnesium concentrations at well MW16A have historically been similar to those at well MW13A and the Site background wells. East Ash Pond surface water samples had magnesium concentrations ranging from 8.4 to 42 mg/L and a median concentration of 30 mg/L.

It is uncertain what factors may have resulted in higher magnesium concentrations at well MW16A during 2002. However, well MW16A also had historically high concentrations of calcium, sulfate, and TDS during 2002. Magnesium and calcium are very highly correlated (R = 0.98, Table 10) in groundwater at the Site and the higher observed concentrations of both these parameters at only one location may be attributed to impacts from the former coal mine.

Manganese

As with magnesium, manganese concentrations in well MW16A are statistically above Site background concentrations. The highest manganese concentrations observed in any of the East Ash Pond or background wells occurs in groundwater at well MW16A. The median manganese concentration at well MW16A during the study was 14 times greater than the median in surface water from the East Ash Pond. Since manganese is highly correlated with magnesium concentrations in groundwater at the Site (R = 0.86, Table 10), the higher manganese concentrations observed at well MW16A would be expected based on the high magnesium concentrations also observed in groundwater at this location.

Manganese concentrations at Well MW13A were also above Site background, but were similar to the concentrations observed at background well MW31. The concentrations at MW13A were also within the range documented by the ISGS from the scientific literature and state databases (Table 11).

The degree to which manganese concentrations at MW13A and MW16A might be impacted by the presence of former coal mines is unknown, although any decrease in pH values or presence of reducing conditions associated with former mines would result in increased manganese concentrations in groundwater.

Phosphorus

Phosphorus concentrations in all of the East Ash Pond wells with the exception of MW24 are either equal to or below background concentrations based on the Wilcoxon Rank-Sum Test. Well MW24 has a median phosphorus concentration of 0.047 mg/L, which is within the range observed in groundwater at wells MW16A and MW31. Phosphorus concentrations at well MW24 are most likely naturally occurring based on concentrations observed in the East Ash Pond, other East Ash Pond wells, and Site background wells.

Sodium

Sodium concentrations at the East Ash Pond wells are generally within the same range as those observed at Site background wells (Figure 38). The highest sodium concentrations

mg/L). The highest TDS concentrations observed in groundwater in 2002, ranging from 2,400 to 2,500 mg/L, occurred at background well MW30. Well MW30 is partially screened across a coal seam. The median TDS concentration of 1,400 mg/L in groundwater at well MW16A is statistically from the same population as the background bedrock wells using the Wilcoxon Rank-Sum Test and 1,000 mg/L below the median TDS concentration in groundwater at background well MW30.

The high TDS concentrations observed at wells MW13A and MW32 can be attributed to the high sodium and chloride concentrations in groundwater at this nested well location. TDS is most highly correlated with sodium (R = 0.93) and chloride (R = 0.88). As discussed earlier, high sodium and chloride concentrations in groundwater at the Site are a function of naturally occurring conditions at most bedrock wells. Naturally elevated concentrations of these major ions are reflected by similarly high TDS concentrations. However, the highest elevated concentrations of TDS (as with sodium and chloride) may occur in some bedrock wells due to coal deposits (i.e., at well MW30) or former coal mines located nearby (MW25, MW13A, and MW16A).

The median TDS concentration of 1,400 mg/L in groundwater at well MW16A in 2002 is significantly higher than the historical median of 760 mg/L for the period 1993 through 2001. The high TDS concentrations observed at well MW16A in 2002 are attributed primarily to calcium, magnesium, and sulfate, all of which were elevated in groundwater at well MW16A relative to other bedrock wells.

Factors contributing to the higher concentrations of these parameters at well MW16A are difficult to determine since this is the only well with elevated calcium, magnesium, and sulfate concentrations relative to background. However, based on an upward hydraulic gradient within the bedrock and the presence of former coal mines in the vicinity of the well, it is surmised that the occurrence of high TDS in groundwater in this area may be impacted by the former coal mines.

Barium

Barium concentrations in the East Ash Pond wells are at statistically significant lower concentrations than observed in the background bedrock wells based on the Wilcoxon Rank-Sum Test. The lowest mean and median concentrations of barium are found in surface water of the East Ash Pond. The highest barium concentrations are found in the background bedrock wells and the nested East Ash Pond bedrock wells MW13A and MW32.

The nested bedrock wells MW13A and MW32 may have higher barium concentrations than other East Ash Pond wells due to either naturally higher concentrations or may be affected by the former coal mines. The influence of former coal mines on groundwater quality of the bedrock at MW13A and MW32 is hypothesized based on the higher barium concentrations observed in background bedrock wells MW25 and MW30. Wells MW25 and MW30 have elevated barium concentrations relative to the other background wells. Well MW25 is located near a former coal mine and well MW30 is partially screened across a coal seam.

Strontium
Strontium concentrations in the East Ash Pond bedrock wells are at statistically significant lower concentrations or from the same population as the background bedrock wells based on the Wilcoxon Rank-Sum Test. Concentrations of strontium in the East Ash Pond water samples are within the range of both background wells and East Ash Pond wells. Based on the data collected, strontium is not a useful parameter for distinguishing groundwater types or the potential influence of anthropogenic sources.

Aluminum, Molybdenum, Selenium, and Vanadium
Concentrations of the trace metals aluminum, molybdenum, selenium, and vanadium in the East Ash Pond during 2002 were all significantly higher than observed in groundwater within the bedrock deposits (background and on-site). Concentrations of aluminum, molybdenum, selenium, and vanadium in groundwater samples from all bedrock wells were typically below or near their detection limits compared to significantly higher concentrations in the East Ash Pond surface water samples. All of the East Ash Pond bedrock well samples for these four trace metals are statistically from the same population as the background samples using the Wilcoxon Rank-Sum Test for comparison of means.

The deficiency of these four trace metals in groundwater within the Pennsylvanian age bedrock at both background and East Ash Pond wells, as compared to their presence within waters of the East Ash Pond, suggests there is no impact to bedrock groundwater quality by the East Ash Pond.

5.2.2 Exceedances of Groundwater Quality Standards

Groundwater samples collected from bedrock wells at the East Ash Pond and background locations in 2002 (Appendix J) exceeded several Class II groundwater standards (IAC Title 35, Part 620.420) for inorganic parameters. The parameters exceeded by one or more groundwater samples from the bedrock wells at the Site include chloride, sulfate, and TDS. As discussed in Section 5.2.1.3 and displayed on Table 11, many parameters detected at elevated concentrations in groundwater were elevated in both background wells and the East Ash Pond wells.

As seen on the following table, the chloride standard was exceeded at four background wells and two East Ash Pond wells, the sulfate standard at one East Ash Pond well, and the TDS standard at two background wells and three East Ash Pond wells.

Parameter	Class II Groundwater Standard (mg/L)	Background Bedrock Wells Exceeding Class II Standard in 2002	East Ash Pond Bedrock Wells Exceeding Class II Standard in 2002
Chloride	200	MW25, MW27, MW29, MW30	MW13A, MW32
Sulfate	400	none	MW16A
TDS	1,200	MW25, MW30	MW13A, MW16A, MW32

The occurrence of parameters in groundwater at sufficiently high concentrations to exceed groundwater standards can be attributed to three sources: natural geochemistry of

the shale bedrock; natural geochemistry associated with coal deposits, particularly at MW30; and, anthropogenic affects on geochemistry associated with former coal mines in the vicinity of background well MW25 and the East Ash Pond wells, particularly wells MW13A, MW16A, and MW32.

5.3 ISOTOPE RESEARCH RESULTS

The carbon and hydrogen (tritium) isotopic data analyzed by the ISGS for groundwater "reveal that some wells produce recent water, while others yield much older water" (Mehnert and Dreher, 2002; Appendix A). Groundwater sampled from the alluvial deposits at wells MW26 and MW28 is indicative of recent water. Tritium values in Illinois precipitation as reported by the ISGS (Appendix A, Table 11) typically range from 3 to 10 tritium units (TU). In the subsurface, tritium has a half-life of 12.3 years and water with tritium concentrations greater than 5 TU is considered recent water. Tritium concentrations in groundwater from the unlithified deposits at wells MW26 and MW28 were 5.3 and 5.8 TU, respectively. Conversely, tritium concentrations in groundwater from the bedrock deposits at wells MW25, MW27, MW29, and MW30 were all below detection limits ranging from 0.43 to 0.52 TU. Water with non-detectable tritium concentrations is considered to be greater than 50 years old.

The Carbon-14 (^{14}C) data for groundwater from the alluvial deposits was consistent with the tritium data. ^{14}C, which has a much longer half-life than tritium, is presented by the ISGS (Appendix A, Table 11) as radiocarbon years before present (RYBP) and as percent (%) modern carbon, both of which provide relative ages. Groundwater from the shallow alluvial wells (MW26 and MW28) had % modern carbon values of 97 and 102 and RYBP values of 210 and "modern", respectively. Based on the tritium and ^{14}C data for groundwater from MW26 and MW28, it is apparent that wells completed in Quaternary geologic materials (i.e., alluvial deposits) "appear to draw water from the local groundwater flow system" (Mehnert and Dreher, 2002).

In contrast to water sampled from the alluvial wells, ^{14}C data from the bedrock wells indicates that the groundwater is significantly older. The ^{14}C data for the background wells installed in the Pennsylvanian bedrock is listed below.

Well Number	Radiocarbon Years Before Present (RYBP)	% Modern Carbon
MW25 (Kelron 25)	13,920	18
MW27 (Kelron 27)	19,400	8.9
MW29 (Kelron 29)	34,610	1.4
MW30 (Kelron 30)	20,850	7.5

The conclusions of the ISGS concerning the four bedrock wells sampled for ^{14}C analysis were that they "apparently draw water from the bedrock and are either only slightly connected to or completely isolated from the local groundwater flow system".

The results of the isotopic analyses of groundwater samples from the background bedrock wells support the hydrogeologic data and conceptualization established earlier. Namely, the Middle Fork of the Vermilion River is a regional discharge area for the bedrock and groundwater within the bedrock is at the end of its flow path, with upward hydraulic gradients, high dissolved mineral content, and significantly older by 13,000 to 35,000 RYBP than groundwater in the overlying unlithified deposits.

6.0 CONCLUSIONS

A comprehensive hydrogeologic and geochemical study of the East Ash Pond System and surrounding region at DMG's Vermilion Power Plant was conducted during 2001-2002. Background geochemical data on the bedrock and groundwater was collected and evaluated by the ISGS for comparison to site-specific data. The collected body of data has been summarized below for the geology, hydrogeology and groundwater chemistry. Utilizing all the available data from the study site and surrounding region, a final section provides the proposed groundwater classification for groundwater at the Vermilion Power Plant and East Ash Pond System.

6.1 GEOLOGY

The deposits covering the bedrock in the region surrounding the study site are derived from recent river deposition (alluvial sediments) in the river valleys and glacial drift deposits occurring below the alluvial sediments and in the upland areas. The glacial and interglacial geologic events that shaped the topography seen today occurred during the Pleistocene Epoch, about 2 million to 12,000 years ago. Thickness of these deposits in the region range from zero thickness along portions of the Middle Fork where bedrock is exposed to over 200 feet in the upland areas.

The unlithified alluvial and glacial deposits in the vicinity of the East Ash Pond and within the floodplain generally range in thickness from 10 to 25 feet. The unlithified deposits increase in thickness as the alluvial deposits pinch out and are supplanted by glacial deposits at higher topographic elevations. Along the western portion of the study site, to the west of the East Ash Pond, the thickest glacial deposits range from 71 feet to the north to 103 feet in the south.

Rocks of Pennsylvanian age form the bedrock surface in the region surrounding the study site. The Danville area is located on the northeast flank of the Illinois basin. Regionally, the Pennsylvanian bedrock consists of mainly shale with thin limestone, sandstone, and coal beds. The upper 75 feet of bedrock at the Site consists of non-marine and marine, silty and micaceous shales of the Pennsylvanian Age Shelburn Formation. The Shelburn Formation contains a major coal seam mined in the region, the Danville Coal, also called the No. 7 Coal.

The top of the Danville Coal, or the void remaining where the coal was removed through mining, was intercepted at depths of 80 to 102.5 feet BLS on the floodplain adjacent to the East Ash Pond. The thickness of the coal seam ranged from 4 to 7 feet with an average thickness of 5.4 feet. A geophysical survey by URS Corp. along 5 lines in 2002 detected 12 anomalies judged to be mine-related voids, collapse features, or partial collapse features in the vicinity of the East Ash Pond System.

The region surrounding the Vermilion Power Plant, including portions of the plant property, has seen extensive coal-mining activity from 1893 to 1970. Two coal mines are located within the vicinity of the East Ash Pond System. Based on data and maps

obtained from the ISGS, the former entrances to the two coal mines beneath the site are located just north of the secondary cell of the East Ash Pond and 600 feet southwest of the primary cell.

6.2 HYDROGEOLOGY

Groundwater within the alluvial and, where present, the glacial (till) deposits within the floodplain generally conforms to the ground surface topography. Groundwater elevations in the till and alluvial deposits demonstrate that groundwater elevations in the unlithified materials are higher than those in the adjacent Middle Fork through much of the year. The groundwater surface in the alluvial deposits fluctuates in response to changes in river stage and variations in precipitation. The groundwater surface is not affected by water levels in the East Ash Pond, which has been hydraulically isolated from both the shale and alluvial deposits by soil/bentonite slurry walls and a compacted clay core. Changes in pond elevation do not result in any corresponding changes in the shallow groundwater levels.

Groundwater elevations in the shale are highest in the topographically highest areas to the west and east of the Middle Fork of the Vermilion River. The lowest groundwater elevations occur at wells located adjacent to the Middle Fork. Flow lines derived from the potentiometric surface maps indicate that the Middle Fork in this area is a zone of discharge for the shale. The occurrence of the Middle Fork in this area as a regional discharge zone for the shallow bedrock is supported by the upward vertical hydraulic gradients measured within the shale and the upward vertical hydraulic gradients observed during various periods and at multiple locations between the shale and the alluvium. The shale outcrops along the banks of the Middle Fork and groundwater moving upward through the shale discharges into both the alluvium and directly into the Middle Fork.

The coal mines in the vicinity of the East Ash Pond System have been shown to have significant collapse features where the overlying shale has collapsed or partially collapsed downward into the void or mined coal seam. The collapse of the shale into the void translates upward through the shale, resulting in fracturing and in some cases surface subsidence. A hydrologic feature noted during the exploratory boring phase of the coal mine investigation was the presence of substantial hydraulic head within the coal and overlying fractured shale in proximity to mined areas. Borings located northwest of the East Ash Pond intercepted groundwater under flowing artesian conditions that resulted in temporary suspension of drilling.

6.3 GROUNDWATER CHEMISTRY

Based on all of the groundwater and surface water quality data collected in 2002, the affects of the East Ash Pond on groundwater quality are either negligible or not present. Groundwater quality data for most major ions and trace constituents is similar to background groundwater quality. In cases where elevated concentrations of a parameter were found to occur in groundwater near the East Ash Pond there were also elevated

concentrations in background wells screened within coal deposits or in the proximity of abandoned coal mines.

Trace metal concentrations in groundwater were compared to East Ash Pond water samples and there was no commonality between the two water types. The deficiency of trace metals such as molybdenum, selenium, and vanadium in groundwater within both the alluvial deposits and the Pennsylvanian age bedrock at both background and East Ash Pond wells, as compared to their ubiquitous presence within waters of the East Ash Pond, suggests that based on trace water quality data there is no impact to unlithified or bedrock groundwater quality by the East Ash Pond.

Finally, the results of the isotopic analyses of groundwater samples from the background bedrock wells by the ISGS resulted in Carbon-14 ages ranging from 13,000 to 35,000 RYBP (radiocarbon years before present). In support of the Carbon-14 results, tritium concentrations for the same set of bedrock groundwater samples were all below detection limits ranging from 0.43 to 0.52 TU (tritium units). Water with non-detectable tritium concentrations is considered to be greater than 50 years old (Mehnert and Dreher, 2002).

The isotopic and other geochemical data supports the hydrogeologic conceptualization established earlier. Namely, the Middle Fork of the Vermilion River is a regional discharge area for the bedrock and groundwater within the bedrock is at the end of its flow path, with upward hydraulic gradients, high dissolved mineral content, and significantly older by 13,000 to 35,000 RYBP than recent groundwater in the overlying unlithified deposits.

6.4 GROUNDWATER CLASSIFICATION

During March through August 2002, no groundwater parameters measured in shallow monitoring wells in the unlithified deposits exceeded Class I or II groundwater standards. However, background well MW28 exceeded the sulfate and TDS standards of 400 and 1,200 mg/L, respectively, during January and February 2002.

Three bedrock monitoring wells at the East Ash Pond and four background wells regularly exceeded standards for at least one of the parameters of chloride, sulfate, and TDS. The occurrence of parameters within the bedrock at sufficiently high concentrations to exceed groundwater standards can be attributed to three sources: natural geochemistry of the shale bedrock; natural geochemistry associated with coal deposits; and, anthropogenic (man-made) affects on geochemistry associated with former coal mines.

Based on the hydrogeology and geochemistry established for the vicinity of the East Ash Pond and surrounding region, and given the influence of former coal mines documented at the Site on the geochemistry of groundwater within the unlithified and bedrock deposits, it is proposed that the groundwater designation in accordance with Section 620.201 of Part 620 (IAC Title 35, Subtitle F, Chapter I) be Class IV – Other Groundwater, as documented by the following excerpt from Section 620.240:

"g) Groundwater within a previously mined area, unless monitoring demonstrates that the groundwater is capable of consistently meeting the standards of Sections 620.410 or 620.420. If such capability is determined, groundwater within the previously mined area shall not be Class IV."

The groundwater quality established at the East Ash Pond is within a previously mined area and has been documented to be influenced by both natural geochemistry and the influences of abandoned coal mines and mine spoils. Groundwater quality at the Vermilion Power Plant and in background wells have consistently not met the Class I and II standards for chloride, sulfate, and TDS as documented in Sections 620.410 and 620.420, respectively, of the IAC. Therefore, groundwater in the unlithified deposits and bedrock at the East Ash Pond and surrounding area of the DMG property at the Vermilion Power Plant should be designated Class IV.

7.0 REFERENCES

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Tables

Table 1. Boring and Monitoring Well Summary

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Boring or Monitoring Well	Drilling / Installation Date	Status / Purpose as of November 2002	Land Surface Elevation (feet) 2001 Survey	State Planar X-Coord (feet)	State Planar Y-Coord (feet)
MW10	1987	Quarterly Monitoring Well	656.3	1,150,091	1,279,665
MW13A	1987	Quarterly Monitoring Well	581.9	1,151,313	1,279,859
MW13B	1987	Quarterly Monitoring Well	582.0	1,151,313	1,279,865
MW16A	1987	Quarterly Monitoring Well	578.3	1,151,425	1,279,349
MW16B	1987	Quarterly Monitoring Well	578.5	1,151,418	1,279,347
MW-11A	1987	destroyed - E.Ash Pond construction	594.7	1,150,764	1,279,956
MW-12A	1987	destroyed - E.Ash Pond construction	590.0	1,151,082	1,280,323
MW-14A	1987	destroyed - E.Ash Pond construction	586.1	1,150,877	1,279,520
MW-15A	1987	destroyed - E.Ash Pond construction	589.0	1,150,650	1,279,242
MW22	2001	2001-2002 Hydrogeologic Investigation / In Use	655.6	1,150,083	1,279,669
MW23	2001	2001-2002 Hydrogeologic Investigation / In Use	599.1	1,150,788	1,280,399
MW24	2001	2001-2002 Hydrogeologic Investigation / In Use	598.8	1,150,783	1,280,404
MW25	2001	2001-2002 Hydrogeologic Investigation / In Use	578.8	1,150,916	1,278,027
MW26	2001	2001-2002 Hydrogeologic Investigation / In Use	580.5	1,150,782	1,280,741
MW27	2001	2001-2002 Hydrogeologic Investigation / In Use	580.4	1,150,787	1,280,744
MW28	2001	2001-2002 Hydrogeologic Investigation / In Use	581.0	1,151,565	1,281,552
MW29	2001	2001-2002 Hydrogeologic Investigation / In Use	580.9	1,151,564	1,281,557
MW30	2001	2001-2002 Hydrogeologic Investigation / In Use	645.7	1,150,347	1,282,360
MW31	2001	2001-2002 Hydrogeologic Investigation / In Use	698.2	1,152,932	1,279,256
MW32	2001	2001-2002 Hydrogeologic Investigation / In Use	581.9	1,151,312	1,279,850
B101	2001	Geotechnical Boring - E.Ash Pond Expansion	604.0	1,150,224	1,279,157
B102	2001	Geotechnical Boring - E.Ash Pond Expansion	642.0	1,150,264	1,279,708
B103	2001	Geotechnical Boring - E.Ash Pond Expansion	653.9	1,150,323	1,279,872
B104	2001	Geotechnical Boring - E.Ash Pond Expansion	652.4	1,150,287	1,279,540
B105	2001	Geotechnical Boring - E.Ash Pond Expansion	652.4	1,150,360	1,279,510
B106	2001	Geotechnical Boring - E.Ash Pond Expansion	659.2	1,150,353	1,279,348
B107	2001	Geotechnical Boring - E.Ash Pond Expansion	658.6	1,150,188	1,279,346
B108	2001	Geotechnical Boring - E.Ash Pond Expansion	658.0	1,150,259	1,279,463
B109	2001	Geotechnical Boring - E.Ash Pond Expansion	655.8	1,150,194	1,279,559
B110	2001	Geotechnical Boring - E.Ash Pond Expansion	654.6	1,149,682	1,279,283
B111	2001	Geotechnical Boring - E.Ash Pond Expansion	653.7	1,149,852	1,279,443
B112	2001	Geotechnical Boring - E.Ash Pond Expansion	652.7	1,149,843	1,279,285
B201	2002	Exploratory Boring - Coal Mine Investigation	599.1	1,150,614	1,280,277
B202	2002	Exploratory Boring - Coal Mine Investigation	606.0	1,150,547	1,280,287
B203	2002	Exploratory Boring - Coal Mine Investigation	627.1	1,150,427	1,280,159
B204	2002	Exploratory Boring - Coal Mine Investigation	588.0	1,150,065	1,278,812
B205	2002	Exploratory Boring - Coal Mine Investigation	589.6	1,150,223	1,278,791
B206	2002	Exploratory Boring - Coal Mine Investigation	589.0	1,150,345	1,278,682
B207	2002	Exploratory Boring - Coal Mine Investigation	595.6	1,150,358	1,278,992
B208	2002	Exploratory Boring - Coal Mine Investigation	657.6	1,149,885	1,278,897

Table 2. Monitoring Well Depths and Screened Elevations

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Monitoring Well	TOC/MP Elevation (feet)	Land Surface Elevation (feet)	Well Stickup (feet)	Screen Top from LS (feet)	Screen Bot from LS (feet)	Screen Length (feet)	Screen Elevation Top (feet)	Screen Elevation Bottom (feet)	Total Well Depth from LS (feet)	Total Well Depth from TOC/MP (feet)
MW10	659.10	656.3	2.8	46.60	56.60	10.00	609.70	599.70	56.6	59.4
MW13A	583.47	581.9	1.6	21.00	41.00	20.00	560.90	540.90	41.0	42.6
MW13B	583.84	582.0	1.8	5.50	10.50	5.00	576.50	571.50	10.5	12.3
MW16A	580.17	578.3	1.9	21.80	41.80	20.00	556.50	536.50	41.8	43.7
MW16B	580.56	578.5	2.1	7.00	12.00	5.00	571.50	566.50	12.0	14.1
MW22	658.60	655.6	3.0	80.00	100.00	20.00	575.60	555.60	100.0	103.0
MW23	601.89	599.2	2.7	11.80	21.80	10.00	587.40	577.40	22.0	24.7
MW24	601.81	598.8	3.0	34.80	54.80	20.00	564.00	544.00	54.8	57.8
MW25	581.65	578.8	2.9	19.10	39.10	20.00	559.70	539.70	39.1	42.0
MW26	583.52	580.5	3.0	7.75	12.75	5.00	572.75	567.75	13.0	16.0
MW27	583.39	580.4	3.0	23.00	43.00	20.00	557.40	537.40	43.0	46.0
MW28	583.79	581.0	2.8	8.00	13.00	5.00	573.00	568.00	13.0	15.8
MW29	583.90	580.9	3.0	23.00	43.00	20.00	557.90	537.90	43.0	46.0
MW30	648.71	645.7	3.0	127.00	147.04	20.04	518.70	498.66	147.0	150.1
MW31	701.21	698.2	3.0	162.00	182.00	20.00	536.20	516.20	182.0	185.0
MW32	585.00	581.9	3.1	45.80	55.80	10.00	536.10	526.10	55.8	58.9

Notes:

Shale
Till or Alluvial

All elevations measured during December 2001 except MW13A,B; and, MW16A,B from 1999 survey.

Table 3. Groundwater and Surface-Water Levels and Elevations: 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Monitoring Well or Surface Water Point	Measuring Point Elevation[1] (feet NGVD)	Groundwater Depth (feet below MP)								Groundwater Elevation (feet NGVD)							
		1 1/22-23/02	2 2/18/2002	3 3/19-21/02	4 4/16-17/02	5 5/22/2002	6 6/18/2002	7 7/16/2002	8 8/27/2002	1 1/22-23/02	2 2/18/2002	3 3/19-21/02	4 4/16-17/02	5 5/22/2002	6 6/18/2002	7 7/16/2002	8 8/27/2002
MW10	659.10	52.99	52.41	51.89	51.62	52.63	51.62	51.81	52.26	606.11	606.69	607.21	607.48	606.47	607.48	607.29	606.84
MW13A	583.47	10.73	10.56	10.32	10.59	10.11	10.73	10.82	8.82	572.74	572.91	573.15	572.88	573.36	572.74	572.65	574.65
MW13B	583.84	dry	12.03	11.79	11.90	10.40	12.12	12.61	10.67	dry	571.81	572.05	571.94	573.44	571.72	571.23	573.17
MW16A	580.17	10.34	10.60	10.36	10.74	9.65	9.86	9.99	6.6	569.83	569.57	569.81	569.43	570.52	570.31	570.18	573.57
MW16B	580.56	dry	dry	10.05	10.22	dry	10.51	dry	9.63	dry	dry	570.51	570.34	dry	570.05	dry	dry
MW22	658.60	56.61	56.52	56.60	58.54	57.42	58.78	59.10	60.35	601.99	602.08	602.00	600.06	601.18	599.82	599.50	598.25
MW23	601.89	13.79	12.98	12.00	12.39	12.06	13.80	14.49	13.46	588.10	588.91	589.89	589.50	589.83	588.09	587.40	588.43
MW24	601.81	22.71	23.86	21.90	22.39	21.80	22.06	22.48	21.20	579.10	577.95	579.91	579.42	580.01	579.75	579.33	580.61
MW25	581.65	16.02	15.89	15.39	15.46	14.82	15.25	15.84	13.97	565.63	565.76	566.26	566.19	566.83	566.40	565.81	567.68
MW26	583.52	10.03	9.11	7.91	7.83	6.40	8.13	9.83	8.86	573.49	574.41	575.61	575.69	577.12	575.39	573.69	574.66
MW27	583.39	8.70	8.52	7.80	7.88	7.00	7.77	8.60	7.54	574.69	574.87	575.59	575.51	576.39	575.62	574.79	575.85
MW28	583.79	9.36	8.53	7.95	7.77	7.42	8.70	10.09	8.44	574.43	575.26	575.84	576.02	576.37	575.09	573.70	575.35
MW29	583.90	4.04	3.42	3.04	2.83	2.71	3.38	4.52	3.95	579.86	580.48	580.86	581.07	581.19	580.52	579.38	579.95
MW30	648.71	63.94	63.18	62.57	62.57	62.34	62.26	62.83	62.70	584.77	585.53	586.14	586.14	586.37	586.45	585.88	586.01
MW31	701.21	88.12	87.94	87.55	87.30	87.00	87.41	87.89	86.06	613.09	613.27	613.66	613.91	614.21	613.80	613.32	615.15
MW32	585.00	0.09	0.12	0.00	0.00	0.00	0.00	1.98	0.00	584.91	584.88	585.00	585.00	585.00	585.00	583.02	585.00
River at MW26/MW27[2]	580.81	na	na	na	na	na	na	na	na	572.01	572.14	573.47	572.86	573.26	573.31	nm	573.83
River at MW25[3]	573.00	12.71	12.33	11.93	11.91	11.60	11.78	nm	11.20	560.29	560.67	561.07	561.09	561.40	561.22	nm	561.80
Secondary Ash Pond[4]	599.43	na	nm	7.20	7.56	7.21	nm	nm	nm	593.17	nm	592.23	591.87	592.22	nm	nm	nm
Primary Ash Pond[5]	599.77	na	nm	6.11	12.8	nm	nm	nm	nm	592.66	nm	593.66	586.97	586.65	nm	nm	nm

Notes:

1 As measured at top of riser pipe for wells and surveyed or measured for surface water points.

2 Control Monument 0109 adjacent to Wells MW26 and MW27.

3 Control Point is scribe mark on lower deck of Pump House.

4 Control Point is scribe mark on concrete base of east catwalk.

5 Control Point is scribe mark on concrete base of north catwalk.

MP	Measuring point.
MW	Monitoring well.
NGVD	National Geodetic Vertical Datum.
MW27	Shale Monitoring Wells
MW26	Till or Alluvial Monitoring Wells
na	not applicable
nm	not measured

Table 4. Field Hydraulic Conductivity Results

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Monitoring Well	Formation	Analytical Solution	Number of Field Tests	Average Hydraulic Conductivity (cm/sec)
MW24	Pennsylvanian Shale	Bouwer-Rice (confined)	1	3.85×10^{-5}
MW25	Pennsylvanian Shale	Bouwer-Rice (confined)	1	2.47×10^{-6}
MW27	Pennsylvanian Shale	Bouwer-Rice (confined)	2	1.04×10^{-4}
MW29	Pennsylvanian Shale	Bouwer-Rice (confined)	1	5.76×10^{-7}
MW30	Pennsylvanian Shale and Coal	Bouwer-Rice (confined)	1	1.80×10^{-6}
MW31	Pennsylvanian Shale	Bouwer-Rice (confined)	1	1.45×10^{-7}
MW32	Pennsylvanian Shale	Bouwer-Rice (confined)	1	1.49×10^{-6}
Geometric Mean Hydraulic Conductivity (all shale wells)				**3.0×10^{-6}**
MW26	Recent Alluvium (sand and gravel)	Bouwer-Rice (unconfined)	2	2.16×10^{-2}
MW28	Recent Alluvium (silt, some sand)	Bouwer-Rice (unconfined)	2	1.02×10^{-2}
Geometric Mean Hydraulic Conductivity (alluvial wells only)				**1.5×10^{-2}**

Table 5. Depths and Elevations of Pennsylvanian Shale Bedrock and Danville Coal

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Boring or Monitoring Well	Land Surface Elevation	Pennsylvanian Shale		Danville (No. 6) Coal			
		Depth (feet)	Elevation (feet)	Top of Coal Seam		Bottom of Coal Seam	
				Depth (feet)	Elevation (feet)	Depth (feet)	Elevation (feet)
MW13A	581.9	11	571	- -	- -	- -	- -
MW16A	578.3	12	566	- -	- -	- -	- -
MW22	655.6	71	585	- -	- -	- -	- -
MW24	598.8	22	577	- -	- -	- -	- -
MW25	578.8	10	569	- -	- -	- -	- -
MW27	580.4	13	567	- -	- -	- -	- -
MW29	580.9	18	566	- -	- -	- -	- -
MW30	645.7	116	530	144.2	501.5	Borehole terminated above base of unit.	
MW31	698.2	155	545	- -	- -	- -	- -
MW32	581.9	11	571	- -	- -	- -	- -
B-11A	594.7	10	585	- -	- -	- -	- -
B-12A	590.0	12	578	- -	- -	- -	- -
B-14A	586.1	10	576	- -	- -	- -	- -
B-15A	589.0	12	578	- -	- -	- -	- -
B101	604.0	29	575	- -	- -	- -	- -
B102	642.0	49	594	- -	- -	- -	- -
B103	653.9	69	585	- -	- -	- -	- -
B104	652.4	64	588	- -	- -	- -	- -
B105	652.4	64	588	- -	- -	- -	- -
B106	659.2	69	590	- -	- -	- -	- -
B107	658.6	70	589	- -	- -	- -	- -
B108	658.0	67	591	- -	- -	- -	- -
B109	655.8	>71	na	- -	- -	- -	- -
B110	654.6	>86	na	- -	- -	- -	- -
B111	653.7	>76	na	- -	- -	- -	- -
B112	652.7	>76	na	- -	- -	- -	- -
B201	599.1	41	559	102.5	496.6	107.5	491.6
				Mined Out Coal Seam. Mine Void Intercepted - Coal Seam Removed.			
B202	606.0	48	558	*Mined Out Coal Seam. Collapsed Mine.*		114.7	491.3
B203	627.1	66	561	127.0	500.1	132.3	494.8
B204	588.0	15	574	83.0	505.0	88.9	499.1
				Sloped Mineshaft (Void) Intercepted from 28 to 37 feet below ground surface.			
B205	589.6	22	568	86.3	503.3	91.8	497.8
B206	589.0	16	573	80.4	508.6	84.4	504.6
				Mined Out Coal Seam. Mine Void Intercepted - Coal Seam Removed.			
B207	595.6	22	574	90.0	505.6	95.5	500.1
B208	657.6	103	554	152.0	505.6	159.0	498.6

Notes:

- - Borehole terminated at a depth shallower than the Danville (No. 6) Coal.

Table 6. Vertical Groundwater Gradients in Shale and Between Shale and Alluvium

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Monitoring Wells for Gradient Calculations with Screened Formations		Groundwater Level Measurement Date During 2002								8-month Average
		22-23 Jan	18-Feb	19-21 March	16-17 April	22-May	18-Jun	16-Jul	27-Aug	
MW13B alluvial	MW13A shale	alluvial dry	**-0.048**	**-0.048**	**-0.041**	0.003	**-0.044**	**-0.061**	**-0.064**	**-0.043**
MW13A shale	MW32 shale	**-0.615**	**-0.605**	**-0.598**	**-0.612**	**-0.588**	**-0.619**	**-0.524**	**-0.523**	**-0.585**
MW16B alluvial	MW16A shale	alluvial dry	alluvial dry	0.031	0.040	alluvial dry	**-0.012**	alluvial dry	alluvial dry	0.020
MW23 alluvial	MW24 shale	0.317	0.386	0.351	0.355	0.346	0.294	0.284	0.275	0.326
MW26 alluvial	MW27 shale	**-0.053**	**-0.020**	0.001	0.008	0.032	**-0.010**	**-0.048**	**-0.052**	**-0.018**
MW28 alluvial	MW29 shale	**-0.240**	**-0.231**	**-0.222**	**-0.223**	**-0.213**	**-0.240**	**-0.251**	**-0.204**	**-0.228**

Notes:
-0.615 Vertical gradient is upwards between the screened well intervals and formations indicated.
0.386 Vertical gradient is downwards between the screened well intervals and formations indicated.
alluvial dry Shallow alluvial monitoring well did not have a measurable water level on the date indicated.

Table 7. Correlation Between Groundwater Quality Parameters in Unlithified Deposits

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

	Aluminum	Alkalinity	Boron	Barium	Calcium	Chloride	Iron	Potassium	Lithium	Magnesium	Manganese	Sodium	Selenium	Sulfate	Strontium	TDS
Aluminum		-0.38	-0.53	0.10	-0.80	-0.28	-0.03	0.07	-0.47	-0.59	-0.20	-0.50	-0.35	-0.80	-0.55	-0.73
Alkalinity			-0.16	0.66	0.63	-0.30	0.49	-0.83	**0.92**	**0.94**	**0.82**	0.42	0.36	0.38	**0.96**	0.72
Boron				-0.51	0.61	**0.89**	-0.11	0.58	-0.15	0.12	-0.18	0.72	-0.01	0.79	0.06	0.53
Barium					0.05	-0.47	0.45	-0.59	0.49	0.47	0.53	-0.06	0.22	-0.09	0.59	0.20
Calcium						0.36	0.18	-0.24	0.66	**0.84**	0.38	0.79	0.36	**0.92**	0.77	**0.97**
Chloride							-0.21	0.66	-0.27	-0.08	-0.32	0.68	-0.08	0.55	-0.11	0.29
Iron								-0.41	0.33	0.37	**0.82**	0.13	-0.13	0.09	0.51	0.28
Potassium									**-0.81**	-0.69	-0.67	0.03	-0.39	0.09	-0.69	-0.33
Lithium										**0.91**	0.59	0.36	0.54	0.40	**0.89**	0.71
Magnesium											0.69	0.59	0.47	0.63	**0.97**	**0.89**
Manganese												0.29	-0.01	0.21	**0.81**	0.49
Sodium													0.07	0.78	0.56	0.78
Selenium														0.26	0.33	0.39
Sulfate															0.57	**0.89**
Strontium																**0.83**
TDS																

Notes:

between the variables. The number of pairs of data values used to compute each coefficient was 18 (6 observations of each chemical parameter in groundwater per well for wells MW23, MW26, and MW28). Generally, correlations greater than 0.50 or less than -0.50 indicate statistically significant non-zero correlations at the 95% confidence level.

Data for determination of correlations are the 6 monthly samples collected from March to August 2002 at unconsolidated wells MW23 at the East Ash Pond and background wells MW26 and MW28.

0.89 Bold-face numbers highlighted in boxes indicate a high level of correlation between two parameters. Positive numbers indicate that the parameters are directly proportional and negative numbers indicate the parameters are inversely proportional.

Table 8. Summary of Groundwater Quality Data in Unlithified Deposits, East Ash Pond, and Middle Fork River

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Aluminum, diss (mg/L)	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	0.013	0.013	0.010	0.017
MW28	6	0.007	0.008	<0.005	0.010
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	0.007	0.008	<0.005	0.010
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	0.015	0.013	<0.005	0.030
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002)	5	**0.124**	**0.140**	0.011	0.25

Comments:
1. East Ash Pond alluvial well MW23 comes from same population as Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Aluminum concentrations in East Ash Pond Surface Water Samples are 10 to 18 times greater than in Background and East Ash Pond alluvial wells.
3. Median Aluminum concentrations upstream on the Middle Fork are equivalent to or slightly greater than the Background Alluvial Wells.

Parameter: Barium, diss (mg/L)	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	0.030	0.029	0.028	0.031
MW28	6	0.033	0.033	0.028	0.041
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	0.025	0.025	0.023	0.027
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	0.041	0.039	0.036	0.054
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002) not applicable	5	**0.14**	**0.13**	0.03	0.28

Comments:
1. East Ash Pond alluvial well MW23 has a statistically significant lower concentration than Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Barium concentrations in East Ash Pond Surface Water Samples are 4 to 5 times greater than in Background and East Ash Pond alluvial wells.
3. Median Barium concentrations upstream on the Middle Fork are slightly greater than (within 35 percent) the Background Alluvial Wells.

Parameter: Boron, diss (mg/L)	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	0.038	0.025	<0.05	0.076
MW28	6	0.122	0.120	0.110	0.140
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	**0.265**	**0.265**	0.20	0.32
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	0.057	0.065	<0.05	0.091
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002) not applicable	5	**10.88**	**10.00**	5.1	18.0

Comments:
1. East Ash Pond alluvial well MW23 has a statistically significant higher concentration than Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Boron concentrations in East Ash Pond Surface Water Samples are 38 times greater than those in East Ash Pond alluvial well MW23.
3. Median Boron concentrations upstream on the Middle Fork are within the range of the Background Alluvial Wells.

Notes:
* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
Highest mean and median concentrations of parameter are shown in boldface.

Table 8. Summary of Groundwater Quality Data in Unlithified Deposits, East Ash Pond, and Middle Fork River

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Calcium, diss (mg/L)	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	89	92	75	100
MW28	6	203	195	180	250
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	185	185	180	190
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	77	82	60	93
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002) not applicable	5	**322**	**350**	150	450

Comments:
1. East Ash Pond alluvial well MW23 comes from same population as Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Calcium concentrations in East Ash Pond Surface Water Samples are 1.9 times greater than those in East Ash Pond alluvial well MW23.
3. Median Calcium concentrations upstream on the Middle Fork are slighly lower than the Background Alluvial Wells.

Parameter: Chloride, total (mg/L)	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	11.1	12.0	7.3	13
MW28	6	13	12.5	11	18
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	35.2	38.5	10	54
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	28.8	29.5	18	41
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002)	5	**172**	**200**	100	240

Comments:
1. East Ash Pond alluvial well MW23 has a statistically significant higher concentration than Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Chloride concentrations in East Ash Pond Surface Water Samples are 5.2 times greater than those in East Ash Pond alluvial well MW23.
3. Median Chloride concentrations upstream on the Middle Fork are about 2.5 times higher than the Background Alluvial Wells.

Parameter: Iron, diss (mg/L)	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	**0.015**	**0.013**	<0.025	0.025
MW28	6	**0.040**	**0.029**	<0.025	0.11
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	nd	nd	<0.025	<0.025
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	nd	nd	<0.025	<0.025
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002)	5	nd	nd	<0.025	<0.025

Comments:
1. East Ash Pond alluvial well MW23 comes from same population as Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. The only detected iron concentrations were in the Background Alluvial Wells; all other locations were below the method detection limit of 0.025 mg/L.

Notes:
* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
nd No samples were above method detection limit.
Highest mean and median concentrations of parameter are shown in boldface.

Table 8. Summary of Groundwater Quality Data in Unlithified Deposits, East Ash Pond, and Middle Fork River

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Lithium, diss (mg/L)	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	0.004	0.003	<0.005	0.007
MW28	6	nd	nd	<0.005	<0.005
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	0.004	0.003	<0.005	0.007
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	0.004	0.003	<0.005	0.007
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	5	**0.19**	**0.27**	<0.005	0.30

Comments:
1. East Ash Pond alluvial well MW23 comes from same population as Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Lithium concentrations in East Ash Pond Surface Water Samples are over 90 times greater than in Background and East Ash Pond alluvial wells.
3. Median Lithium concentrations upstream on the Middle Fork are equivalent to the Background Alluvial Wells.

Parameter: Magnesium, diss (mg/L)	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	34	35	28	42
MW28	6	**98**	**100**	90	110
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	56	55	53	62
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	35.3	36	24	41
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	5	26.5	30	8.4	42

Comments:
1. East Ash Pond alluvial well MW23 comes from same population as Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Magnesium concentrations in East Ash Pond Surface Water Samples are lower than those observed in East Ash Pond alluvial well MW23 and the Middle Fork.
3. Median Magnesium concentrations upstream on the Middle Fork are within the range of the Background Alluvial Wells.

Parameter: Manganese, diss (mg/L)	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	nd	nd	<0.005	<0.005
MW28	6	**0.062**	**0.065**	0.019	0.11
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	nd	nd	<0.005	<0.005
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	0.011	0.010	0.005	0.019
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	5	0.025	0.024	0.003	0.057

Comments:
1. Background alluvial wells MW26 and MW28 have a statistically significant higher concentration than East Ash Pond alluvial well MW23 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Manganese concentrations upstream on the Middle Fork are within the range of the Background Alluvial Wells.

Notes:
* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
nd No samples were above method detection limit.
Highest mean and median concentrations of parameter are shown in boldface.

Table 8. Summary of Groundwater Quality Data in Unlithified Deposits, East Ash Pond, and Middle Fork River

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Molybdenum, diss (mg/L)	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)					
MW26	6	nd	nd	<0.010	<0.010
MW28	6	nd	nd	<0.010	<0.010
East Ash Pond Bedrock Wells (2002 Kelron Study)					
MW23	6	nd	nd	<0.010	<0.010
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002)	5	**0.22**	**0.24**	0.130	0.298

Comments:
1. All Bedrock Wells (Background and East Ash Pond wells) had no detectable concentrations of Molybdenum.
2. East Ash Pond Surface Water Samples had Molybdenum in all samples, ranging from 0.13 to 0.298 mg/L.

Parameter: Phosphorus, diss (mg/L)	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	0.060	0.057	0.018	0.095
MW28	6	0.019	0.022	<0.010	0.029
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	0.011	0.010	<0.010	0.017
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)					
	6	**0.104**	**0.063**	0.014	0.310
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002)	5	0.071	0.031	0.010	0.23

Comments:
1. Background alluvial wells MW26 and MW28 have a statistically significant higher concentration than East Ash Pond alluvial well MW23 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Phosphorus concentrations upstream on the Middle Fork are two times greater than those observed in the East Ash Pond Surface Water Samples.
3. East Ash Pond alluvial well MW23 has the lowest phosphorus concentrations compared to all other locations.

Parameter: Potassium, diss (mg/L)	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	2.35	2.35	2.2	2.5
MW28	6	0.97	0.82	0.7	1.8
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	3.32	3.25	2.8	4.0
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)					
	6	1.60	1.20	1.1	3.0
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002)	5	**24.0**	**25.0**	17	31

Comments:
1. East Ash Pond alluvial well MW23 has a statistically significant higher concentration than Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Potassium concentrations in East Ash Pond Surface Water Samples are 7.7 times greater than those in East Ash Pond alluvial well MW23.
3. Median Potassium concentrations upstream on the Middle Fork are within the range of the Background Alluvial Wells.

Notes:
* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
nd No samples were above method detection limit.
Highest mean and median concentrations of parameter are shown in boldface.

Table 8. Summary of Groundwater Quality Data in Unlithified Deposits, East Ash Pond, and Middle Fork River

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Selenium, diss (mg/L)	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)					
MW26	6	nd	nd	<0.005	<0.005
MW28	6	0.004	0.003	<0.005	0.005
East Ash Pond Bedrock Wells (2002 Kelron Study)					
MW23	6	***	0.003	<0.005	0.006
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	***	0.003	<0.005	0.005
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002)	5	***	**0.022**	<0.005	0.043

Comments:
1. All Alluvial Wells (Background and East Ash Pond wells) had Selenium concentrations equal to or less than 0.006 milligrams per Liter.
2. East Ash Pond Surface Water Samples had median Selenium concentrations at least 7 times greater than in Background Wells or East Ash Pond alluvial well MW23.

Parameter: Sodium (mg/L)	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	4.2	4.2	3.1	5.1
MW28	6	17.0	17.0	15.0	19.0
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	17.7	19.5	8.4	26
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	9.4	9.2	7	14
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002)	5	**160**	**140**	100	240

Comments:
1. East Ash Pond alluvial well MW23 has a statistically significant higher concentration than Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Sodium concentrations in East Ash Pond Surface Water Samples are 7.2 times greater than those in East Ash Pond alluvial well MW23.
3. Median Sodium concentrations upstream on the Middle Fork are within the range of the Background Alluvial Wells.

Parameter: Strontium, diss (mg/L)	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	0.07	0.07	0.067	0.076
MW28	6	0.33	0.32	0.300	0.390
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	0.14	0.14	0.128	0.160
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	0.12	0.12	0.094	0.160
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002) not applicable	5	**0.51**	**0.57**	0.27	0.65

Comments:
1. East Ash Pond alluvial well MW23 comes from same population as Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Strontium concentrations in East Ash Pond Surface Water Samples are 4 times greater than those in East Ash Pond alluvial well MW23.
3. Median Strontium concentrations upstream on the Middle Fork are within the range of the Background Alluvial Wells.

Notes:
* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
nd No samples were above method detection limit.
Highest mean and median concentrations of parameter are shown in boldface.

Table 8. Summary of Groundwater Quality Data in Unlithified Deposits, East Ash Pond, and Middle Fork River

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Sulfate (mg/L)	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	23.8	23.5	18	30
MW28	6	273	270	170	360
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	327	320	280	380
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	40	41.5	26	52
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002)	5	**808**	**780**	440	1,500

Comments:
1. East Ash Pond alluvial well MW23 has a statistically significant higher concentration than Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median Sulfate concentrations in East Ash Pond Surface Water Samples are 2.4 times greater than those in East Ash Pond alluvial well MW23.
3. Median Sulfate concentrations upstream on the Middle Fork are within the range of the Background Alluvial Wells.

Parameter: TDS (mg/L)	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Alluvial Wells (2002 Kelron Study)					
MW26	6	403	395	290	520
MW28	6	1,038	1,040	900	1,200
East Ash Pond Alluvial Wells (2002 Kelron Study)					
MW23	6	868	860	810	970
Upstream Middle Fork at Higginsville Bridge (2002 Kelron Study)	6	382	385	290	430
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002)	5	**1,650**	**1,800**	950	2,100

Comments:
1. East Ash Pond alluvial well MW23 comes from same population as Background alluvial wells MW26 and MW28 based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Median TDS concentrations in East Ash Pond Surface Water Samples are 2 times greater than those in East Ash Pond alluvial well MW23.
3. Median TDS concentrations upstream on the Middle Fork are slighly lower than the Background Alluvial Wells.

Parameter: Vanadium (mg/L)	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)					
MW26	6	nd	nd	<0.010	<0.010
MW28	6	nd	nd	<0.010	<0.010
East Ash Pond Bedrock Wells (2002 Kelron Study)					
MW23	6	nd	nd	<0.010	<0.010
East Ash Pond Surface Water Samples (2002 Kelron Study)					
(monthly samples from Jan-May 2002)	5	**0.04**	**0.03**	<0.010	0.078

Comments:
1. All Alluvial Wells (Background and East Ash Pond wells) had Vanadium concentrations below 0.01 milligrams per Liter.
2. East Ash Pond Surface Water Samples had median Vanadium concentrations at least 3 times greater than in Background Wells or East Ash Pond Alluvial Wells.

Notes:
* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
na Not analyzed.
nd No samples were above method detection limit.
Highest mean and median concentrations of parameter are shown in boldface.

Table 9. Summary of Impacts on Groundwater Quality in Unlithified Deposits

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter	COLUMN 2 Mean Groundwater Concentrations in Alluvial Wells[1] at East Ash Pond Compared to Background Alluvial Wells[2]	COLUMN 3 Groundwater Quality in East Ash Pond Alluvial Wells[1] Compared to East Ash Pond Surface Water	Impact by East Ash Pond on Groundwater Quality in Alluvial Deposits	Other Conclusions
Aluminum	**0**	LT	No impact	
Barium	**LT**	LT	No impact	
Boron	GT	LT	**Uncertain**	Median B in MW23 is above background by 0.15 mg/L, but at 0.27 mg/L the source of impact, if any, is uncertain. Slightly higher B may be from natural variation, presence of former coal mine, or East Ash Pond.
Calcium	**0**	LT	No impact	
Chloride	GT	LT	**Uncertain**	Median Cl in MW23 is above background by 26 mg/L and only 9 mg/L above Middle Fork. Slighly higher Cl may be due to natural variation, presence of former coal mine, or East Ash Pond.
Iron	**0**	**All non-detect**	No impact	
Lithium	**0**	LT	No impact	
Magnesium	**0**	GT	No impact	
Manganese	**LT**	LT	No impact	
Molybdenum	**All wells non-detect**	LT	No impact	
Phosphorus	**LT**	LT	No impact	
Potassium	GT	LT	**Uncertain**	Median K in MW23 is above background by 0.9 mg/L, but at 3.25 mg/L may be due to either natural variation or impacts from former coal mine. Concentrations are similar to bedrock.
Selenium	**0**	LT	No impact	
Sodium	GT	LT	**Uncertain**	Median Na in MW23 is above background by 2.5 mg/L, but at 19.5 mg/L the source of impact, if any, is uncertain. Slightly higher Na may be from natural variation, presence of former coal mine, or East Ash Pond.
Strontium	**0**	LT	No impact	
Sulfate	GT	LT	**Uncertain**	Median sulfate in MW23 is above background by 50 mg/L. Higher concentrations are most likely from natural variation. Impacts by East Ash Pond or nearby coal mine are relatively minor or negligible.
TDS	**0**	LT	No impact	
Vanadium	**0**	LT	No impact	

Key to Symbols

COLUMN 2

0 Groundwater quality for given parameter in East Ash Pond wells is statistically from the same population as Background Wells (26 and 28) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.

LT Groundwater quality for given parameter in East Ash Pond wells has a statistically significant lower mean concentration compared to Background Wells (26 and 28) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.

GT Groundwater quality for given paramter in East Ash Pond wells has a statistically significant higher mean concentration compared to Background Wells (26 and 28) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.

COLUMN 3

LT Groundwater concentrations in East Ash Pond Alluvial Wells are less than East Ash Pond surface water for given parameter.

GT Groundwater concentrations in East Ash Pond Alluvial Wells are greater than East Ash Pond surface water for given parameter.

1 Alluvial wells at East Ash Pond include MW13B, MW16B, and MW23. Only MW23 had sufficient water for sampling in 2002.

2 Background alluvial wells used for statistical comparison to East Ash Pond wells using Wilcoxon Rank-Sum Test include the following: MW26 and MW28.

Table 10. Correlation Between Groundwater Quality Parameters in Bedrock

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

	Aluminum	Alkalinity	Boron	Barium	Calcium	Chloride	Iron	Potassium	Lithium	Magnesium	Manganese	Sodium	Selenium	Sulfate	Strontium	TDS
Aluminum		-0.17	-0.02	-0.01	0.16	-0.09	0.06	0.68	0.63	0.10	0.05	-0.05	0.65	0.09	0.27	-0.03
Alkalinity			0.39	0.39	-0.14	0.46	0.46	0.56	0.42	-0.07	0.05	0.70	0.21	0.01	0.46	0.67
Boron				0.13	-0.20	0.65	-0.02	0.25	0.47	-0.10	-0.04	0.63	-0.02	-0.19	0.17	0.61
Barium					-0.11	0.77	**0.87**	0.38	0.28	-0.04	-0.16	0.73	-0.06	-0.23	0.54	0.72
Calcium						-0.30	0.06	0.18	0.01	**0.98**	**0.81**	-0.34	0.51	**0.86**	0.57	0.00
Chloride							0.55	0.32	0.48	-0.17	-0.23	**0.94**	-0.17	-0.37	0.33	**0.88**
Iron								0.40	0.31	0.11	0.10	0.58	0.22	0.06	0.56	0.62
Potassium									0.67	0.15	0.07	0.37	0.50	0.06	0.73	0.42
Lithium										0.05	0.08	0.45	0.48	-0.08	0.38	0.47
Magnesium											**0.86**	-0.21	0.46	**0.86**	0.58	0.14
Manganese												-0.18	0.52	**0.91**	0.38	0.15
Sodium													-0.08	-0.29	0.33	**0.93**
Selenium														0.63	0.36	0.06
Sulfate															0.36	0.01
Strontium																0.54
TDS																

Notes:

between the variables. The number of pairs of data values used to compute each coefficient was 60 (6 observations of each chemical parameter in groundwater per well for wells MW13A, MW16A, MW22, MW24, MW25, MW27, MW29, MW30, MW31, and MW32.
Generally, correlations greater than 0.50 or less than -0.50 indicate statistically significant non-zero correlations at the 95% confidence level.

Data for determination of correlations are the 6 monthly samples collected from March to August 2002 at bedrock wells MW13A, MW16A, MW22, MW24, MW25, MW27, MW29, MW30, MW31, and MW32.

0.89 Bold-face numbers highlighted in boxes indicate a high level of correlation between two parameters. Positive numbers indicate that the parameters are directly proportional and negative numbers indicate the parameters are inversely proportional.

Table 11. Summary of Groundwater Quality Data in Bedrock and East Ash Pond
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Aluminum, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	0.006	0.007	<0.005	0.009
MW27	1	6	0.011	0.011	0.010	0.013
MW29	1	6	0.006	0.007	<0.005	0.009
MW30	1	6	0.016	0.010	0.009	0.044
MW31	1	5	0.006	0.009	<0.005	0.009
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	27	1	***	**0.20**	<0.02	8.47
ISGS Background Wells (2002 ISGS Study) see Appendix A						
(wells 1349,21903,23343,25531)	4	1	<0.1	<0.1	<0.1	<0.1
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	0.008	0.007	<0.005	0.017
MW16A	1	6	0.008	0.008	0.005	0.013
MW22	1	6	0.008	0.007	0.005	0.013
MW24	1	6	0.016	0.010	0.007	0.040
MW32	1	6	0.036	0.042	<0.005	0.047
East Ash Pond Surface Water Samples (2002 Kelron Study)						
(monthly samples from Jan-May 2002)	not applicable	5	**0.124**	**0.140**	0.011	0.25

Comments:
1. All East Ash Pond Bedrock Wells except MW32 come from same population as Background Bedrock Wells (2002 Kelron Study) based on Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. East Ash Pond Bedrock Well MW32 has a higher mean and median concentration than the Background Bedrock Wells (2002 Kelron Study) and other shallower East Ash Pond Bedrock Wells.
3. Highest mean and median concentrations of Aluminum are found in East Ash Pond water samples and in ISGS Background Wells (Scientific Literature and State Databases).
4. Median Aluminum concentrations in East Ash Pond Surface Water Samples are 12 to 20 times greater than in Background Bedrock Wells (2002 Kelron Study) and 3 to 20 times greater than in East Ash Pond Bedrock Wells (2002 Kelron Study).

Parameter: Barium, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	**1.66**	**1.60**	1.6	1.7
MW27	1	6	**0.66**	**0.67**	0.63	0.69
MW29	1	6	**0.47**	**0.47**	0.45	0.49
MW30	1	6	**4.57**	**4.30**	4.2	5.3
MW31	1	6	**0.57**	**0.67**	0.052	0.71
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	27	1	***	0.28	0.02	2.44
ISGS Background Wells (2002 ISGS Study) see Appendix A						
(wells 1349,21903,23343,25531)	4	1	**0.46**	**0.37**	0.14	0.98
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	**0.41**	**0.41**	0.39	0.43
MW16A	1	6	0.07	0.04	0.04	0.18
MW22	1	6	0.06	0.06	0.06	0.071
MW24	1	6	0.16	0.14	0.13	0.25
MW32	1	6	**0.48**	**0.49**	0.45	0.50
East Ash Pond Surface Water Samples (2002 Kelron Study)						
(monthly samples from Jan-May 2002)	not applicable	5	0.14	0.13	0.03	0.28

Comments:
1. Each of the East Ash Pond Bedrock Wells have a statistically significant lower mean concentration than the Background Bedrock Wells (2002 Kelron Study) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Lowest mean and median concentrations of Barium are found in East Ash Pond water samples. Highest Barium concentrations are found in the Background Bedrock Wells (2002 Kelron Study) and in the East Ash Pond Bedrock Wells MW13A and MW32.

Notes:
* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
Highest mean and median concentrations of parameter are shown in boldface.

Table 11. Summary of Groundwater Quality Data in Bedrock and East Ash Pond
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Boron, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	1.17	1.15	1.10	1.30
MW27	1	6	0.83	0.83	0.79	0.87
MW29	1	6	1.12	1.10	1.10	1.20
MW30	1	6	0.90	0.99	0.85	0.96
MW31	1	6	0.68	0.77	0.20	0.82
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	30	1	***	0.28	ND	2.08
ISGS Background Wells (2002 ISGS Study) see Appendix A (wells 1349,21903,23343,25531)	4	1	0.85	0.85	0.29	1.4
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	**1.40**	**1.40**	1.30	1.60
MW16A	1	6	0.79	0.77	0.70	0.92
MW22	1	6	0.33	0.32	0.30	0.38
MW24	1	6	0.55	0.47	0.43	0.86
MW32	1	6	**1.45**	**1.50**	1.30	1.50
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	not applicable	5	**10.88**	**10.00**	5.1	18.0

Comments:
1. East Ash Pond Bedrock Wells MW16A, MW22, and MW24 have statistically significant lower concentrations than Background Wells (2002 Kelron Study) based on Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
   Bedrock Wells MW13A and MW32 have statistically significant higher concentrations than Background Wells (2002 Kelron Study).
2. Median Boron concentrations in East Ash Pond Surface Water Samples are 9 to 13 times greater than in Background Bedrock Wells (2002 Kelron Study) and 7 to 31 times greater than in East Ash Pond Bedrock Wells.

Parameter: Calcium, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	84.7	85.0	80	89
MW27	1	6	31.8	32.0	30	33
MW29	1	6	28.7	29.5	26	30
MW30	1	6	34.5	34.0	31	38
MW31	1	6	79.3	85.5	13	110
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	31	1	***	83	<1	951
ISGS Background Wells (2002 ISGS Study) see Appendix A (wells 1349,21903,23343,25531)	4	1	69.9	55.8	36.8	131
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	19.8	20.0	18	21
MW16A	1	6	**149.3**	**135.0**	96	210
MW22	1	6	48.7	49.0	45	51
MW24	1	6	34.0	35.5	25	38
MW32	1	6	15.2	16.0	13	17
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	not applicable	5	**322**	**350**	150	450

Comments:
1. East Ash Pond Bedrock Wells MW13A and MW32 have a statistically significant lower mean concentration than the Background Bedrock Wells (2002 Kelron Study) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
   East Ash Pond Bedrock Wells MW22 and MW24 are statistically from the same population as the Background Bedrock Wells.
   East Ash Pond Bedrock Well MW16A is has a statistically significant higher mean concentration than the Background Bedrock Wells.
2. Highest mean and median concentrations of Calcium are found in East Ash Pond water samples.
3. Median Calcium concentrations in East Ash Pond Surface Water Samples are 4 to 11 times greater than in Background Bedrock Wells (2002 Kelron Study) and 2.6 to 22 times greater than in East Ash Pond Bedrock Wells.

Notes:
* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
Highest mean and median concentrations of parameter are shown in boldface.

Table 11. Summary of Groundwater Quality Data in Bedrock and East Ash Pond
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Chloride, total (mg/L)	Number of Wells	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	**820**	**840**	720	910
MW27	1	6	353	370	290	390
MW29	1	6	333	285	270	570
MW30	1	6	**1,233**	**1,200**	1,100	1,400
MW31	1	6	60	69	19	79
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	31	1	1,689	13	2.1	30,269
ISGS Background Wells (2002 ISGS Study) see Appendix A (wells 1349,21903,23343,25531)	4	1	244	165	5	640
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	**630**	**570**	500	1000
MW16A	1	6	90	71	45	170
MW22	1	6	11	11	9.9	13
MW24	1	6	65	40	31	190
MW32	1	6	**860**	**845**	830	930
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	not applicable	5	172	200	100	240

Comments:

1. East Ash Pond Bedrock Wells MW16A, MW22, and MW24 have statistically significant lower concentrations than Background Wells (2002 Kelron Study) based on Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level. Wells MW13A and MW32 are statistically from the same population as the Background Wells (2002 Kelron Study).
2. Median Chloride concentrations in East Ash Pond Surface Water Samples are 3 to 18 times greater than in East Ash Pond Bedrock Wells MW16A, MW22, and MW24 (2002 Kelron Study). East Ash Pond Bedrock Wells MW13A and MW32 are 3 to 4 times greater than the East Ash Pond Surface Water Samples.

Parameter: Iron, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	0.13	0.05	<0.025	0.27
MW27	1	6	0.19	0.18	0.10	0.22
MW29	1	6	0.22	0.23	<0.025	0.40
MW30	1	6	**1.66**	**1.70**	0.83	2.20
MW31	1	6	0.37	0.33	0.26	0.55
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	31	1	***	**0.69**	<0.006	26.8
ISGS Background Wells (2002 ISGS Study) see Appendix A (wells 1349,21903,23343,25531)	4	1	**1.95**	**2.00**	<0.01	3.8
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	0.15	0.16	0.067	0.25
MW16A	1	6	0.34	0.33	0.063	0.79
MW22	1	6	0.12	0.13	0.096	0.15
MW24	1	6	0.036	0.013	<0.025	0.11
MW32	1	6	0.037	0.024	<0.025	0.11
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	not applicable	5	0.013	0.013	0.013	0.013

Comments:

1. All East Ash Pond Bedrock Wells have a statistically significant lower mean concentration than the Background Bedrock Wells (2002 Kelron Study) or are statistically from the same population based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
2. Highest mean and median concentrations of Iron are found in ISGS Background Wells (2002 ISGS Study and Scientific Literature and State Databases), and in Background Bedrock Well MW30 (Kelron Study).

Notes:

* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
Highest mean and median concentrations of parameter are shown in boldface.

Table 11. Summary of Groundwater Quality Data in Bedrock and East Ash Pond
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Lithium, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	**0.11**	**0.08**	0.071	0.18
MW27	1	6	0.04	0.04	<0.005	0.086
MW29	1	6	0.04	0.04	<0.005	0.089
MW30	1	6	**0.11**	**0.10**	0.010	0.26
MW31	1	6	0.09	0.05	<0.005	0.40
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A						
	31	1	na	na	na	na
ISGS Background Wells (2002 ISGS Study) see Appendix A						
(wells 1349,21903,23343,25531)	4	1	0.025	0.015	0.01	0.07
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	**0.11**	**0.08**	0.070	0.19
MW16A	1	6	0.04	0.04	0.022	0.069
MW22	1	6	0.04	0.03	<0.005	0.089
MW24	1	6	0.02	0.02	<0.005	0.070
MW32	1	6	**0.12**	**0.09**	<0.087	0.23
East Ash Pond Surface Water Samples (2002 Kelron Study)						
(monthly samples from Jan-May 2002)	not applicable	5	**0.19**	**0.27**	<0.005	0.30

Comments:

1. East Ash Pond Bedrock Wells MW16A, MW22, and MW24 have statistically significant lower concentrations than Background Wells (2002 Kelron Study) or are statistically from the same population based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level. Wells MW13A and MW32 have a statistically significant higher mean concentration than the Background Bedrock Wells.
2. Median Lithium concentrations in East Ash Pond Surface Water Samples are 3 to 14 times greater than in East Ash Pond Bedrock Wells (2002 Kelron Study) and IGSG Background Wells (2002 ISGS Study).

Parameter: Magnesium, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	44.7	44.5	44	46
MW27	1	6	19.5	19.5	19	20
MW29	1	6	15.0	15.0	14	16
MW30	1	6	25.2	25.0	24	27
MW31	1	6	33.7	37.0	4.1	46
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A						
	31	1	***	31.1	<0.5	454
ISGS Background Wells (2002 ISGS Study) see Appendix A						
(wells 1349,21903,23343,25531)	4	1	39.3	37.0	27	56
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	18.2	18.0	18	19
MW16A	1	6	**77.0**	**72.5**	53	100
MW22	1	6	26.3	26.0	26	27
MW24	1	6	16.2	16.5	14	17
MW32	1	6	15.5	16.0	14	16
East Ash Pond Surface Water Samples (2002 Kelron Study)						
(monthly samples from Jan-May 2002)	not applicable	5	26.5	30.0	8.4	42

Comments:

1. East Ash Pond Bedrock Wells MW13A , MW24, and MW32 have a statistically significant lower mean concentration than the Background Bedrock Wells (2002 Kelron Study) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.
   East Ash Pond Bedrock Well MW22 is statistically from the same population as the Background Bedrock Wells.
   East Ash Pond Bedrock Well MW16A is has a statistically significant higher mean concentration than the Background Bedrock Wells.
2. Highest median concentrations of Magnesium are found in ISGS Background Wells (Scientific Literature and State Databases) and in East Ash Pond Bedrock Well MW16A.

Notes:

* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
na Not analyzed.
Highest mean and median concentrations of parameter are shown in boldface.

Table 11. Summary of Groundwater Quality Data in Bedrock and East Ash Pond
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Manganese, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	**0.041**	**0.041**	0.028	0.053
MW27	1	6	0.023	0.022	0.018	0.029
MW29	1	6	0.015	0.016	0.010	0.020
MW30	1	6	**0.043**	**0.041**	0.034	0.059
MW31	1	6	**0.085**	**0.081**	0.072	0.110
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	31	1	***	**0.100**	0.015	1.47
ISGS Background Wells (2002 ISGS Study) see Appendix A						
(wells 1349,21903,23343,25531)	4	1	**0.057**	**0.041**	0.035	0.11
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	**0.082**	**0.087**	0.018	0.120
MW16A	1	6	**0.330**	**0.345**	0.200	0.390
MW22	1	6	0.017	0.017	0.014	0.019
MW24	1	6	0.012	0.012	0.010	0.012
MW32	1	6	0.014	0.013	0.011	0.022
East Ash Pond Surface Water Samples (2002 Kelron Study)						
(monthly samples from Jan-May 2002)	not applicable	5	0.025	0.024	0.003	0.057

Comments:
1. East Ash Pond Bedrock Wells MW22, MW24, and MW32 have statistically significant lower concentrations than Background Wells (2002 Kelron Study) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level. Wells MW13A and MW16A have a statistically significant higher mean concentration than the Background Bedrock Wells.
2. Median Manganese concentrations in Background Bedrock Wells MW25, MW30, and MW31 (2002 Kelron Study), ISGS Background Wells (ScientificLiterature and State Databases), and ISGS Background Wells (2002 ISGS Study) are significantly greater than in East Ash Pond Surface Water Samples and East Ash Pond Bedrock Wells MW22, MW24, and MW32 (2002 Kelron Study).
3. Median Manganese concentrations in East Ash Pond Bedrock Well MW16A is 14 times greater than median concentrations for the East Ash Pond Surface Water Samples.

Parameter: Molybdenum, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	nd	nd	<0.010	<0.010
MW27	1	6	nd	nd	<0.010	<0.010
MW29	1	6	nd	nd	<0.005	<0.010
MW30	1	6	nd	nd	<0.010	<0.010
MW31	1	6	nd	nd	<0.010	<0.010
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	31	1	na	na	na	na
ISGS Background Wells (2002 ISGS Study) see Appendix A						
(wells 1349,21903,23343,25531)	4	1	nd	nd	<0.01	<0.01
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	nd	nd	<0.010	<0.010
MW16A	1	6	nd	nd	<0.010	<0.010
MW22	1	6	nd	nd	<0.010	<0.010
MW24	1	6	nd	nd	<0.010	<0.010
MW32	1	6	nd	nd	<0.010	<0.010
East Ash Pond Surface Water Samples (2002 Kelron Study)						
(monthly samples from Jan-May 2002)	not applicable	5	**0.22**	**0.24**	0.130	0.298

Comments:
1. All Bedrock Wells (Background and East Ash Pond wells) had no detectable concentrations of Molybdenum.
2. East Ash Pond Surface Water Samples had Molybdenum in all samples, ranging from 0.13 to 0.298 mg/L.

Notes:
* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
na Not analyzed.
nd No samples were above method detection limit.
Highest mean and median concentrations of parameter are shown in boldface.

Table 11. Summary of Groundwater Quality Data in Bedrock and East Ash Pond
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Phosphorus, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	0.012	0.008	<0.010	0.031
MW27	1	6	0.028	0.027	0.019	0.038
MW29	1	6	0.023	0.024	<0.010	0.036
MW30	1	6	0.037	0.036	0.027	0.053
MW31	1	6	0.067	0.041	0.032	0.19
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	31	1	na	na	na	na
ISGS Background Wells (2002 ISGS Study) see Appendix A (wells 1349,21903,23343,25531)	4	1	na	na	na	na
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	0.038	0.033	0.022	0.070
MW16A	1	6	0.069	0.093	<0.010	0.110
MW22	1	6	0.015	0.017	<0.010	0.022
MW24	1	6	0.048	0.047	0.023	0.081
MW32	1	6	0.027	0.023	0.016	0.045
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	not applicable	5	0.071	0.031	0.010	0.23

Comments:

1. East Ash Pond Bedrock Wells MW13A, MW16A, MW22, and MW32 are statistically from the same population or have statistically significant lower concentrations than Background Wells (2002 Kelron Study) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level. Well MW24 has a statistically significant higher mean concentration than Background Wells (2002 Kelron Study).

Parameter: Potassium, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	5.2	5.2	4.9	5.4
MW27	1	6	3.3	3.4	3.1	3.6
MW29	1	6	3.2	3.2	3.1	3.4
MW30	1	6	6.6	6.6	6.2	7.4
MW31	1	6	9.4	8.2	6.6	17
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	30	1	7.4	2.1	0.67	63
ISGS Background Wells (2002 ISGS Study) see Appendix A (wells 1349,21903,23343,25531)	4	1	4.5	4.25	3.0	5.0
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	4.8	4.9	4.5	5.2
MW16A	1	6	3.5	3.6	2.5	4.6
MW22	1	6	2.6	2.6	2.5	2.7
MW24	1	6	2.0	1.8	1.8	2.5
MW32	1	6	5.4	5.4	5.1	6.0
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	not applicable	5	**24.0**	**25.0**	17	31

Comments:

1. East Ash Pond Bedrock Wells MW16A, MW22, and MW24 have a statistically significant lower mean concentration than the Background Bedrock Wells (2002 Kelron Study) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level. East Ash Pond Bedrock Well MW13A and MW32 are statistically from the same population as the Background Bedrock Wells.
2. Median Potassium concentrations in the East Ash Pond Surface Water Samples are 3 to 12 times greater than median concentrations in Background Bedrock Wells (2002 Kelron Study), ISGS Background Wells (Scientific Literature and State Databases), or ISGS Background Wells (2002 ISGS Study).

Notes:

* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
na Not analyzed.
nd No samples were above method detection limit.
Highest mean and median concentrations of parameter are shown in boldface.

Table 11. Summary of Groundwater Quality Data in Bedrock and East Ash Pond
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Selenium, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	nd	nd	<0.005	<0.005
MW27	1	6	***	***	0.005	<0.005
MW29	1	6	nd	nd	<0.005	<0.005
MW30	1	6	***	***	0.005	<0.005
MW31	1	6	***	***	0.005	<0.005
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	30	1	***	0.001	<0.001	0.002
ISGS Background Wells (2002 ISGS Study) see Appendix A (wells 1349,21903,23343,25531)	4	1	nd	nd	<0.1	<0.1
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	nd	nd	<0.005	<0.005
MW16A	1	6	nd	nd	<0.005	<0.005
MW22	1	6	nd	nd	<0.005	<0.005
MW24	1	6	nd	nd	<0.005	<0.005
MW32	1	6	nd	nd	<0.005	<0.005
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	not applicable	5	***	**0.022**	<0.005	0.043

Comments:
1. All Bedrock Wells (Background and East Ash Pond wells) had Selenium concentrations equal to or less than 0.005 milligrams per Liter.
2. East Ash Pond Surface Water Samples had median Selenium concentrations 22 times greater than in Background Wells or East Ash Pond Bedrock Wells.

Parameter: Sodium (mg/L)	Number of Wells	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	385	390	360	400
MW27	1	6	267	270	250	280
MW29	1	6	257	250	250	280
MW30	1	6	**887**	**890**	850	910
MW31	1	6	176	195	88	210
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	31	1	1,083	28.7	6	18,078
ISGS Background Wells (2002 ISGS Study) see Appendix A (wells 1349,21903,23343,25531)	4	1	241	154	67	590
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	**507**	**505**	490	520
MW16A	1	6	180	185	120	240
MW22	1	6	102	100	100	110
MW24	1	6	130	110	100	210
MW32	1	6	**730**	**735**	680	760
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	not applicable	5	160	140	100	240

Comments:
1. East Ash Pond Bedrock Wells MW16A, MW22, and MW24 have a statistically significant lower mean concentration than the Background Bedrock Wells (2002 Kelron Study) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level. East Ash Pond Bedrock Well MW13A and MW32 have a statistically significant higher mean concentration than the Background Bedrock Wells.
2. Median Sodium concentrations in Background Bedrock Wells (2002 Kelron Study) are 1.4 to 6.4 times greater than the median East Ash Pond Surface Water Samples.
3. Median Sodium concentrations in East Ash Pond Bedrock Wells MW13A and MW32 are a 3.6 and 5.3 times greater, respectively, than the median concentration in the East Ash Pond Surface Water Samples and 6.4 times greater than East Ash Pond samples.

Notes:
* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means or medians.
na Not analyzed.
nd No samples were above method detection limit.
Highest mean and median concentrations of parameter are shown in boldface.

Table 11. Summary of Groundwater Quality Data in Bedrock and East Ash Pond
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: Strontium, diss (mg/L)	Number of Wells	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	0.57	0.56	0.54	0.60
MW27	1	6	0.36	0.36	0.34	0.38
MW29	1	6	0.33	0.33	0.31	0.35
MW30	1	6	0.65	0.64	0.61	0.70
MW31	1	6	0.67	0.78	0.14	0.79
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	30	1	na	na	na	na
ISGS Background Wells (2002 ISGS Study) see Appendix A (wells 1349,21903,23343,25531)	4	1	0.71	0.55	0.23	1.5
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	0.35	0.38	<0.366	0.39
MW16A	1	6	0.55	0.54	0.44	0.67
MW22	1	6	0.32	0.31	0.30	0.34
MW24	1	6	0.22	0.22	0.21	0.23
MW32	1	6	0.38	0.38	0.36	0.40
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	not applicable	5	0.51	0.57	0.27	0.65

Comments:

1. East Ash Pond Bedrock Wells MW22 and MW24 have a statistically significant lower mean concentration than the Background Bedrock Wells (2002 Kelron Study) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level. East Ash Pond Bedrock Wells MW13A, MW16A, and MW32 are statistically from the same population as the Background Bedrock Wells.

Parameter: Sulfate (mg/L)	Number of Wells	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	***	2.5	<5.0	7
MW27	1	6	nd	nd	<5.0	<5.0
MW29	1	6	nd	nd	<5.0	<5.0
MW30	1	6	4.5	4.3	<5.0	7
MW31	1	6	**123**	**125**	58	160
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A	31	1	***	31	<1	847
ISGS Background Wells (2002 ISGS Study) see Appendix A (wells 1349,21903,23343,25531)	4	1	38	5.8	<0.1	140
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	nd	nd	<5.0	<5.0
MW16A	1	6	**415**	**510**	120	620
MW22	1	6	30	31	27	32
MW24	1	6	35	34	30	41
MW32	1	6	nd	nd	<5.0	<5.0
East Ash Pond Surface Water Samples (2002 Kelron Study) (monthly samples from Jan-May 2002)	not applicable	5	**808**	**780**	440	1,500

Comments:

1. East Ash Pond Bedrock Wells MW16A, MW22, and MW24 have a statistically significant higher mean concentration than the Background Bedrock Wells (2002 Kelron Study) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level. East Ash Pond Bedrock Wells MW13A and MW32 are statistically from the same population as the Background Bedrock Wells.
2. Mean and median Sulfate concentrations in East Ash Pon Bedrock Wells MW13A, MW22, MW24, and MW32 are within range of Background Bedrock Wells (2002 Kelron Study), ISGS Background Wells (Scientific Literature and State Databases), and ISGS Background Wells (2002 ISGS Study).
3. Median Sulfate concentration in East Ash Pond Bedrock Well MW16A is 4 times greater than highest concentration in Background Bedrock Wells (i.e., Well MW31).
4. Median Sulfate concentration in East Ash Pond Surface Water Samples is 1.5 times greater than in East Ash Pond Bedrock Well MW16A.

Notes:

* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
na Not analyzed. nd No samples were above method detection limit.
Highest mean and median concentrations of parameter are shown in boldface.

Table 11. Summary of Groundwater Quality Data in Bedrock and East Ash Pond
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter: TDS (mg/L)	Number of Wells	Samples per Location	Mean*	Median	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	**1,450**	**1,400**	1,400	1,600
MW27	1	6	910	905	850	980
MW29	1	6	838	825	800	900
MW30	1	6	**2,433**	**2,400**	2,400	2,500
MW31	1	6	863	940	410	1,000
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A						
	28	1	3,540	426	280	52,100
ISGS Background Wells (2002 ISGS Study) see Appendix A						
(wells 1349,21903,23343,25531)	4	1	633	510	210	1,300
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	**1,467**	**1,450**	1,400	1,600
MW16A	1	6	**1,383**	**1,400**	1,200	1,600
MW22	1	6	532	525	470	620
MW24	1	6	532	495	410	750
MW32	1	6	**1,933**	**1,900**	1,900	2,000
East Ash Pond Surface Water Samples (2002 Kelron Study)						
(monthly samples from Jan-May 2002)	not applicable	5	**1,650**	**1,800**	950	2,100

Comments:
1. East Ash Pond Bedrock Wells MW13A and MW32 have a statistically significant higher mean concentration than the Background Bedrock Wells (2002 Kelron Study) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level. East Ash Pond Bedrock Well MW16A is statistically from the same population as the Background Bedrock Wells. Wells MW22 and MW24 have a statistically significant lower mean concentration than the Background Wells (2002 Kelron Study).
2. Median TDS concentrations in the East Ash Pond Surface Water Samples are within the same range of values as Background Bedrock Wells (2002 Kelron Study) MW25 and MW30 and East Ash Pond Bedrock Wells MW13A, MW16A, and MW32.

Parameter: Vanadium (mg/L)	Number of Wells	Samples per Location	Mean*	Median*	Minimum**	Maximum
Background Bedrock Wells (2002 Kelron Study)						
MW25	1	6	nd	nd	<0.010	<0.010
MW27	1	6	nd	nd	<0.010	<0.010
MW29	1	6	nd	nd	<0.010	<0.010
MW30	1	6	nd	nd	<0.010	<0.010
MW31	1	6	nd	nd	<0.010	<0.010
ISGS Background Wells (Scientific Literature and State Databases) see Appendix A						
	31	1	na	na	na	na
ISGS Background Wells (2002 ISGS Study) see Appendix A						
(wells 1349,21903,23343,25531)	4	1	nd	nd	<0.01	<0.01
East Ash Pond Bedrock Wells (2002 Kelron Study)						
MW13A	1	6	nd	nd	<0.010	<0.010
MW16A	1	6	nd	nd	<0.010	<0.010
MW22	1	6	nd	nd	<0.010	<0.010
MW24	1	6	nd	nd	<0.010	<0.010
MW32	1	6	nd	nd	<0.010	<0.010
East Ash Pond Surface Water Samples (2002 Kelron Study)						
(monthly samples from Jan-May 2002)	not applicable	5	**0.04**	**0.03**	<0.010	0.078

Comments:
1. All Bedrock Wells (Background and East Ash Pond wells) had Vanadium concentrations below 0.01 milligrams per Liter.
2. East Ash Pond Surface Water Samples had median Vanadium concentrations at least 3 times greater than in Background Wells or East Ash Pond Bedrock Wells.

Notes:
* Less than points were replaced by one-half the detection limit.
** Some parameters had multiple detection limits. Lowest detection limit is reported.
*** Sample data contained censored values, did not compute means.
na Not analyzed.
nd No samples were above method detection limit.
Highest mean and median concentrations of parameter are shown in boldface.

Table 12. Summary of Impacts on Groundwater Quality in Bedrock
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant, Illinois

Parameter	COLUMN 2 Mean Groundwater Concentrations in Bedrock Wells[1] at East Ash Pond Compared to Background Bedrock Wells[2]		COLUMN 3 Groundwater Quality in East Ash Pond Bedrock Wells[1] Compared to East Ash Pond Surface Water	Impact by East Ash Pond on Groundwater Quality in Bedrock	Other Conclusions
Aluminum	**0**	all wells	LT	No impact	
Barium	**LT**	all wells	GT	No impact	Wells 13A and 32 may be affected by past coal mining activities.
Boron	**LT** GT	16A,22,24 13A,32	LT	No impact	Wells 13A and 32 may be affected by past coal mining activities.
Calcium	**0** **LT** GT	22,24 13A,32 16A	LT	No impact	Well 16A has higher Ca concentrations than background wells. Ca is higly correlated with Mg at 0.98. Ca is either naturally occurring or influenced by former coal mines.
Chloride	**0** **LT**	13A,32 16A,22,24	LT (16A,22,24) GT (13A,32)	No impact	Wells 13A and 32 may be affected by past coal mining activities. Background well 25 may also be affected by coal mining. Background well 30 is in coal and shale and has highest Cl concentrations at study site.
Iron	**0** **LT**	16A 13A,22,24,32	GT	No impact	Well 30, background well installed in coal and shale, has the highest Fe concentration at the study site.
Lithium	**0** **LT** GT	16A 22,24 13A,32	LT	No impact	Wells 13A and 32 may be affected by past coal mining activities. Background well 25 may also be affected by coal mining. Background well 30 is in coal and shale and has similar Li concentrations to 13A, 32, and 25.
Magnesium	**0** **LT** GT	22 13A,24,32 16A	LT (13A,22,24,32) GT (16A)	No impact	Well 16A has higher Mg concentrations than background wells and East Ash Pond and is not impacted by surface water from East Ash Pond. All other East Ash Pond wells are either equal to or below background concentrations.
Manganese	**LT** GT	22,24,32 13A,16A	LT (22,24,32) GT (13A,16A)	No impact	Wells 13A and 16A may be affected by past coal mining activities. These wells have higher concentrations than most background wells and East Ash Pond water.
Molybdenum	**0**	all wells	LT	No impact	All background wells and East Ash Pond wells have no detectable concentrations of Mo. Only East Ash Pond water samples have detected concentrations of Mo.
Phosphorus	**0** **LT** GT	13A,16A,32 22 24	Variable (no determination)	No impact	
Potassium	**0** **LT**	13A,32 16A,22,24	LT	No impact	
Selenium	**0**	all wells	LT	No impact	Almost all samples from background wells and East Ash Pond wells have no detectable concentrations of Se. Only East Ash Pond water samples have detectable Se levels.
Sodium	**LT** GT	16A,22,24 13A,32	Variable (no determination)	No impact	Wells 13A and 32 may be affected by past coal mining activities. Background well 30 is in coal and shale and has similar high Na concentrations as wells 13A and 32.
Strontium	**0** **LT**	13A,16A,32 22,24	LT	No impact	
Sulfate	**0** GT	13A,32 16A,22,24	LT	No impact	Well 16A is the only bedrock well in the vicinity of East Ash Pond with elevated sulfate relative to background. Water quality is most likely affected by past coal mining.
Total Dissolved Solids	**0** **LT** GT	16A 22,24 13A,32	Variable (no determination)	No impact	Wells 13A, 16A and 32 may be affected by past coal mining activities. Background well 25 may also be affected by coal mining. Background well 30 is in coal and shale and has the highest mean and median TDS concentrations.
Vanadium	**0**	all wells	LT	No impact	All samples from background wells and East Ash Pond wells were below detection limits for Vanadium. Only East Ash Pond water samples have detectable Vanadium.

Key to Symbols

COLUMN 2

0 Groundwater quality for given parameter in East Ash Pond wells is statistically from the same population as Background Wells (25,27,29,30, and 31) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.

LT Groundwater quality for given parameter in East Ash Pond wells has a statistically significant lower mean concentration compared to Background Wells (25,27,29,30, and 31) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.

GT Groundwater quality for given parameter in East Ash Pond wells has a statistically significant higher mean concentration compared to Background Wells (25,27,29,30, and 31) based on the Wilcoxon Rank-Sum Test for Comparison of Means, 95 % confidence level.

COLUMN 3

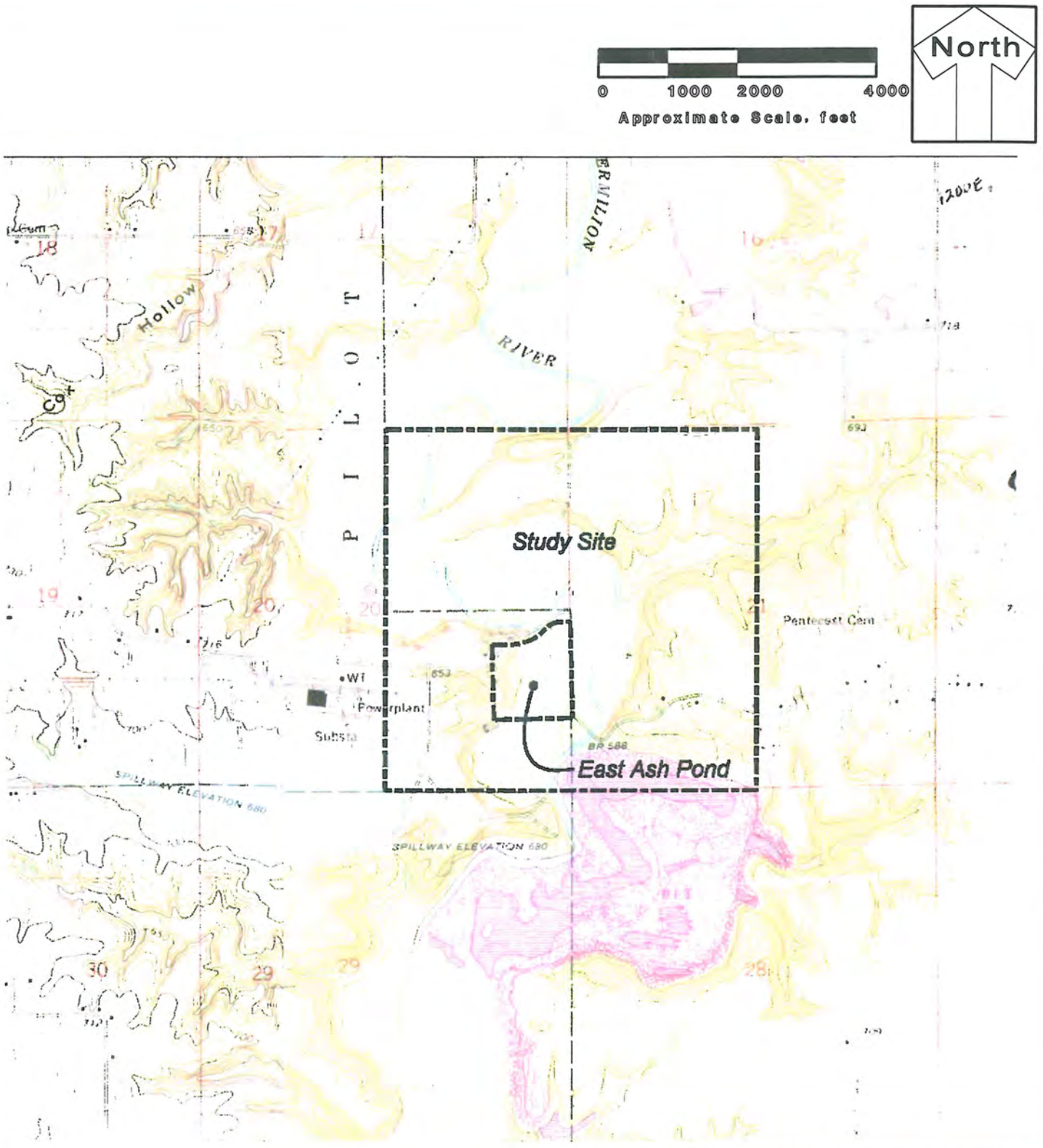
LT Groundwater concentrations in East Ash Pond Bedrock Wells are less than East Ash Pond surface water for given parameter.

GT Groundwater concentrations in East Ash Pond Bedrock Wells are greater than East Ash Pond surface water for given parameter.

[1] Bedrock wells at East Ash Pond include MW13A (13A), MW16A (16A), MW22 (22), MW24 (24), and MW32 (32).

[2] Background bedrock wells used for statistical comparison to East Ash Pond wells using Wilcoxon Rank-Sum Test include the following: MW25 (25), MW27 (27), MW29 (29), MW30 (30), and MW31 (31).

Figures

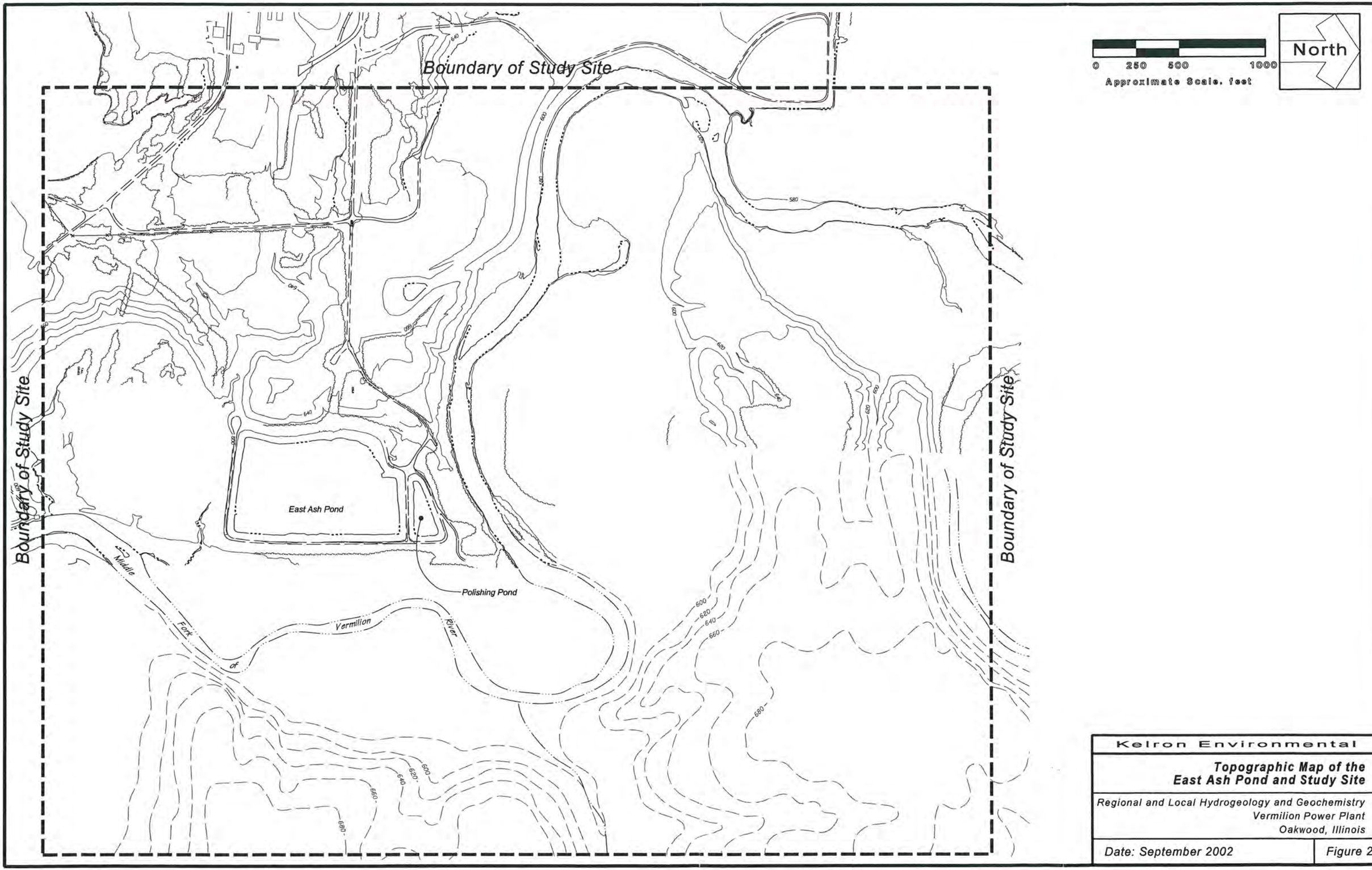


Kelron Environmental

Site Location Map of the Vermilion Power Station and East Ash Pond

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 1*

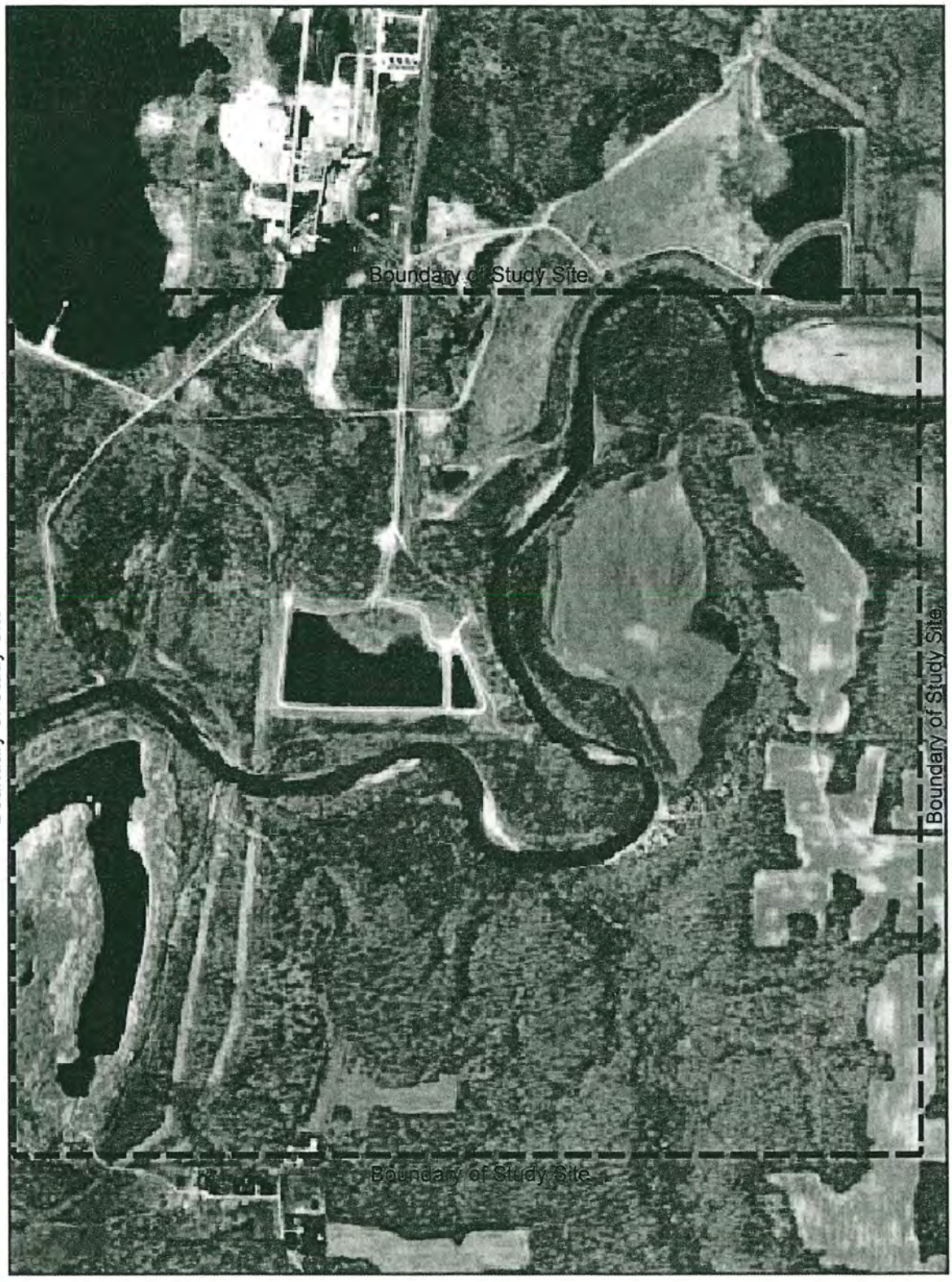


Kelron Environmental

Topographic Map of the East Ash Pond and Study Site

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 2*



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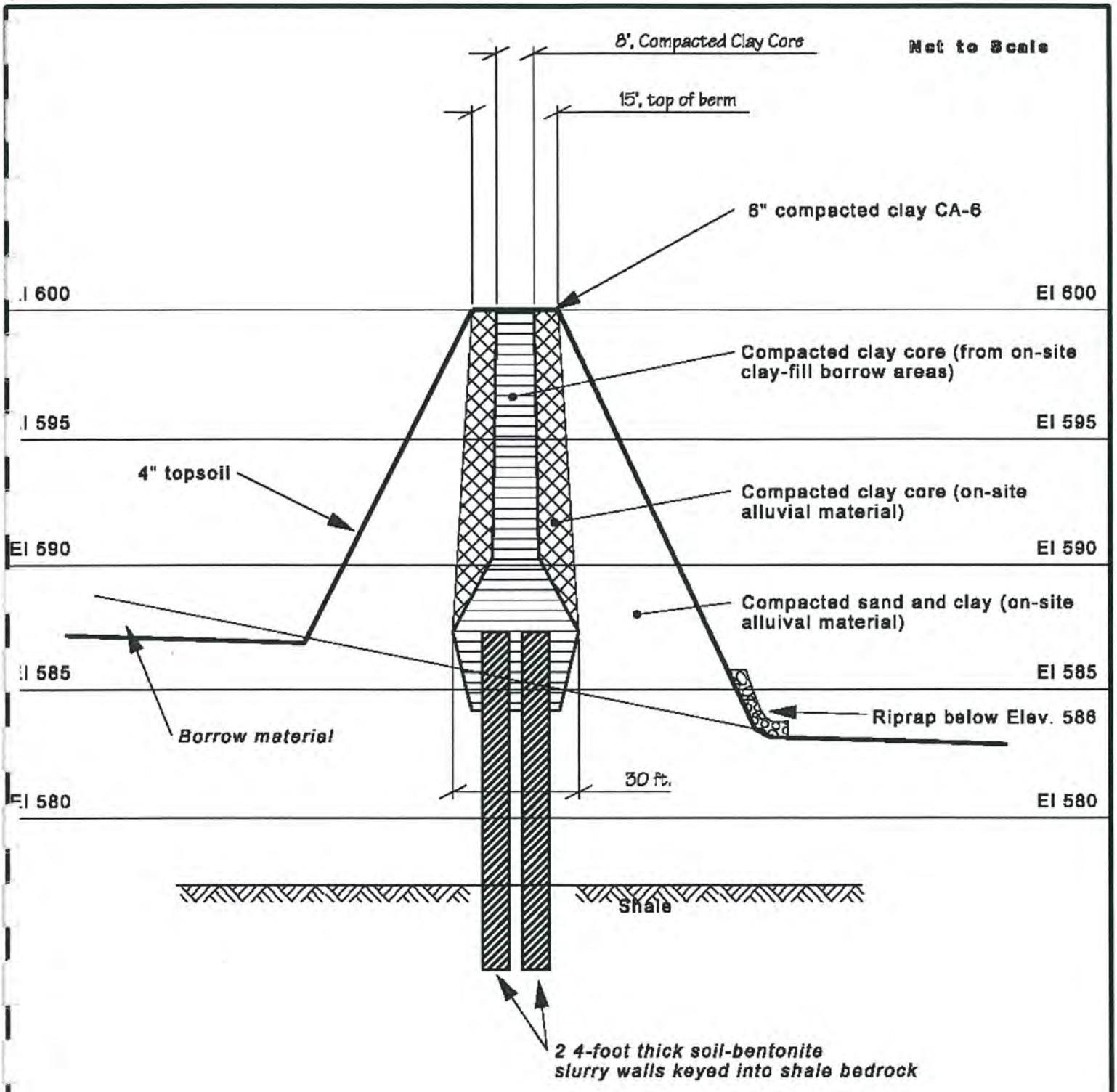
Aerial Photograph of the East Ash Pond and Study Site

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 3*

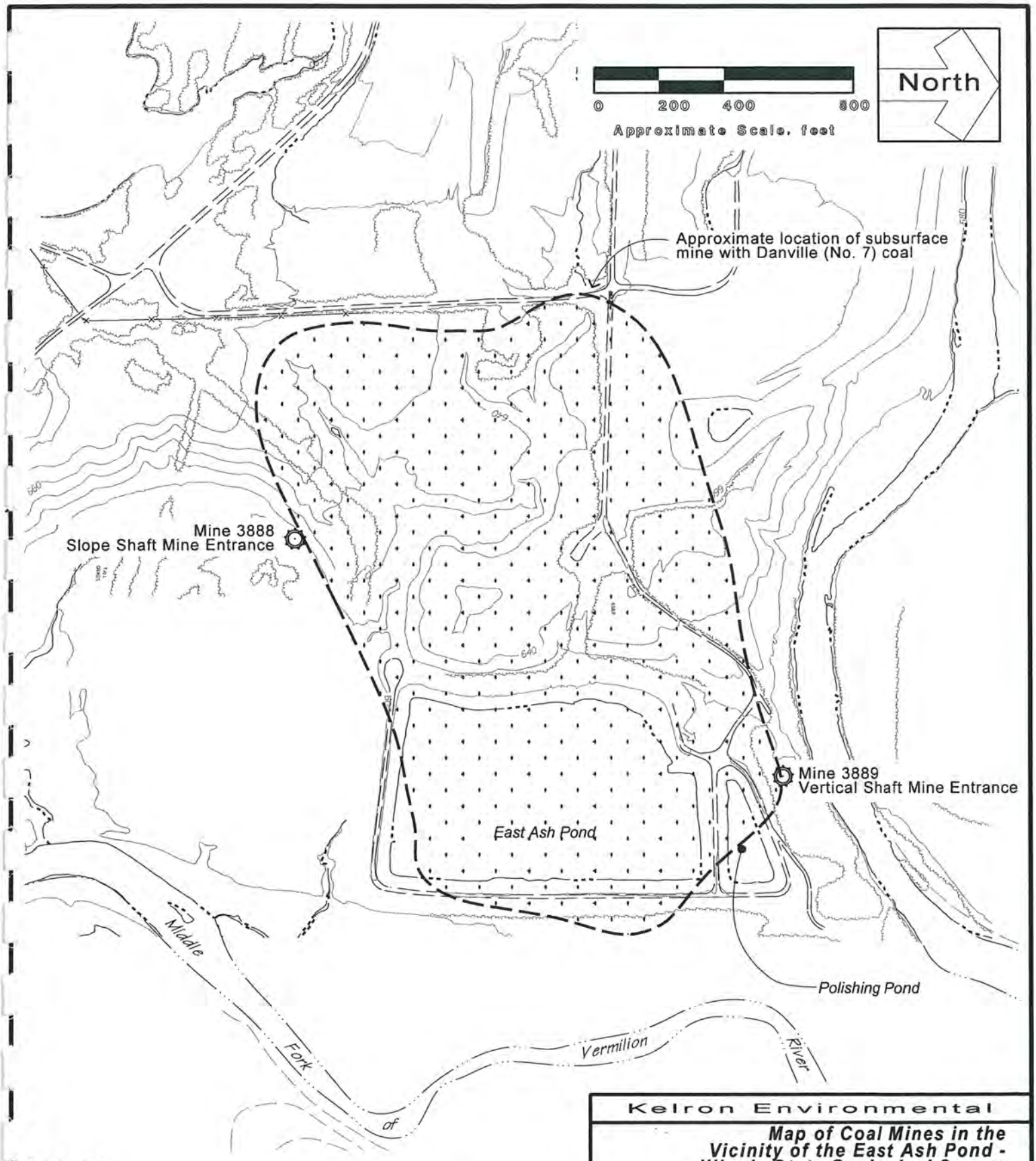


Kelron Environmental

Typical Cross-Section of Original East Ash Pond Berm

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 4*



Legend

Location of Mine Entrance

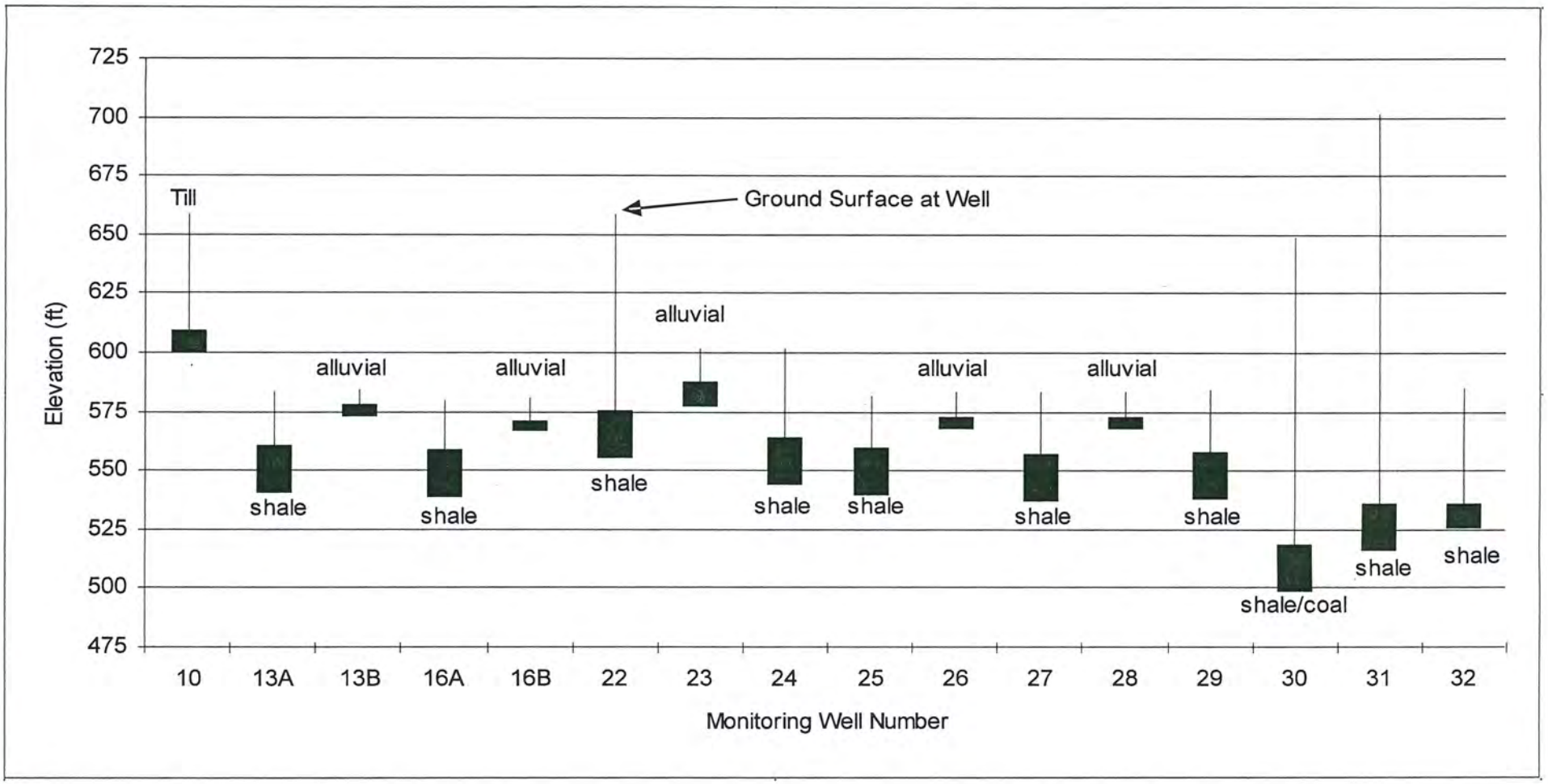
Note: Modified after " Directory of Coal Mines in Illinois - Vermilion County "; ISGS 1996.

Kelron Environmental

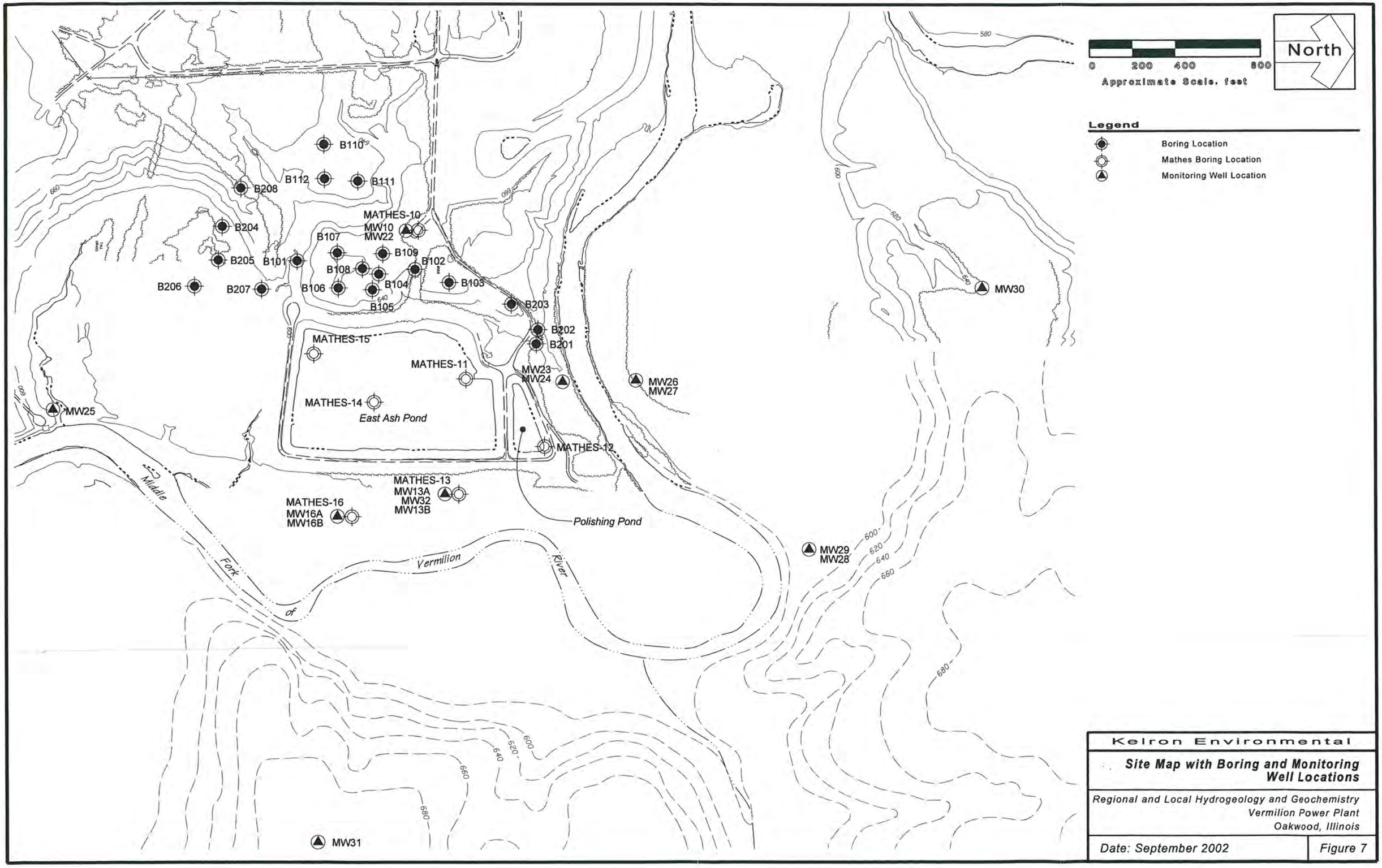
Map of Coal Mines in the Vicinity of the East Ash Pond - Illinois State Geological Survey

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 5*



Kelron Environmental	
Monitoring Well Screen Intervals	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 6*

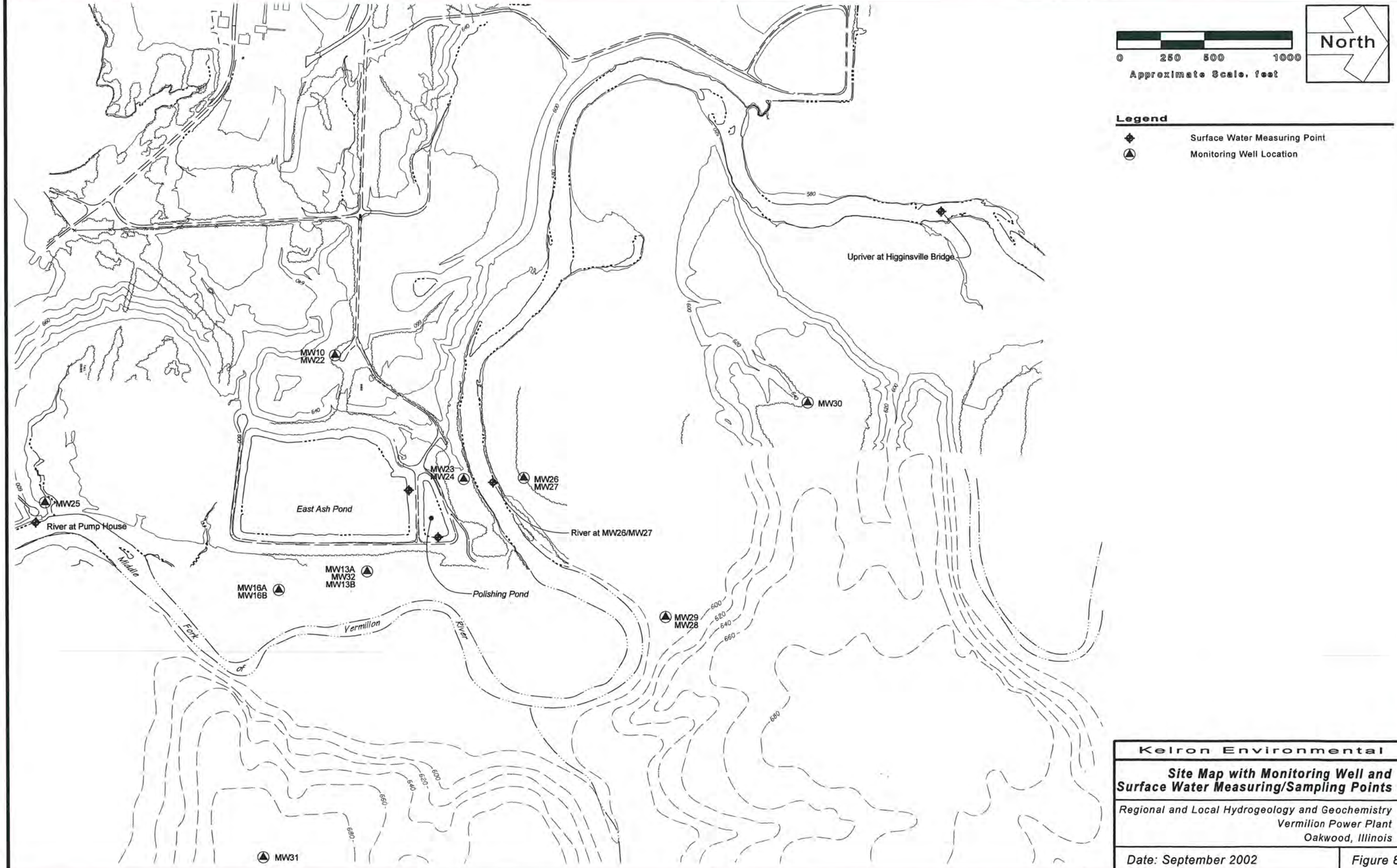


Kelron Environmental

Site Map with Boring and Monitoring Well Locations

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 7*

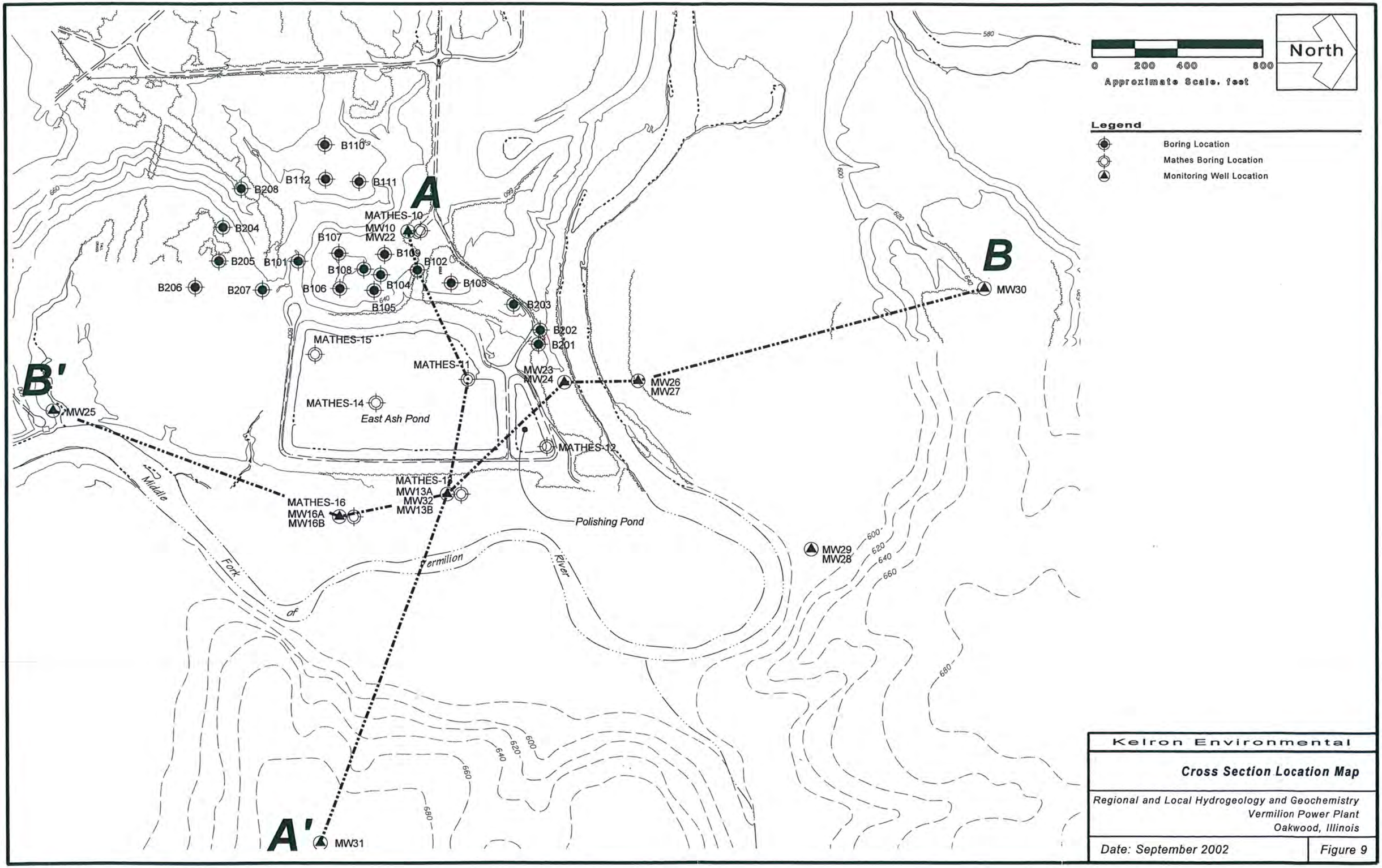


Kelron Environmental

Site Map with Monitoring Well and Surface Water Measuring/Sampling Points

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 8*



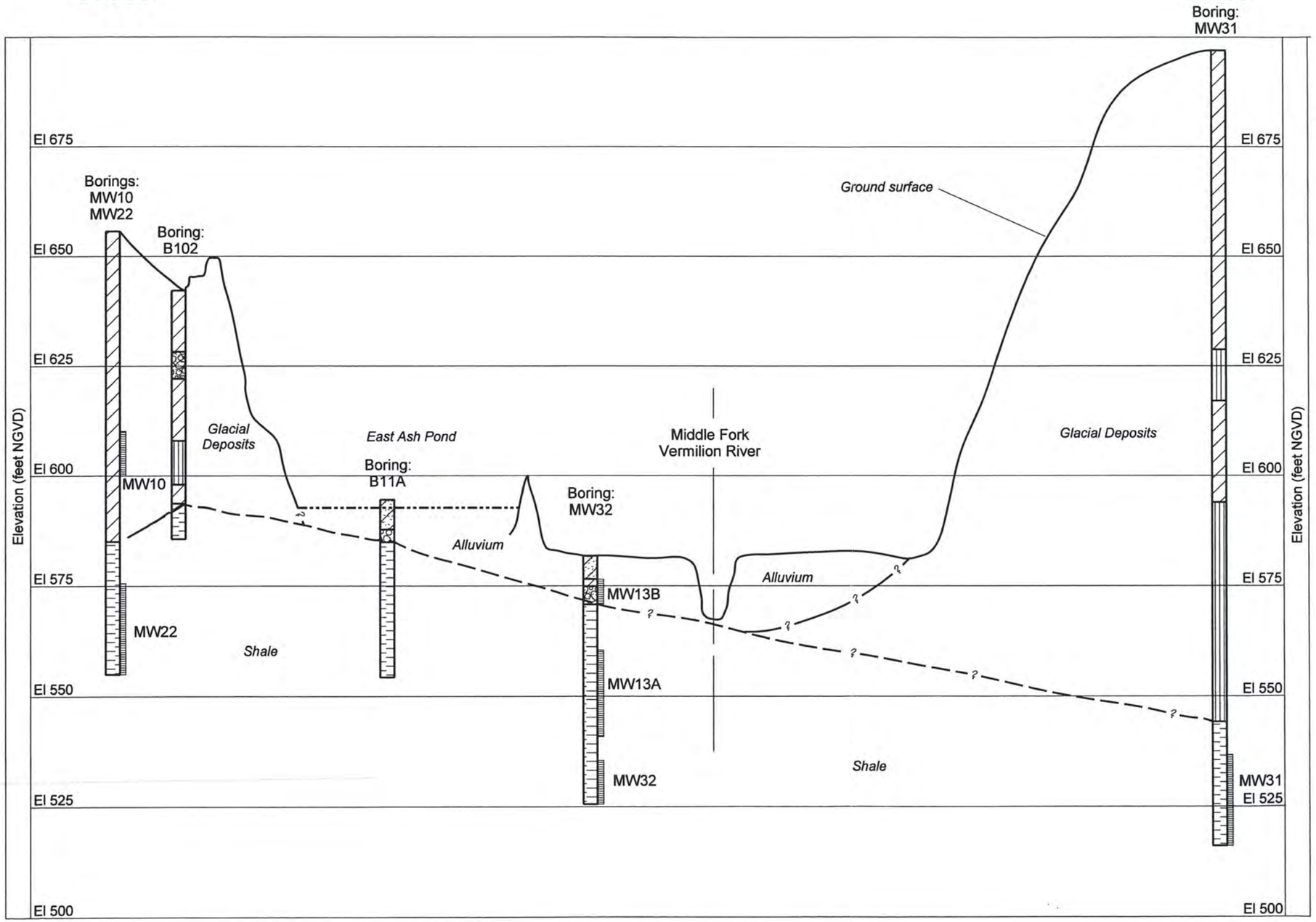
Kelron Environmental

Cross Section Location Map

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 9*

A West — A' East



0 150 300 600

Approximate Horizontal Scale: 1 in - 300 ft.
Approximate Vertical Scale: 1 in - 25 ft.
Vertical Exaggeration: 12x

Legend

Geology

- CL — Clay, silty clay, sandy clay, gravelly clay
- ML — Silts, clayey silts
- SC-SM — Clayey to silty sand
- SP-SW — Sand, gravelly sand
- GC-GM — Gravel. with silt and/or clay
- GP-GW — Gravel; gravel-sand mix
- SH — Shale

Monitoring Well Screen Interval

Kelron Environmental

East-West Geologic Cross-Section

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

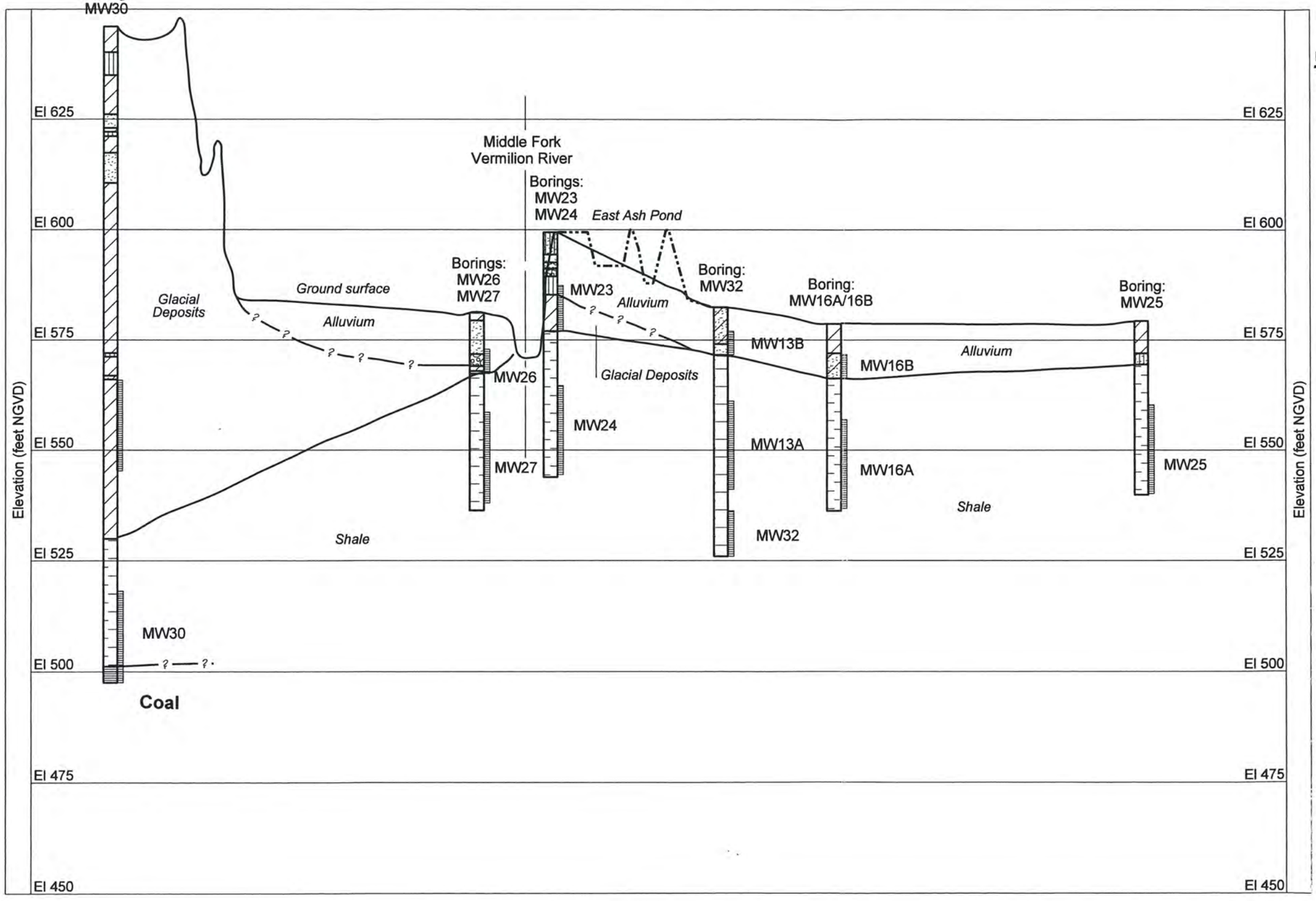
Date: September 2002 | *Figure 10*

B North

B' South

0 250 500 1000

Approximate Horizontal Scale: 1 in - 500 ft.
Approximate Vertical Scale: 1 in - 25 ft.
Vertical Exaggeration: 20x



Legend

Geology

CL	Clay, silty clay, sandy clay, gravelly clay
ML	Silts, clayey silts
SC-SM	Clayey to silty sand
SP-SW	Sand, gravelly sand
GC-GM	Gravel. with silt and/or clay
GP-GW	Gravel; gravel-sand mix
SH	Shale
	Coal

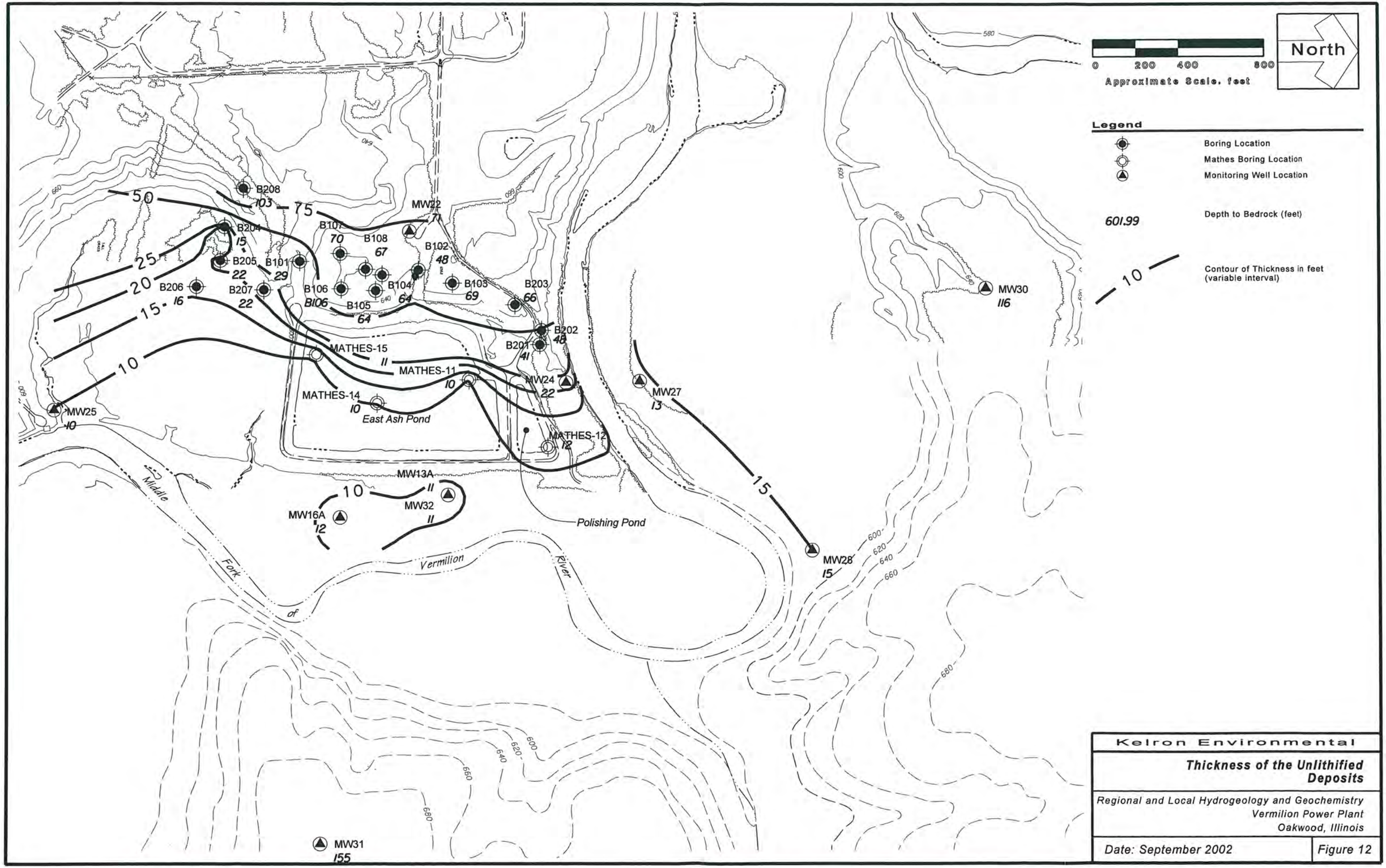
Monitoring Well Screen Interval

Kelron Environmental

North-South Geologic Cross-Section

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 11*

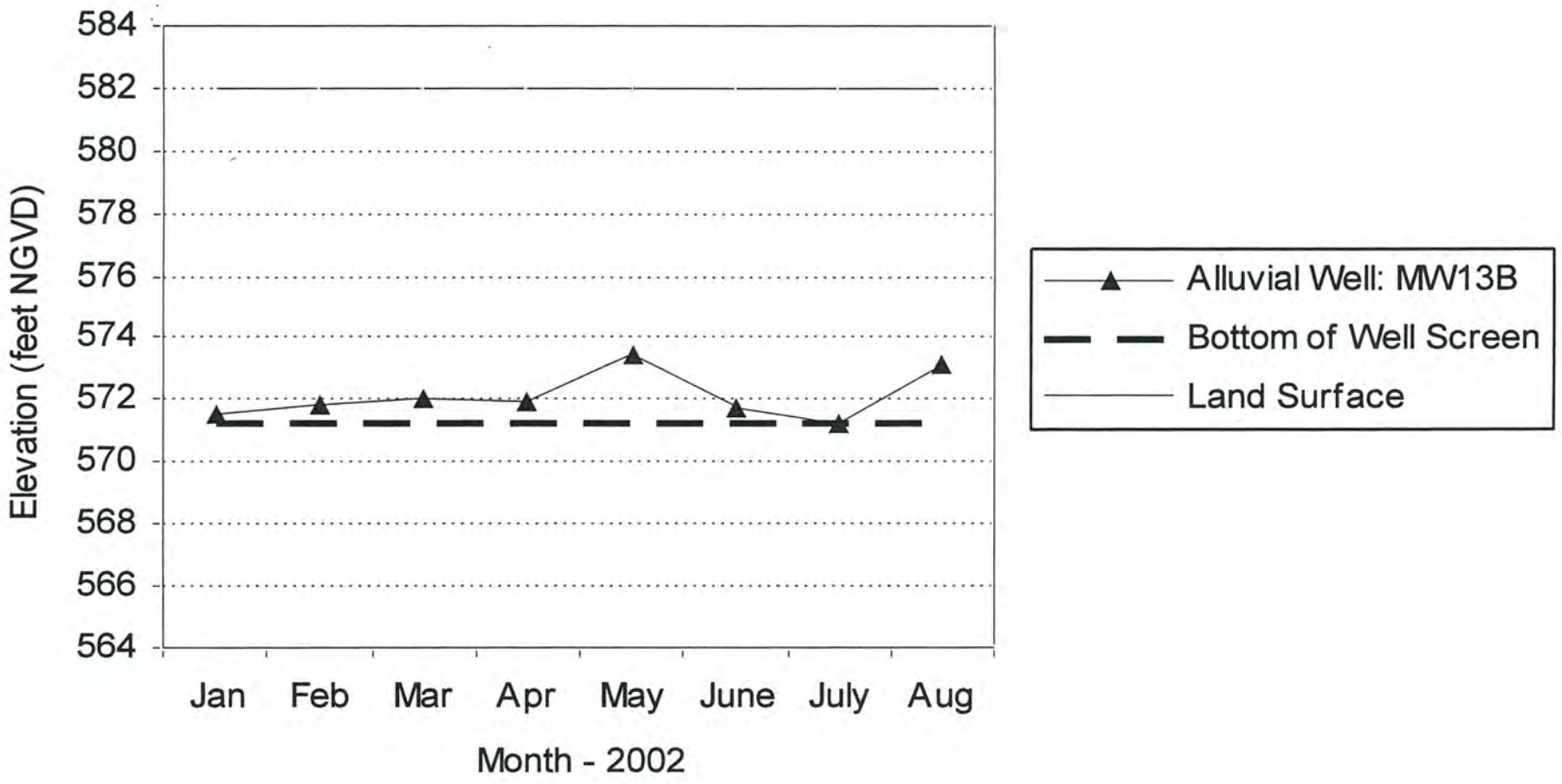


Kelron Environmental

Thickness of the Unlithified Deposits

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 12*

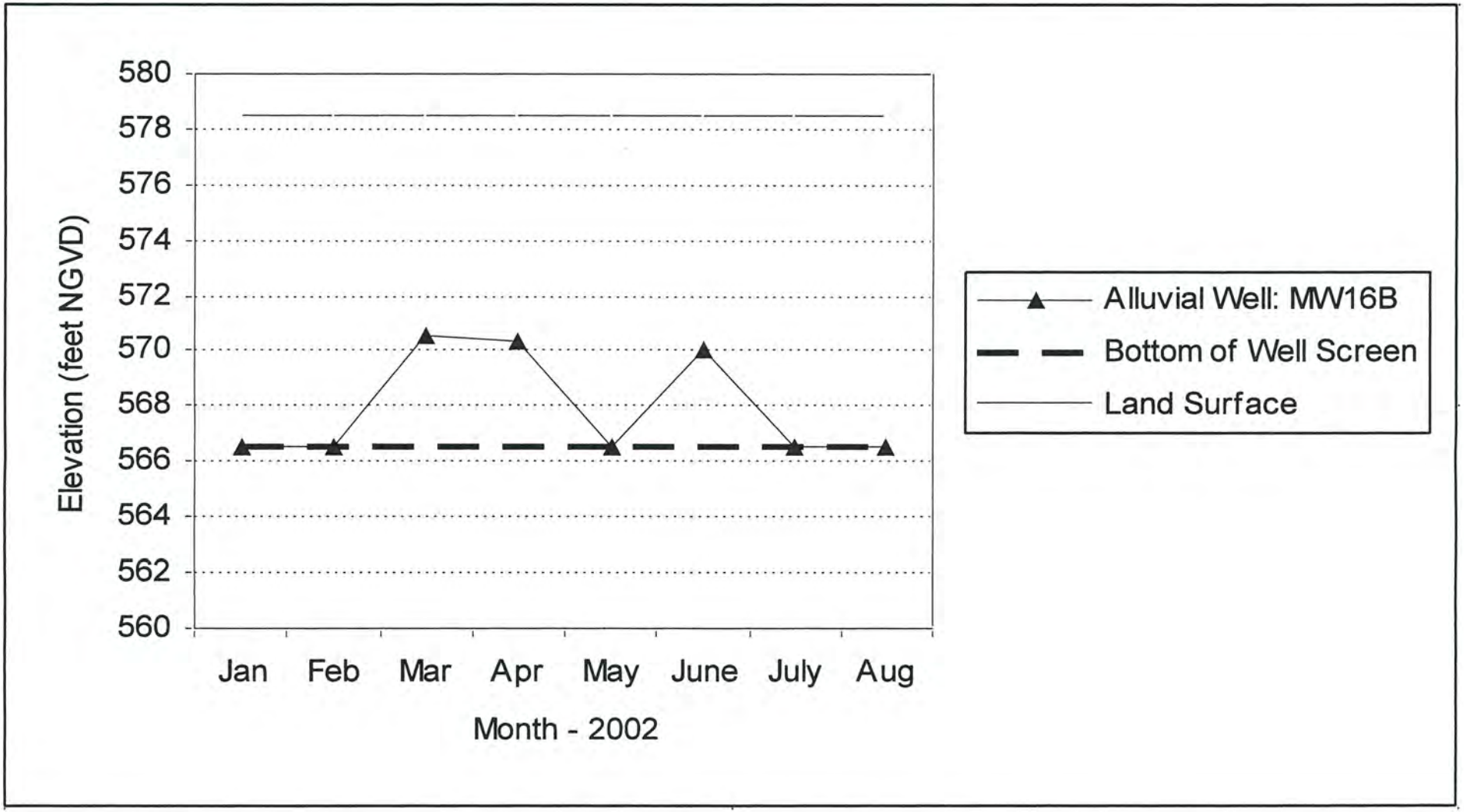


Kelron Environmental

Groundwater Hydrograph of Alluvial Well MW13B

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 13*

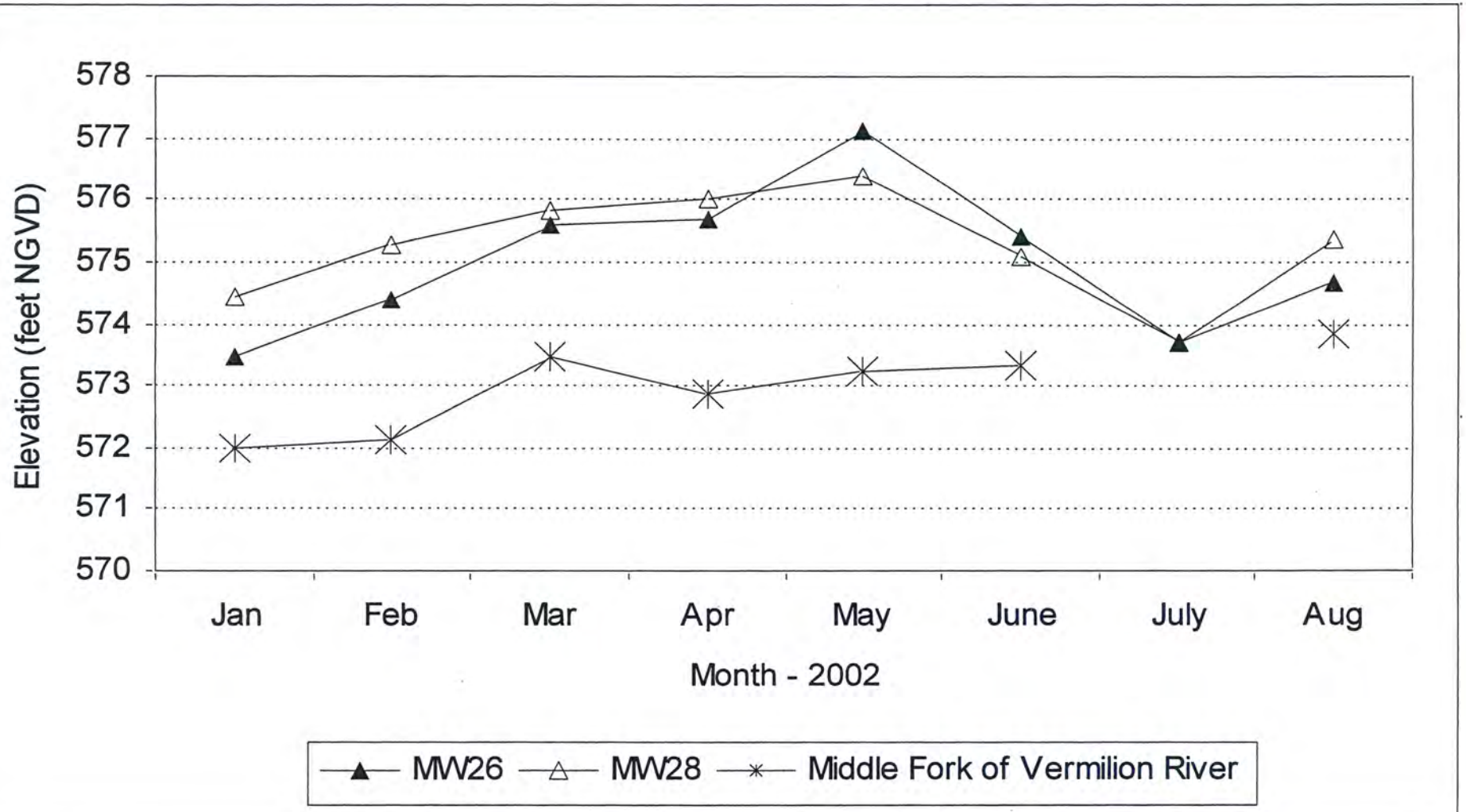


Kelron Environmental

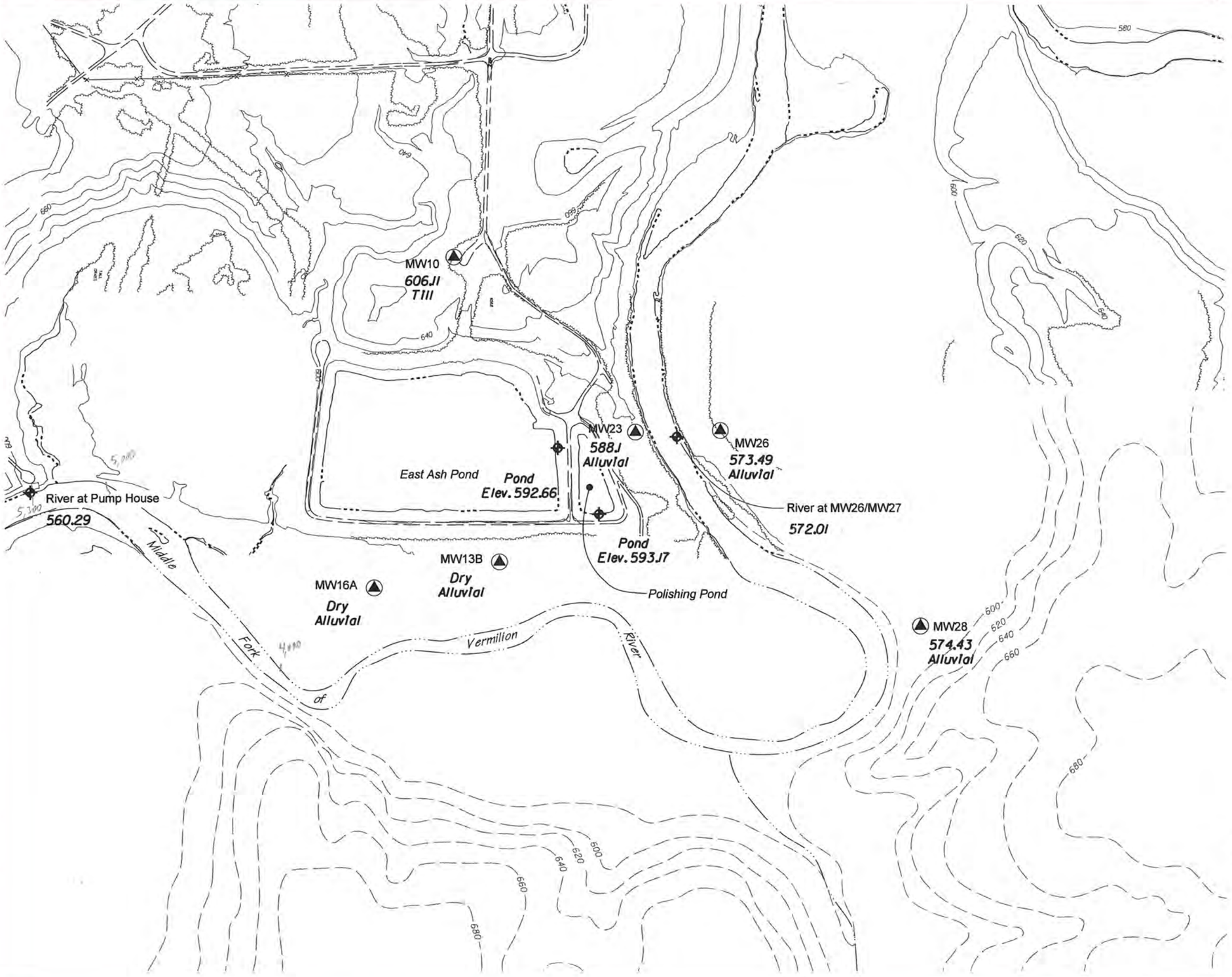
Groundwater Hydrograph of Alluvial Well MW16B

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 14*



Kelron Environmental	
Hydrographs of Alluvial Wells MW26, MW28, and Middle Fork of Vermilion River	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 15*



Kelron Environmental

Groundwater Elevations in Till and Alluvial Deposits: January 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 16*

North

0 200 400 800

Approximate Scale, feet

Legend

- Boring Location
- Mathes Boring Location
- Monitoring Well Location
- 601.99 — Top of Shale Elevation (feet)
- 560 — Top of Shale Elevation Contour, feet NGVD, (interval 10 feet)

B208 554.2
B204 573.5
B205 568.1
B101 575
B107 589
B108 591
MW22 585
B102 594
B206 573
B207 573.85
B106 590
B104 588
B105 588
B103 585
B203 561.1
B202 558
B201 558.6
MATHES-15 578
MATHES-11 585
MATHES-14 576
East Ash Pond
MW24 577
MW27 567
MW30 530
MW25 569
MATHES-12 578
MW13A 571
MW32 571
MW16A 566
Polishing Pond
MW28 566
MW31 544
Middle Fork of Vermilion River

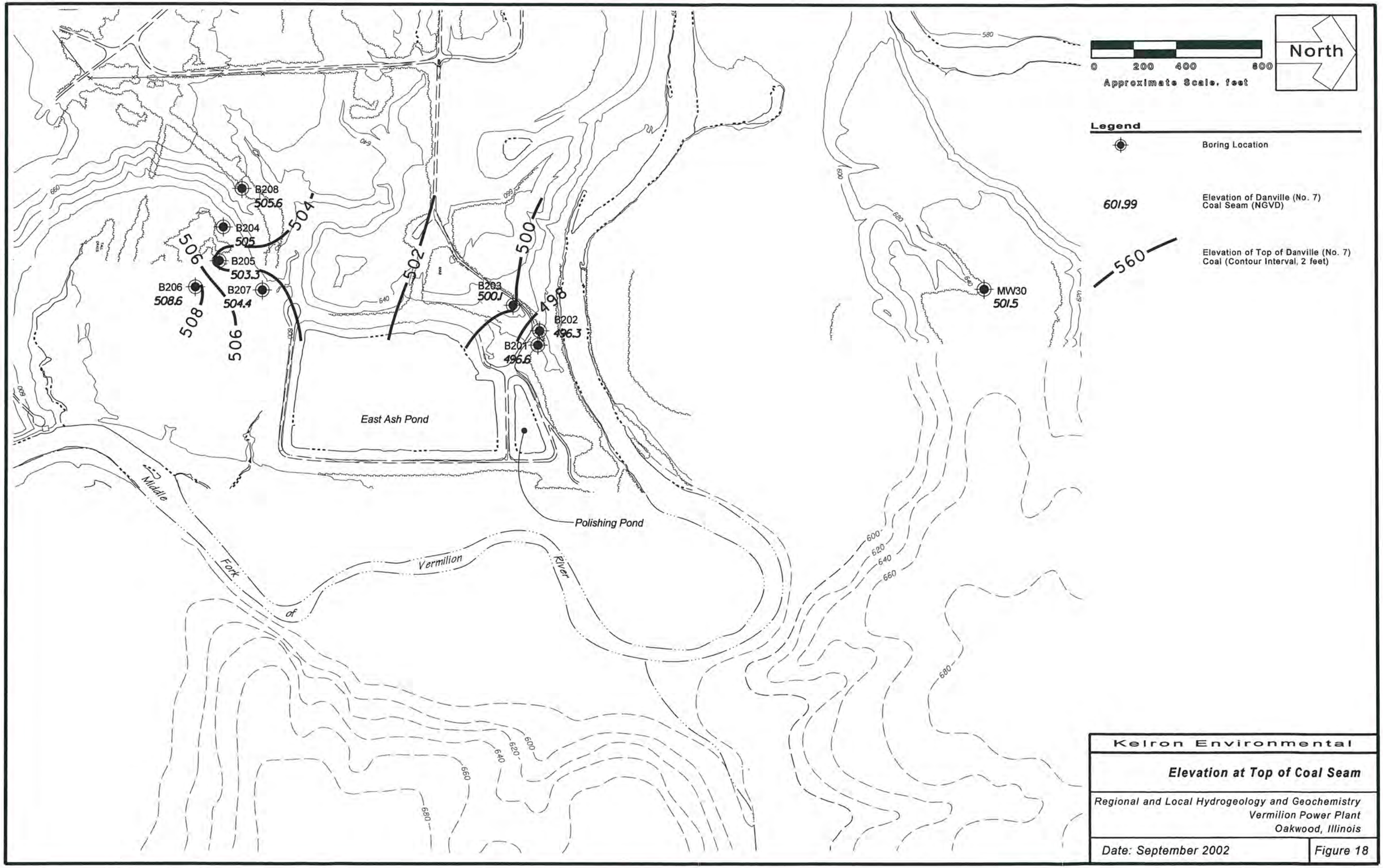
570 580 570 560 550 560 560 550

Kelron Environmental

Elevation of Top of the Pennsylvanian Bedrock

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | Figure 17

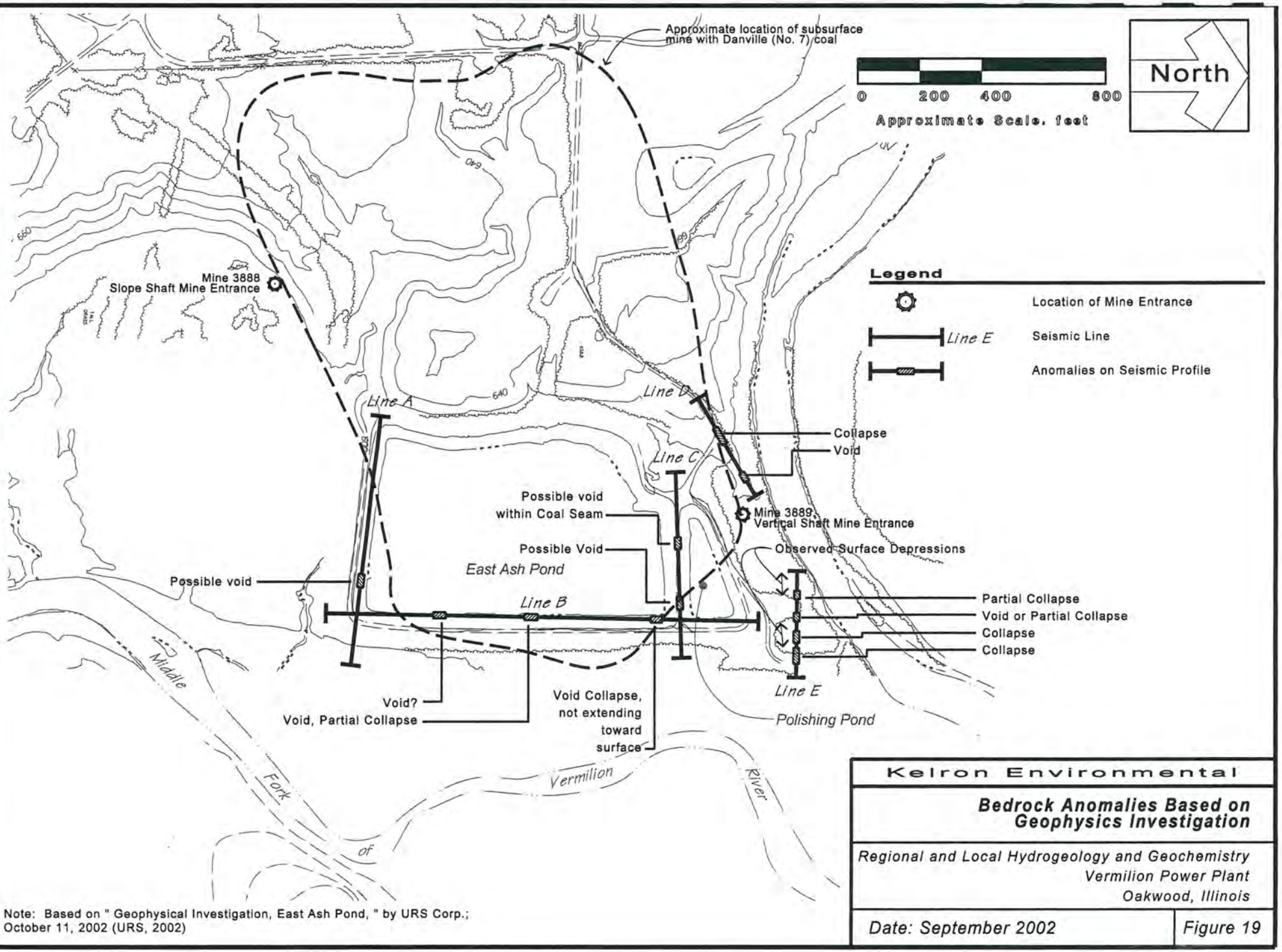


Kelron Environmental

Elevation at Top of Coal Seam

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 18*



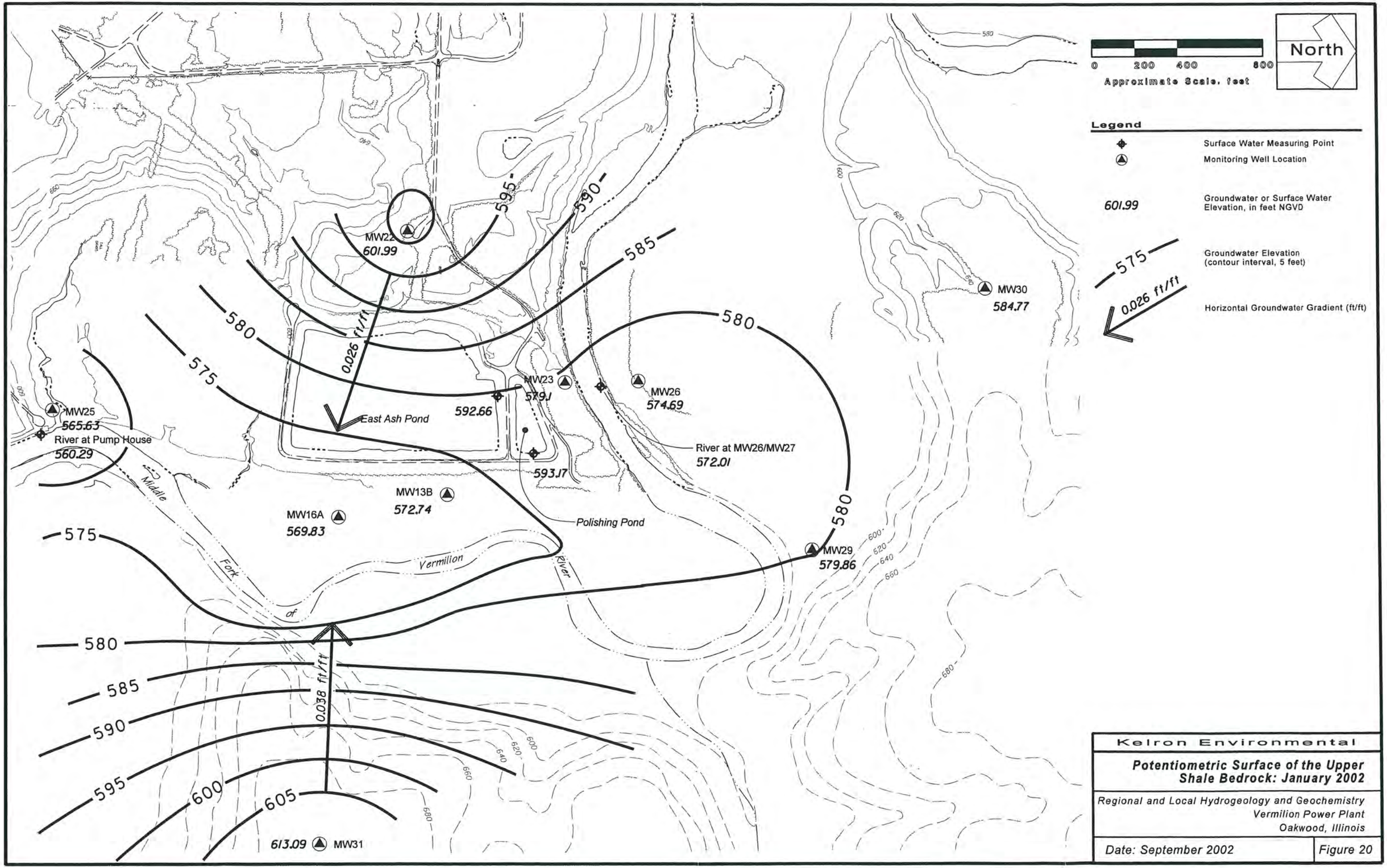
Note: Based on " Geophysical Investigation, East Ash Pond, " by URS Corp.; October 11, 2002 (URS, 2002)

Kelron Environmental

Bedrock Anomalies Based on Geophysics Investigation

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 19*

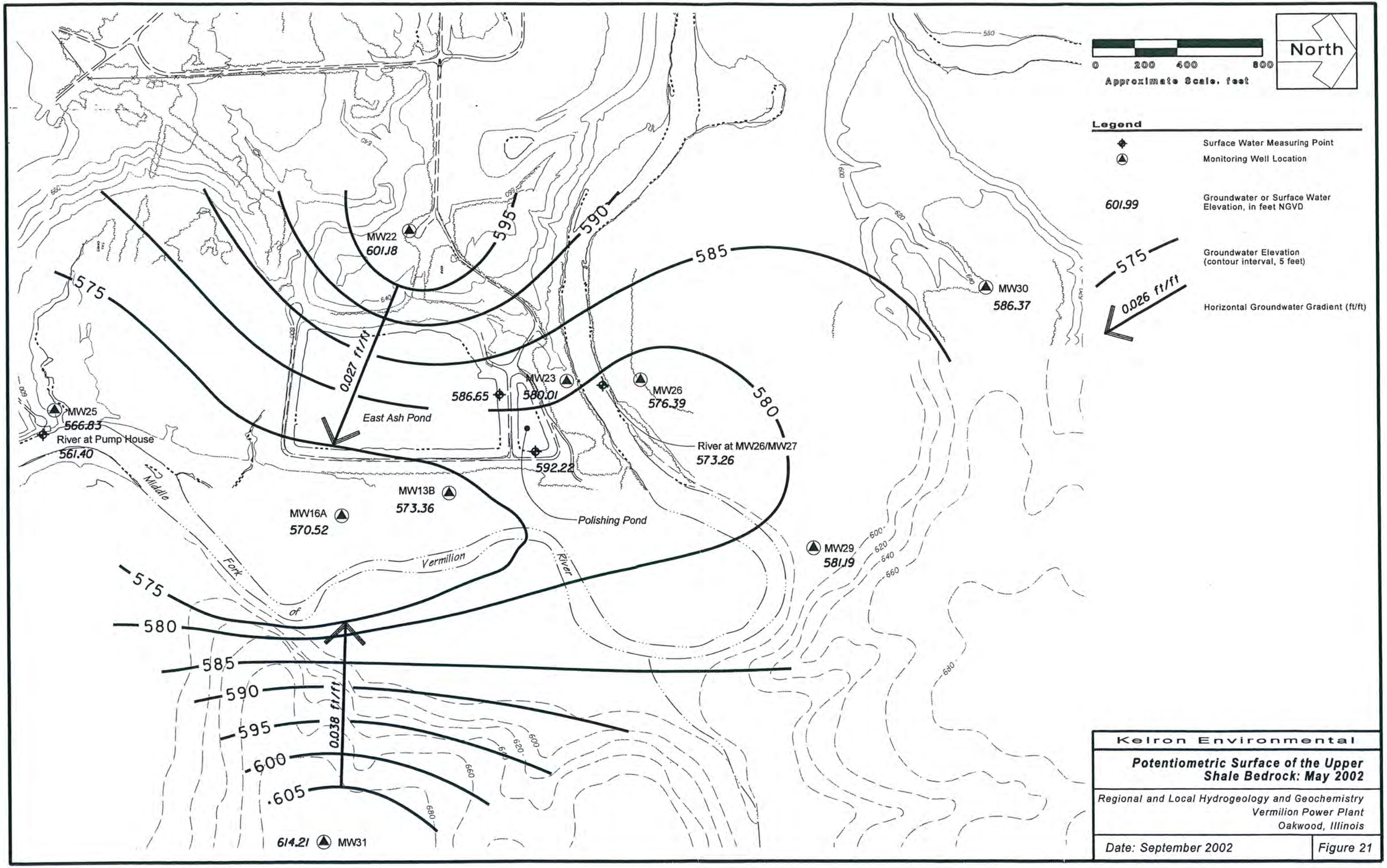


Kelron Environmental

Potentiometric Surface of the Upper Shale Bedrock: January 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 20*



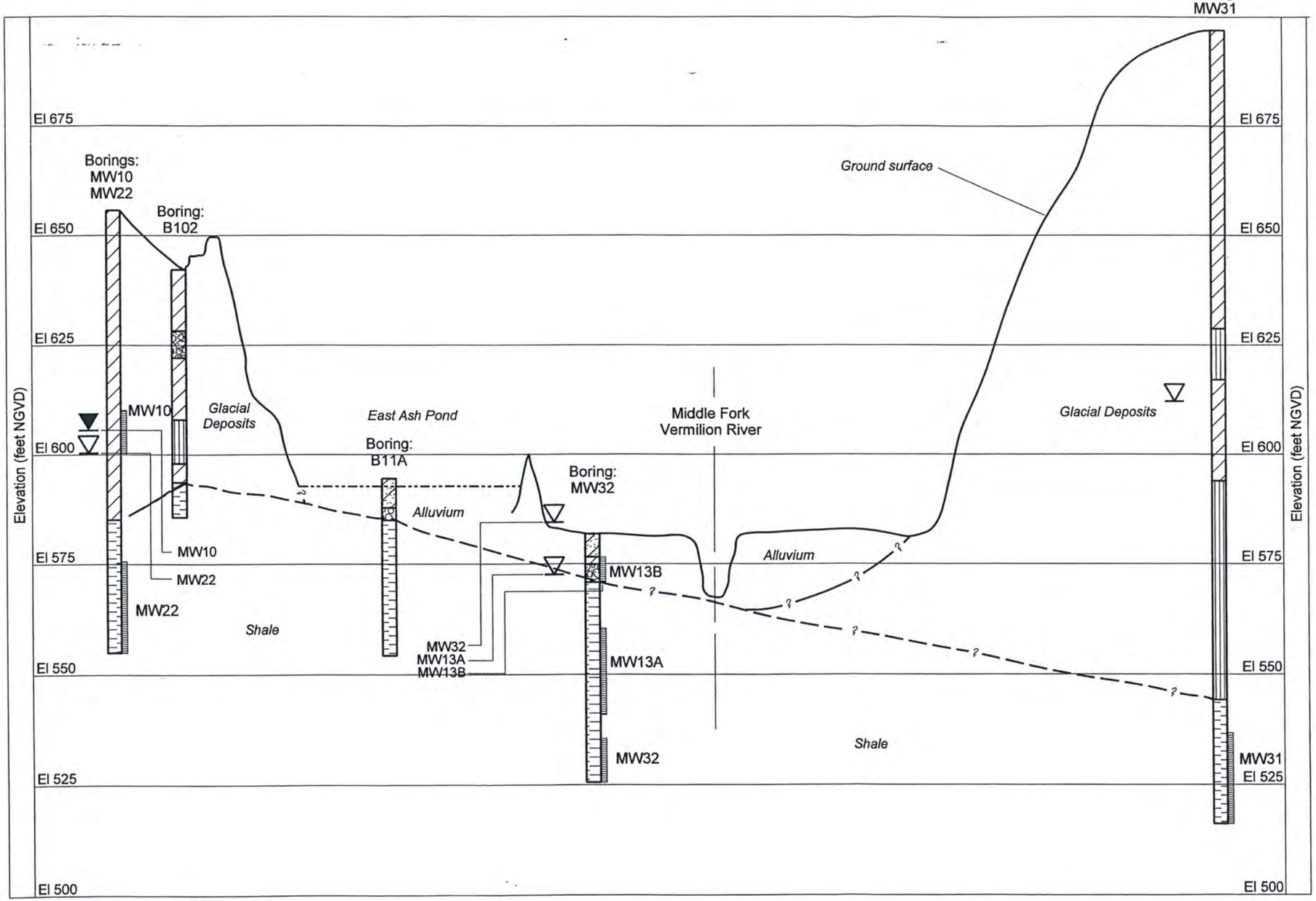
Kelron Environmental

Potentiometric Surface of the Upper Shale Bedrock: May 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 21*

A West — A' East



0 150 300 600

Approximate Horizontal Scale: 1 in - 300 ft.
Approximate Vertical Scale: 1 in - 25 ft.
Vertical Exaggeration: 12x

Legend

Geology

CL	Clay, silty clay, sandy clay, gravelly clay
ML	Silts, clayey silts
SC-SM	Clayey to silty sand
SP-SW	Sand, gravelly sand
GC-GM	Gravel. with silt and/or clay
GP-GW	Gravel; gravel-sand mix
SH	Shale

Monitoring Well Screen Interval

Water-level Elevation in Shale Well (feet NGVD) Jan '02

Water-level Elevation in Till or Alluvial Deposits (feet NGVD) Jan '02

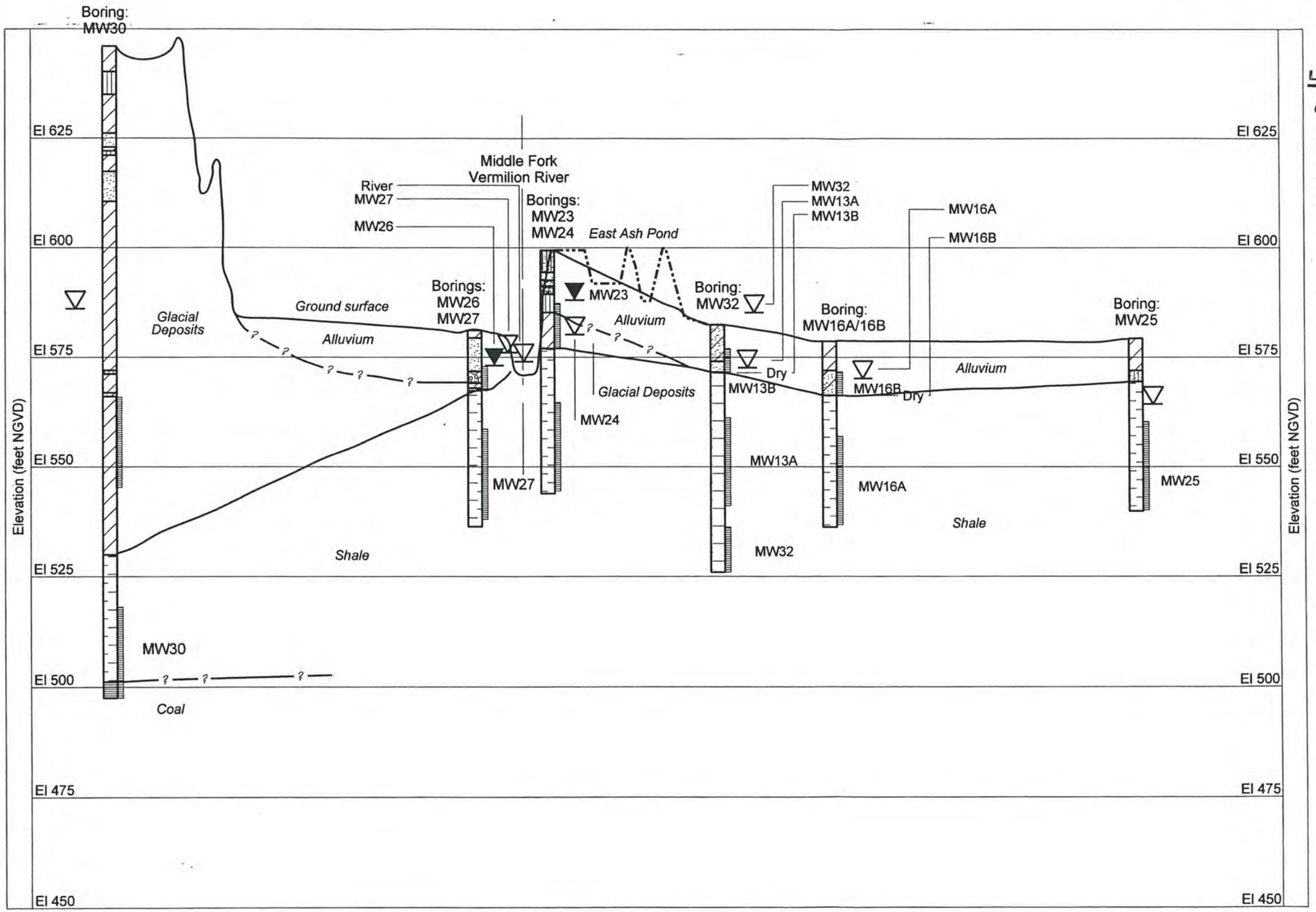
Kelron Environmental

East-West Geologic Cross-Section with Ground-Water Elevations: January 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 22*

B North — B' South



0 250 500 1000

Approximate Horizontal Scale: 1 in - 500 ft.
Approximate Vertical Scale: 1 in - 25 ft.
Vertical Exaggeration: 20x

Legend

Geology

- CL — Clay, silty clay, sandy clay, gravelly clay
- ML — Silts, clayey silts
- SC-SM — Clayey to silty sand
- SP-SW — Sand, gravelly sand
- GC-GM — Gravel. with silt and/or clay
- GP-GW — Gravel; gravel-sand mix
- SH — Shale
- Coal

Monitoring Well Screen Interval

Water-level Elevation in Shale Well (feet NGVD) Jan '02

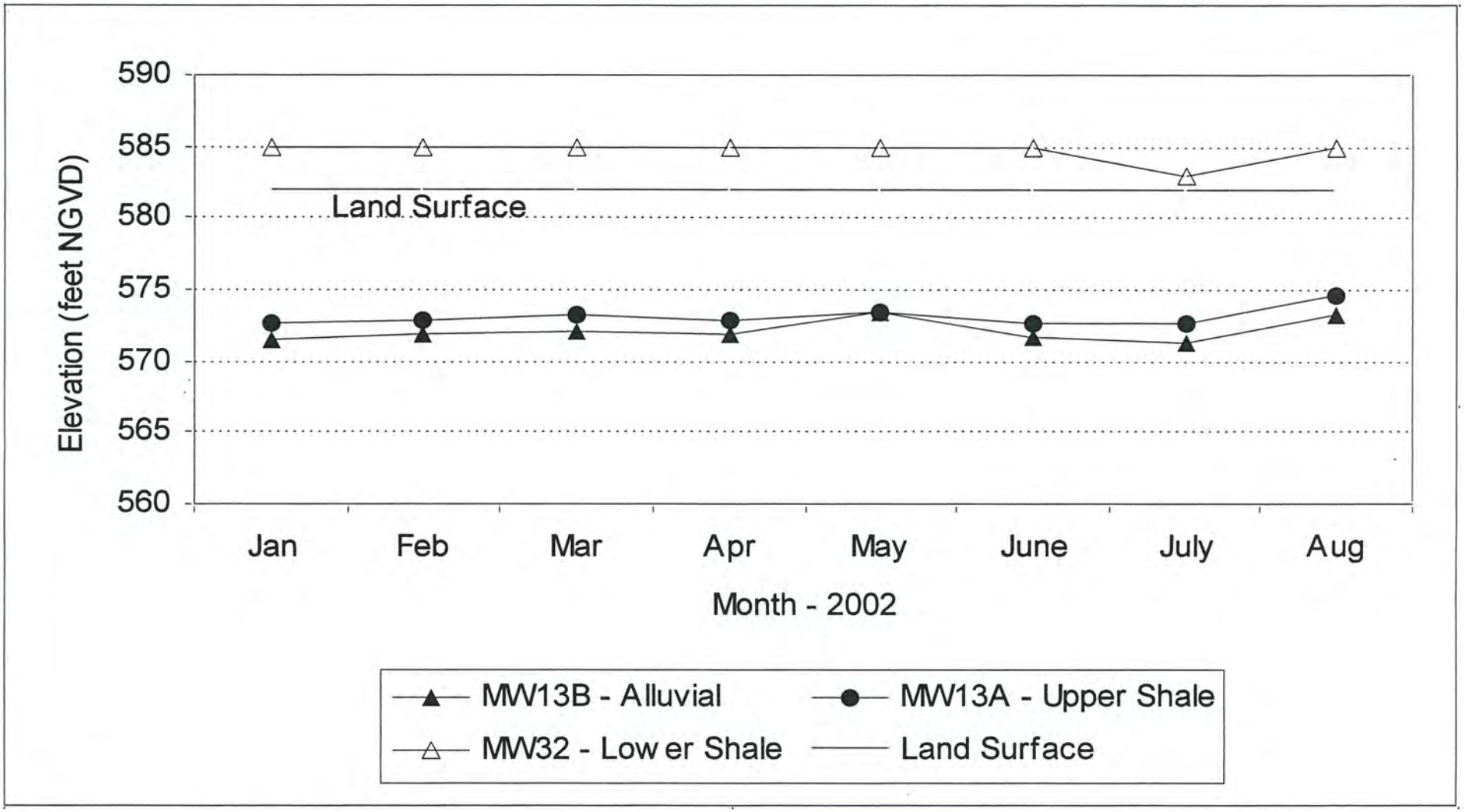
Water-level Elevation in Till or Alluvial Deposits (feet NGVD) Jan '02

Kelron Environmental

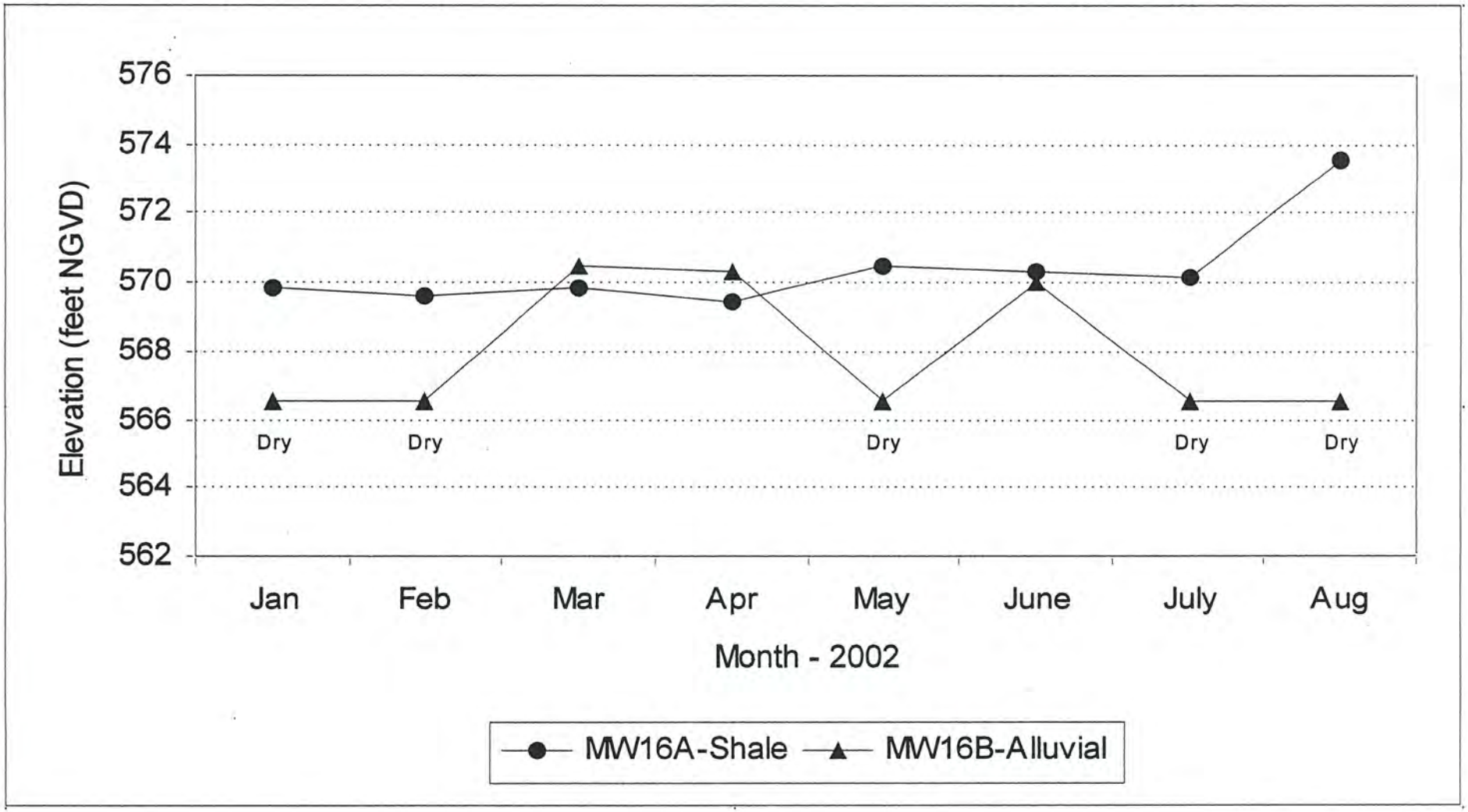
North-South Geologic Cross-Section with Ground-Water Elevations: January 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

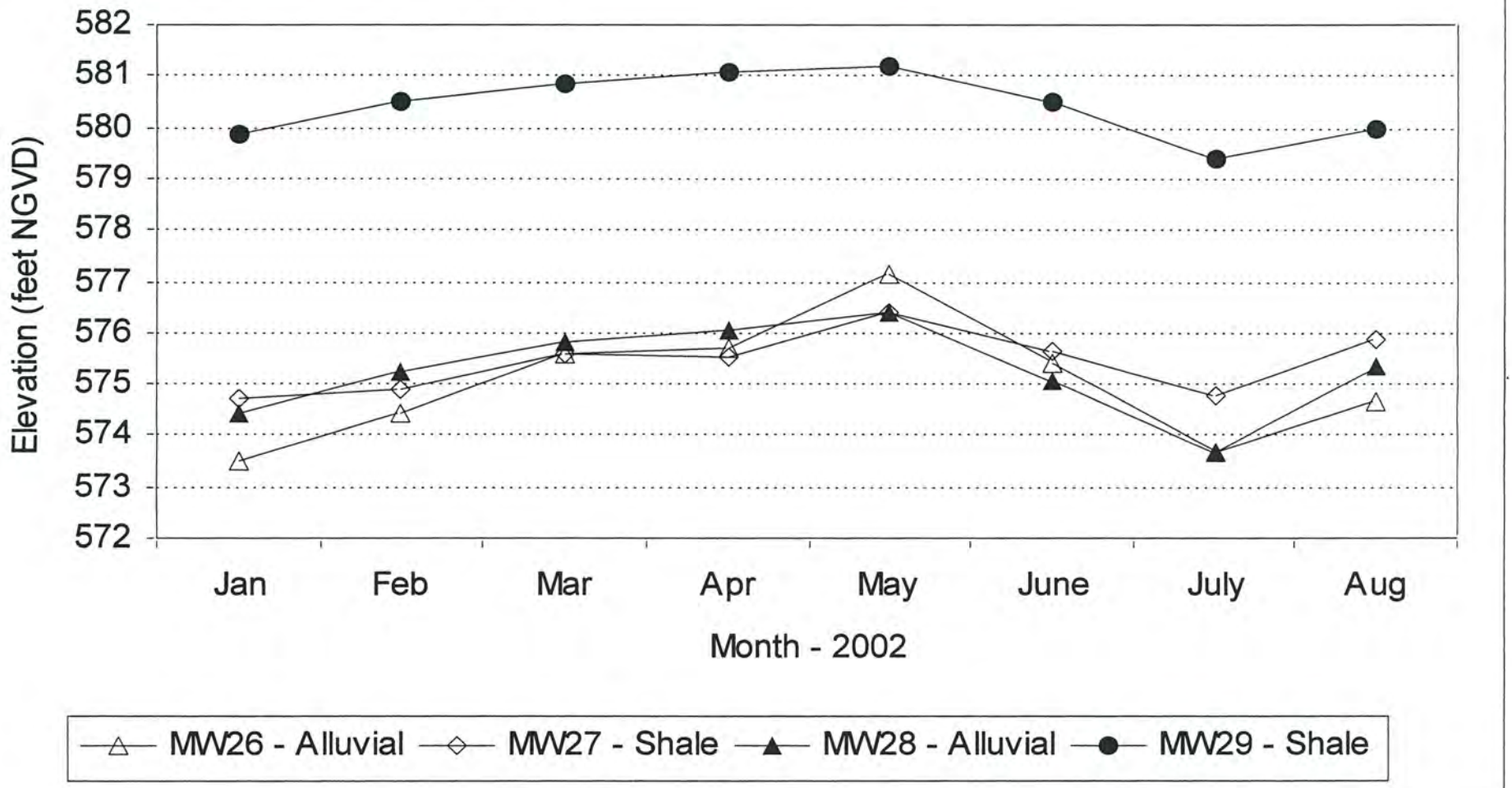
Date: September 2002 | *Figure 23*



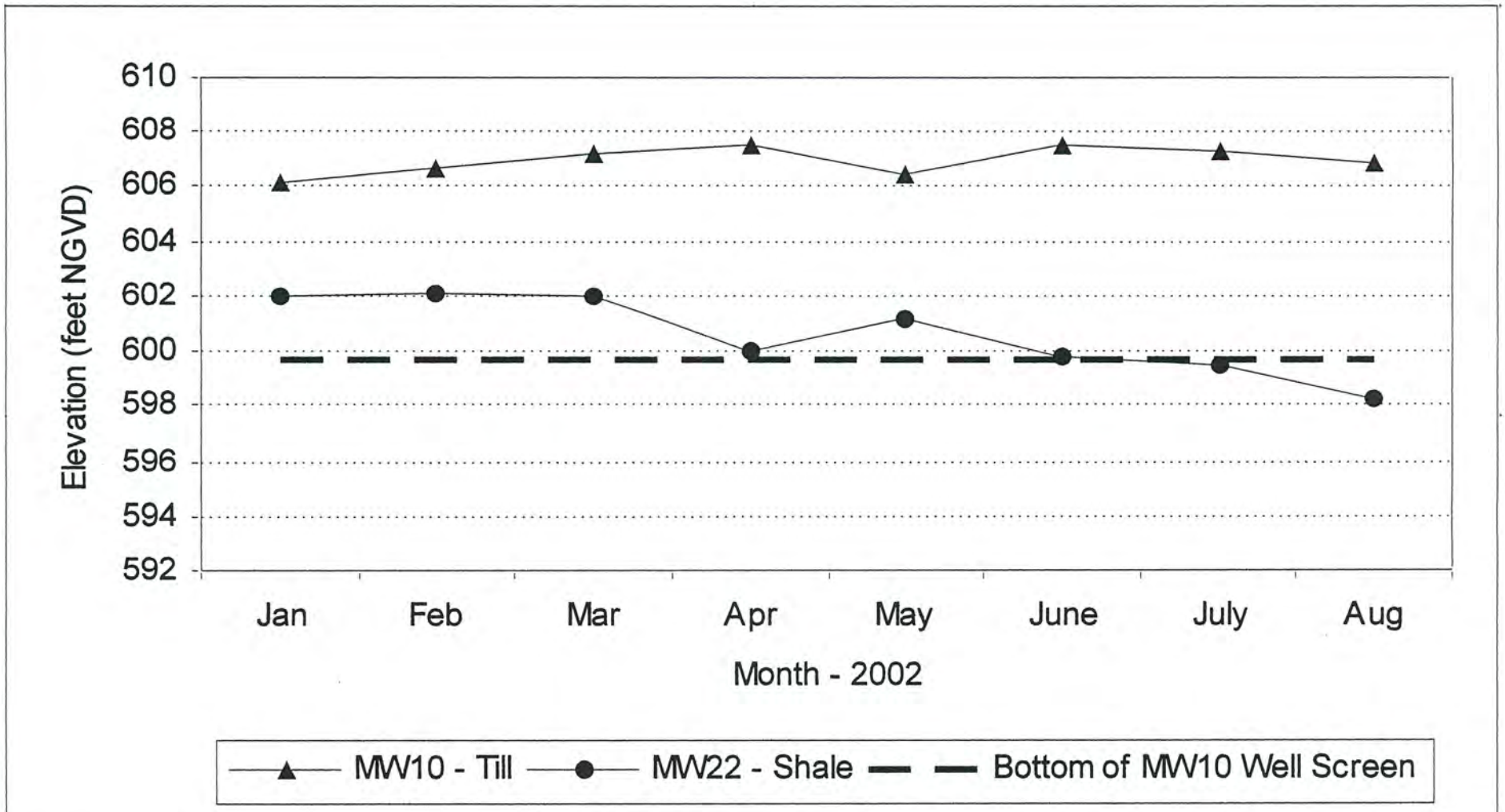
Kelron Environmental	
Groundwater Hydrographs of Nested Wells MW13A, MW13B and MW32	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 24*



Kelron Environmental	
Groundwater Hydrographs of Nested Wells MW16A and MW16B	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 25*



Kelron Environmental	
Groundwater Hydrographs of Nested Wells MW26 / MW27 and MW28 / MW29	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 26*



Kelron Environmental	
Groundwater Hydrographs of Nested Wells MW10 and MW22	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 27*

A West — A' East

Boring: MW31

0 150 300 600

Approximate Horizontal Scale: 1 in = 300 ft.
Approximate Vertical Scale: 1 in = 25 ft.
Vertical Exaggeration: 12x

Elevation (feet NGVD)

El 675
El 650
El 625
El 600
El 575
El 550
El 525
El 500

Borings: MW10, MW22
Boring: B102
Boring: B11A
Borings: MW32, MW13B, MW13A
Boring: MW31

MW10

Ground surface
Glacial Deposits
East Ash Pond
Middle Fork Vermilion River
Alluvium
Shale

602
570
573
585
613

580
575
590
600
610

Legend

Geology

- *CL* — Clay, silty clay, sandy clay, gravelly clay
- *ML* — Silts, clayey silts
- *SC-SM* — Clayey to silty sand
- *SP-SW* — Sand, gravelly sand
- *GC-GM* — Gravel. with silt and/or clay
- *GP-GW* — Gravel; gravel-sand mix
- *SH* — Shale

Monitoring Well Screen Interval

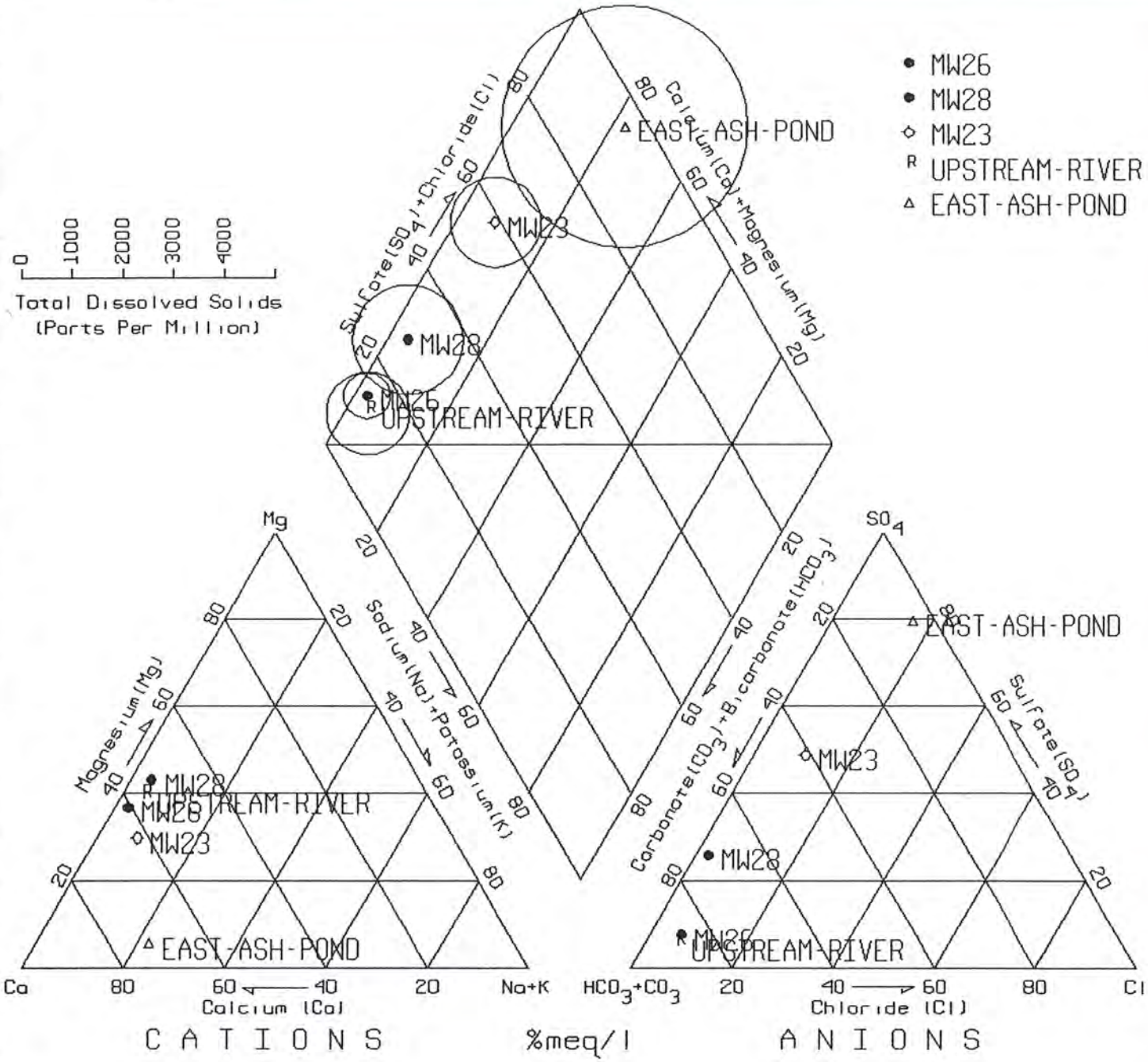
580 — Estimated Equipotential Lines (Lines of Equivalent Head)

Kelron Environmental

Equipotential Lines and Flowlines for Groundwater in the Shale Based on Observed Hydraulic Head in January 2002

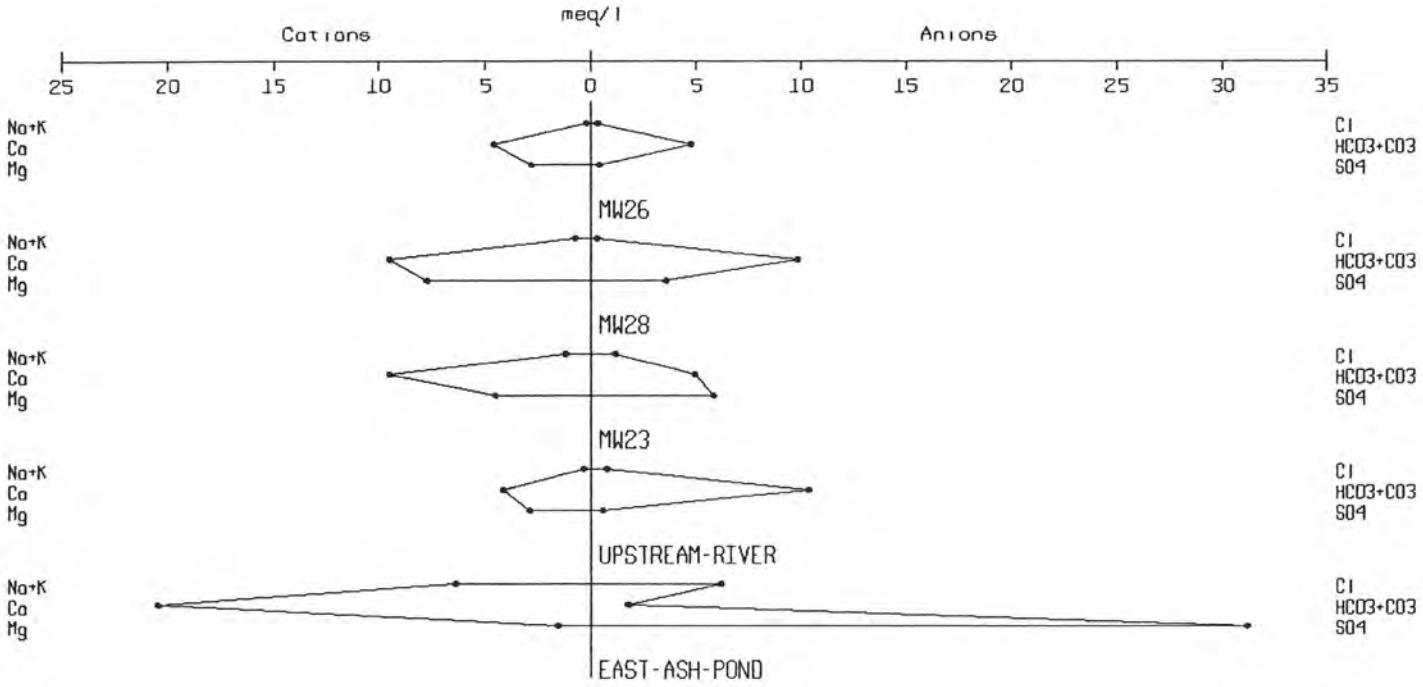
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 28*



Kelron Environmental	
Piper Diagram of Water Samples from Unlithified Deposits, Middle Fork River, and East Ash Pond	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 29*

Note: Groundwater samples and Middle Fork River Sample are from June 2002; East Ash Pond sample is from March 2002



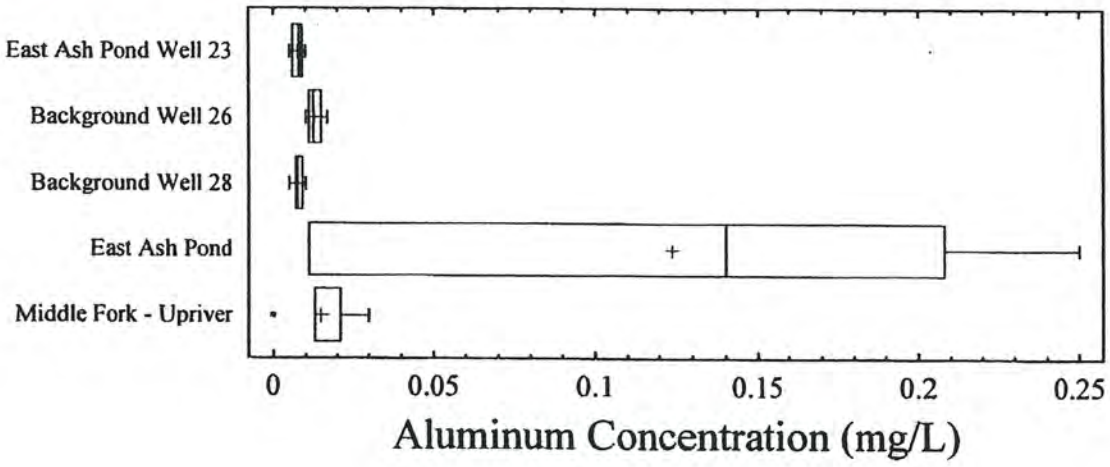
Note: Groundwater samples and Middle Fork River Sample are from June 2002; East Ash Pond sample is from March 2002

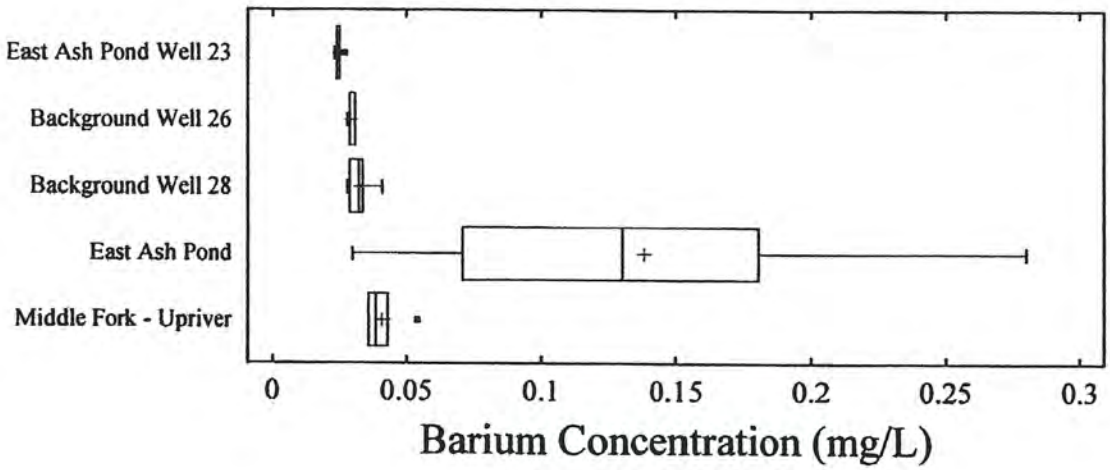
Kelron Environmental

Stiff Diagrams of Water Samples from Unlithified Deposits, Middle Fork River, and East Ash Pond

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 30*



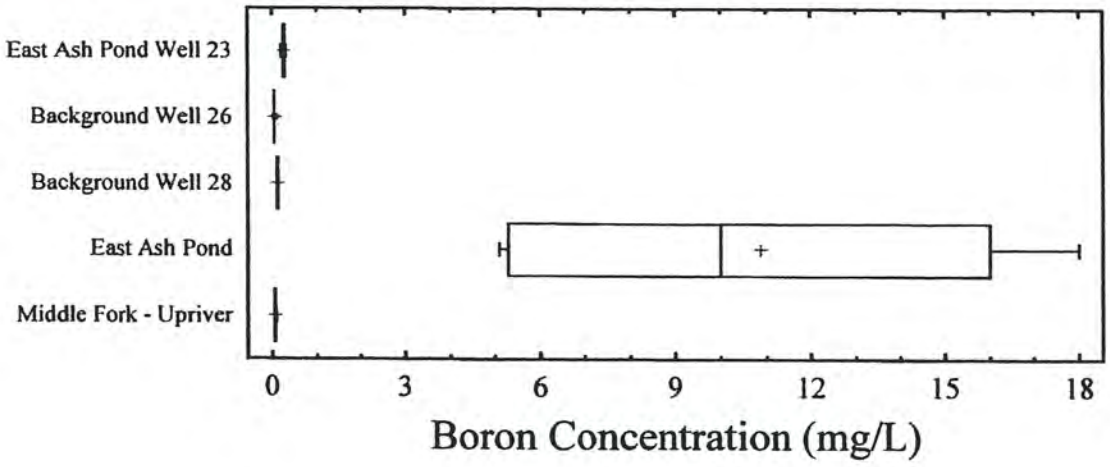


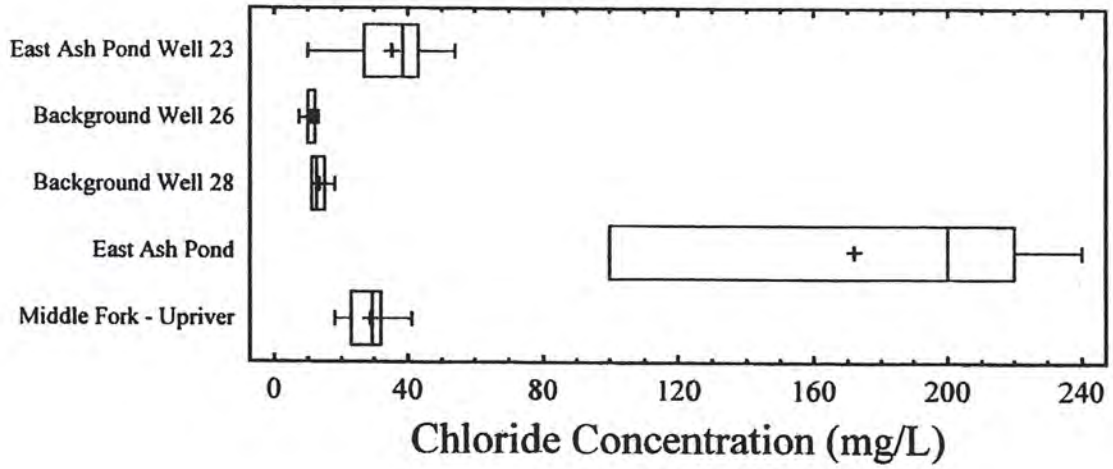
Kelron Environmental

Box-and-Whisker Diagrams for Water Samples from Unlithified Deposits, Middle Fork River, and East Ash Pond in 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 31a*





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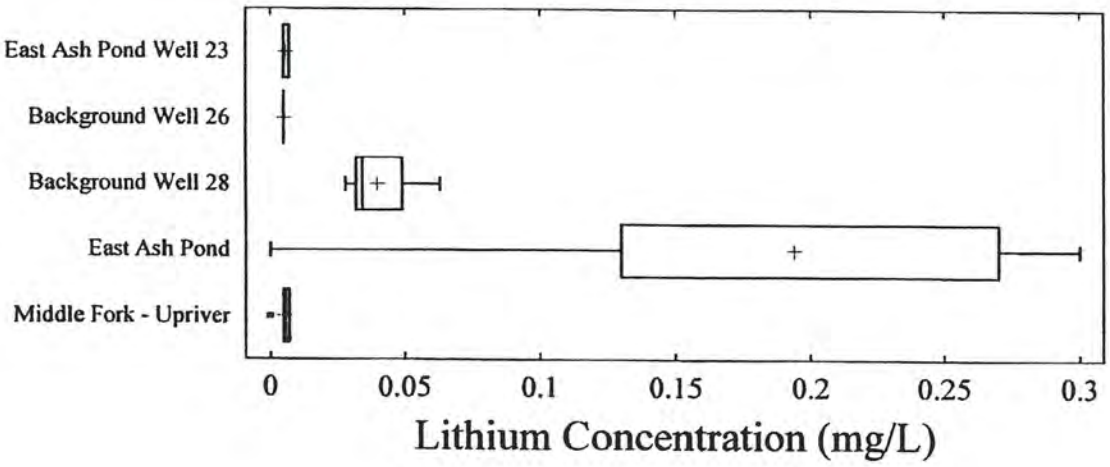
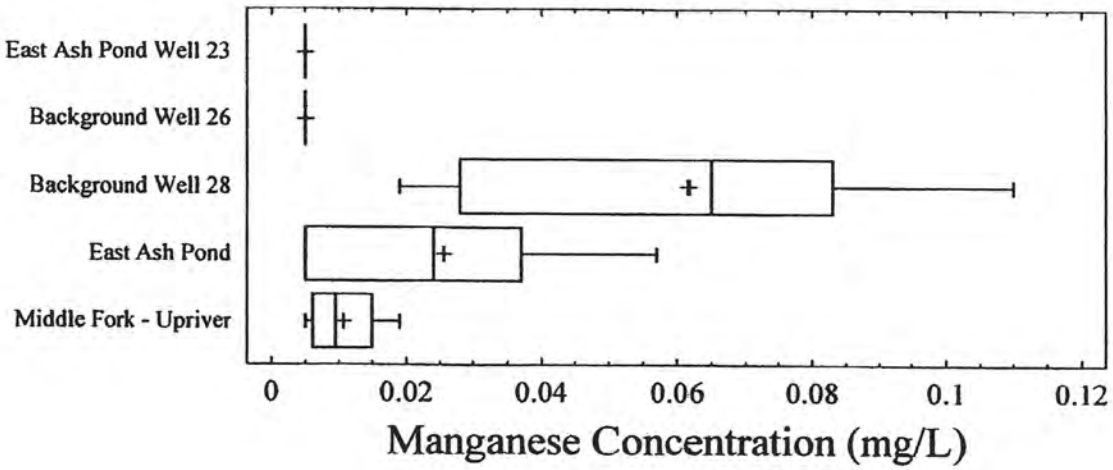
Box-and-Whisker Diagrams for Water Samples from Unlithified Deposits, Middle Fork River, and East Ash Pond in 2002

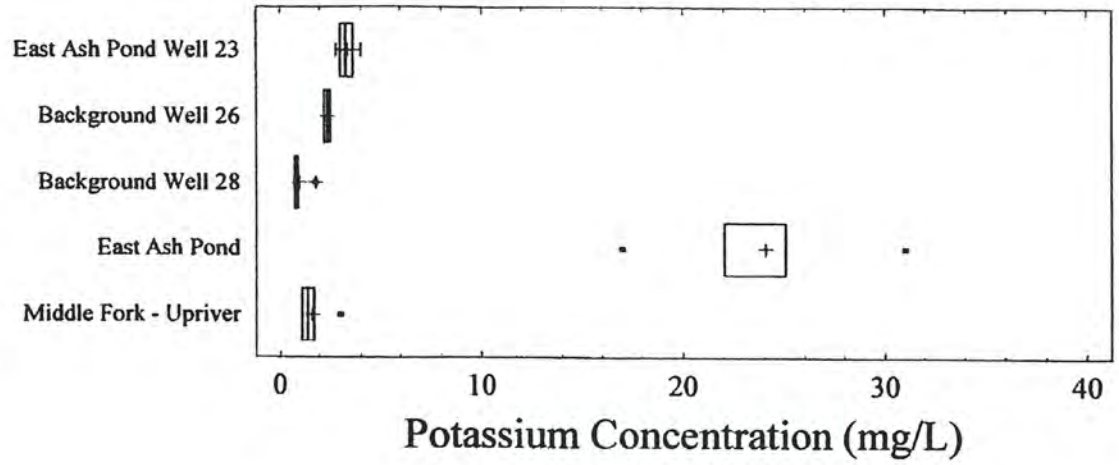
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

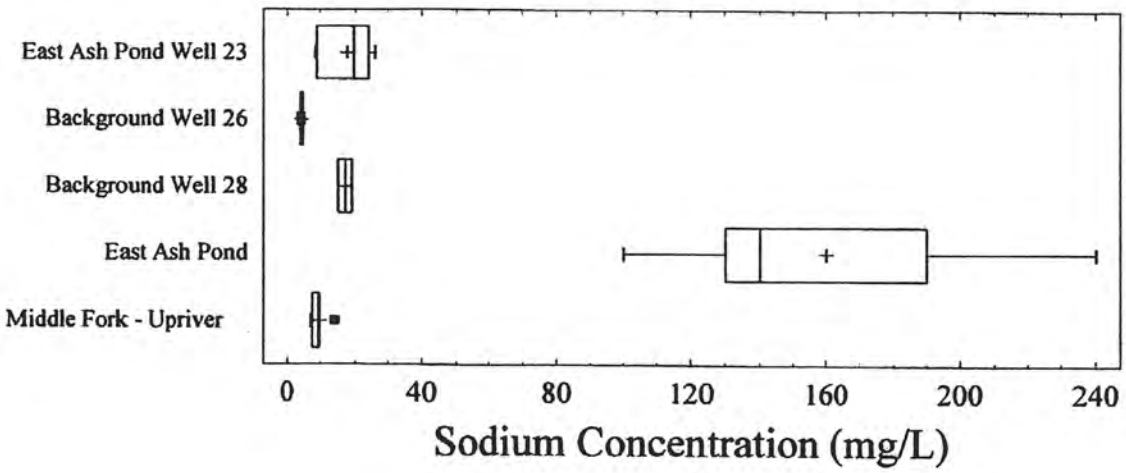
Date: September 2002 | *Figure 31b*





Kelron Environmental	
Box-and-Whisker Diagrams for Water Samples from Unlithified Deposits, Middle Fork River, and East Ash Pond in 2002	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 31c*



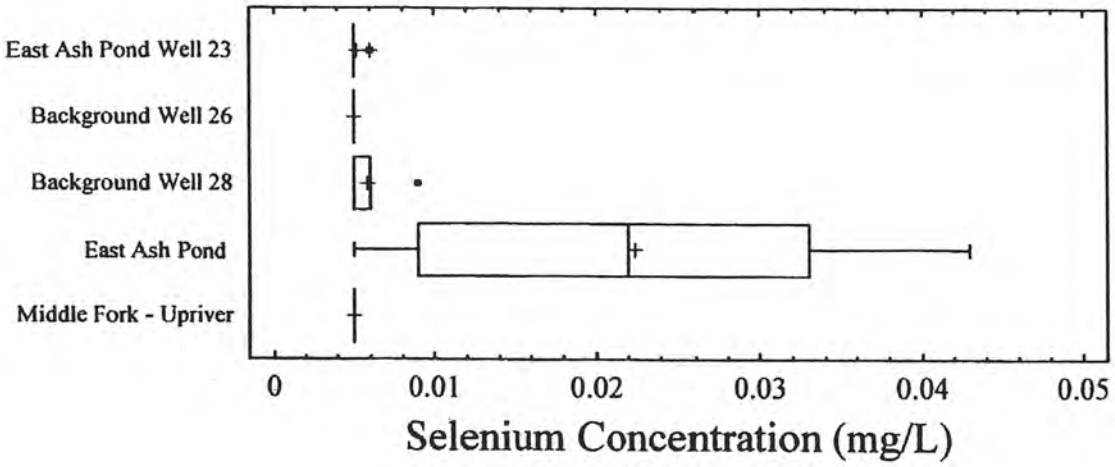


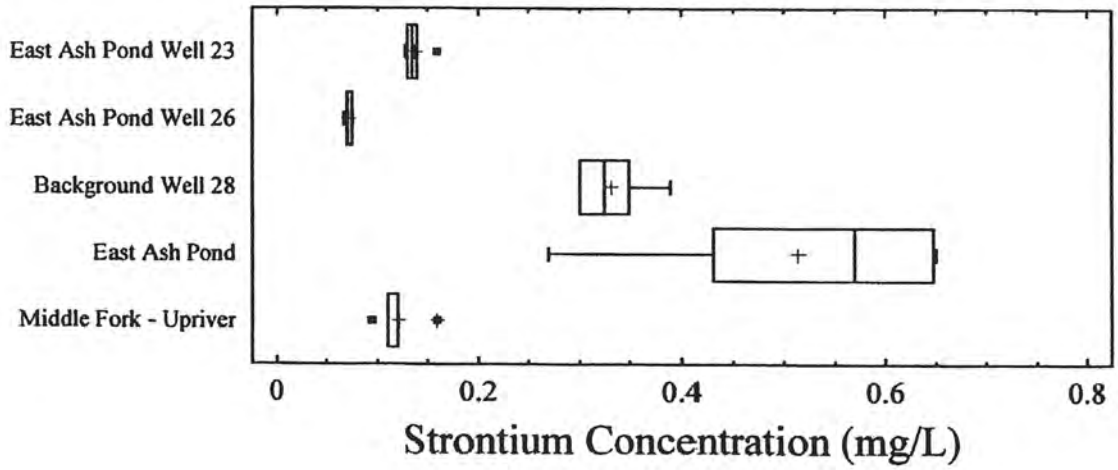
Kelron Environmental

Box-and-Whisker Diagrams for Water Samples from Unlithified Deposits, Middle Fork River, and East Ash Pond in 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 31d*



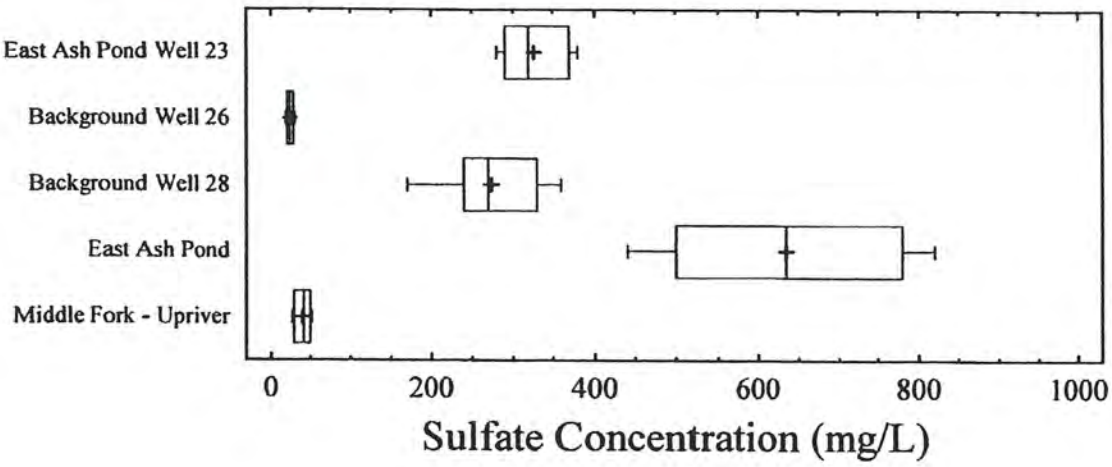


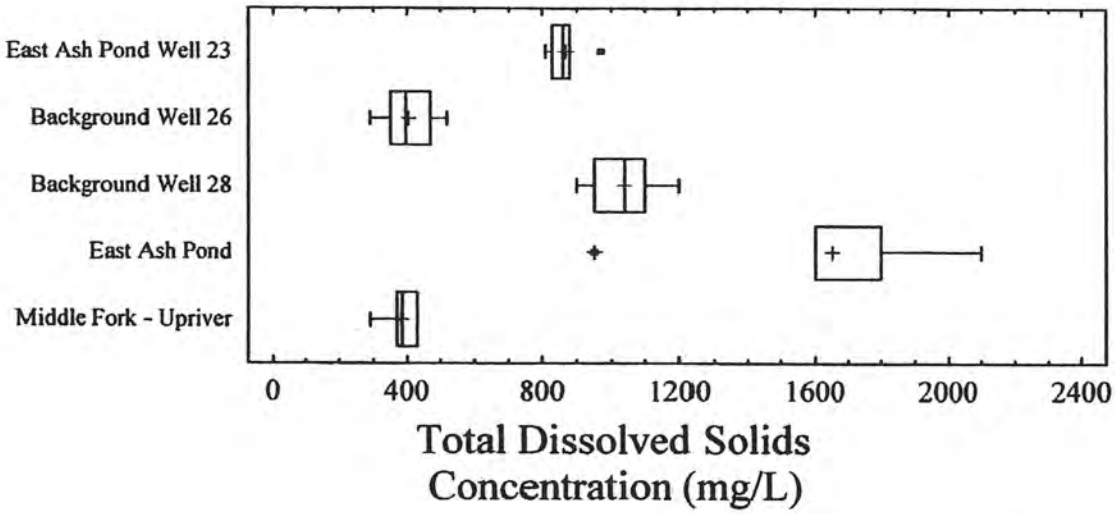
Kelron Environmental

Box-and-Whisker Diagrams for Water Samples from Unlithified Deposits, Middle Fork River, and East Ash Pond in 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 31e*



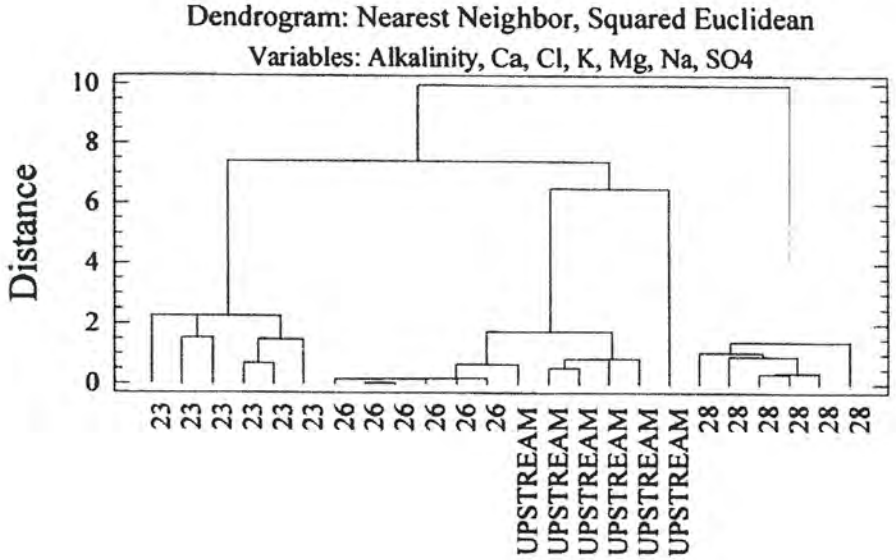


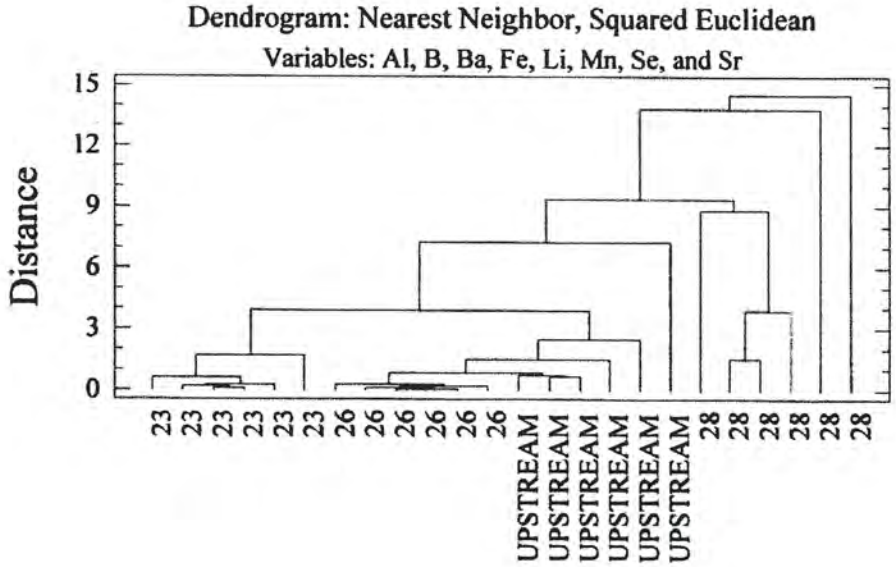
Kelron Environmental

Box-and-Whisker Diagrams for Water Samples from Unlithified Deposits, Middle Fork River, and East Ash Pond in 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

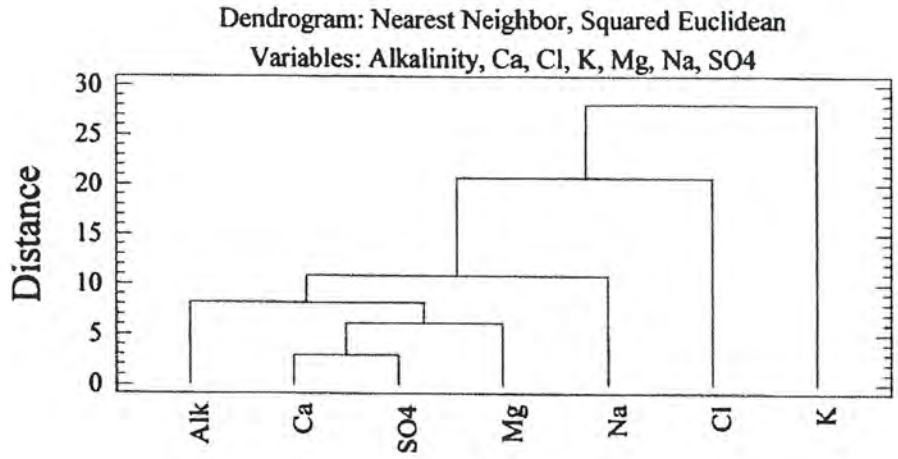
Date: September 2002 | *Figure 31f*

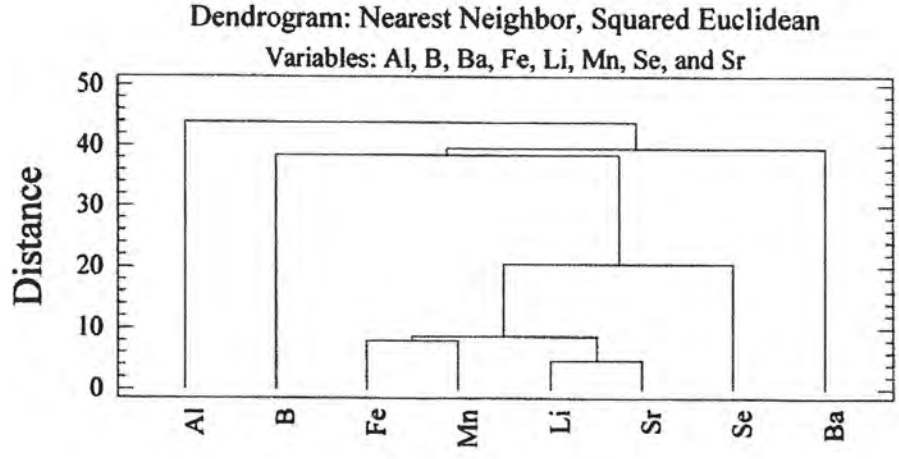




Note: Wells used in dendograms are: background wells MW26 and MW28; and, East Ash Pond well MW23. Upstream surface water quality is from Middle Fork of Vermilion River)

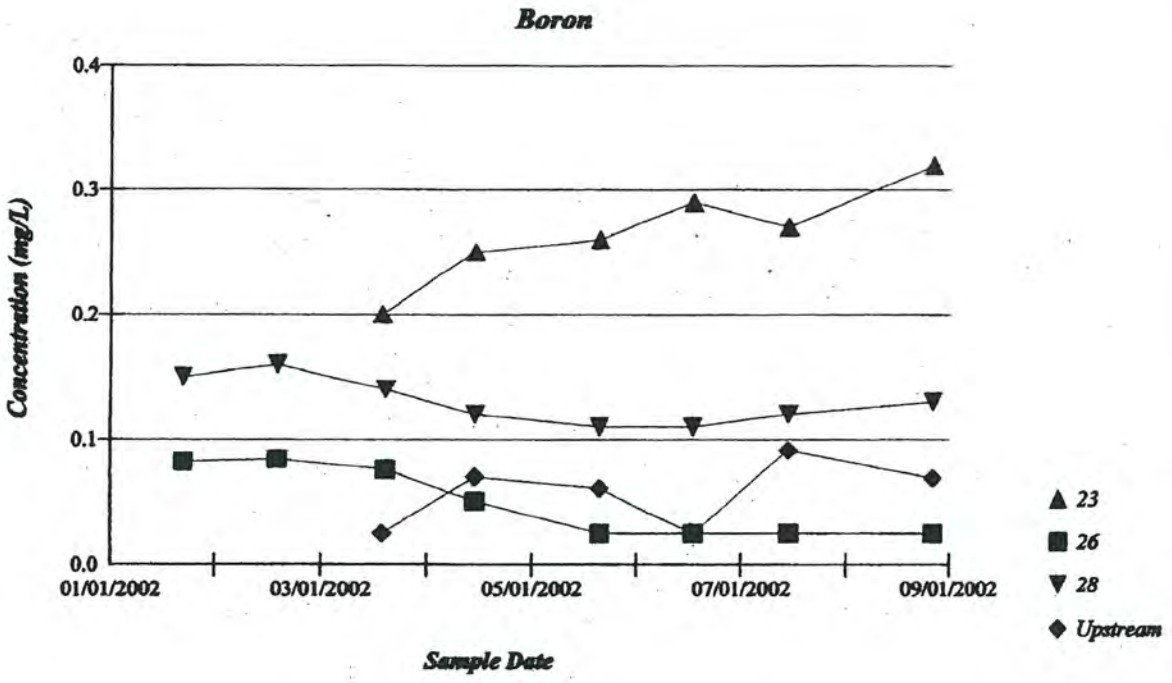
Kelron Environmental	
Dendrograms of Monthly Water Chemistry Data in Unlithified Deposits and Middle Fork River Based on Major Ions and Trace Metals	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 32*

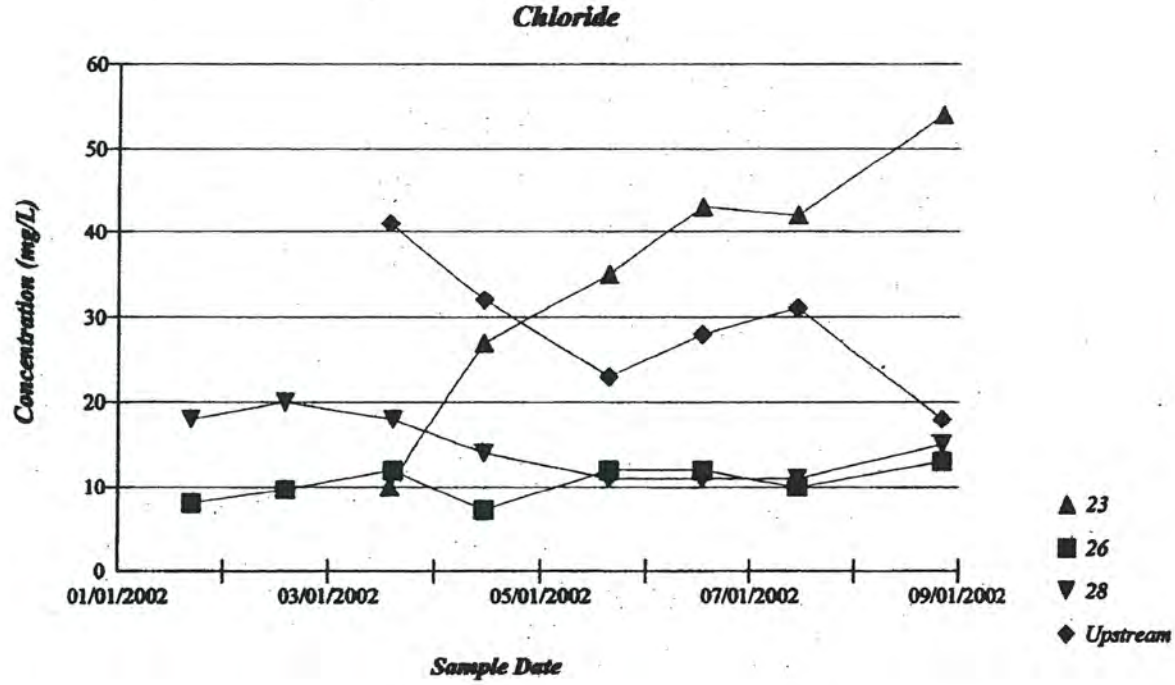




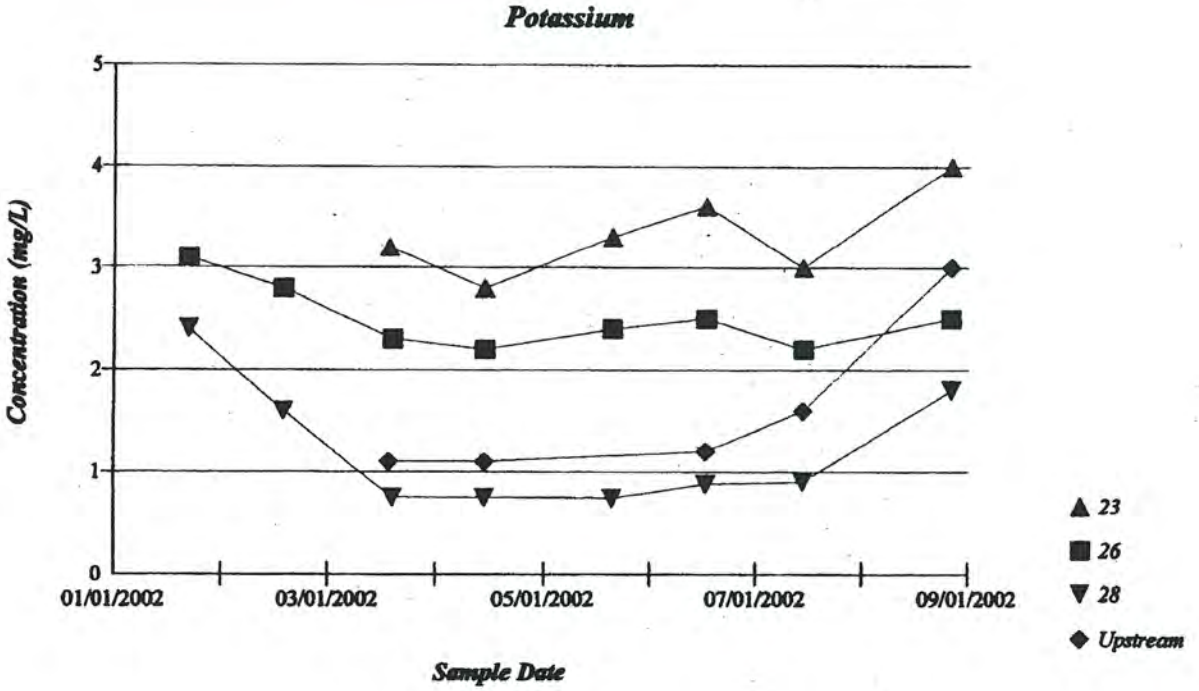
Note: Data used in dendograms are for background wells MW26 and MW28, East Ash Pond well MW23, and upstream surface water from the Middle Fork of Vermilion River)

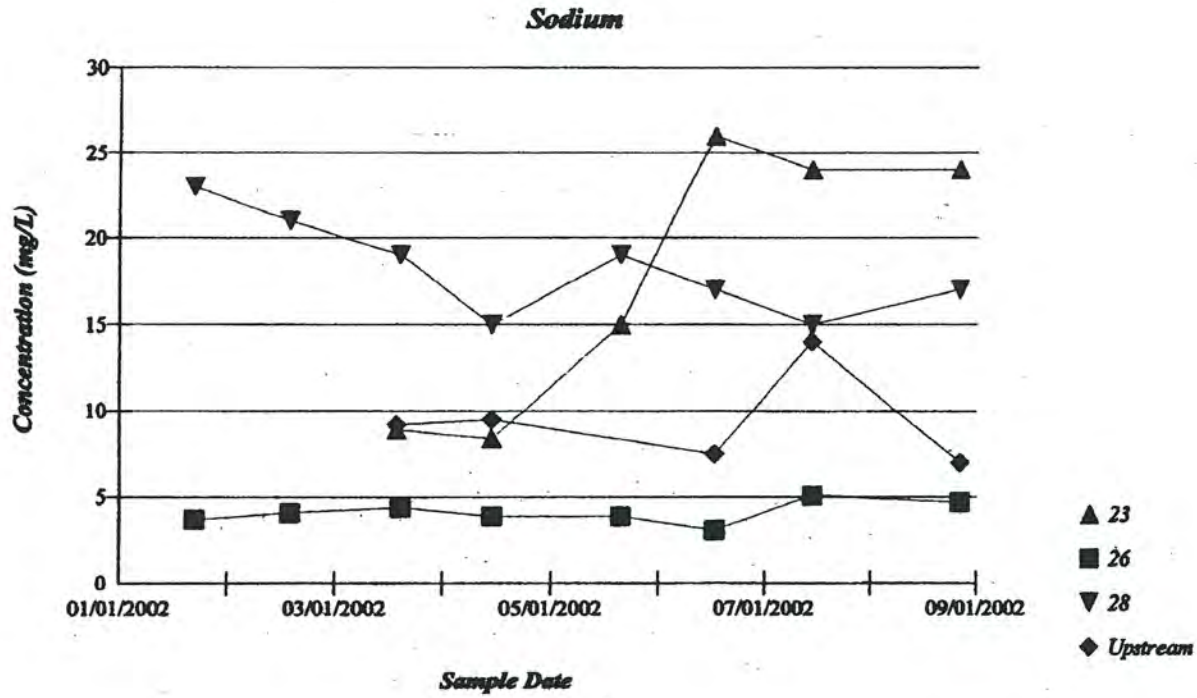
Kelron Environmental	
Dendrograms of Major Ions and Trace Metals in Water from Unconsolidated Deposits and Middle Fork River	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 33*



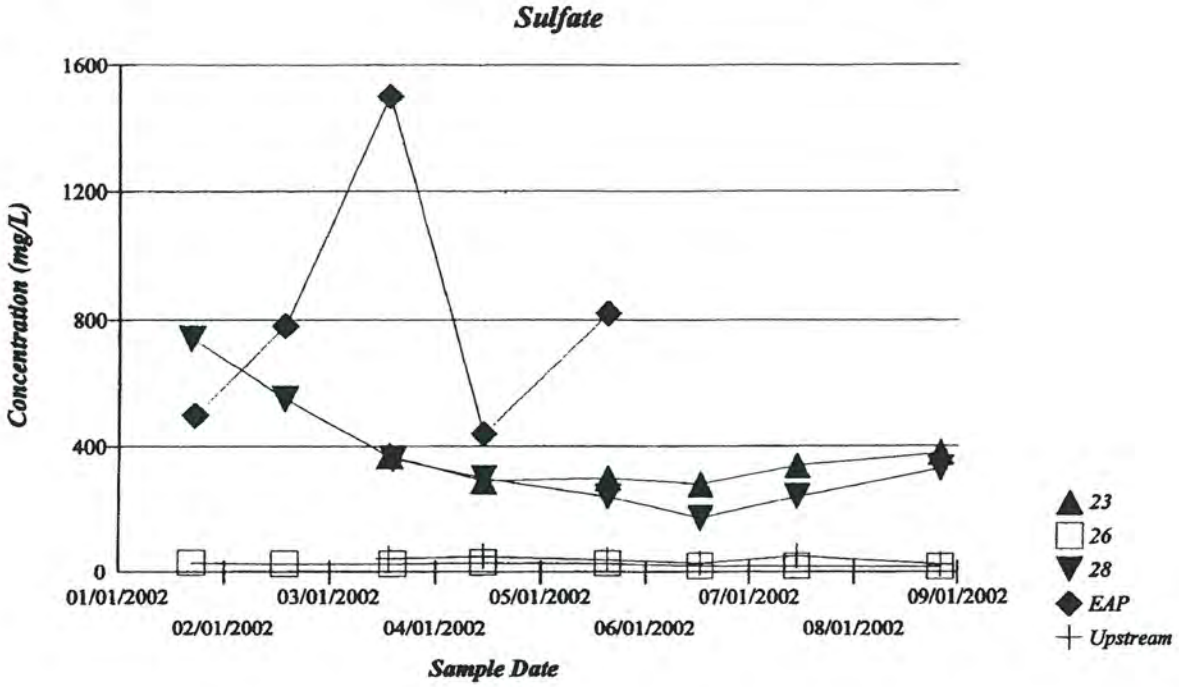


Kelron Environmental	
Chloride Trends in Unlithified Deposits and Upstream on Middle Fork River	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 34A*

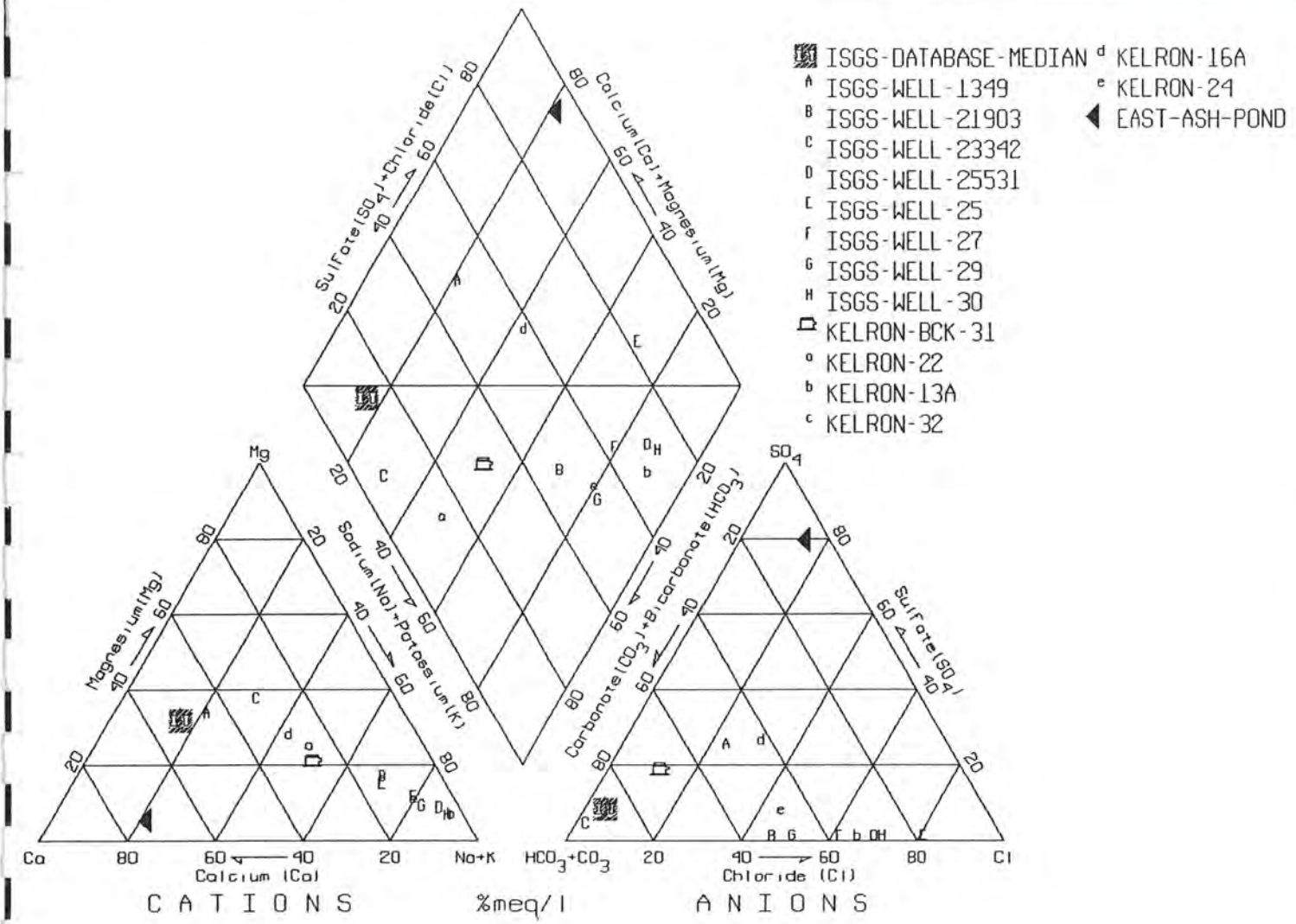




Kelron Environmental	
Potassium and Sodium Trends in Unlithified Deposits and Upstream on Middle Fork River	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 34B*

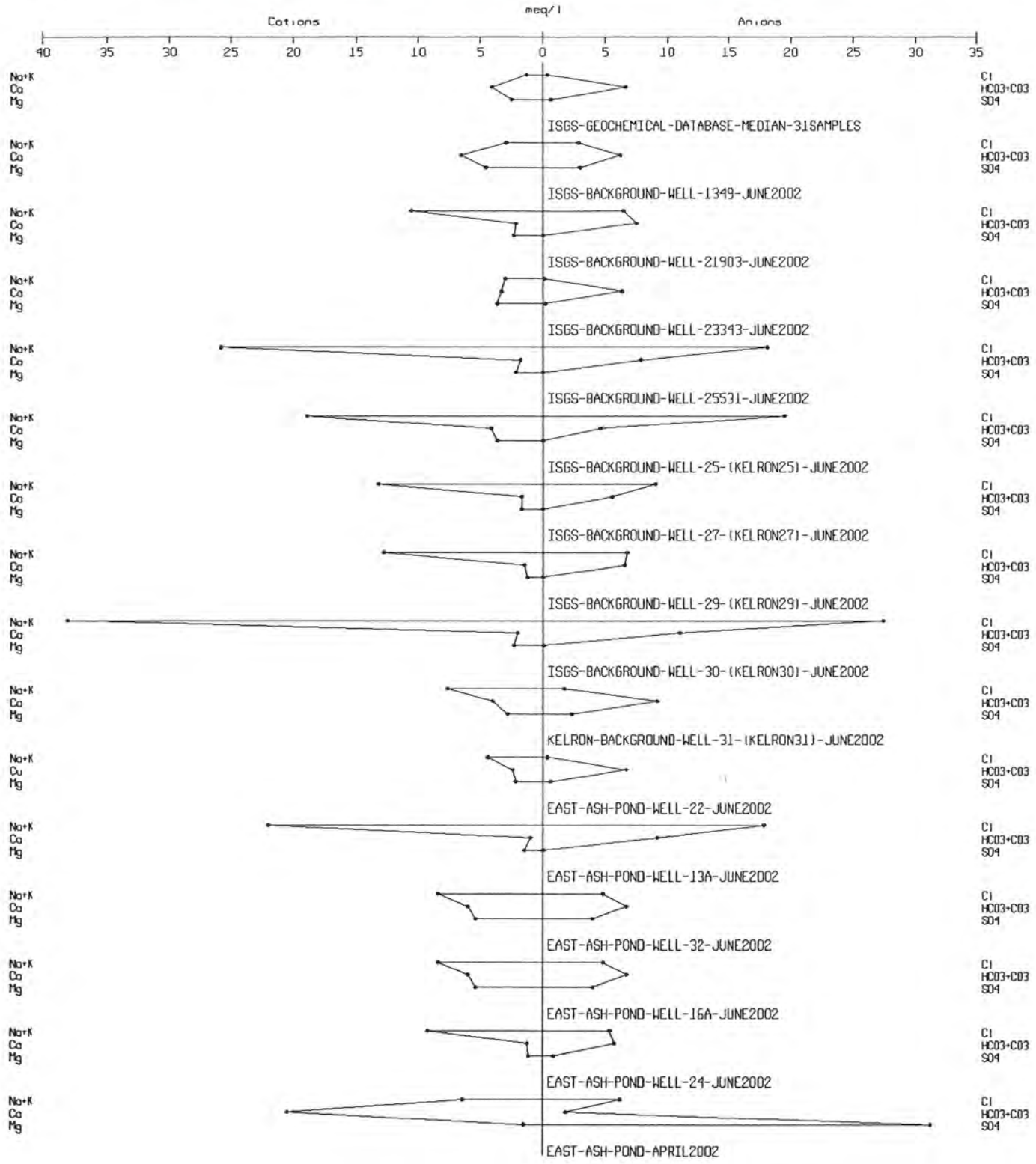


Kelron Environmental	
Sulfate Trends in Unlithified Deposits, Upstream on Middle Fork River, and East Ash Pond	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 34C*



Note: Groundwater samples are from June 2002; East Ash Pond sample is from March 2002)

Kelron Environmental	
Piper Diagram of Groundwater Samples from Bedrock and Surface Water Samples from East Ash Pond	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 35*



Note: Groundwater samples are from June 2002; East Ash Pond sample is from March 2002)

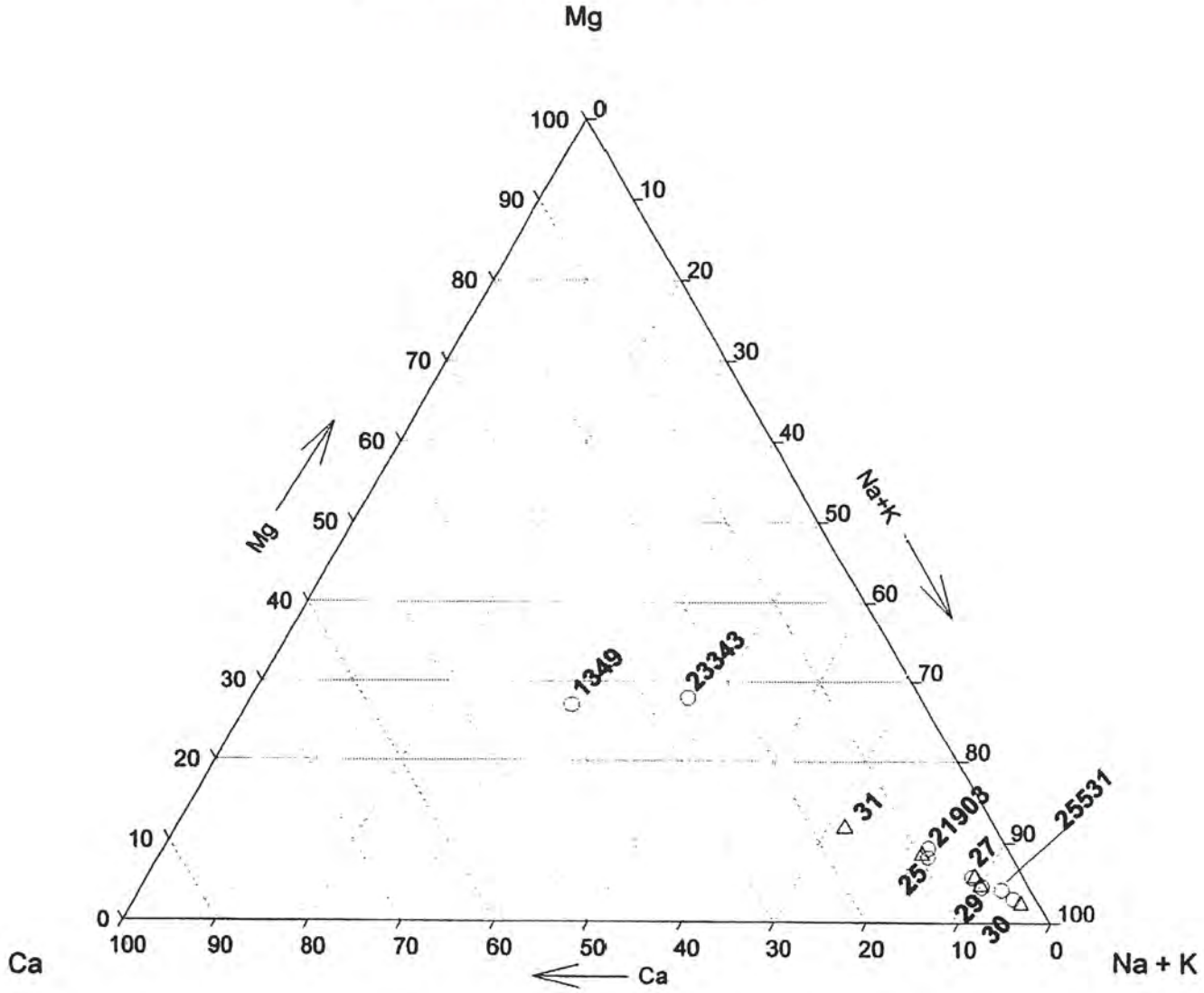
Kelron Environmental

Stiff Diagrams of Groundwater Samples from Bedrock and Surface Water Samples from East Ash Pond

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 36*

Cation Plot of Piper Diagram

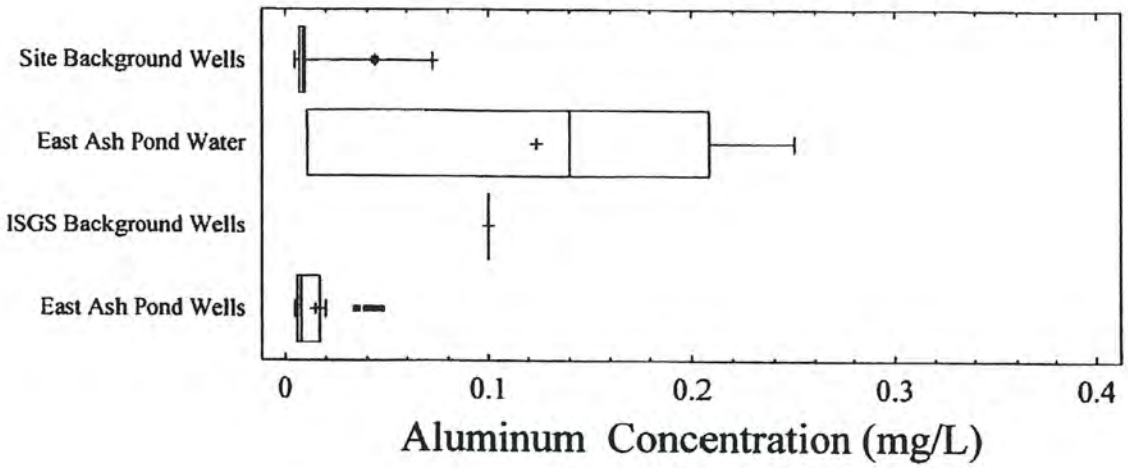


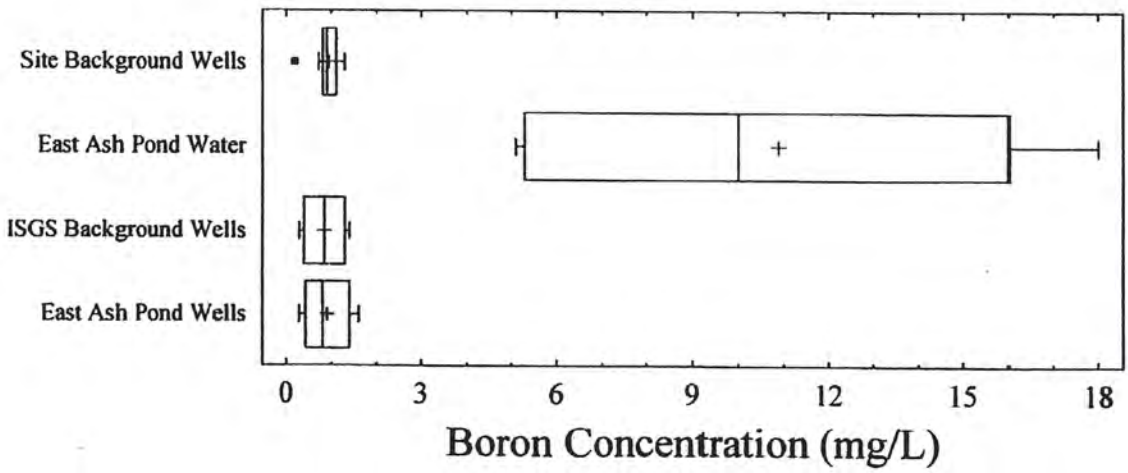
○ Shale well (ISGS)

△ Shale well (Kelron)

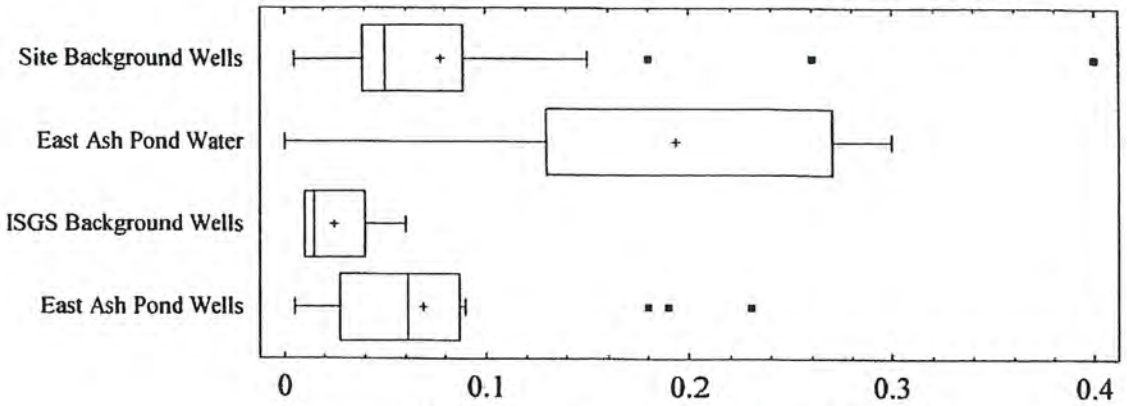
Note: modified after Figure 13, Appendix A (Mehnert and Dreher, 2002)

Kelron Environmental	
Cation Plot of Piper Diagram for June 2002 Groundwater Samples Collected by the ISGS and Kelron	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 37*

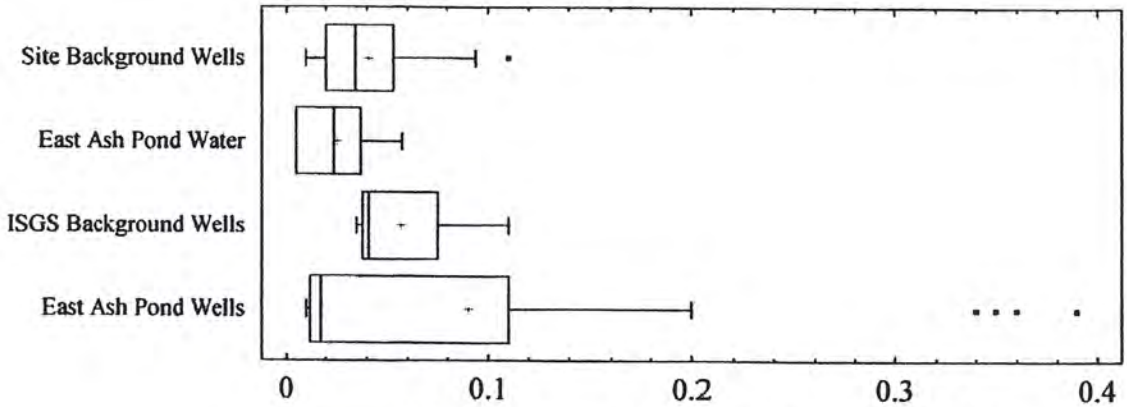




Kelron Environmental	
Box-and-Whisker Diagrams for Groundwater Samples from Bedrock and Surface Water Samples from East Ash Pond in 2002	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 38A*

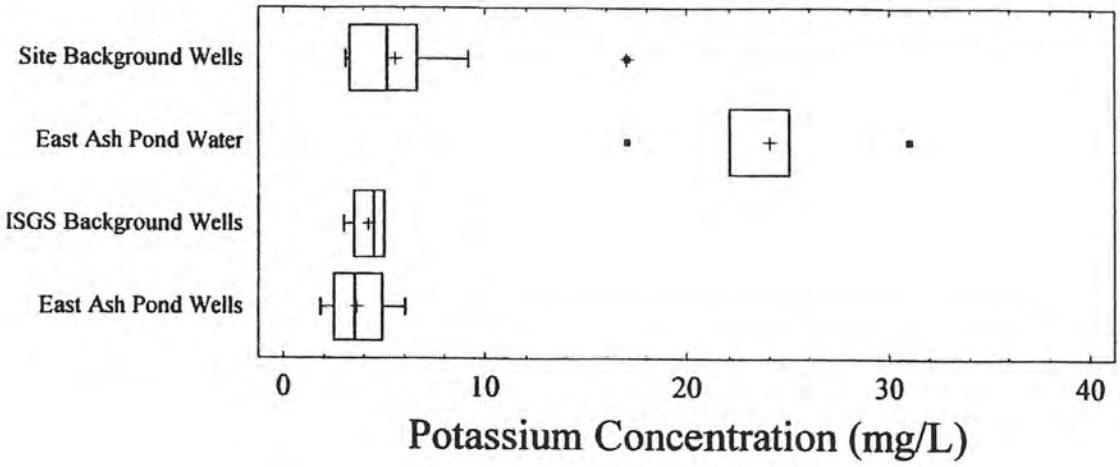


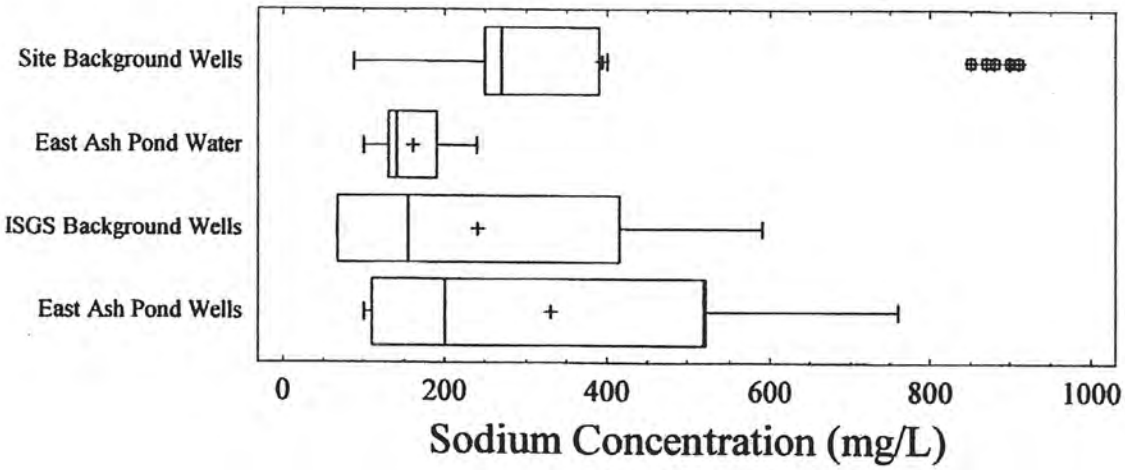
Lithium Concentrations (mg/L)



Manganese Concentration (mg/L)

Kelron Environmental	
Box-and-Whisker Diagrams for Groundwater Samples from Bedrock and Surface Water Samples from East Ash Pond in 2002	
Regional and Local Hydrogeology and Geochemistry *Vermilion Power Plant* *Oakwood, Illinois*	
Date: September 2002	*Figure 38C*



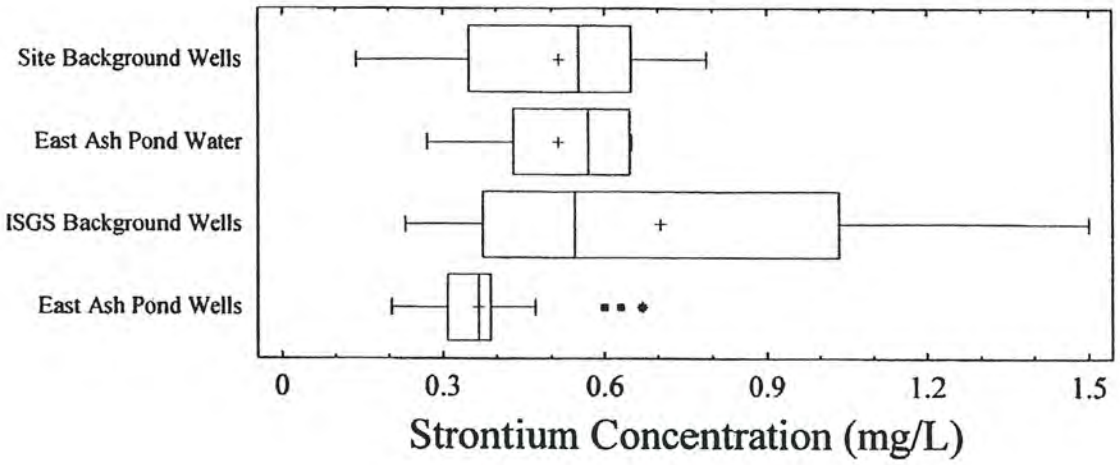


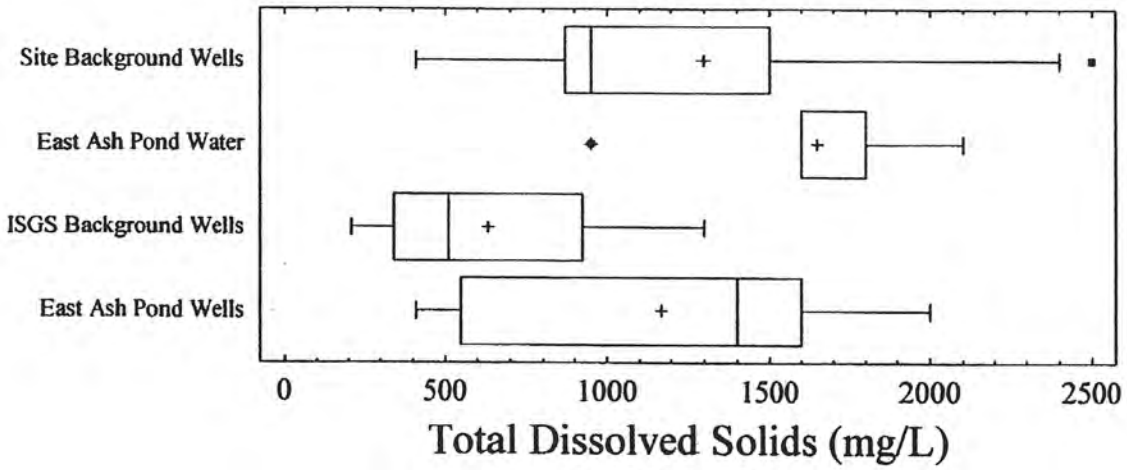
Kelron Environmental

Box-and-Whisker Diagrams for Groundwater Samples from Bedrock and Surface Water Samples from East Ash Pond in 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 38D*





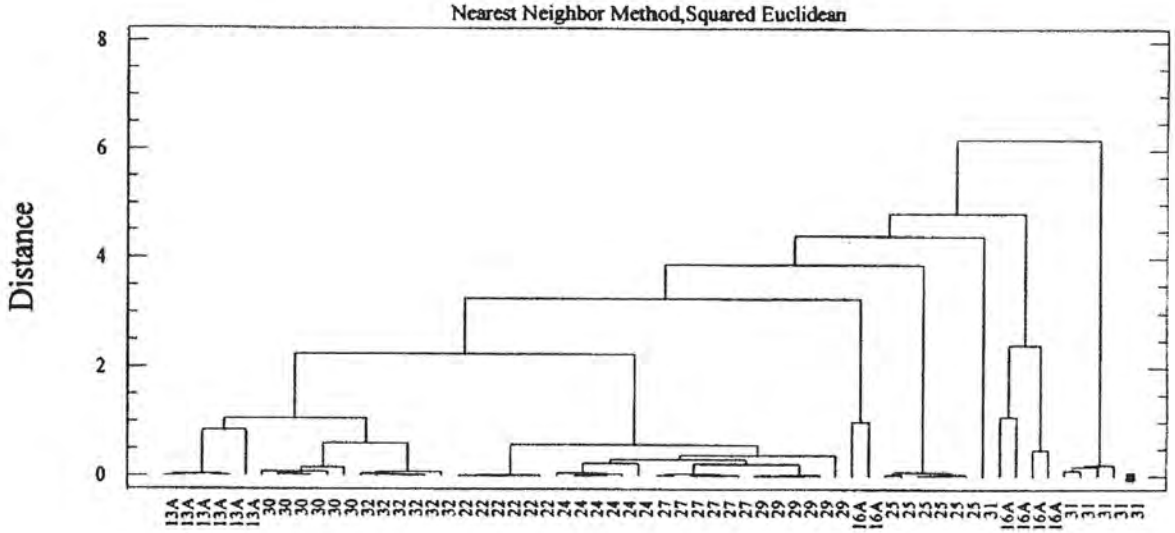
Kelron Environmental

Box-and-Whisker Diagrams for Groundwater Samples from Bedrock and Surface Water Samples from East Ash Pond in 2002

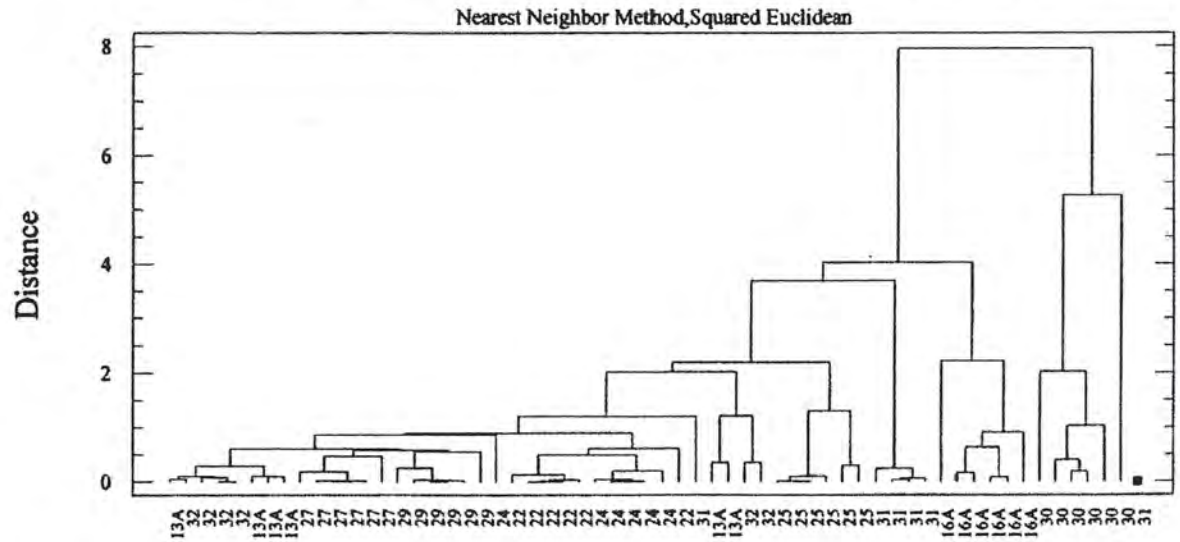
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 38E*

Dendrogram: Variables - Na, K, Ca, Mg, Cl, SO4, Alkalinity



Dendrogram: Variables - Trace Metals (Al, B, Ba, Fe, Li, Mn, Sr)



Note: Wells used in dendogram are background and East Ash Pond wells: MW13A, MW16A, MW22, MW24, MW25, MW27, MW29, MW30, and MW31)

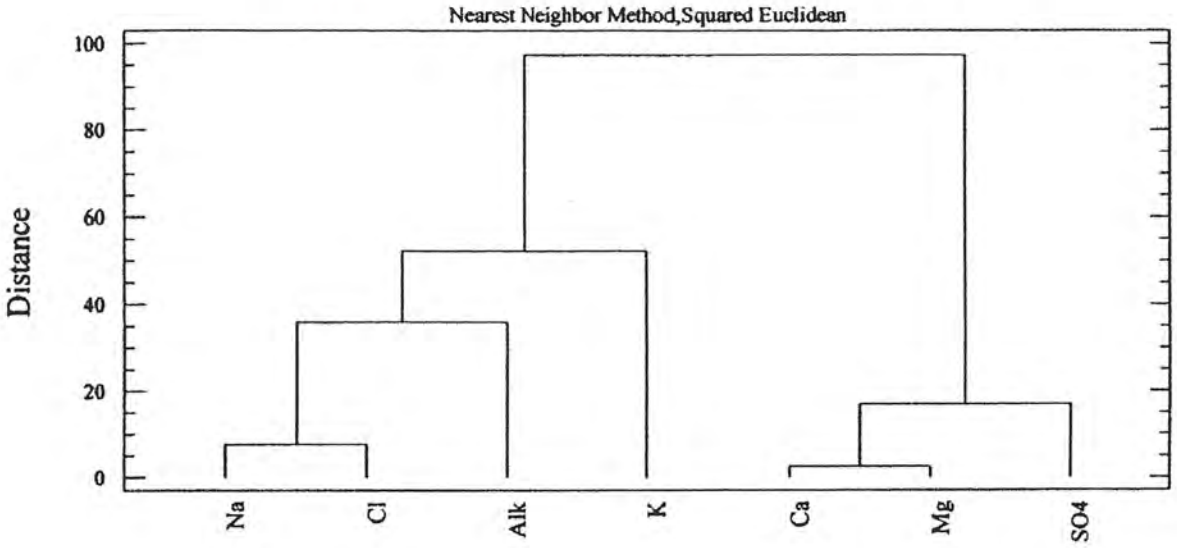
Kelron Environmental

Dendrograms of Monthly Groundwater Chemistry Data in Bedrock Deposits Based on Major Ions and Trace Metals

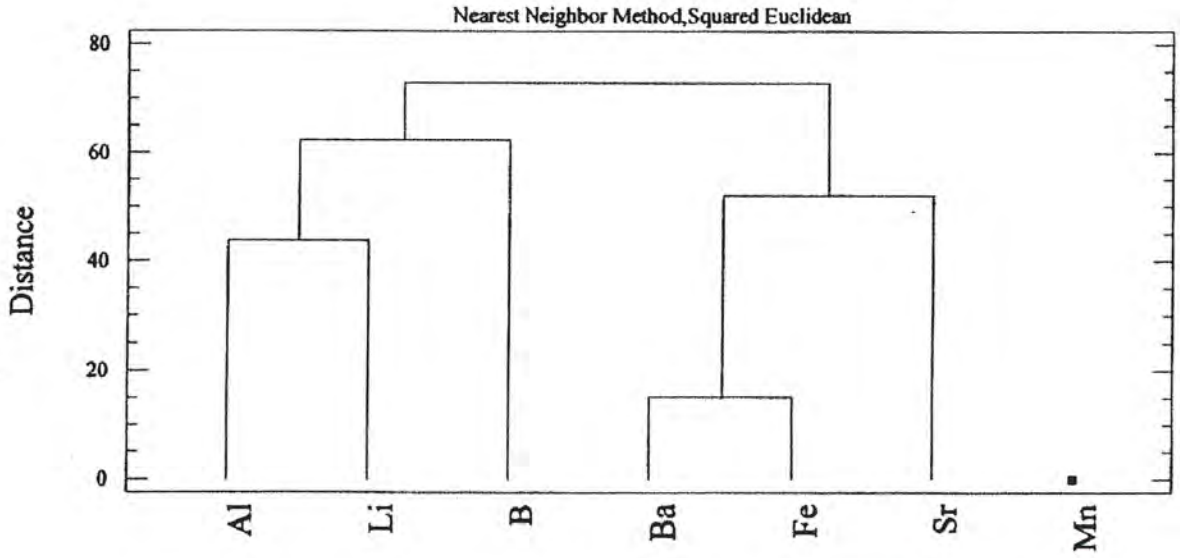
Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 39*

Dendrogram Variables: Na, K, Ca, Mg, Cl, SO4, Alkalinity



Dendrogram: Variables - Trace Metals (Al, B, Ba, Fe, Li, Mn, Sr)



Note: Data used in dendogram are for background and East Ash Pond wells: MW13A, MW16A, MW22, MW24, MW25, MW27, MW29, MW30, and MW31)

Kelron Environmental

Dendrograms of Major Ions and Trace Metals in Groundwater of Bedrock Deposits

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 40*

Appendix A

Volume 1

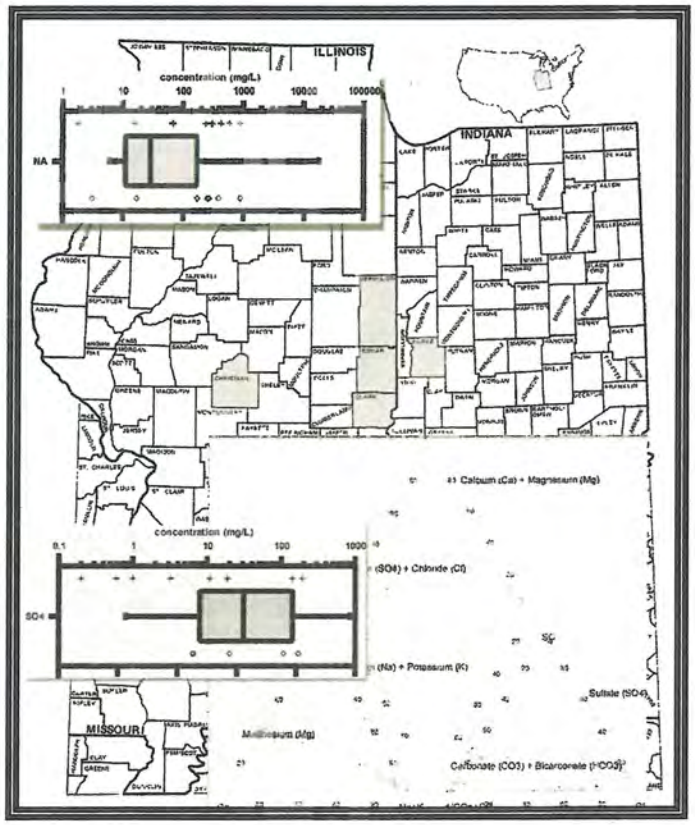
Geochemistry of Groundwater from the Shallow Bedrock in Central Vermilion County, Illinois.

Edward Mehnert and Gary B. Dreher, Illinois State Geological Survey. Illinois State Geological Survey Open-File Series Report 2002-4.

The Geochemistry of Groundwater from the Shallow Bedrock in Central Vermilion County, Illinois

Edward Mehnert and Gary B. Dreher
Illinois State Geological Survey

Illinois State Geological Survey
Open-File Series Report 2002-4



ISGS
Illinois State Geological Survey

ILLINOIS
DEPARTMENT OF
NATURAL
RESOURCES

The Geochemistry of Groundwater from the Shallow Bedrock in Central Vermilion County, Illinois

ABSTRACT

The background groundwater conditions in the shallow bedrock of central Vermilion County, Illinois, were assessed by reviewing available geochemical data and by analyzing a limited number of water and rock samples. Water samples were collected from monitoring wells and water-supply wells and were analyzed for anions, cations, and carbon and hydrogen isotopes. Rock samples were obtained from cores collected by KELRON and were analyzed using a portable infrared mineral analyzer and x-ray diffraction.

Great variability was observed in the geochemical data for the Pennsylvanian bedrock, Pennsylvanian groundwater, and other data collected for this project. Some of this variability is due to the different lithologies which included sandstone, shale, coal, limestone, and sand and gravel. Some of this variability is also due to the depth of the sample. For example, groundwater samples from KELRON 26 and 28 are significantly different from other samples because they were from shallow wells and are completely connected to the local groundwater system, whereas water samples from deeper wells were largely isolated from the local groundwater flow system. Overall, the geochemical data collected for this project are similar to the available data from Vermilion and surrounding counties.

1. INTRODUCTION

Using available data and limited sampling, we sought to define the background groundwater conditions in the shallow bedrock of central Vermilion County. Most of the wells sampled for this study were concentrated around the Middle Fork of the Vermilion River, as shown in figures 1 and 2. We had access to and sampled monitoring wells on land owned by Dynegy, Inc. as well as private and public water supply wells (figure 2) . Because of the limited number of Vermilion County wells completed in the bedrock, we sought and used available data from surrounding counties in Illinois and Indiana.

2. GEOLOGY

The surficial bedrock geology in Vermilion County is variable. The youngest formation, the Pennsylvanian-aged Bond Formation, is found beneath southwestern Vermilion County (figure 3). Pennsylvanian-aged bedrock underlies most of Vermilion County, except in the northern portion of the county where Mississippian and Devonian rocks are present. Older units can be found at the bedrock surface to the west and north, which reflects the erosional surface of the Mahomet Bedrock Valley and the structure of the Illinois Basin. In Vermilion County, the thickness of the Pennsylvanian bedrock varies from 0 feet in the

Figure 1. Map showing sampling locations in Illinois and Indiana

Figure 2. Map showing sampling locations in Vermilion County, Illinois

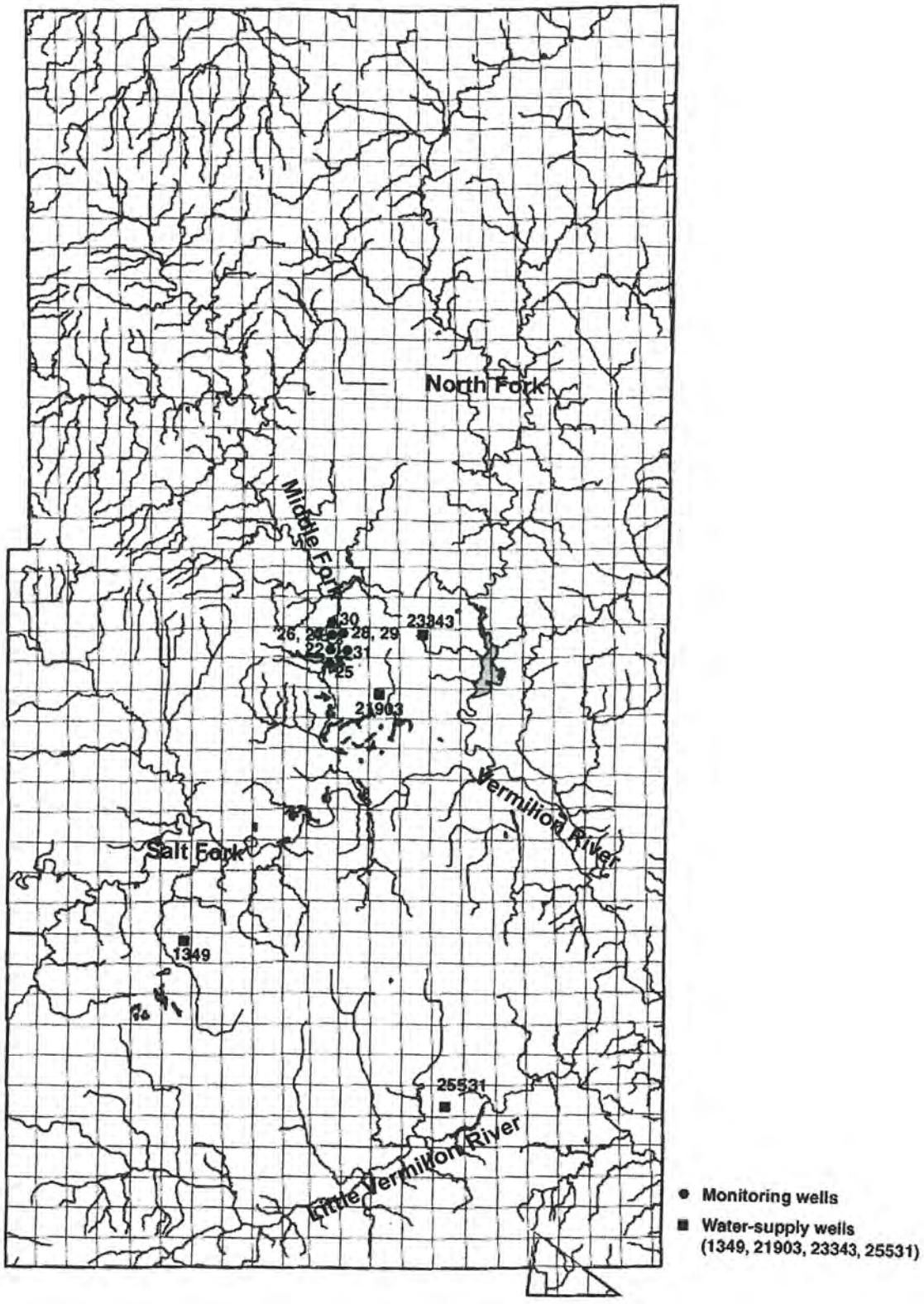
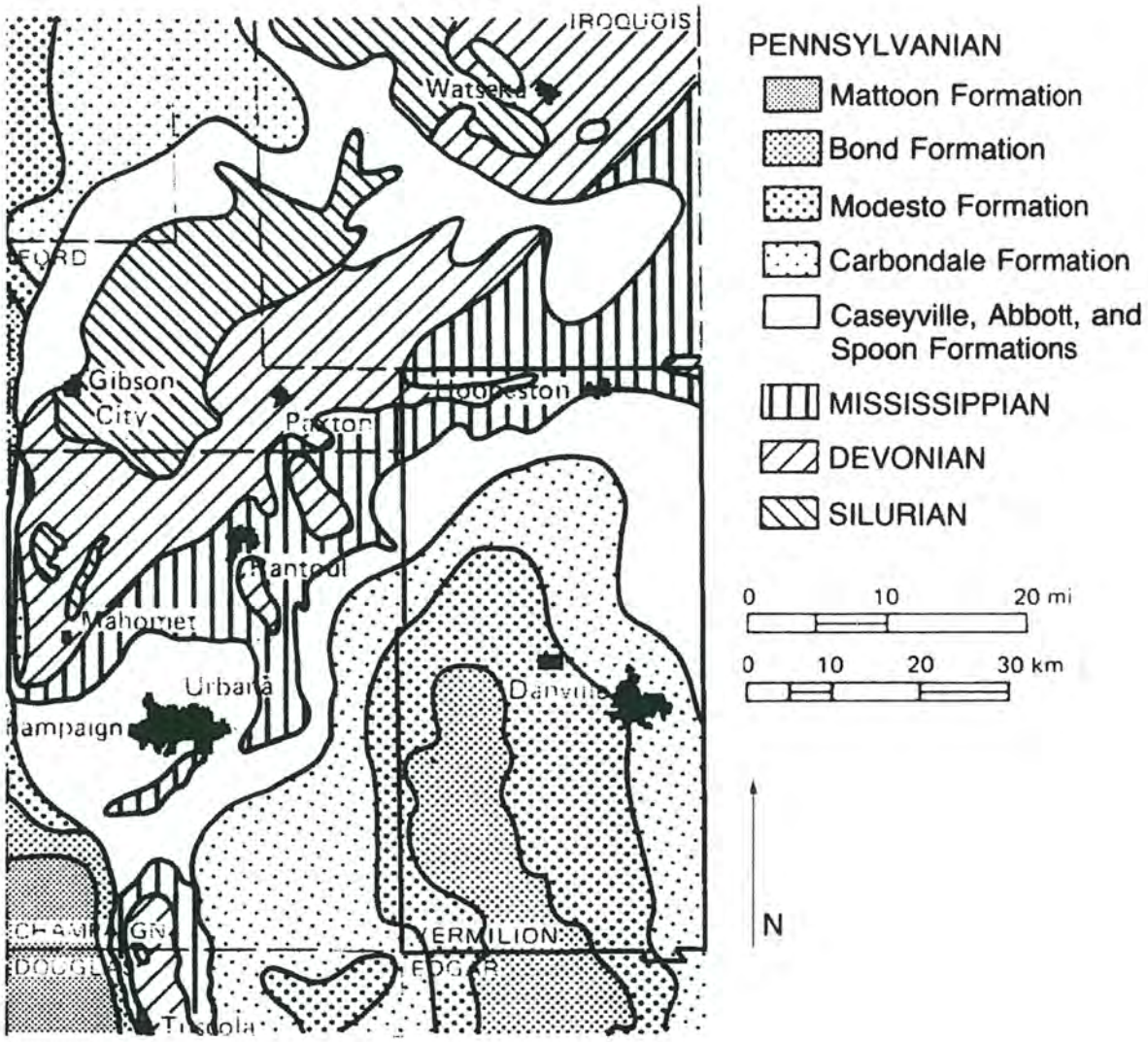


Figure 3. Surficial Bedrock Geology in Vermilion County (adapted from Kempton et al., 1982)



north to greater than 400 feet in the southeast (Willman et al., 1975).

The location of the Mahomet Bedrock Valley can be seen in the drift thickness map (figure 4). The thalweg of the valley, defined by the 400-foot thickness contour, runs east-west through the northern tier of townships in Vermilion County. In addition, a northwest-southeast trending tributary underlies parts of T23N R13W, T22N R13W, T22N R12W, and T21N R12W. The drift thickness also exceeds 200 feet in the southwest portion of the county. However, in the central portion of the county, the drift is generally less than 100 feet thick and bedrock outcrops are common in the river valleys (Piskin and Bergstrom, 1975).

KELRON collected core at 3 locations in T20N R12W (KELRON 25, KELRON 30, and KELRON 31). Descriptions of these cores appear in Appendices A and B. At this location, the uppermost bedrock was mapped as the Pennsylvanian-aged, Modesto Formation by Willman et al. (1975). The core from KELRON 30 penetrated 3 feet into the Danville (No. 7) Coal Member, which was considered the uppermost member of the Carbondale Formation. The stratigraphic nomenclature of the Pennsylvanian system was recently revised by the Tri-State Committee (2001). Using this new nomenclature, the bedrock from the three cores collected by KELRON (KELRON 25, KELRON 30, and KELRON 31) was assigned to the Shelburn Formation (Appendix A). Natural gamma logs for these wells, collected by the ISGS, appear in Appendix B.

In west-central Indiana, the surficial bedrock is Pennsylvanian-age along the IL-IN state line and Mississippian-age to the east (figure 5).

3. GEOCHEMISTRY

We reviewed the available geochemical data for both groundwater and bedrock from Vermilion County and surrounding counties in Illinois and Indiana. In addition, during June 2002, we collected groundwater samples from several monitoring wells and water wells. We also analyzed samples from core collected from three KELRON monitoring wells. To determine the geochemistry of the groundwater in chemical equilibrium with the host rock, equilibrium geochemical modeling was conducted.

3.1 Review of Available Data

To obtain data on the geochemistry of groundwater from Pennsylvanian bedrock and the Pennsylvanian
bedrock itself, we searched the scientific literature and databases at the Illinois State Geological Survey, Illinois State Water Survey, Illinois Environmental Protection Agency, and the Indiana Geological Survey. These data are summarized in tables 1 through 5. The locations for available groundwater samples are summarized by county in table 1. The geochemical data for these 31 samples are presented in table 2. The lithologies of the Pennsylvanian bedrock samples are summarized in table 3. We obtained data for 56 bedrock samples– 35 coal and 21 non-coal samples. The geochemistry of the non-coal samples (table 4) and the coal samples (table 5) has been summarized. Table 5 includes 1 sample from the Springfield (No.

Figure 4. Drift Thickness in Vermilion County (adapted from Piskin and Bergstrom, 1975)

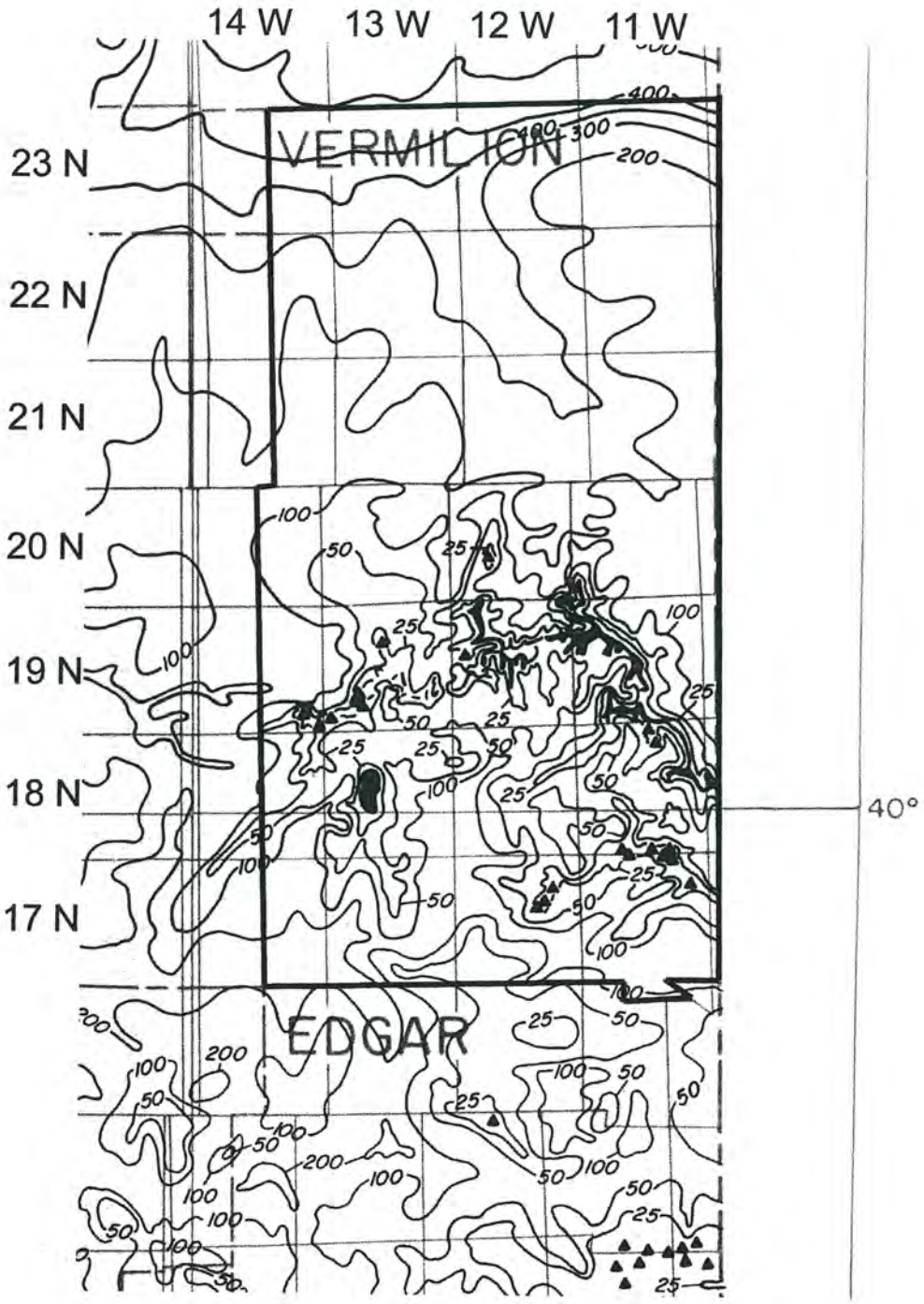


Figure 5. Surficial Bedrock Geology of west-central Indiana including Parke County (from Indiana Geological Survey, 1970) The dashed line shows the limit of the Wisconsin Episode glacial sediments.

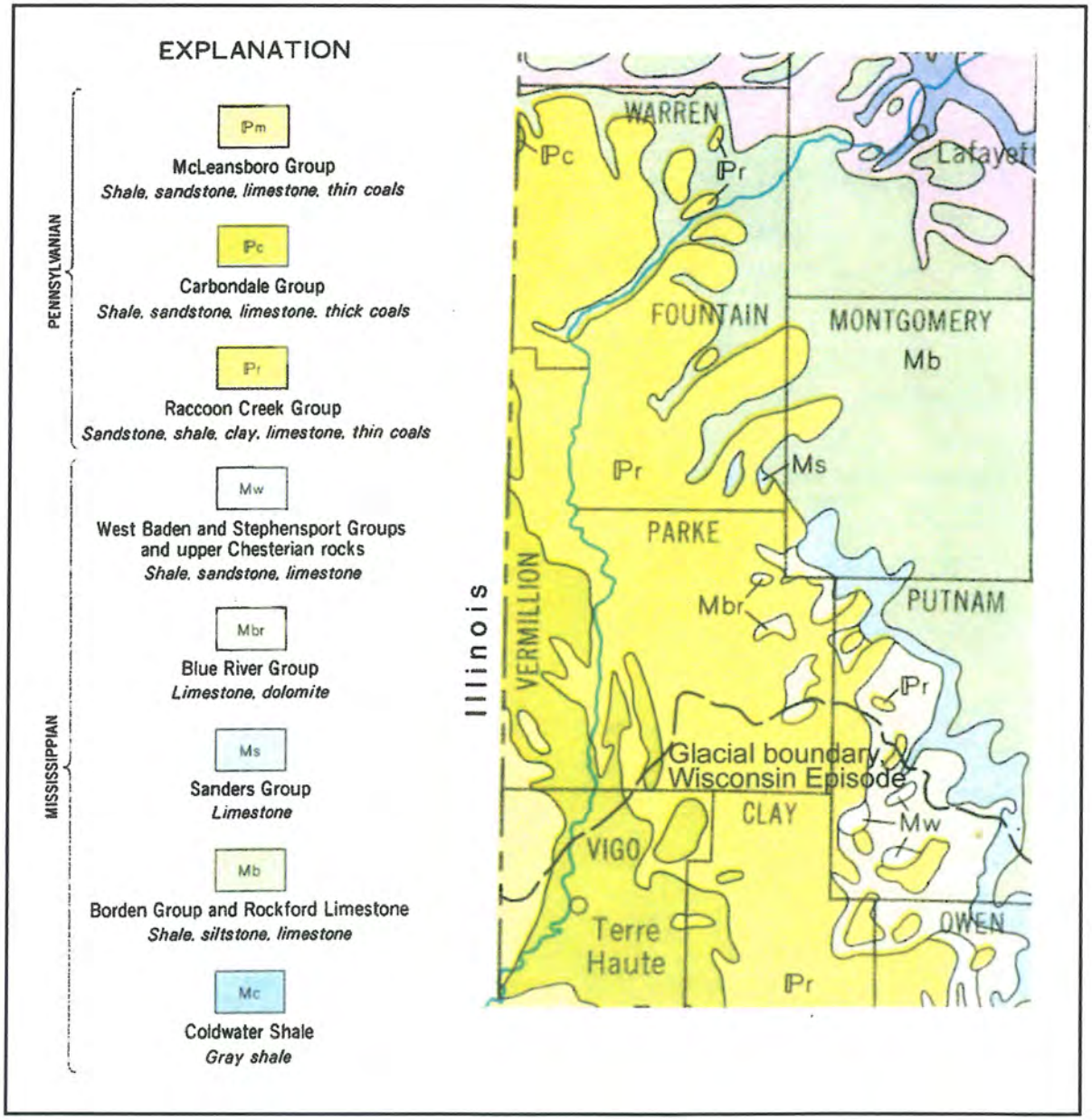


Table 1: Summary of available well data

County	# of Wells	Sampling Dates	Well Depths (ft)
Vermilion	6	10/9/74 - 11/9/93	72 - 220
Clark	1	6/3/99	155
Edgar	1	8/7/48	422
Christian	4	1/22/97 - 2/20/97	276 - 344
Parke (IN)	19	7/10/95 - 7/20/95	100 - 307
TOTAL	31	10/9/74 - 2/20/97	72 - 422

Table 2: Geochemical summary for available water samples
(Sources: Chugh et al., 1997; ISGS Geochemical Database, Meents et al., 1952)

	Units	# of Records	Minimum*	Maximum	Mean	Median
TDS	ppm	28	280	52100	3540	426
Alkalinity	mg/L as $CaCO_3$	30	56	485	321	335
pH	--	27	6.5	10.0	7.5	7.3
Temperature	°C	23	11.0	22.8	15.5	14.8
Bicarbonate	mg/L	31	63	591	389	407
Chloride	mg/L	31	2.1	30269	1689	13
Fluoride	mg/L	26	0.09	1.06	0.49	0.47
Nitrate	mg/L	31	<0.01	29.0	***	2.95
Sulfate	mg/L	31	<1	847	***	31
Aluminum	mg/L	27	<0.02	8.47	***	0.20
Arsenic	mg/L	30	<0.001	0.023	***	0.0050
Barium	mg/L	30	0.02	2.44	***	0.28
Boron	mg/L	30	ND**	2.08	***	0.0047
Cadmium	mg/L	30	<0.0002	0.0044	***	0.00020
Calcium	mg/L	31	<1	951	***	83
Chromium	mg/L	30	<0.001	0.005	***	0.0015
Iron	mg/L	31	<0.006	26.8	***	0.69
Lead	mg/L	29	<0.001	0.018	***	0.003
Magnesium	mg/L	31	<0.5	454	***	31.1
Manganese	mg/L	31	0.015	1.47	***	0.10
Mercury	mg/L	30	<0.00005	1.0	***	0.000025
Potassium	mg/L	30	0.67	63	7.4	2.1
Selenium	mg/L	30	<0.001	0.002	***	0.001
Silicon	mg/L	31	0.69	10.0	6.51	7.12
Sodium	mg/L	31	6	18078	1083	28.7
Zinc	mg/L	30	<0.01	1.43	***	0.21

* Some parameters had multiple detection levels. The lowest detection level is reported.
** Not detected, detection limit was not reported.
*** Sample data contain censored values, did not compute mean.

Table 3: Lithology of the available Pennsylvanian bedrock samples

Lithology	Number of Samples
Sandstone	2
Limestone	2
Shale	4
Carbonaceous Shale	13
Coal	35
TOTAL	56

Table 4: Geochemical summary for available non-coal solid samples
(Sources: Bradbury et al., 1962; Chugh et al., 1997; Schultz and Coveney, 1992)

Analyte	Units	# of Records	Minimum	Maximum	Mean	Median
Al_2O_3	wt. %	21	0.42	20.8	11.7	11.1
CaO	wt. %	21	0.15	54.1	7.57	1.27
Fe_2O_3	wt. %	21	0.63	21.4	8.65	7.02
K_2O	wt. %	21	0.09	4.20	2.51	2.61
MgO	wt. %	21	0.36	2.17	1.44	1.63
MnO	wt. %	18	0.017	1.83	0.20	0.045
Na_2O	wt. %	21	0.030	1.68	0.59	0.58
P_2O_5	wt. %	17	0.030	18.4	2.31	0.53
SiO_2	wt. %	21	2.09	85.7	37.0	33.8
TiO_2	wt. %	21	<0.1	0.92	***	0.51
As	mg/kg	18	19.8	119	57.7	53.8
B	mg/kg	18	31	385	123	112
Ba	mg/kg	18	122	543	***	333
Be	mg/kg	16	<1	4.8	***	2.0
Ce	mg/kg	18	52	233	134	125
Co	mg/kg	18	15.9	68.5	28.3	24.6
Cr	mg/kg	18	68.5	643	289	281
Cs	mg/kg	18	<2	13.4	***	7.0
Cu	mg/kg	16	9.0	192.3	94.3	84.3
Ga	mg/kg	18	6.5	29.3	18.7	17.9

Analyte	Units	# of Records	Minimum	Maximum	Mean	Median
Hg	mg/kg	6	<0.5	5.4	***	2.8
La	mg/kg	18	16.4	99.2	50.8	44
Li	mg/kg	16	11	130.	51.2	37.0
Ni	mg/kg	18	50.	530.	288	280
Pb	mg/kg	16	32	812	167	79
Rb	mg/kg	18	<3.	201	***	127
Sb	mg/kg	18	1.9	56.0	27.2	29.7
Sc	mg/kg	18	9.3	23.6	15.5	14.9
Se	mg/kg	18	4.0	260	104	97
Sr	mg/kg	18	<80	699	210	147
V	mg/kg	18	80.	5600	1770	790
Zn	mg/kg	18	30.3	3350	1000	522
Zr	mg/kg	16	20.8	103	***	49.3
Cl	mg/kg	7	240	698	532	563
Total Carbon	wt. %	17	0.91	>33	***	6.0
Inorganic Carbon	wt. %	17	0.02	11.7	1.7	0.49
Organic Carbon	wt. %	16	0.48	>33	***	3.7

*** Sample data contain censored values, did not compute mean.

Table 5: Geochemical summary for available coal samples
(Sources: Bradbury et al., 1962; Chugh et al., 1997; Schultz and Coveney, 1992; Yates, 1984)

	Sample Data						Illinois Basin Coals*		
	Units	# of Records	Min.	Max.	Mean	Median	Min.	Max.	Mean
Al	mg/kg	34	2300	16800	10400	10400	4300	30000	12000
As	mg/kg	35	0.4	52	***	5.1	1	120	14
B	mg/kg	32	37	149	97.3	99.0	12	230	110
Ba	mg/kg	33	8.9	231	64.6	38.8	5	750	100
Be	mg/kg	35	<0.12	2.5	***	1.5	0.5	4	1.7
Ca	mg/kg	34	1500	21300	8740	8100	100	27000	6700
Ce	mg/kg	33	2.0	30	10.0	8.0	4.4	46	14
Co	mg/kg	35	0.9	23.9	5.1	4.0	2	34	7.3
Cr	mg/kg	35	4.0	32	14.7	13.0	4	60	18
Cs	mg/kg	33	<0.3	3.2	***	0.9	0.5	3.6	1.4
Cu	mg/kg	35	2.0	39	10.6	9.0	5	44	14
Fe	mg/kg	35	4300	57900	19500	18600	4500	41000	20000
Ga	mg/kg	35	1.7	5.55	3.4	3.3	0.8	10	3.2
Hg	mg/kg	34	0.07	0.52	0.14	0.11	0.03	1.6	0.2
K	mg/kg	35	300	3800	1610	1500	400	5600	1700
La	mg/kg	33	1.2	12.7	***	4.2	2.7	20	6.8
Li	mg/kg	30	2.0	39.7	13.7	12.5	Not determined		
Mg	mg/kg	34	<100	2200	***	600	100	1700	500
Na	mg/kg	35	400	2300	989	1000	40	2000	500
Ni	mg/kg	35	2.0	93	15.7	9.0	7.6	68	21
Pb	mg/kg	35	2.0	191	***	8.0	0.8	220	32
Rb	mg/kg	33	1.6	44	13.1	11.5	2	46	19
Sb	mg/kg	35	0.06	3.3	1.0	0.8	0.1	8.9	1.3
Sc	mg/kg	33	0.8	5.2	2.7	2.6	1.2	7.7	2.7
Se	mg/kg	35	0.7	12.3	2.2	1.8	0.4	7.7	2.2
Si	mg/kg	34	3300	37800	21200	20700	5800	47000	24000
Sr	mg/kg	33	9	127	***	20.6	10	130	35
Ti	mg/kg	34	100	1000	550	500	200	1500	600
V	mg/kg	35	3.3	59	14.2	11	11	90	32
Zn	mg/kg	35	7.0	318	***	51.5	10	5300	250

	Sample Data						Illinois Basin Coals*		
	Units	# of Records	Min.	Max.	Mean	Median	Min.	Max.	Mean
Zr	mg/kg	33	3.1	42	20.3	18.0	12	130	47
Cl	mg/kg	22	400	4600	1700	1600	100	5400	1400
Org. S	wt. %	33	0.6	2.04	1.6	1.7	0.37	3.2	1.6
Pyr. S	wt. %	33	0.36	4.18	1.8	1.8	0.29	4.6	2
Su. S	wt. %	33	0.01	0.42	0.1	0.1	0.01	1.1	0.1
Tot. S	wt. %	33	1.68	6.01	3.5	3.5	0.56	6.4	3.6
Ash	wt. %	34	3.71	19.7	12.1	11.5	4.6	20	11

* Gluskoter et al.,1977

*** Sample data contain censored values, did not compute mean.

5) coal, 23 samples from the Herrin (No. 6) coal, 10 samples from the Danville (No. 7) coal, and one other sample whose stratigraphic source is unknown.

For the liquid samples, the available data have been plotted on box plots and a Piper diagram. A box plot shows the distribution of concentrations. The left side of the box shows the 25th percentile. The center of the box shows the 50th percentile or the median. The right side of the box shows the 75th percentile. The difference between the 75th percentile and 25th percentile is the Hspread, which is used to define outliers. The whiskers on the box show approximately the 5th percentile (left) and the 95th percentile (right). Additional data outside these ranges are shown with asterisks (points between 1.5*Hspread and 3*Hspread) and circles (points >3*Hspread). Box plots were constructed for major cations (figure 6) and anions (figure 7) using SYSTAT version 9. A Piper diagram (figure 8) was constructed for the water samples using RockWorks (Rockware Inc.).

Of the major cation concentrations, sodium (Na) had the greatest variability and calcium (Ca) and magnesium (Mg) had the least variability. Of the major anion concentrations, chloride (Cl) had the greatest
variability and bicarbonate (HCO_3) had the least variability. The Piper diagram will be discussed later in this report.

3.2 Summary of New Chemical and Mineralogical Data

New chemical and mineralogical data were obtained from samples of cores previously collected by KELRON (KELRON 25, KELRON 30, and KELRON 31). In addition, we collected groundwater samples from 6 KELRON wells and 4 water-supply wells in central Vermilion County. KELRON provided geochemical data for 7 wells.

Figure 6. Box plot of major cations for the available groundwater samples

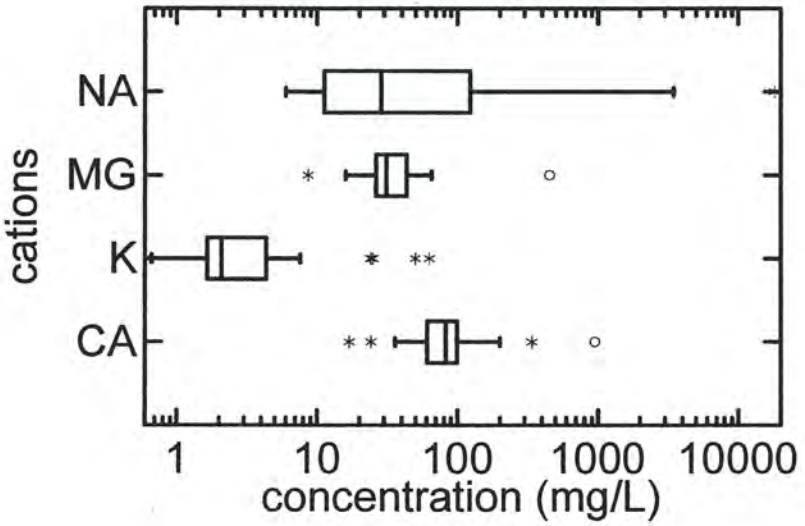


Figure 7. Box plot of major anions for the available groundwater samples

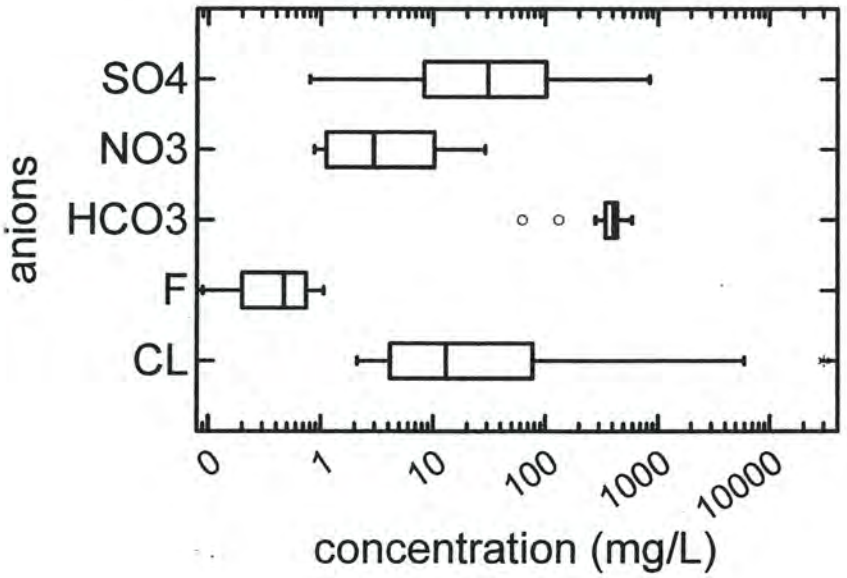
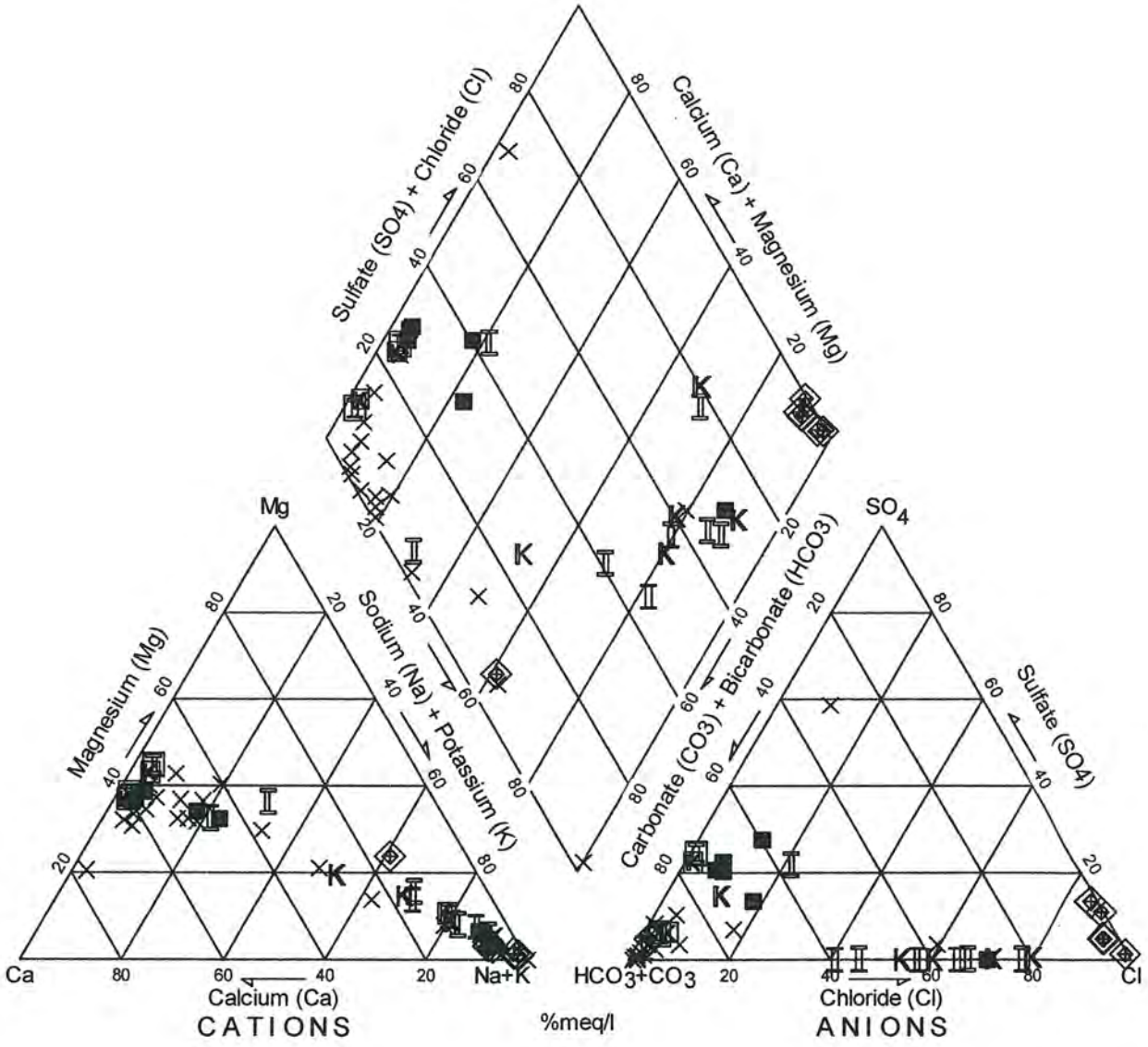


Figure 8. A Piper diagram of the groundwater samples (Vermilion Co., IL= squares, other IL counties= diamond, Parke Co., IN= x, ISGS samples= I and KELRON samples= K, non-bedrock samples from ISGS & KELRON are boxed.)



Analytical Methods

PIMA and X-ray diffraction (XRD) analyses. Core samples were analyzed using a portable infrared mineral analyzer (PIMA), manufactured by Integrated Spectronics Pty. Ltd. (Baulkham Hills, New South Wales, Australia). The PIMA-SP™ reflectance spectrometer (figure 9) provided analyses as quickly as one per minute, portability, and good data from irregular, round or flat core- or hand-specimen samples. The instrument's 1.25 cm-diameter window allowed close-interval core logging and determinations on small features in samples. In the analysis mode, the PIMA's 1300 to 2500 nm spectra were matched with reference spectra to determine percentages for up to six minerals. Quartz and feldspar produce no PIMA spectra, thus PIMA sees through these grains to give better-than-expected spectra for minerals that are usually of primary concern, e.g., clay minerals, iron hydroxides, and carbonates. Custom reference spectra can be created for the specific minerals of concern, and the spectral processing programs provide several methods for analyzing spectra, including instantaneous display of calculated features in each spectrum in a "special stack" from outcrop or borehole samples (figure 10).

For six geochemical-PIMA-XRD samples, the core was sawed and about a 15-cm-thick composite of half of the core was crushed and split. The other 13 samples of the three cores were removed, either by drilling perpendicular to bedding with a ¼ inch carbide drill bit, or, for core segments that broke into thin bedding layers, by breaking a 5 to10 g fragment of the layer. For PIMA and XRD analyses, all 19 samples were hand ground with a mortar and pestle, and packed into end-loading XRD sample holders. The samples were x-rayed using standard operating procedures (SOPs) on file at the ISGS. The same sample surface was later inverted into a calibrated petri dish for PIMA analyses. Hughes and Warren (1989) Hughes et al. (1994) and Hughes et al. (2002) summarize the methods used. Demir et al. (2001), Hughes et al. (1987), Hughes et al. (1989), Hughes et al. (1992), Hughes (1993), Hughes et al. (1994), and Hughes et al. (2002) summarize the range of composition normally found for these types of
sediments.

Smear samples. Smears of the particles with diameters <8μm were prepared by placing 1 to 3 g of sample in a 150 mL beaker, adding 100 mL of deionized H_2O, dispersing the slurry with an ultrasonic probe for 60 seconds, and allowing the samples to soak overnight. For samples that flocculated and had clear supernates, the clear water was decanted and the beakers refilled with deionized water. Five drops of dispersant solution were added to each of the beakers, each beaker was stirred for 30 seconds, and the samples were allowed to settle 3 minutes per cm of slurry depth. After settling, the fine fractions were poured into 400 mL glass beakers and flocculated with $CaCl_2 \cdot nH_2O$. The glass beakers were refilled, two drops of dispersant were added, the mixtures were stirred, allowed to settle, and the fine fractions were added to the glass beakers containing the first settlings. A third settling was completed, and the >8 μm fractions were allowed to dry, after which, the sample and beaker were weighed, to estimate the weights of the coarse and fine fractions. The <8 μm fractions were flocculated and allowed to settle overnight, the clear supernate was decanted, the fines were transferred to 40 mL centrifuge tubes, and after centrifuging 20 minutes @ 2000 RPM, the clear supernates were decanted, the sediment plugs were thoroughly mixed with a microspatula, and the paste was smeared on a round, glass XRD slide. After the smear dried in air, the slides were x-rayed using ISGS SOPs.

Figure 9. A typical laboratory setup for PIMA showing the power supply at left, a limestone sample on the PIMA's analysis window on the tabletop, and a laptop computer with a spectrum for pure calcite from a limestone sample.

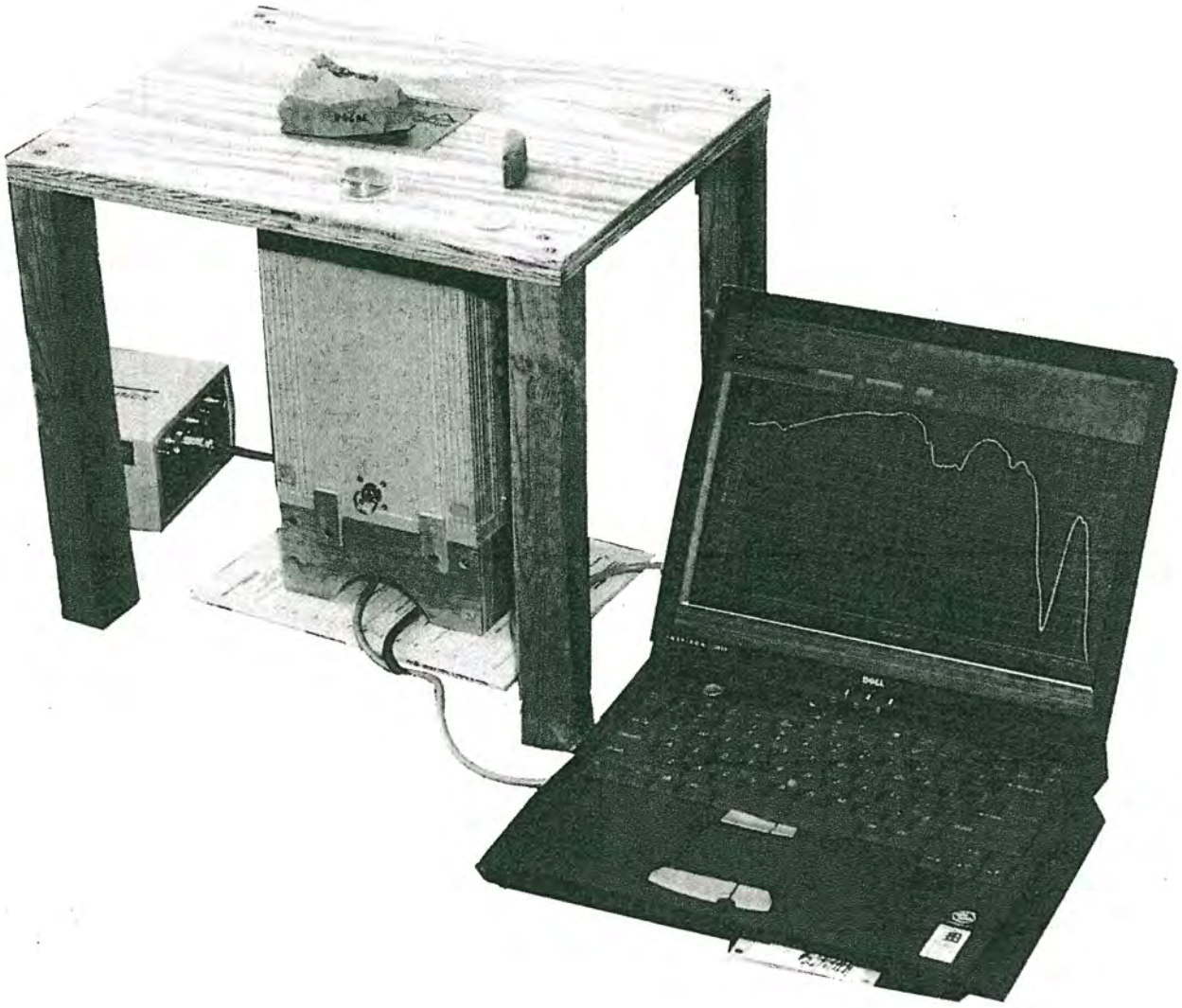
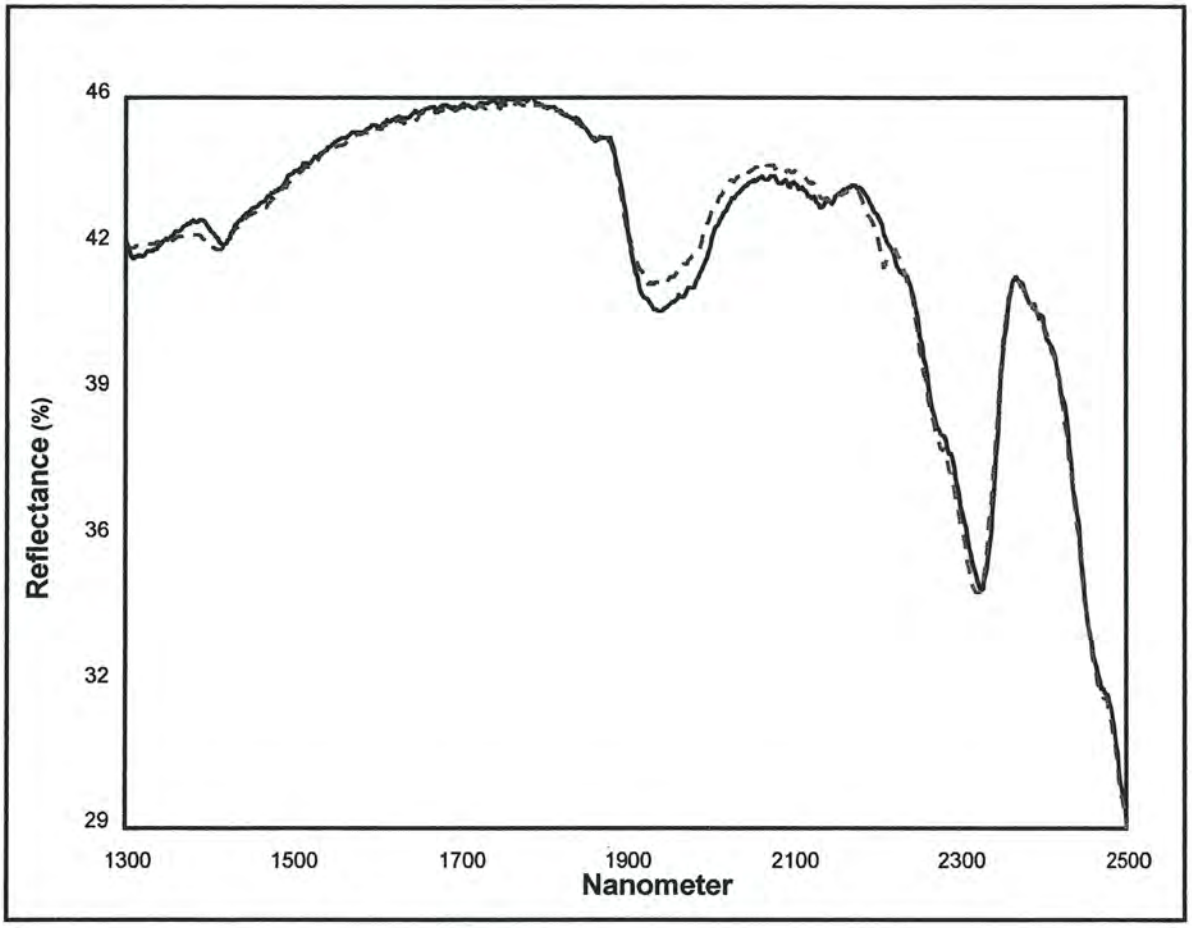


Figure 10. Overlay of the spectrum for western Illinois dolomite (dark trace) and a calculated spectrum (light, dashed trace) for 100% dolomite (PIMA's MinIDB reference standards library).



Water samples. Water samples were collected from monitoring and water-supply wells. Groundwater samples from the KELRON monitoring wells were collected using Dynegy-owned equipment including dedicated, low-flow sampling pumps. The June 18, 2002 samples were collected as split samples during Dynegy's regular sampling. Groundwater samples from water-supply wells were collected using the installed pumps, from taps prior to any water treatment such as water softeners. Prior to sample collection, field parameters (temperature, dissolved oxygen, pH, Eh, and specific conductance) were monitored and were allowed to stabilize, unless the well appeared to be running out of water. Water samples were transported on ice and stored at 4°C until analyzed.

Water samples collected by the ISGS were analyzed for anions and cations by the ISGS Geochemistry Laboratory. Anions were determined using a Dionex DX-120 Ion Chromatograph with Ionpac AG14 Guard Column, Ionpac AS14 Analytical Column, and ASRS-ULTRA (4mm) suppressor module. Analytes were measured with a CDM-3 conductivity detector cell with a DS4 detection stabilizer. The eluent was 3.5mM sodium carbonate and 1.0 mM sodium bicarbonate. The following were approximate retention times in minutes: fluoride, 2.9; chloride, 4.0; bromide, 5.6; nitrate, 6.4; phosphate, 8.0; and sulfate, 9.5. Instrument operation and data collection were controlled using PeakNet 5.01 software. A calibration check standard and blank were run with each analysis set.

Cations were determined with a Thermo Jarrell-Ash Model ICAP 61e inductively coupled plasma spectrometer. The list of elements and their wavelengths in nanometers are: Al(308.2), As(193.6), B(249.6), Ba(493.4), Be(313.0), Ca(393.3, 317.9), Cd(228.8), Co(228.6), Cr(267.7), Cu(324.7), Fe(259.9, 271.4), K(766.4), Li(670.7), Mg(279.5, 383.2), Mn(257.6), Mo(202.0), Na(588.9, 330.2), Ni(231.6), P(214.9), Pb(220.3), S(182.0), Sb(206.8), Sc(361.3), Se(196.0), Si(288.1), Sr(421.5), Te(214.2), Ti(334.9), Tl(190.8), V(292.4), and Zn(213.8). Instrument operation, inter-element interference correction, background correction, and data collection were controlled using ThermoSPEC/AE 6.20 software. Blanks, calibration check standards, and reference standards were run with each analysis set.

For tritium analyses, water samples were collected in 1L HDPE bottles. Tritium was determined with 200 mL of water using the enrichment technique (Ostlund and Dorsey, 1977). The tritium enriched samples were purified by vacuum distillation, mixed with a scintillation cocktail, and counted in a low-level scintillation counter (Packard 2000 CA/LL). The tritium results are reported in tritium units (TU), which is defined as one tritium atom per 10^{18} hydrogen atoms.

The dissolved inorganic carbon (DIC) in water was analyzed at the ISGS for carbon-14 activity using conventional techniques (Hackley, 2002). The DIC is extracted from water samples by the addition of acid. The carbon dioxide released from water samples is quantitatively collected and cryogenically purified on a vacuum line. The purified carbon dioxide is converted to high-purity benzene following the technique described in Coleman (1976). The carbon-14 activity is measured using the liquid scintillation spectrometry method developed by Noakes et al. (1965, 1967).
Groundwater samples from the KELRON wells also were collected and analyzed by Dynegy. Prior

to sample collection, Dynegy monitored several field parameters (temperature, dissolved oxygen, pH, Eh, and specific conductance) using a calibrated Hydrolab Minisonde. Cations were determined by inductively coupled plasma emission spectroscopy (ICP) (USEPA method 200.7). Alkalinity was determined by a titrimetric method (USEPA method 310.1). Total dissolved solids were determined by a gravimetric method (USEPA method 160.1). Sulfate was determined using a turbidimetric method (USEPA method 375.4). Total phosphorus was determined using an ascorbic acid/colorimetric method (USEPA 365.2). Finally, chloride was determined using a potentiometric method (Standard method 4500-Cl).

Solid Samples

Detailed descriptive logs (see DeMaris logs, Appendix A) were compiled for three new holes drilled by KELRON and used to select 19 samples for PIMA-SP™ and XRD analyses. Table 6 gives the lab number, core number, depth, and material type for the 19 samples. The coal in core KELRON 30 had been sealed, and a sample of the white oxidation product on top of the coal was analyzed by PIMA and XRD. Separately, one or two siderite nodules were analyzed, and 19 PIMA and XRD samples were chosen to contrast the mineralogical composition of silt- and clay-rich zones. Over 90 PIMA analyses were run for this project, 54 on the cores, and 39 on bulk and <8μm smear samples. The results from the PIMA analyses of the cores were quite uniform, suggesting that little mineralogical variation was present. Table 6 gives the XRD analysis results for bulk sample preparations that show: a) 10 to 60% clay minerals, b) 35 to 75% quartz, 0 to 3% K-feldspar, 2 to 13% plagioclase feldspar, and 0 to 10% siderite. Samples 3955S and T also contained 2.3 and 10% pyrite/marcasite, respectively. The iron sulfide in both samples is mostly marcasite, a form of the compound that oxidizes very quickly. The needle-like white precipitate above the coal in core KELRON 30 is undoubtedly the result of this rapid oxidation. In general, silt-rich samples had lower clay mineral contents and higher quartz and feldspar contents than shaly zones.

The XRD analyses of the <8μm smear samples (table 7) showed that the clay mineral suites were composed mostly of illite, kaolinite, chlorite, and small amounts of mixed-layered illite/smectite (I/S). Coarser, more permeable zones normally have higher fluid flow rates and this results in higher kaolinite contents, and so as expected, the silt-rich samples in this set contained relatively more kaolinite, a higher kaolinite:chlorite ratio, and less illite, I/S, and chlorite. Table 8 gives the ranges of the clay mineral contents from the smear slides- 50 to 65% illite, 12 to 32% kaolinite, 9 to 22% chlorite, and 3 to 7% I/S (atypical sample 3955T had 19% I/S).

PIMA analyses of core, hand specimen, bulk powder, and smear samples confirmed the generally uniform composition of these strata, but showed significant differences in the compositions of the silty and shaly samples. These results also are qualitatively consistent with the XRD results. Finally, the PIMA analyses of the core required only a few minutes each, and these results confirmed the value of the PIMA to identify compositional changes and refine the sample selection process.

Table 6. PIMA-XRD sample description and mineral percentages from XRD analysis

Well	Sample No.	Depth (ft)	Material	% Clay minerals	% Quartz	%K-Feldspar	%Plagiclase feldspar	% Siderite
KELRON 25	3955A1	18.17	siltstone	14	72	2.3	10	1.2
	3955A2	18.13	siltstone	14	69	0.9	12	3.6
	3955A3	18.10	shale	25	61	0.8	8.8	4.5
	3955B	28.17	shale	11	74	0.0	12	2.6
	3955C	36.0	shale	26	59	1.1	8.1	5.8
	3955E	12.55-12.75	silty-shale	21	63	1.8	11	3.6
	3955G	32.0-32.25	shale	23	61	0.0	9.0	6.5
KELRON 31	3955I	156.6-156.8	shale	24	60	1.5	10	3.8
	3955J1	154.22	shale	27	56	1.2	11	4.5
	3955J2	162.0	shale	22	55	0.0	13	10
	3955K	165.7-165.95	shale	26	60	1.5	8.4	4.0
	3955L	178.18	shale	36	53	0.0	7.8	2.8
	3955M	174.4-174.62	shale	34	53	0.0	7.4	5.0
KELRON 30	3955N	120.3	shale	24	67	0.0	9.1	0.0
	3955O	127.2-127.45	shale	34	52	1.4	8.8	4.2
	3955P	132.5	shale	36	55	0.0	7.2	2.6
	3955Q	136.25-136.43	shale	40	51	0.0	5.1	3.2
	3955S	141.15-141.4	shale	39	49	0.0	6.2	3.1
	3955T	144.0	C-Py-shale	56	30	2.5	2.0	0.0

Key: C = carbonaceous; Py = pyritic (pyrite or marcasite)

Samples 3955S and T had pyrite/marcasite, which was mostly marcasite; percentages = 2.3 and 6.7%, respectively.

Table 7. Percentages of mixed-layered illite/smectite, illite, kaolinite, and chlorite from X-ray diffraction data based on 8μm smear samples. The ratio of kaolinite:chlorite (K:C), the clay index (CI), and %<8μm also are given.

Sample	%I/S	%I	%K	%C	K:C	CI	%<8μm
3955A1	3.6	48	32	16	0.67	0.73	35
3955A2	3.9	48	30	18	0.63	0.78	49
3955A3	4.0	62	15	19	0.44	0.87	54
3955B	3.3	51	29	16	0.64	0.81	38
3955C	4.5	62	16	17	0.48	0.84	59
3955E	5.0	59	17	18	0.49	0.91	31
3955G	4.5	60	17	19	0.47	0.89	39
3955I	5.8	58	15	21	0.42	0.88	40
3955J1	5.8	60	16	18	0.47	0.90	44
3955J2	4.9	60	17	18	0.49	0.83	57
3955K	4.3	64	13	19	0.40	0.89	47
3955L	5.0	60	13	22	0.36	0.86	79
3955M	5.1	60	14	21	0.39	0.85	72
3955N	4.8	57	18	20	0.48	0.88	47
3955O	5.4	62	13	20	0.41	0.88	75
3955P	6.0	59	14	21	0.39	0.85	75
3955Q	6.4	58	13	22	0.38	0.85	91
3955S	6.6	61	12	20	0.39	0.86	88
3955T	19	60	13	8.6	0.60	0.81	62

Key: I/S = mixed-layered illite/smectite; I = illite; K = kaolinite; C = chlorite; K:C = the ratio of the kaolinite 002 peak to the chlorite 004 peak; CI = the clay index, which equals the corrected sum of the peaks for the clay minerals divided by the sum of the corrected intensities of the clay and nonclay minerals; the higher the ratio, the higher the clay mineral content; the %<8μm was estimated from the initial weight of the sample minus the final weight of the >8μm.

Water Samples

The ISGS sampled the wells described in table 8 in mid- to late June 2002. These wells included 6 monitoring wells and 4 water-supply wells located in Vermilion County. All but two wells were completed in shallow bedrock. Two monitoring wells (KELRON 26 & 28), completed in shallow Quaternary materials, were sampled to provide data on shallow groundwater. The chemical data for the ISGS samples are summarized in table 9. Dynegy sampled numerous monitoring wells from February through August 2002 (table 10). Some of these data are reported here. On June 18th, split samples were collected from 6 KELRON wells and sent to ISGS and Dynegy laboratories. The results for these split samples were within 20%, except for a few samples for chloride, iron, and potassium.

Table 8. Description of wells sampled by the ISGS and/or Dynegy

Well #	Location	Total Depth (ft)	Lithology @ screen
1349	T18N, R13W, Sec 9	72	sandstone & shale
21903	T20N, R12W, Sec 34	147	sandstone & shale
23343	T20N, R12W, Sec 23	175	sandstone & shale
25531	T17N, R12W, Sec 1	140	rock & shale
KELRON 25	T20N, R12W, Sec 29	39	shale
KELRON 26	T20N, R12W, Sec 20	16	sand & shale
KELRON 27	T20N, R12W, Sec 20	44	shale
KELRON 28	T20N, R12W, Sec 21	15	sand & silt
KELRON 29	T20N, R12W, Sec 21	45	shale
KELRON 30	T20N, R12W, Sec 20	148	shale & coal
KELRON 31	T20N, R12W, Sec 21	184	shale

The range of concentrations of major anions (figure 11) and major cations (figure 12) for the samples collected for this study (by the ISGS and Dynegy) are shown by the dots, while the box plots display the available data. These box plots were generated using GRAPHER version 3. The whiskers cover the entire range of data, which differs from the whiskers for the SYSTAT box plots (e.g., figure 6).

The dot and box plots are similar; thus, the data collected from the sampled wells are similar to the available data, which cover a broader geographic area. Only 2 sampled wells (well 23343 and KELRON 26) had TDS values below 250 mg/L. Well 23343 is a 175-foot, domestic well completed in bedrock. KELRON 26 is a 16-foot monitoring well completed in Quaternary geologic materials. Another shallow monitoring well, KELRON 28, had a TDS similar to the bedrock wells.

Some of the concentration data can be explained by the lithology of the aquifer materials (table 8). KELRON 30 was completed in shale and coal, wells 1349, 21903 and 23343 in sandstone and shale, well
25531 in rock and shale, KELRON 26 and 28 in sand, while the remaining wells were completed in shale. For example, a groundwater sample from KELRON 30 (the only well completed in coal) had the highest concentration of Ba, Li, Na, and Cl. Data from tables 4 and 5 show that coal generally has higher concentrations of Cl than other geologic materials.

Table 9. Geochemical data for ISGS sampled wells

	Well Number									
	1349	21903	23343	25531	KELRON 25	KELRON 26	KELRON 27	KELRON 28	KELRON 29	KELRON 30
n*	1	1	1	1	2	2	2	2	2	2
Al	<0.1**	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
As	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
B	0.29	0.50	1.4	1.2	1.14	.055	.086	0.09	1.2	0.93
Ba	0.14	0.98	0.26	0.47	2.0	0.031	0.77	0.034	0.55	5.3
Be	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ca	131	44.2	67.4	36.8	84.4	87.3	34.8	186	30.4	42.0
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	2.4	<0.01	1.6	3.8	0.06	<0.01	0.20	0.04	0.22	1.9
K	3.0	4.0	5.0	5.0	6.5	3.5	4.5	<1	4.0	7.0
Li	0.01	0.02	0.01	0.06	0.07	<0.01	0.04	0.03	0.04	0.10
Mg	56	29	45	27	45	34	21	98	15	29
Mn	0.11	0.041	0.035	0.041	0.057	<0.001	0.020	0.081	0.015	0.047
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na	67	240	68	590	430	1.9	300	16	290	870
Ni	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.005	0.005	<0.01
Pb	<0.02	<0.02	<0.02	<0.02	<0.02	0.015	0.015	<0.02	<0.02	<0.02
S	49	0.03	5.4	0.38	0.46	7.9	0.19	72	0.3	1.5
Sb	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Sc	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Se	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Si	8.0	3.4	7.5	3.3	5.4	4.4	6.1	6.2	5.8	4.7
Sr	0.23	0.52	1.5	0.57	0.7	0.1	0.4	0.3	0.4	0.8
Ti	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tl	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
V	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

	1349	21903	23343	25531	KELRON 25	KELRON 26	KELRON 27	KELRON 28	KELRON 29	KELRON 30
Zn	0.055	<0.001	0.018	0.074	<0.001	<0.001	<0.001	0.004	<0.001	0.003
F	0.2	0.2	0.5	0.5	0.5	0.1	0.7	0.1	0.8	0.7
Cl	100	230	5.0	640	690	7.0	320	7.0	240	970
Br	<0.05	<0.05	<0.05	0.72	1.3	<0.05	0.61	<0.05	0.51	2.5
NO_3-N	<0.02	<0.02	<0.02	<0.02	<0.02	6.7	<0.02	<0.02	<0.02	0.15
PO_4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
SO_4	140	<0.1	11	0.6	1.0	19	0.2	190	0.6	3.2
Total Alk	380	460	390	480	280	280	340	600	400	670
pH	7.7	7.8	8.2	8.0	7.8	7.9	8.0	7.9	8.1	8.2
TDS	470	550	210	1300	1300	150	700	450	590	1900

* n= number of samples. For n>1, average values are reported.

**: All values are reported in units of mg/L except pH.

Table 10. Geochemical data from KELRON well samples

Parameter	Units	Well Number						
		KELRON 25	KELRON 26	KELRON 27	KELRON 28	KELRON 29	KELRON 30	KELRON 31
n*	–	7	1	7	1	7	7	7
pH	--	7.3	7.2	7.6	7.0	7.5	7.4	7.2
Temperature	°C	12.5	11.6	12.0	13.6	13.0	14.5	12.4
TDS	mg/L	1500	350	900	900	830	2400	860
Alkalinity	mg/L	280	290	330	600	390	670	560
B	mg/L	1.2	<0.05	0.83	0.11	1.1	0.9	0.7
Ba	mg/L	1.6	0.03	0.7	0.03	0.47	4.6	0.58
Ca	mg/L	85	92	32	190	29	34	82
Fe	mg/L	0.15	<0.025	0.18	0.05	0.26	1.8	0.40
K	mg/L	5.8	2.2	3.7	0.88	3.7	7.7	9.5
Li	mg/L	0.11	<0.005	0.04	0.03	0.05	0.12	0.10
Mg	mg/L	45	34	20	94	15	25	35
Mn	mg/L	0.05	<0.005	0.02	0.07	0.01	0.04	0.08
Na	mg/L	390	3.1	270	17	260	890	170
Sr	mg/L	0.57	0.07	0.4	0.3	0.3	0.7	0.7
Cl	mg/L	820	12	360	11	320	1200	59
PO_4	mg/L	0.03	0.10	0.02	0.01	0.03	0.04	0.06
SO_4	mg/L	6.6	20	<5	170	<5	6.5	110

* n= number of samples. For n>1, average values are reported.

Figure 11. Major anions: box plot for the available wells along with dot plots of the ISGS (+) and Dynegy (◇) samples

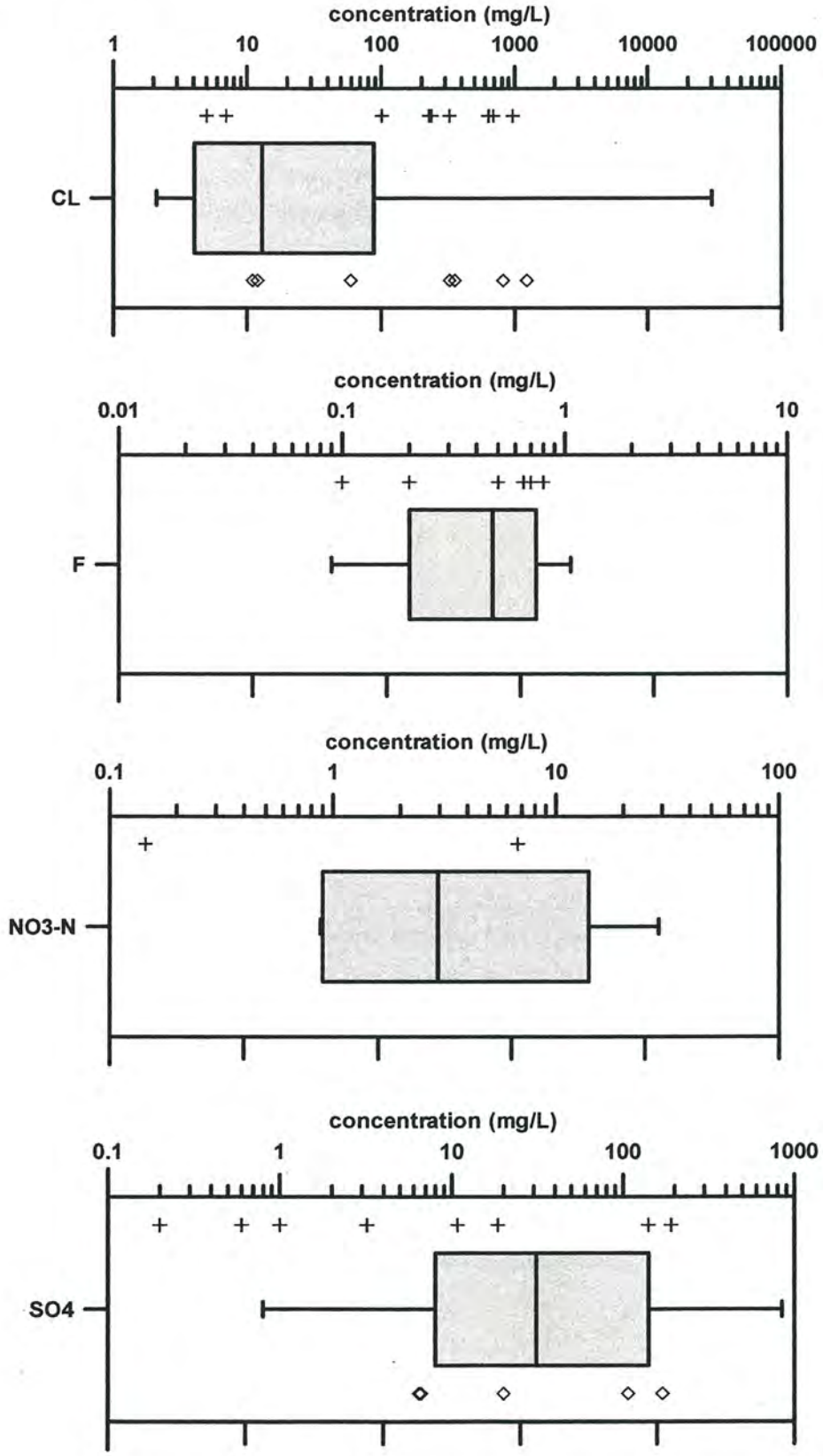
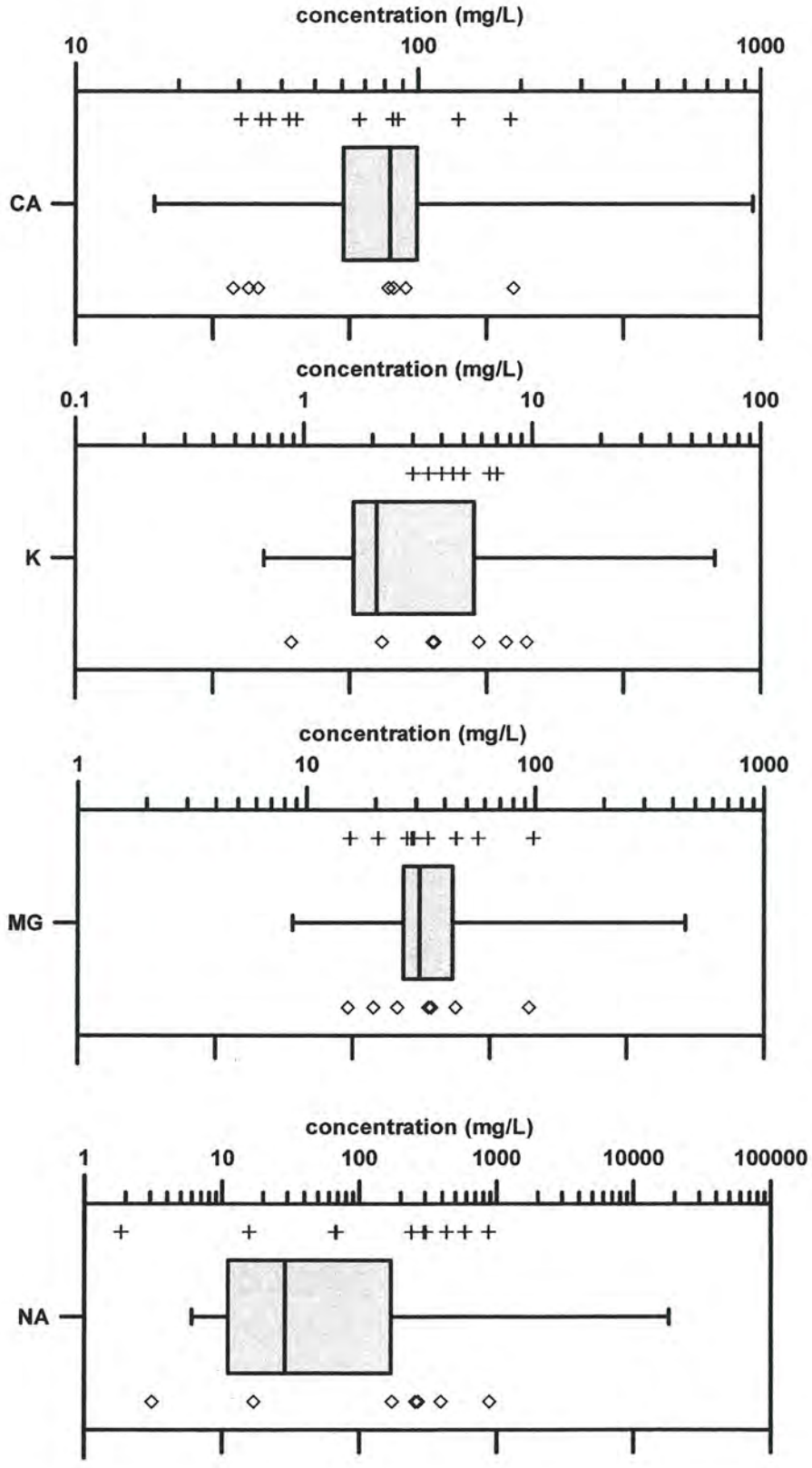


Figure 12. Major cations: box plot for the available wells along with dot plots of the ISGS (+) and Dynegy (◇) samples



The concentration data for the ISGS and Dynegy groundwater samples were also plotted on a Piper diagram (figure 8). The major cation concentrations for these groundwater samples appear in the left-hand ternary plot of the Piper diagram (figures 8 & 13). The linear nature of the data points leads to the hypothesis that groundwater with the greater concentrations of sodium plus potassium (Na+K, e.g., KELRON 27 or KELRON 29) migrated over a longer distance from the recharge area to the respective well than samples with lower concentrations of Na+K (e.g., well 23343). During migration, the groundwater dissolved increasingly greater amounts of sodium from the aquifer rocks and increasing amounts of calcium and magnesium were removed from the water, probably by adsorption by clay minerals in the aquifer rocks. In general, the chemistry of the water samples tends to cluster based on the lithology of the geologic materials in which they are screened. For example, the two wells completed in Quaternary materials plot to the far left in figure 13, and wells 1349 and 23343 (sandstone and shale) in the center of the plot. Well 25531 is the only well that does not fit this pattern.

The diamond-shaped plot in the Piper diagram (figure 8) indicates that for the water samples collected in June 2002, 35% displayed temporary hardness (moderate amounts of Mg, Ca, and HCO_3^-); 41% of these samples are classified as saline (contained relatively large amounts of Na and Cl); the remaining samples were of intermediate classification between temporary hardness and saline.

The position of water quality results plotted on a Piper diagram can be misleading, however, because the Piper diagram is based on the mole percent of four major cations and four major anions. For a given water sample, the number of moles of each of the eight major ions is calculated, then the mole percent is calculated on the basis of the total moles of either cations or anions, respectively. The mole percent of sodium, for example, in a water sample that contains low concentrations of the major cations and anions can be the same as in a water sample that contains high concentrations of major anions and cations. A water that is classified as temporarily hard might not be hard at all, according to the accepted definition of hard water. The hardness of water is defined by the concentration of calcium carbonate in the water. Water containing 0 to 60 mg $CaCO_3$/L is defined as "soft," whereas water that contains 121 to 180 mg $CaCO_3$/L is defined as "hard" (Hem, 1970).

The carbon and hydrogen (tritium) isotopic data (table 11) reveal that some wells produce recent water, while others yield much older water. Tritium values in Illinois precipitation typically range from 3 to 10 tritium units (TU) (Hackley et al., 1996; Hackley, personal communication, 2002). Tritium is generated in the atmosphere. In the subsurface, tritium decays exponentially with a half-life of 12.3 years (Freeze and Cherry, 1979). Thus, water with tritium concentrations greater than 5 TU is considered recent water (wells 1349, KELRON 26, and KELRON 28), while water with nondetectable tritium concentrations is considered to be >50 years old. ^{14}C has a longer half-life than tritium and is expressed as radiocarbon years before present (RYBP) and as % modern carbon. Both units provide relative ages. Due to the complexities of carbon chemistry, a great deal of additional analysis is needed to obtain definitive dates. The ^{14}C data are consistent with the tritium data, showing that three wells (wells 1349, KELRON 26 and KELRON 28) yield recent water and the others yield much older water. Two wells (KELRON 26 and

Figure 13. Cation plot of the Piper diagram for ISGS and Dynegy samples

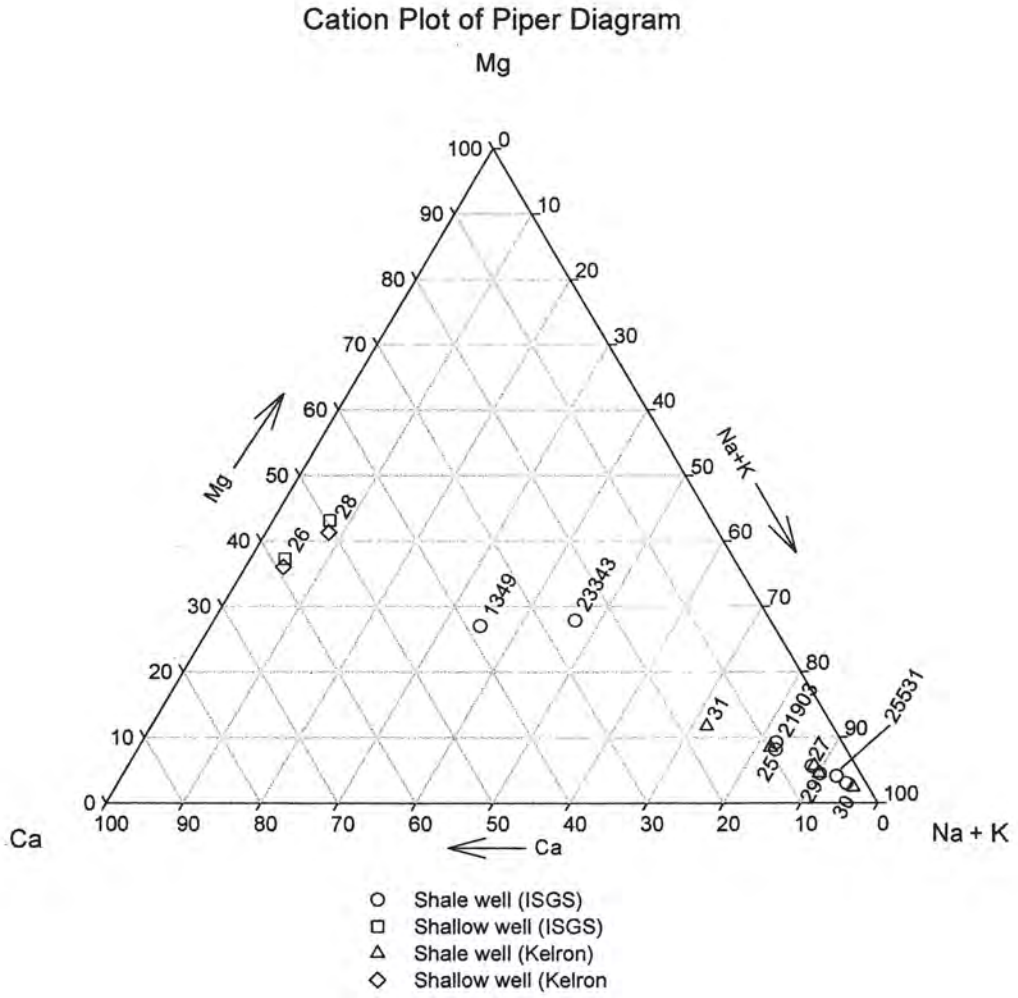


Table 11. Isotopic data for ISGS sampled wells

Parameter	Units	Well Number							
		1349	25531	KELRON 25	KELRON 26	KELRON 27	KELRON 28	KELRON 29	KELRON 30
^{14}C	RYBP	2,180	21,160	13,920	210	19,400	modern	34,610	20,850
	% modern carbon	76	7.2	18	97	8.9	102	1.4	7.5
Tritium	TU	7.8	<0.43	<0.43	5.3	<0.43	5.8	<0.52	<0.43

KELRON 28) were completed in Quaternary geologic materials and appear to draw water from the local groundwater flow system. The third well (well 1349) is completed in the shallow bedrock, but apparently draws some recent water from the overlying Quaternary geologic materials. The remaining wells (KELRON 25, KELRON 27, KELRON 29, KELRON 30, and KELRON 31) apparently draw water from the bedrock and are either only slightly connected to or completely isolated from the local groundwater flow system.

When expressing ^{14}C as % modern carbon, ^{14}C has an inverse linear relationship with TDS, sodium, and chloride and a positive linear relationship with calcium. These relationships were determined using linear regression and had coefficients of determination or R^2 ranging from 0.46 (for TDS) to 0.73 (for Ca).

3.3 Equilibrium Geochemical Modeling

The geochemical model, MINTEQA2 (Allison et al., 1990), is an equilibrium geochemical model used to calculate the theoretical composition of an aqueous solution at equilibrium, with or without contacting solids (minerals). Because they are in dynamic relationships with their environment, most groundwater systems are not at equilibrium. The use of a geochemical equilibrium model, however, provides an approximation of the geochemical reactions that might occur in a groundwater system.

Input data for MINTEQA2 from the two KELRON wells screened in Pennsylvanian shale (KELRON 25 and KELRON 30) included major element water chemistry and selected mineral components of the shale in the screened interval of the wells. The aqueous components input to the model were carbonate (from alkalinity determinations), calcium, iron (as Fe^{2+}), magnesium, potassium, sodium, silicon (as H_4SiO_4), chloride, sulfate, Eh, and pH. Trace elements were not used because of their negligible influence on the water chemistry. The only minerals included in the model were kaolinite, quartz, and siderite. Thermodynamic data for other minerals present in the shale, such as illite, K-feldspar, plagioclase feldspar, and chlorite, were not available in the model's database. Kaolinite, quartz, and siderite were set as infinitely available, i.e., they were assumed to never completely dissolve from the rock.

In operation, MINTEQA2 initially calculates the charge balance of the input solution. The errors for the charge balances between anions and cations were 2% and 6% for KELRON 25 and KELRON 30, respectively, using data derived by the ISGS for the aqueous composition. After the initial calculation of the charge balance, the model determines which minerals in its database could potentially precipitate, due to the components in the aqueous phase. For example, if manganese were not present as an aqueous component, then rhodochrosite ($MnCO_3$) would not be among the potential precipitates. The model then calculates which of the potential solid phases is most supersaturated according to a comparison of the mineral's solubility product (K_{sp}) with the activity product of the relevant components of the aqueous phase. For example, if calcite ($CaCO_3$) is the most supersaturated mineral, MINTEQA2 calculates the activity product of $(Ca^{2+})(CO_3^{2-})$ and compares this product with the K_{sp} for calcite. Sufficient Ca^{2+} and CO_3^{2-} are subtracted from the aqueous phase and added to the solid phase so that the resulting aqueous activity product equals the K_{sp}. At this point, the solid and aqueous phases are in equilibrium with respect to calcite. MINTEQA2 then calculates the next most supersaturated solid phase and repeats the above procedure. Dissolution of minerals is also accomplished in an iterative manner, by addition of solutes from the solid phase to the aqueous phase.

The modeling results for KELRON 25 and KELRON 30 were that calcite ($CaCO_3$) and wustite (FeO) are allowed to precipitate from the water in both wells. In addition, magnesite ($MgCO_3$) is allowed to precipitate from the water in KELRON 30. The mass of minerals that were calculated to precipitate per liter of water were small: 0.1 to 0.2 g calcite, 0.08 to 0.4 g wustite, and approximately 0.09 g magnesite. The calculated equilibrium pH values for the water in KELRON 25 and KELRON 30 were 8.55 and 9.20 while the mean observed pH values at the time of collection were 7.78 and 8.24, respectively.

When the mean observed pH values were imposed as the equilibrium values, then only about 0.09 g of calcite was calculated to precipitate per liter of water in both wells, with neither wustite nor magnesite precipitating. This is the most likely scenario. Given sufficient time, calcite will probably precipitate in the wells screened in the Pennsylvanian shale. If water were removed from the wells and stored (e.g., in a tank), then calcite and siderite ($FeCO_3$) were calculated to precipitate when the observed pH was imposed as the equilibrium pH.

4. SUMMARY & CONCLUSIONS

Great variability was observed in the geochemical data for the Pennsylvanian bedrock, Pennsylvanian groundwater, and other data collected for this project. Some of this variability is due to the different lithologies which includes sandstone, shale, coal, limestone, and sand and gravel. Some of this variability is also due to the depth of the sample. For example, groundwater samples from KELRON 26 and 28 are significantly different from other samples because they were from shallow wells and are completely connected to the local groundwater system, whereas water samples from deeper wells were largely isolated from the local groundwater flow system. Although little data are available regarding the hydraulic connection between the Vermilion River and the shallow bedrock which crops out locally, we suspect that a well's position relative to recharge and discharge areas affects the concentrations of major cations and anions in the groundwater samples.

Some general observations can be made regarding the groundwater compositions, although exceptions can be found for most of these observations.

The samples collected for this study have a similar range in the concentrations of major anions and cations as those from available groundwater samples collected over a broader geographic area.

The average concentrations of calcium, magnesium, sulfate, and alkalinity were higher in water from two shallow wells (KELRON 26 and 28) than in the wells developed in shale (KELRON 25, 27, 29, 30, and 31). This indicates a possibility that the aquifer rocks of the shallow wells contained greater contents of calcite/dolomite and gypsum or magnesite than the wells completed in shale. Water from the wells completed in shale contained higher concentrations of aluminum, barium, bromide, boron, chloride, fluoride, iron, lithium, potassium, sodium, and strontium. The greater aluminum concentration in the water suggests greater clay contents in the shale aquifer rocks than in the shallow wells.

For samples from bedrock wells, sodium and chloride concentrations apparently increase at the expense of calcium, magnesium, and other higher valence cations due to adsorption as groundwater moves away from recharge areas.

Compared to samples from the deeper bedrock wells, samples from shallow wells generally have higher tritium and % modern carbon, suggesting the addition of recent water.

Equilibrium modeling showed that calcite is expected to precipitate from water derived from the shale wells, given enough time for equilibrium to become established. The calcite might eventually plug well screens. If water is pumped from the shale aquifer and stored in a tank, calcite is expected to precipitate in the tank and accumulate slowly on the tank walls and bottom.

The mineralogy of an aquifer governs the chemical composition of the associated groundwater. Mineralogical analyses were conducted to aid in understanding the chemical composition of the groundwater, and to provide information for geochemical modeling. The mineralogical analyses showed that three cores collected during this project (KELRON 29, KELRON 30, and KELRON 31) consisted principally of shale, composed of clay minerals and quartz with minor amounts of K-feldspar, plagioclase feldspar, siderite, and marcasite or pyrite. Coal was penetrated while drilling KELRON 30, and a small amount was recovered at the bottom of that core. The most abundant clay minerals in the cores were illite, kaolinite, and chlorite, with minor amounts of illite/smectite mixed-layer clay.

ACKNOWLEDGMENTS

This study was partially funded by a grant from KELRON Environmental, Inc. of Champaign, IL. We gratefully acknowledge the well owners who allowed us to sample their wells. In addition, we received technical assistance with sampling from Gina Eversole, Dynegy, Inc., Lindsay Hagemeyer, Dynegy, Inc. and Stuart Cravens, KELRON.

Chris Stohr, ISGS, collected the natural gamma logs from 3 wells.

Randy Hughes, Phil DeMaris, Makiko Otao, and Mary Hynes of the ISGS conducted the PIMA and XRD analyses.

The ISGS Isotope Geochemistry Lab ran the tritium and ^{14}C analyses. Keith Hackley, ISGS, assisted with the interpretation of the isotopic data.

Alec M. Davis, ISGS, compiled much of the geochemical data and prepared some of the figures for this report.

Mike Knapp, ISGS, drafted figures 1 & 2 for this report.

Tracy D. Branam, Indiana Geological Survey, provided data for the Indiana wells included in this report.

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Appendix A. Geologic Logs of Selected Bedrock Core

The core descriptions by Kolata and Jacobson include a stratigraphic interpretation of the core and appear first. The core descriptions by DeMaris emphasize lithologic and structural features of the core.

Kelron Environmental MW 25

Vermilion Power Station
Danville, Vermilion County, IL
(NW, NW, NW, Sec. 29, T. 20 N., R. 12 W.)
Description by Dennis R. Kolata and Russell J. Jacobson, March 14, 2002

Pennsylvanian System
Shelburn Formation
Unnamed Shale above the Danville Coal

9' to at 39' (TD)
Shale, light to medium gray, massive beds, blocky fracture, silty, micaceous, abundant carbonized plant material, bioturbated; interbeds of very light gray shale between 1 mm and 30 mm thick.

Kelron Environmental MW 30

Vermilion Power Station
Danville, Vermilion County, IL
(SW, NE, NE, Sec. 20, T. 20 N., R. 12 W.)
Description by Dennis R. Kolata and Russell J. Jacobson, March 14, 2002

Pennsylvanian System
Shelburn Formation

Farmington Shale
116' to 135'
Shale, medium gray, massive beds, blocky fractures, silty, micaceous; 1-2 " thick brownish-gray siderite nodules beginning a 128', non-marine.

135' to 144'
Shale, medium to dark gray, somewhat less silty than above, brownish-gray siderite nodules mostly 1 cm thick; first appearance of marine fossils 135.5' (strophomenid brachiopods, gastropods, and bivalves increase in abundance downward).

144' to 145'
Shale, dark gray to black, organic-rich, contains white needle-like crystals.

Danville Coal
145' to 148'
Coal, abundant pyrite along cleats

Kelron Environmental MW 31
Vermilion Power Station
Danville, Vermilion County, IL
(SW, NE, NE, Sec. 20, T. 20 N., R. 12 W.)
Description by Dennis R. Kolata and Russell J. Jacobson, March 14, 2002

Pennsylvanian System
Shelburn Formation?

Unnamed Shale above the Danville Coal
154' to 173'
Shale, medium gray, massive beds, blocky fractures, bioturbated, silty, micaceous, not fossiliferous.

173' to 183' (TD)
Shale, medium to dark gray, siderite nodules up to 3 cm thick, bioturbated, silty, micaceous; small bivalves suggest that this is a marine shale.

Boring: **KELRON 25** (HQ or 2.5 inch core)
Location: NW/4 of NW/4 of NW/4, Sec 29, T20N, R12W, Vermilion County, IL

Total Depth= 39 feet, Surface Elevation= 578.8 feet
Description by Philip J. DeMaris, June 2002

Interval (ft)			**Description**
Top	Bottom	Thickness	
9.00	11.25	2.25	Shale– light to medium gray, slightly silty, especially as silt lenses from 10.35 to 11.25', slightly micaeous, horizontal bedding, slightly weathered at top
11.25	30.60	19.35	Shale– medium gray, silty, slightly micaeous and finely carbonaceous, multiple siltstone bands in interval from 18.10 to 30.60', planar bedding
30.60	36.87	6.27	Shale– medium gray, slightly silty, some pyrite, predominantly planar bedding
36.87	38.82	1.95	Shale– medium gray, very slightly silty, some clay lenses, silt lenses and carbonaceous debris rare, faint planar bedding with some bioturbation
			total core= 29.82'

Boring: **KELRON 30** (HQ or 2.5 inch core)
Location: SW/4 of NE/4 of NE/4, Sec 20, T20N, R12W, Vermilion County, IL

Total Depth= 148 feet, Surface Elevation= 645.7 feet
Description by Philip J. DeMaris, June 2002

Interval (ft)			**Description**
Top	Bottom	Thickness	
119.00	126.92	7.92	Shale– light to medium gray, slightly silty, sparsely micaeous above 123', slightly weathered at top, fractured on multiple low-angle planes in top 1.5', generally planar bedding throughout, two medium-angle faults from 121.1 to 121.7'
126.92	131.20	4.28	Shale– medium gray, nonmicaeous, multiple siderite bands/nodules

Interval (ft)			Description
Top	Bottom	Thickness	
131.20	138.68	7.48	Shale– medium gray, finely carbonaceous, many siderite bands/ nodules throughout, scattered marine fossils in interval 136-138'
138.68	144.38	5.70	Shale– dark gray, becoming more carbonaceous and pyritic downward, siderite nodules present in top 1.3', sulfide-rich carb. claystone at base, strongly weathered
144.38	148.00	3.62	Coal (Danville Coal)– normally bright banded, well cleated, pyritic, calcite and kaolinite on cleat, some fusain present throughout
			total core= 29.0'

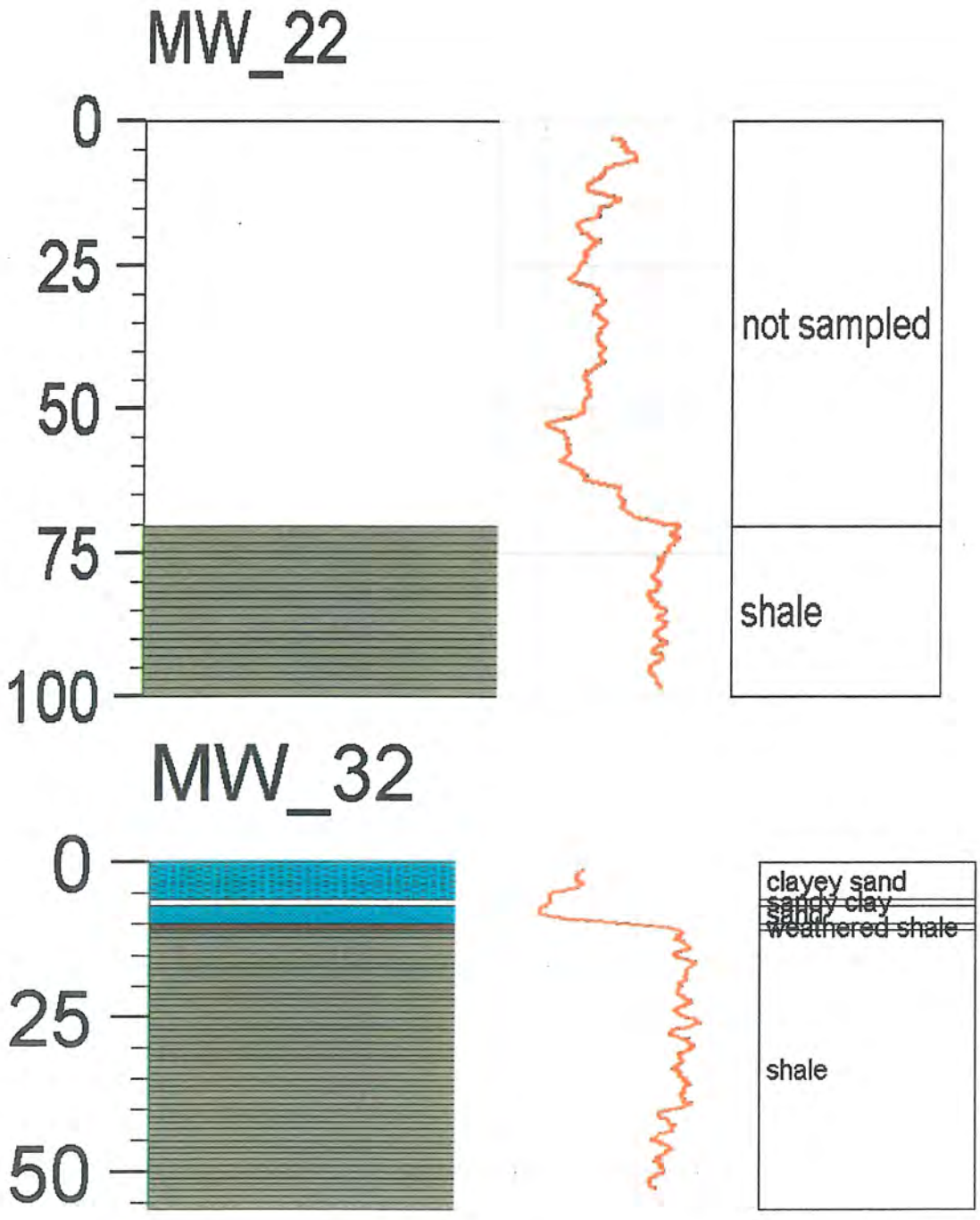
Boring: **KELRON 31** (HQ or 2.5 inch core)
Location: NE/4 of SW/4 of SW/4, Sec 21, T20N, R12W, Vermilion County, IL

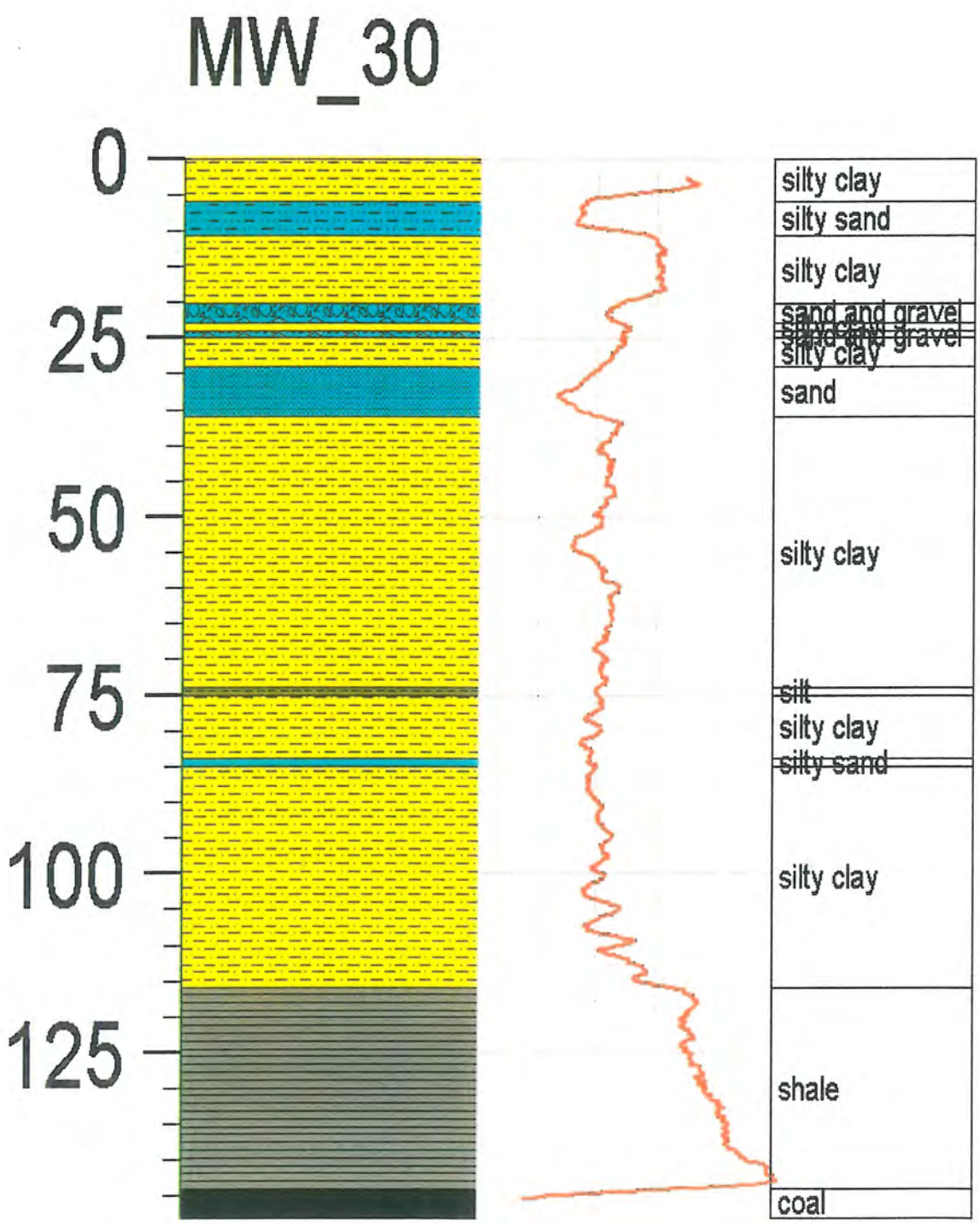
Total Depth= 184 feet, Surface Elevation= 698.2 feet
Description by Philip J. DeMaris, June 2002

Interval (ft)			Description
Top	Bottom	Thickness	
153.00	157.55	4.55	Shale– light to medium gray, slightly silty, well weathered in top 1.2', carbonaceous debris rare, several low angle faults
157.55	170.30	12.75	Shale– light to medium gray, silty, slightly micaeous, unweathered, competent, uniformly faintly laminated, less silty below 164', very faintly horizontally bedded, planar fault (59° dip) centered at 168.8'
170.30	180.80	10.50	Shale– medium gray, slightly silty at top, minor sideritized banding near top of interval, many siderite bands and nodules from 173.7' to base
180.80	182.82	2.02	Shale– dark gray, with multiple siderite bands, very finely carbonaceous
			total core= 29.82'

Appendix B. Natural Gamma Logs of Selected KELRON Wells

Natural gamma logs for three KELRON wells (KELRON 22, KELRON 30, and KELRON 32) were collected by Chris Stohr of the ISGS in May 2002. The natural gamma logs shown in this appendix are scaled from 0 to 100 cps. In general, higher gamma counts reflect geologic materials with higher clay content such as shales and clayey diamictons.




MW_30
0
25
50
75
100
125
silty clay
silty sand
silty clay
sand and gravel
silty clay
sand
silty clay
silt
silty clay
silty sand
silty clay
shale
coal

APPENDIX A-4

Panno, S.V., and K.C. Hackley, 2010. Geologic influences on water quality. In Geology of Illinois, ed. D.R. Kolata and C.K. Nimz, 337-350. Champaign, Illinois: Illinois State Geological Survey

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Geological Influences on Groundwater Quality

19

Samuel V. Panno and Keith C. Hackley

Introduction

The quality of groundwater is determined by the type and concentration of its chemical and biological constituents. These constituents, depending on their nature and concentrations, can produce water that is unsafe to drink or that has an objectionable taste or odor. Because naturally occurring substances are dissolved in or suspended as fine-grained solids in groundwater, in many cases, some water treatment is necessary before groundwater quality becomes acceptable for drinking purposes or industrial uses. This chapter discusses these naturally occurring substances, their common sources, and the general quality of the groundwater observed within the different aquifers in Illinois.

As municipal and industrial water supplies grew in importance during the early twentieth century, scientists began to study the chemical composition of groundwater and its relationship to the geological framework and associations with the host sediment or bedrock aquifers. The chemical interactions between aquifers and groundwater were identified during the first half of the century and rigorously examined during the latter half (Back and Freeze 1983). Water quality of municipal and private water supplies in Illinois has been routinely analyzed by the Illinois State Water Survey since its founding in 1895 as a means of tracing waterborne diseases (Illinois State Water Survey 2003). Today, studies of the chemical composition of groundwater are routinely performed on both public and private water supplies. The composition of groundwater is used to determine its potability and serves as a tool to determine the sources of naturally occurring and human-related contaminants.

Groundwater is derived from precipitation, such as rainfall or snow melt. Precipitation contains very low concentrations of dissolved minerals (approaching that of distilled water). The major ions—or electrically charged particles—present in rainwater and snow melt are calcium, magnesium, sodium, silica (as $Si(OH)_4$), sulfate, chloride, and nitrogen compounds (nitrate, ammonium, and organic nitrogen). The total concentration of all constituents typically is less than 5 to 10 mg/L (parts per million) (Table 19-1). The natural sources of these ions include airborne dust (calcium, magnesium, and silica) and aerosols from seawater (sodium and chloride), which are highest near the coastal areas (Drever 1997). The majority of the remaining ions are typically from airborne particulate matter and gases from industrial emissions, automobile exhaust, and the evaporation of volatile chemicals (e.g., anhydrous ammonia fertilizers). These latter constituents are discussed in Chapter 28, Karst Terrane.

Once rainfall and snowmelt seep into the ground, the water begins its journey to the water table through the connected pores and crevices in soil, unconsolidated sediment, and rocks. The water table is the elevation at which the geological sediments and rocks become saturated with water. Permeable sediments and bedrock below the water table constitute aquifers. Aquifers supply private citizens and municipalities with potable water and are also used as a source of water for irrigation and industrial purposes throughout much of the state.

Water is a solvent and, as such, is capable of dissolving and interacting with organic and inorganic components of soils, the minerals that make up unconsolidated deposits (e.g., sand and gravel), and with various types of bedrock. Dissolution of minerals within the soil, sediment, and bedrock is a slow process that can take days, years, or eons, depending on the solubility of the materials. These materials contribute to the amount of total dissolved solids (TDS) that are present in all groundwater. Major dissolved constituents of groundwater include the cations (positively charged ions) sodium, potassium, calcium, magnesium, and silica and the anions (negatively charged ions) bicarbonate, sulfate, chloride, and nitrate (Table 19-1). When trace-level ions, such as ammonium, iron, manganese, and arsenic, are present in relatively high concentrations, they create water-quality problems. These constituents come from the dissolution of rocks such as limestone and dolomite, the weathering of less-soluble rocks such as granite, the degradation of organic debris in the soil zone (e.g., trees and leaves), and man-made contaminants (discussed in Chapter 29, Pollution of Natural Waters).

In general, the chemistry of groundwater is controlled by the type of geological materials through which the water flows and the amount of time the water is in contact with these materials. For example, precipitation percolating into a limestone aquifer would dissolve the limestone (made of calcium carbonate), and the water (now groundwater) would contain predominantly calcium and bicarbonate ions. The dominant cations and anions are used to describe the gen-

eral chemical composition, or "type," of groundwater. For example, limestone aquifers contain "calcium bicarbonate type" groundwater, and deep, granitic rock eventually produces "sodium chloride type" groundwater.

Aquifers and Aquitards: Effects on Groundwater Quality

Aquifers in Illinois are made up of two types of material: (1) sand and gravel deposits found in association with glacial till or along stream valleys, and (2) porous and permeable bedrock units. Sand and gravel aquifers are scattered throughout the state, but the largest deposits occur in northeastern and central Illinois. Bedrock aquifers containing usable groundwater are located throughout the state, but potable water is found only in the bedrock aquifers of the northern third and, to a lesser extent, the western and southern parts of the state. For example, fresh groundwater with less than 1,000 mg of TDS/L can be pumped from wells over 1,000 feet (305 m) deep in the northern part of the state, but saline (salty) groundwater is encountered several hundred feet or less below the surface in southern Illinois (Lloyd and Lyke 1995). Groundwater from bedrock found in the southern two-thirds of the state is usually too saline for human use (Figure 19-1). Salinity of groundwater generally increases with depth. Bedrock aquifers in the northern portion include shallow carbonate rocks (dolomite and limestone) as well as deep sandstones that are primarily made up of quartz and silicate minerals. The bedrock aquifers in the western and southern parts of the state are primarily shallow carbonate rocks.

Sand and gravel deposits typically contain abundant clasts (i.e., sand grains, pebbles, and cobbles) of limestone and dolomite that dissolve much faster than do clasts of other composition (e.g., quartz). Consequently, calcite and dolomite, once dissolved, dominate the chemical composition of the groundwater in these aquifers, forming a calcium-magnesium bicarbonate type of groundwater (Table 19-1). Similarly, bedrock aquifers are often made of fractured limestone and dolomite, resulting in groundwater with the same general chemical composition as that found in sand and gravel aquifers. Groundwater circulating through fractured sandstone aquifers, such as the Aux Vases Sandstone in southwestern Illinois, typically form a sodium bicarbon-

Table 19-1 Chemical composition[1] of averaged rainwater samples and single samples of different types of groundwater in Illinois. All parameters are reported in milligrams per liter except pH.

		Groundwater type								
	Rain[2]	Ca-Mg bicarbonate[3]	Na bicarbonate[4]	High NaCl[5]	High F[6]	High As[7]	High Mn, Fe[8]	High ammonium[9]	High sulfate[10]	Seawater[11]
pH	4.5	7.2	8.6	6.6	6.8	7.4	7.49	7.2	7.1	8.0
SC	21.1*	688	2,100	—	694	515	750	670	2,000	58,500*
Na	0.08	27.4	559	44,923	27.4	17.4	47.6	15.8	104	10,556
K	0.03	<1	<2	—	<2	1.74	1.82	3	4	380
Ca	0.24	90.1	6.0	5,740	109	67.9	82.3	82.3	279	400
Mg	0.04	33.9	3.1	2,173	20.5	32.9	41.8	36.6	96.7	1,272
SiO_2	—	19.1	8.6	15	14.8	18.1	21.8	22.7	20.1	6.43
HCO_3	—	443	1,108	61	385	479	560	480	301	140
SO_4	2.28	33.1	165	329	25.3	<0.09	16.3	0.34	981	2,649
Cl	0.15	7.4	37	85,569	25.1	1.1	41.8	0.55	8.5	18,908
F	—	0.37	—	—	1.46	0.2	0.1	—	0.28	1
NO_3	1.46	<1.9	0.26	0.0	0.09	<0.02	<0.2	0.35	<1.7	<0.5
NH_4	0.40	0.98	—	64	—	2.8	3.7	6.02	—	<0.5
Fe	—	1.89	<0.01	20	1.65	4.57	3.67	4.32	0.27	0.01
Mn	—	<0.03	<0.01	2.0	0.76	0.04	0.21	0.03	1.2	0.002
As	—	—	—	—	—	0.096	—	—	—	0.003
TDS	4.68*	661*	1,887*	142,194	611*	626*	821*	652*	1,796	34,477

[1]Abbreviations: SC, specific conductance; Na, sodium; K, potassium; Ca, calcium; Mg, magnesium; SiO_2, silicon dioxide, or silica; HCO_3, bicarbonate; SO_4, sulfate; Cl, chlorine; F, fluorine; NO_3, nitrate; NH_4, ammonia; Fe, iron; Mn, manganese; As, arsenic; TDS, total dissolved solids. Values followed by asterisk were calculated. —, data are unavailable.
[2]Average values from six active collection sites throughout Illinois from 1980 to 2003 (http://www.nadp.isws.illinois.edu).
[3]Hackley (2002); sample WRD-55, Mahomet aquifer, Champaign County.
[4]Panno (unpublished data 1995); Aux Vases Sandstone, Monroe County.
[5]Meents et al. (1952); sample 930, Ste. Genevieve Formation, Wayne County.
[6]Panno and Hackley (1997a); Valmeyeran Series limestones, Rosiclare, Hardin County.
[7]Holm (1995); sample 93-24A, Mackinaw Valley aquifer, Tazewell County.
[8]Holm (1995); sample 93-14, Mackinaw Valley aquifer, Tazewell County.
[9]Hackley (unpublished data); Mahomet aquifer, Mc Lean County.
[10]Hackley (2002); sample VER-94b, Mahomet aquifer, Vermilion County.
[11]Mason (1966).

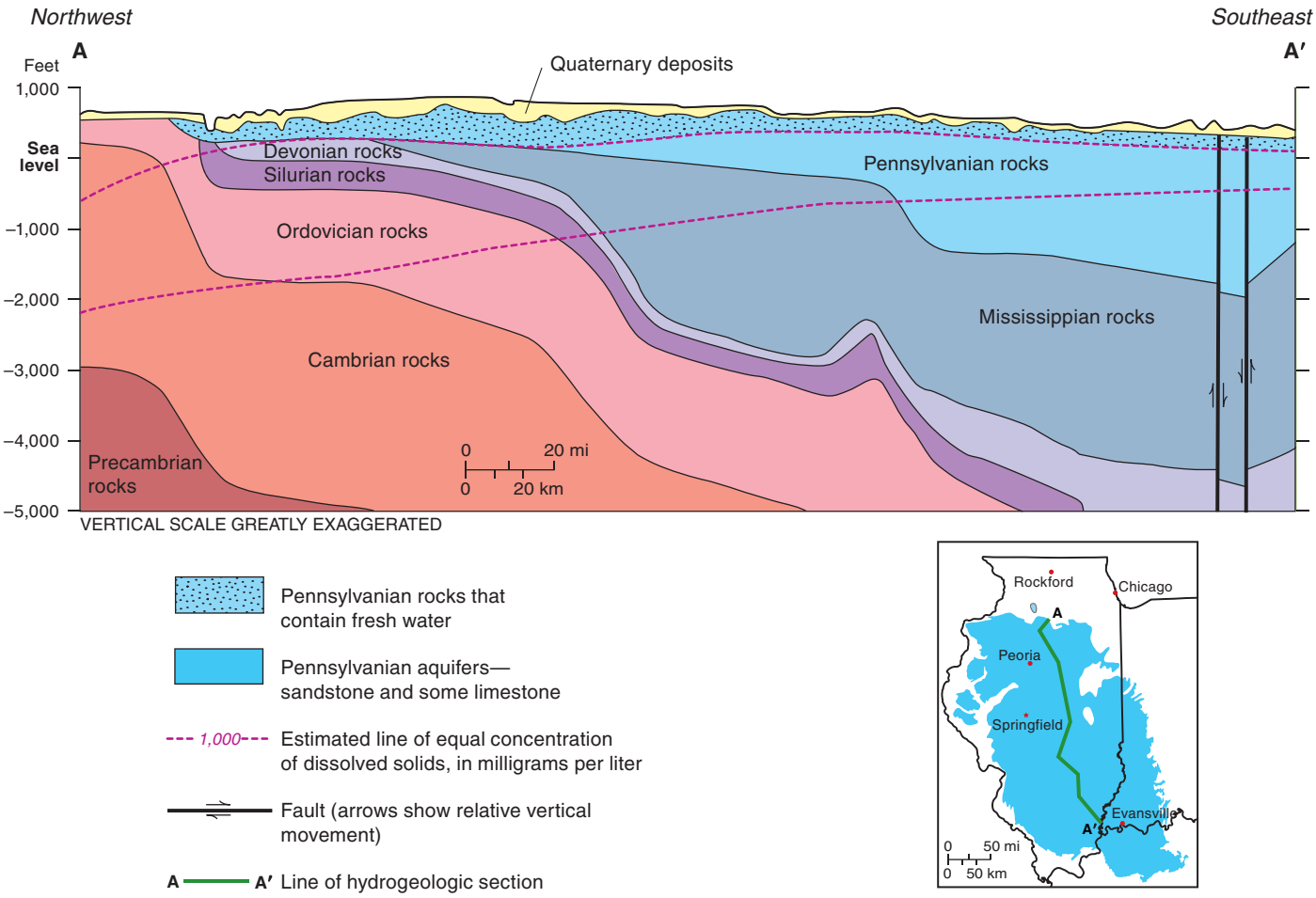

Figure 19-1 North-south cross section of Illinois showing estimated lines of equal concentration of total dissolved solids in groundwater (Lloyd and Lyke 1995).

ate type groundwater (Table 19-1). One way such groundwater is formed is for calcium bicarbonate groundwater to enter the sandstone, and, through ion exchange, calcium ions replace sodium ions on clay minerals (sodium is often present due to degradation of feldspars in the sandstone). This process is similar to that occurring when a water softener causes calcium and magnesium to exchange positions on a resin within the softener; the result in both cases is a "soft" sodium bicarbonate water.

Aquitards are those deposits or rocks that do not allow recharge water or groundwater to penetrate very easily (e.g., clay-rich glacial till and shale) (Chapter 18, Aquifers). These deposits or rock units protect groundwater from surface-borne contaminants, isolate groundwater from the atmosphere, and confine groundwater to a single aquifer or channel it to a series of connected aquifers. The isolation of groundwater for hundreds to thousands to tens of thousands of years can affect its chemistry by fostering reducing conditions, as is discussed later in this chapter. Additionally, the interaction of groundwater with the minerals of an aquitard can alter the chemical composition of the groundwater flowing through it and the chemical composition of adjacent aquifers. For example, recharge water interacting with the shale that bounds an aquifer often encounters the mineral pyrite (iron sulfide), which can be easily oxidized to form groundwater that has very high concentrations of sulfate (perhaps hundreds to thousands of milligrams per liter) (Table 19-1). Such sulfate-enriched groundwater, as it enters an underlying aquifer, can enrich the aquifer with sulfate even though there may have been no mineralogical source of sulfate in the aquifer.

Chemical Composition

There are a number of constituents that can be found in groundwater, and water quality depends on the type and concentration of these constituents. For example, groundwater in some locations is immediately potable; elsewhere it may have an objectionable taste and/or odor and may even be unsafe to drink. The U.S. Environmental Protection Agency (U.S. EPA) has developed a list of acceptable concentrations of natural and man-made contaminants for municipal drinking water. These standards, the National Pri-

mary Drinking Water Regulations (NPDWR), are enforced by the U.S. EPA (1991, 2009). National Secondary Drinking Water Regulations (NSDWR) are U.S. EPA guidelines pertaining to constituents of drinking water based on cosmetic effects, taste, odor, and appearance. Both guidelines may be found on the U.S. EPA (2009) Web site.

The chemical components that are typically measured to help determine the general quality of groundwater include suspended solids, hardness, sodium, chloride, fluoride, sulfate, chemicals associated with reduction-oxidation (e.g., arsenic, iron, manganese, nitrate, and ammonium), assorted minor and trace constituents, dissolved gases (e.g., air, carbon dioxide, methane, and hydrogen sulfide), and stable and radioactive isotopes. Some of these constituents are occasionally referred to as "contaminants," but they can be naturally occurring.

Suspended Solids

Suspended solids in groundwater are occasionally observed in wells tapping aquifers that have relatively large porosity and permeability (e.g., sand and gravel, karst limestone/dolomite). Suspended solids include soil and other fine-grained material (e.g., clay, silt, and organic debris) small enough to pass through the tiny spaces between sand and gravel and through crevices in carbonate rock. Suspended solids can also include compounds that may precipitate in the water as it is withdrawn from the aquifer due to dramatic changes in temperature, pressure, pH, or oxygen content. Examples of dissolved constituents that can emerge from apparently clear water are calcium carbonate, which forms small white flakes when dissolved carbon dioxide is released from the water, and iron and manganese oxides, which form orange and black granules or coatings when water is exposed to oxygen. Such materials can make the water cloudy and can affect its taste unfavorably.

An extreme example of suspended solids in groundwater comes from the karst aquifers of southwestern Illinois. Karst aquifers have large crevices and conduits that can carry relatively large concentrations of suspended solids in the water. Several wells in one subdivision in southwestern Illinois intersected crevices that were in direct contact with at least one large sinkhole. During and following large rainstorms, soil washed into the sinkhole(s) and through the crevices that led to the wells. Pumps in the wells sent the sediment-laden water, now a muddy slurry, into the plumbing systems of several houses, and mud oozed from the fixtures (Figure 19-2) (Panno et al. 1996). In most cases, however, suspended solids in groundwater are not so extreme and can be removed by commercially available filters.

Figure 19-2 Examples of muddy tap water from a residential home in southwestern Illinois' karst region. Left and center: Water containing sediment from erosion of cropland adjacent to a sinkhole during and following relatively large rainfall events (1 inch [2.5 cm] or greater). Right: Fireplace ashes in water caused by dumping fireplace ashes into the sinkhole in the home's backyard. (Photograph by Joel M. Dexter.)

Rock-Water Interaction

The chemical characteristics of groundwater are determined by the interaction between groundwater and the minerals that make up the rock or sediment through which the water is moving (Figure 19-3). That is, the materials of the soil zone and the aquifer are dissolved and incorporated into the water moving through them. Some components may provide a characteristic taste to the water and some may make the water undrinkable based on taste, toxicity, or both.

Calcium, Magnesium, Bicarbonate, and Hardness

In areas where bedrock is dominated by limestone and/or dolomite or where sand and gravel aquifers contain abundant clasts of these carbonate minerals, the groundwater is typically a calcium bicarbonate type or calcium-magnesium bicarbonate type (Table 19-1; Figure 19-4). These rocks are dominated by calcite (calcium carbonate) and dolomite (calcium-magnesium carbonate), and both are soluble in slightly acidic rainwater (Table 19-1) and snowmelt and in carbon dioxide-enriched soil water (soil water made more acidic by the generation of carbon dioxide from root respiration and microbial degradation of organic debris). Carbonate minerals dissolve relatively fast when exposed to carbon dioxide-enriched waters.

Groundwater from aquifers made up of or containing carbonate rock is often referred to as "hard." Hard water contains calcium and magnesium that react with soap and produce soap scum or react with other anions to produce a solid scale or coating when the water is boiled and evapo-

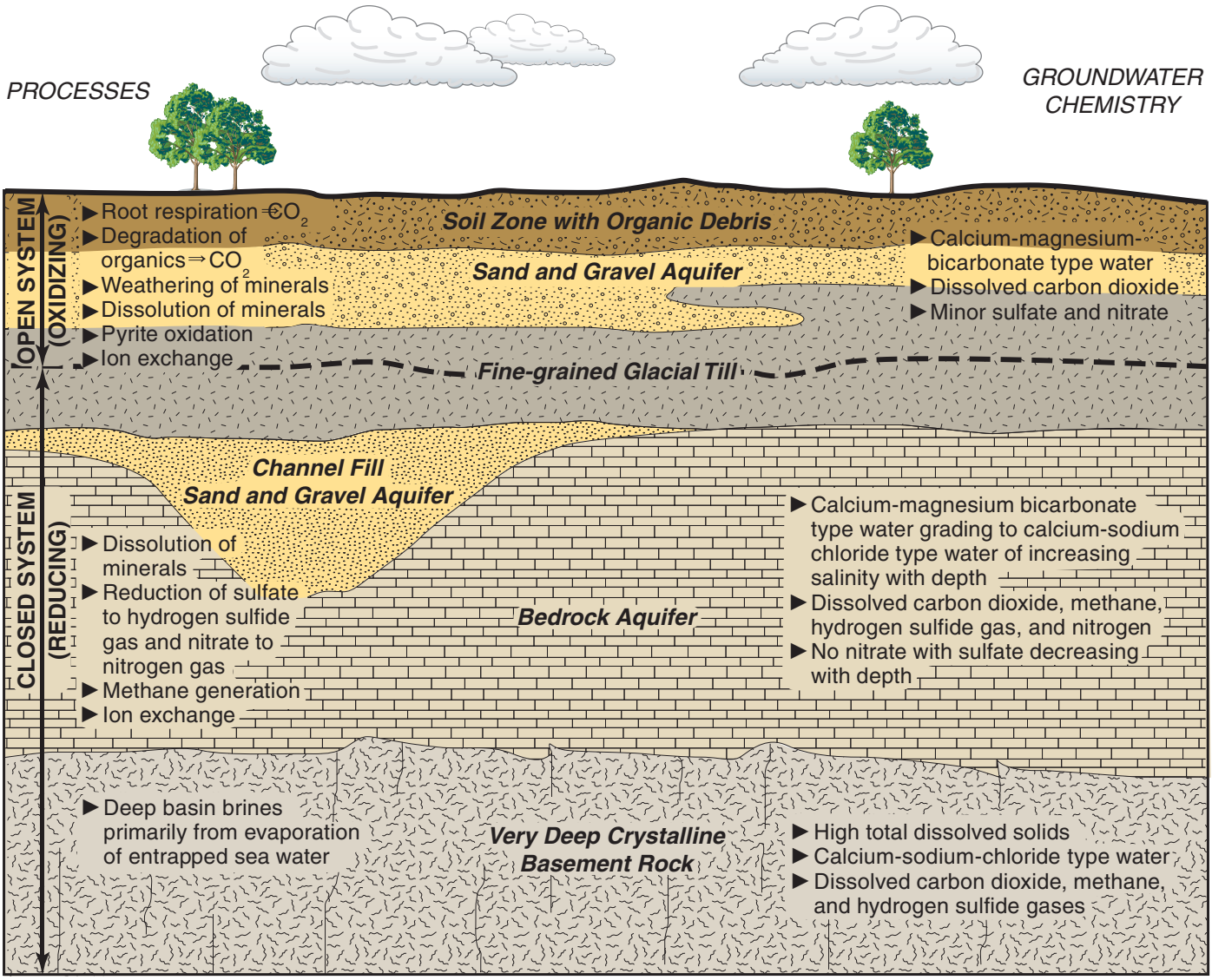

Figure 19-3 Conceptual model of the processes and chemical composition of groundwater in Illinois. Abbreviation: CO_2, carbon dioxide.

rated. Hardness and its components are not toxic, have no offensive taste or odor, and are under no U.S. EPA guidelines. Chemically, hardness is defined (Freeze and Cherry 1979) as (total calcium concentration × 2.5) + (magnesium × 4.1) and is expressed as milligrams per liter, or parts per million. For example, if water contains 5 mg of calcium/L and 5 mg of magnesium/L, then the hardness is 33 mg/L. Water with a hardness value greater than 120 mg/L is considered to be hard, and greater than 180 mg/L is considered to be very hard (Lehr et al. 1980). Because the presence of these minerals controls water chemistry, groundwater from carbonate mineral-rich aquifers is typically very hard. For example, the average hardness value for the groundwater of the karst limestone aquifers of Illinois is about 230 mg/L (Panno et al. 1996, 1997). Groundwater from sand and gravel aquifers in northern Illinois has hardness values of over 300 to 400 mg/L (Panno et al. 2005a).

The scale or coating from these dissolved minerals that can be found in pots used for boiling hard water and on the bottom of hot water heaters is a deposit of carbonate minerals. In some cases, hard water may be desirable because it tends to coat the interior of metal pipes containing copper or lead or joined by lead-bearing solder, thereby protecting the metals from leaching into the water supply (Lehr et al. 1980). However, continued coating of pipes with scale may eventually (after tens of years) constrict the interior of water pipes so that the water flow slows to a trickle. Hardness can be treated easily by commercially available water softening treatment systems. Water softeners typically consist of an ion-exchange system that exchanges sodium for calcium and magnesium. What enters the water softener as a hard, calcium-magnesium bicarbonate water discharges as a soft, sodium bicarbonate water.

Figure 19-4 Groundwater discharging from a spring at Weldon Springs State Park near Clinton, Illinois. The dilute, calcium-bicarbonate groundwater that is recharged in the higher elevations to the north percolates into and flows through a sand and gravel layer in glacial till and discharges as springs in the low-lying area of the park. A pipe was inserted into this spring's discharge point and channeled to this facade; unlike its Wyoming namesake, Illinois' Old Faithful flows constantly (Panno and Hackley 2001b). (Photograph by Samuel V. Panno.)

Sodium and Chloride

Water may be classified according to its TDS content (Table 19-2). In Illinois, most groundwater from shallow aquifers is fresh, whereas relatively deep groundwater from within the Illinois Basin is saline to briney. Water containing chloride concentrations of approximately 250 mg/L or greater may have a salty taste. This concentration is the U.S. EPA recommended limit for drinking water (U.S. EPA 1991, 2009); chloride concentrations exceeding 1,000 mg/L may be unsafe for human consumption (Lin 1977, Lehr et al. 1980, U.S. EPA 1991). Sodium concentrations are not regulated by the U.S. EPA. However, high-sodium intake may be associated with hypertension in some individuals (U.S. EPA 1991), and the sodium concentration in drinking water should be considered by those for whom dietary sodium is a concern (Haman and Bottcher 1986).

Most shallow groundwater is relatively fresh and typically has little sodium and chloride dissolved in it. Usually, naturally occurring sodium and chloride concentrations in sand and gravel aquifers in Illinois are between about 1 and 15 mg/L (Panno et al. 2006a). However, sodium chloride is present in large concentrations in groundwater from deep aquifers of northern Illinois, in parts of central Illinois, and many parts of southern Illinois (Clayton et al. 1966).

Table 19-2 Classification of groundwater relative to total dissolved solids (TDS) contents (Hem 1986).

Water classification	TDS (mg/L)
Fresh	<1,000
Slightly saline	1,000 to 3,000
Moderately saline	3,000 to 10,000
Very saline	10,000 to 35,000
Brine	>35,000

Much of the bedrock in Illinois, however, is part of an underlying midcontinental sedimentary basin known as the Illinois Basin. Sedimentary basins such as this contain abundant saline groundwater that typically increases in salinity with depth (Figures 19-1 and 19-3); in the case of the Illinois Basin, salinity increases to a depth of about 1.2 miles (2 km) or so before it levels out (McIntosh et al. 2002). The source of the salinity of this groundwater has generated much interest. Walter et al. (1990) and Steuber et al. (1991, 1993) suggested that the salinity was due to the evaporation of seawater short of the precipitation of halite in Silurian and Devonian strata and a mixture of evaporated seawater and dissolution of evaporites in shallower Mississippian and Pennsylvanian strata. Recent work by Hanor and McIntosh (2006) suggests that saline groundwater of the Illinois Basin underwent extensive alteration as a result of rock-water interaction and were transformed from sodium chloride brines to calcium-sodium chloride brines with salinities up to 200,000 mg/L TDS.

Saline springs can be seen along structural features, such as along folds and faults in the Starved Rock area (the Old Salt Well) in La Salle County, in southwestern Illinois in the vicinity of oil fields near Columbia in Monroe County, and in southern Illinois near the Equality Fault Zone and the town of Equality in Saline County (Figure 19-5). Water from these springs is about as saline as seawater with about 35,000 mg/L TDS and is dominated by sodium and chloride; seawater is dominated by sodium and chloride and contains about 34,477 mg/L TDS (Table 19-1).

Saline groundwater and brines can be brought near or to the land surface by natural conditions, such as migrating up prominent fractures and/or faults in bedrock, or by anthropogenic activities, such as exploration for and exploitation of petroleum. The mixing of upward-migrating saline groundwater with fresh groundwater from shallow aquifers can make groundwater from private wells undrinkable and can present a very expensive problem for municipalities. An example of saline groundwater seeping into a freshwater aquifer can be found in east-central Illinois where the Mahomet aquifer crosses a major, roughly north-south–trending structural feature called the La Salle Anticlinorium (Figure 19-6). Saline water seeps up into the base of the aquifer from bedrock at a depth of about 300 feet (91 m) below the land surface near the Champaign-Piatt County line. Groundwater that normally has chloride concentra-

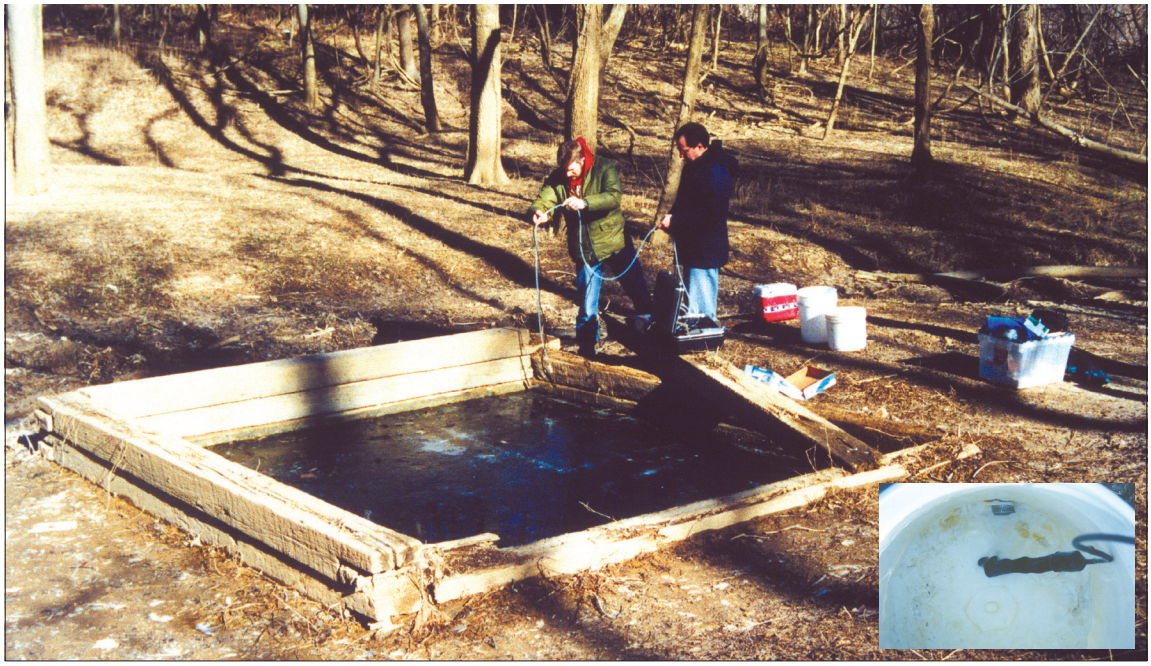

Figure 19-5 Equality Spring in Saline County in southern Illinois is a saline spring containing over 13,000 mg/L of sodium and chloride. The spring is over 6 feet deep (2 m), is encased by railroad ties, and was used as a commercial source of salt by early settlers of Illinois. (Photograph by Samuel V. Panno.)

tions less than or about 1 mg/L here exceeds 300 mg/L (Panno et al. 1994). Samples of groundwater from bedrock beneath the sand and gravel aquifer have chloride concentrations in the thousands of milligrams per liter (Panno et al. 2005a).

In addition, naturally saline springs in northern (e.g., Starved Rock State Park) and southern Illinois, usually located along fault zones or structural folds, discharge highly saline water into surface streams (Panno et al. 2005a, 2006a). Streams in areas where there are saline seeps have names such as the Saline River (Saline County) and the Salt Fork of the Vermilion River (Vermilion County). Because salt was an important commodity during early Illinois settlement by Europeans during the early 1800s, such seeps and their "salt works," initially used by Native Americans, became the nucleus of early settlements. Saline water was boiled in large iron kettles, and the residual salt was harvested and sold (Fliege 2002).

Fluoride

Fluoride typically is added to municipal water supplies because of its protective effects on teeth. However, fluoride in drinking water at concentrations greater than 3 mg/L can cause problems with tooth mottling, brown staining, and pitting in the teeth (dental fluorosis) in children with developing teeth (U.S. EPA 2009). The primary U.S. EPA drinking water standard is 4 mg/L. Fluoride concentrations greater than 4 mg/L can result in bone disease and bone and joint deformation (skeletal fluorosis) (Appelo and Postma 1994). The NSDWR for fluoride in drinking water is 2.0 mg/L (U.S. EPA 1991, 2009).

Groundwater from wells in most aquifers in Illinois has relatively low fluoride concentrations (usually about 0.5 mg/L) (Panno, unpublished data). Fluoride concentrations in groundwater are a function of the chemical composition of the groundwater and the presence or absence of fluorine-bearing minerals within an aquifer. Fluorine-bearing minerals include apatite (calcium phosphate), fluorite (calcium fluoride), and minerals that can exchange hydroxyl ions for fluoride ions (hornblende, mica, and clay minerals) (Hem 1986). Conrad et al. (1999) found that the greatest fluoride concentrations in Kentucky were associated with relatively deep, sodium bicarbonate-type groundwater with pH values between 7.6 and 8.0. The fluoride concentrations in Illinois aquifers are relatively low, in part, because calcium bicarbonate-type groundwater (found in limestone and sand and gravel aquifers of northern Illinois) limits the amount of the fluorite that can be dissolved (Hem 1986). Fluorite (calcium fluoride) deposits are found in southeastern Illinois within and near the town of Rosiclare, in Hardin County, site of the largest known fluorite deposits in the United States. Groundwater samples drawn from limestone for Rosiclare's municipal water supply contained 1.5 mg of fluoride/L (Panno and Hackley 2001a) (Table 19-1). Private wells that tapped into the groundwater of the Aux Vases Sandstone in southern Illinois have intersected groundwa-

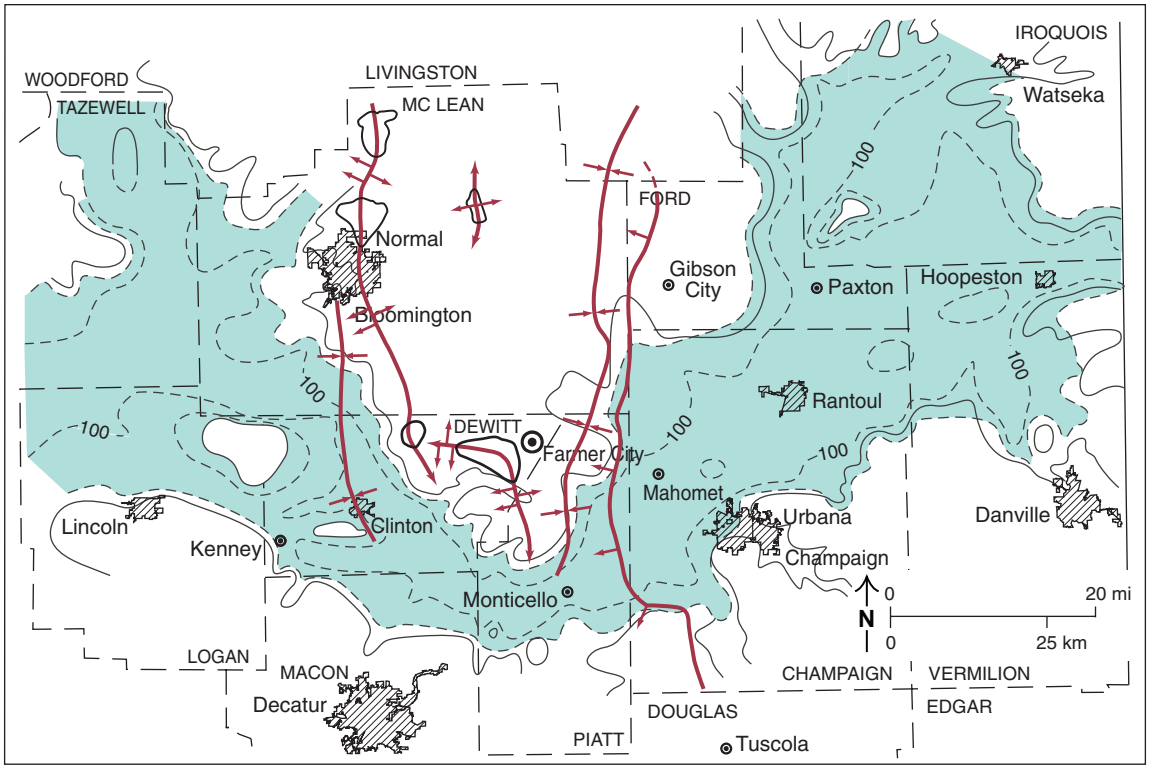

Figure 19-6 Saline groundwater can seep into a freshwater aquifer to contaminate it. Such a situation occurs in east-central Illinois where the Mahomet aquifer crosses the north-south cluster of folds known as the La Salle Anticlinorium. Dashed lines are thickness contours (in feet). (Modified from Panno et al. 1994.)

ter with fluoride concentrations as high as 9 mg/L (J. Bade, former sanitarian with the Monroe-Randolph Bi-County Health Department, personal communications 1997).

Sensitivity to Reduction-Oxidation

Oxygen

Oxygen, one of the most abundant elements on earth, very commonly combines with other elements. Depending on the nature of the bond, the bonded element is either reduced or oxidized. In simplest terms, reduction-oxidation (commonly shortened to redox) involves the gaining (reduction) or losing (oxidation) of electrons between elements, one of which is oxygen. The term "reduction" refers to the charge; an atom, molecule, or ion that gains an electron now has a reduced, or negative, charge. The loss of electrons through oxidation results in a positive charge. Redox reactions happen in pairs; there is no oxidation without a concurrent reduction. Redox-sensitive elements are those that either precipitate or dissolve in the presence or absence of dissolved oxygen and other electron-bearing, often oxygen-bearing, ions (e.g., nitrate and sulfate). The abundance of dissolved oxygen (and oxygen-bearing ions) usually decreases with depth and confinement of an aquifer. Groundwater in shallow, unconfined aquifers typically has dissolved oxygen contents similar to that of surface water (about 8 mg/L). Groundwater in deeper aquifers and shallow, confined aquifers has little or no dissolved oxygen because it is readily used up by bacterial activity and other oxygen- and electron-consuming chemical reactions that occur within the aquifers (e.g., decomposition of organic matter and oxidation of pyrite); such groundwater is referred to as being under reducing conditions. Consequently, redox-sensitive elements are more readily dissolved in deeper, oxygen-depleted groundwater.

Arsenic

Arsenic is an element that is soluble in water, is redox-sensitive, and occurs naturally in minute concentrations in groundwater. The routine ingestion of water containing very low concentrations of arsenic has been linked to skin disease and cancer (Smith et al. 1992). The arsenic standard for community supply wells has been lowered by the U.S. EPA from 50 to 10 µg/L (parts per billion) for finished drinking water (Vorman 2001). Health problems, such as arsenic-induced cancers, have resulted, in other parts of the world, from drinking water with relatively large concentrations of arsenic (e.g., Bagla and Kaiser 1996). Arsenic concentrations of shallow glacial and alluvial aquifers of Illinois range from less than 1 to as high as 107 µg/L; the greatest arsenic concentrations are in the southern part of the state and in the Mahomet aquifer (glacial drift aquifer) (Table 19-1) (Figure 19-7) (Warner et al. 2003).

Iron and Manganese

The solubilities of iron and manganese, metals that are commonly present in groundwater, are sensitive to changes in redox conditions. The concentrations of these metals are low in groundwater from shallow aquifers because the presence of dissolved oxygen in the water causes these metals to precipitate from solution. However, in deeper aquifers where dissolved oxygen has long been consumed by biological and chemical reactions, groundwater often contains abundant concentrations of dissolved iron and manganese (Table 19-1).

Groundwater containing relatively high concentrations of these dissolved metals may appear to turn yellow rapidly (within minutes) in a container. Such water can form orange to black coatings on porcelain fixtures and laundry due to precipitation of manganese oxides and iron oxyhydroxides upon exposure to oxygen (Figure 19-8). The presence of these metals in water can thus be a nuisance. Iron and manganese also can precipitate on well screens and eventually plug them. Such plugging is very likely one of the causes for reduced efficiency of a municipal well in an east-central Illinois municipal well field (Panno et al. 2005b). Iron and manganese can impart a metallic taste to water. The U.S. EPA limits for iron and manganese are 0.30 and 0.05 mg/L, respectively. The U.S. EPA limit is an NSDWR, based on taste and the problems just mentioned rather than on health risk (U.S. EPA 1991). Commercially available water softeners with salt and filters can effectively remove these metals.

Figure 19-8 Falling Springs, located near Dupo, in St. Clair County in southwestern Illinois, is an example of reduced groundwater. The spring discharges from a cave located 50 feet above the base of a cliff. As the groundwater is oxygenated, it precipitates manganese oxide and iron oxyhydroxide intermixed with calcite to form a black apron on the cliff. (Photograph by Joel M. Dexter.)

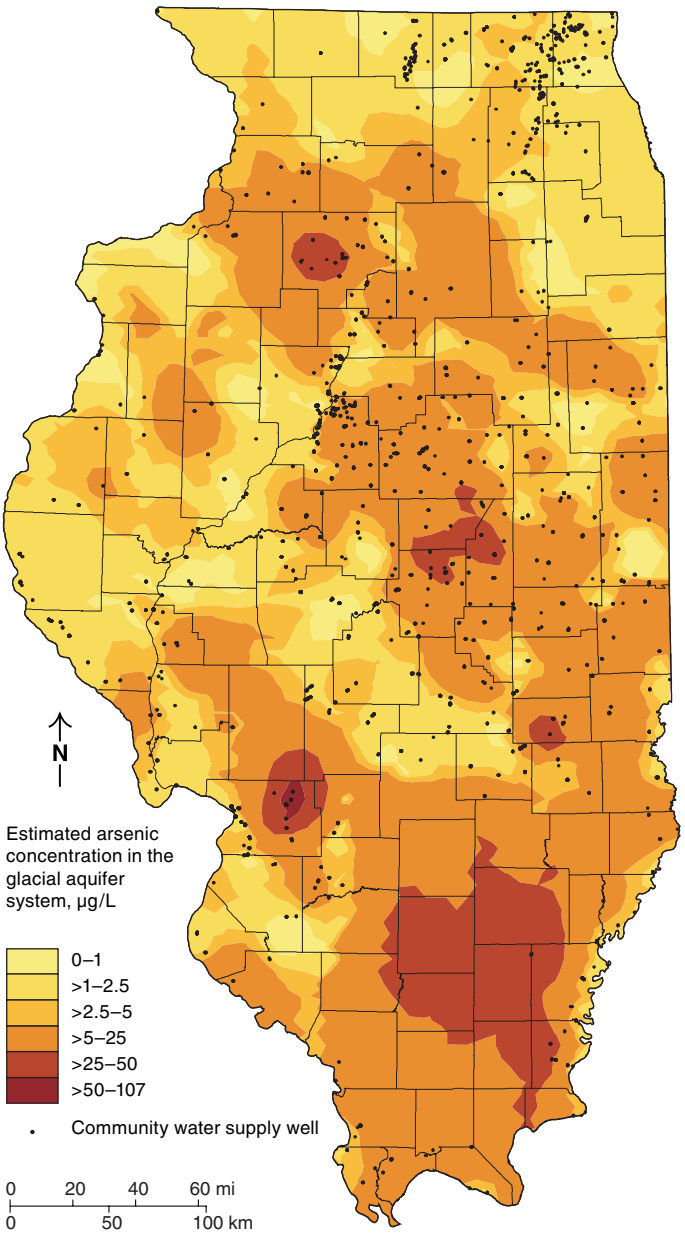

Figure 19-7 Contour map of estimated arsenic concentrations in Illinois groundwater (Warner et al. 2003).

Nitrogen Compounds

Nitrogen compounds (nitrate, nitrite, ammonium, and

organic nitrogen) are naturally occurring components of groundwater. Nitrate is the most common dissolved nitrogen compound in surface and shallow groundwater environments where the water is relatively oxidized. Usually the concentrations of these compounds are small. Naturally occurring nitrate concentrations (NO_3-N) are typically between 2.0 mg/L and 2.5 mg/L (Panno et al. 2006b). However, groundwater in some shallow aquifers in Illinois exceeds the U.S. EPA NPDWR of 10 mg of NO_3-N/L; water with concentrations at or exceeding 10 mg of NO_3-N/L may pose health problems. The potential sources of such high-nitrate concentrations are discussed in Chapter 29, Pollution of Natural Waters. Nitrate concentrations can be naturally reduced through denitrification, a process by which denitrifying bacteria convert nitrate to nitrogen gas. As a result, nitrate in groundwater is often stratified or layered; the greatest concentrations occur near the top of the water table and continually decrease with depth. Ammonium becomes more prevalent in the reducing conditions of deeper and confined aquifers. For example, the Mahomet aquifer of east-central Illinois has ammonium concentrations up to 6 mg/L (Table 19-1) (Hackley 2002). Roy et al. (2003) indicated that the source of ammonium in a deep sand and gravel of the Mahomet aquifer in east-central Illinois is the subsurface degradation of organic materials present in buried ancient soils (paleosols).

Sulfate

Sulfate is typically present in groundwater at concentrations in the tens of milligrams per liter, but it can be much higher. Sulfate concentrations of 250 mg/L or greater is a U.S. EPA NSDWR. Drinking water with such high sulfate concentrations may have objectionable taste and odor; however, there is no evidence of ill effects from drinking such water (Centers for Disease Control, U.S. EPA 1999). In Illinois, sulfate concentrations of several hundred to 2,000 mg/L were found from the deep bedrock Cambrian and Ordovician aquifers in northeastern Illinois (Gilkeson et al. 1981) and in east-central Illinois in the unconsolidated sands and gravels of the Onarga Valley portion of the Mahomet aquifer (Hamdan 1970). Gilkeson et al. (1981) determined that the large sulfate concentrations found in the Cambrian and Ordovician aquifers were from the dissolution of marine evaporites (the calcium sulfate mineral gypsum). Sulfate in the Onarga Valley is due to circulation of groundwater through the bedrock and the leaching of secondary sulfate minerals produced from pyrite oxidation (Table 19-1) (Panno et al. 1994, Hackley 2002).

Dissolved Gases

A variety of dissolved gases are commonly associated with groundwater (Figure 19-3): nitrogen, oxygen, carbon dioxide, methane, and hydrogen sulfide. Other gases that are often present but usually in low concentrations are the noble (inert) gases, hydrogen, chlorofluorocarbons, and radon. As water penetrates into the ground, gases typically found in the atmosphere are dissolved in the water. Thus, nitrogen is common in groundwater. Nitrogen also may be produced from microbial denitrification reactions. Due to biochemical reactions within the aquifers, oxygen is quickly consumed during oxidation of organic matter and other reduced compounds such as the sulfides found in the soils and deeper sediments. Carbon dioxide is added to the infiltrating water in the soil zone due to root respiration and oxidation of organic matter. The addition of carbon dioxide increases the carbonic acid, lowering the water's pH, which has important impacts on the solubility of the rocks and minerals through which the groundwater flows.

In reducing environments, hydrogen sulfide and methane become more prevalent. Hydrogen sulfide results in a rotten egg odor that is sometimes present in well water. The sources of hydrogen sulfide include the bacterial reduction of naturally occurring sulfate dissolved in groundwater and decomposing organic matter within confined aquifers or in aquitards. Although the odor is objectionable, the concentrations of hydrogen sulfide gas typically found in drinking water do not pose a health problem. Hydrogen sulfide can be tasted at concentrations at or exceeding 0.05 mg/L (Lehr et al. 1980). At concentrations of 0.2 mg/L, hydrogen sulfide can be corrosive to silverware, fixtures, and plumbing (Lin 1977). Most water treatment companies can install equipment capable of removing hydrogen sulfide from domestic water supplies using oxidation, chlorination, aeration, and filtration or ion exchange with chemically active compounds (Lemley et al. 1999, Ross et al. 1999).

Dissolved methane is quite common in Illinois groundwater (Figure 19-9). Methane occurs naturally from the microbial degradation of buried organic debris present in the glacial drift deposits throughout much of central and northeastern Illinois (Meents 1958, 1960; Coleman 1976). Many residents of Illinois have used this "drift gas" to run appliances or heat their homes (Meents 1960). Using isotope geochemistry, methane from glacial drift deposits can be distinguished from other sources, such as thermogenic methane associated with petroleum formation or generated in landfills (Coleman et al. 1977, 1988, 1995; Hackley et al. 1996). The ability to determine these differences is important when exploring possible environmental problems from methane-generating sources such as landfills.

Total Dissolved Solids

Total dissolved solids, or TDS, refers to the total mass

of all dissolved constituents (as ions) present in groundwater. The U.S. EPA's NSDWR puts a suggested limit of 500 mg/L on this parameter. The TDS can easily be approximated by using a specific conductance or electrical conductance meter to measure the electrical conductivity of water (its ability to conduct electricity). Conductivity has the following relationship with TDS (Hem 1986):

TDS = specific conductance × 0.59.

Distilled water, having almost no dissolved minerals, would have a specific conductance of near zero. Rainwater is very dilute with a low specific conductance of about 20 microsiemens per centimeter (μS/cm), and water with a large TDS load (such as seawater) has a very high value (close to 60,000 μS/cm in the case of seawater) (Table 19-2). The specific conductance of the 500 mg/L standard would be about 850 μS/cm.

ENVIRONMENTAL ISOTOPES

Isotopes are atoms of an element that have a different number of neutrons in the nucleus. Isotopes can be stable or radioactive. Because the number of protons and the electron configuration are the same as other atoms of that element, isotopes of a particular element behave similarly during chemical reactions. However, because the atomic weights are different, the isotopes of an element react at different rates, which results in different concentrations of isotopes in the coexisting phases of a compound or in the reaction products of chemical, physical, and biological processes. This natural partitioning process is very important in the field of stable isotope geochemistry and is quite useful for determining the source of water or certain dissolved constituents and for figuring out the geochemical processes that have occurred to give the present-day chemical composition of a certain groundwater. The use of environmental isotopes can help solve groundwater quality problems by establishing the source of contaminants (natural or human-induced). The isotopes can also be used to protect groundwater by helping to identify groundwater recharge areas and groundwater flow velocities. Elements with stable isotopes that are commonly used in groundwater studies include oxygen, hydrogen, carbon, sulfur, nitrogen, and, to a lesser degree, chlorine, strontium, helium, and beryllium.

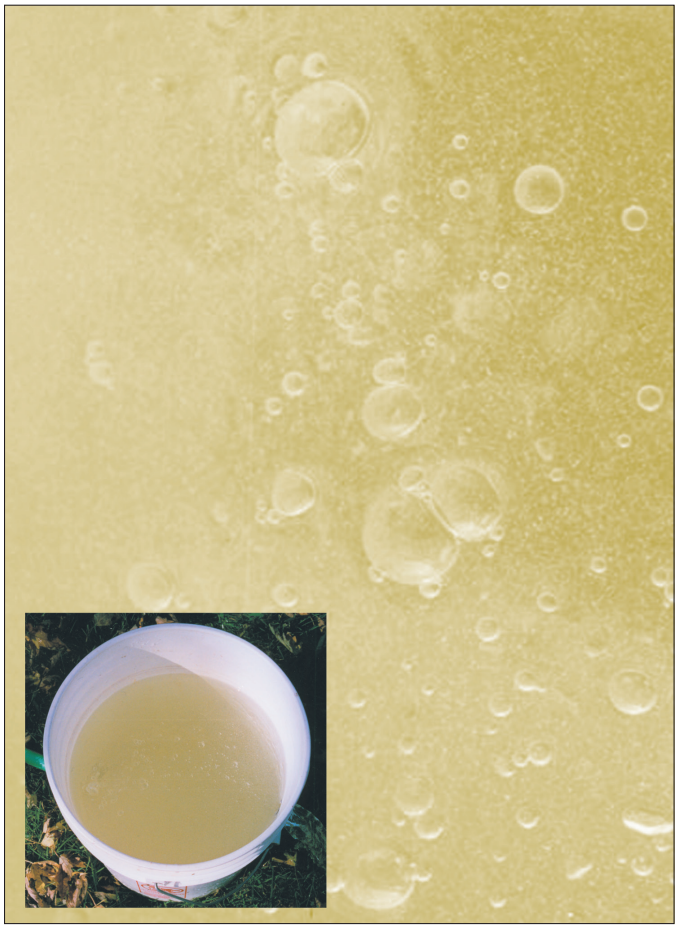

Figure 19-9 Gas (predominantly methane) bubbling out of groundwater pumped from the Mahomet aquifer in central Illinois. The largest bubbles were up to 1 inch (2.54 cm) in diameter. The presence of methane indicates reducing conditions within the aquifer. (Photographs by Samuel V. Panno.)

Radioactive isotopes have unstable nuclei and change into different atomic elements through spontaneous decay involving the emission of particles and energy. The rates of decay differ widely for the various radioactive isotopes, ranging from a fraction of a second to billions of years. The rate of decay is usually referred to as the half-life, the time needed for the concentration of the radioactive isotope to decrease by one-half. In hydrology, radioactive isotopes are typically used to determine the relative age of water and as tracers to help determine the source of water or of dissolved constituents in the water. Several radioactive isotopes are used in groundwater research; however, the most common are tritium (^{3}H), with a 12.3-year half-life, and carbon-14 (^{14}C), which has a 5,730-year half-life.

Two very good sources for information about isotope geochemistry applied to groundwater hydrology are Clark and Fritz (1997) and Kendall and McDonnell (1998). Examples of the use of isotope geochemistry applied to Illinois groundwater include the determination of origin of high-sulfate concentrations in deep aquifers of northern Illinois (Gilkeson et al. 1981), the processes controlling the enrichment of radium-226 and uranium-234 in the Cambrian and Ordovician aquifers of northern Illinois (Gilkeson et al. 1983), the origin of methane in glacial drift and Paleozoic bedrock (Coleman et al. 1988), detection of the impacts of landfill leachate and gases on local groundwater chemistry (Hackley et al. 1996, 1999), determination of sources of elevated nitrate concentrations (Panno et al. 2001, Hackley et

al. 2007, Roadcap et al. 2002, Hwang et al. 2003), the origin of the Illinois Basin brines and Mississippi Valley-type ore deposits (Clayton et al. 1966, Richardson et al. 1988, Stueber and Walter 1991), and the age of groundwater in a buried bedrock valley of central Illinois (Hackley 2002).

Although the concentrations of most radioactive isotopes measured in Illinois groundwater are low and do not detrimentally affect groundwater quality, dissolved radium from the deep Cambrian and Ordovician aquifers of northern Illinois is often present in relatively high concentrations. More than 300 wells in this area exceeded the U.S. EPA NPDWR for radium (Gilkeson et al. 1983). Radium-226 and radium-228 concentrations in groundwater ranged from 2.3 to 50.2 picocuries per liter (pCi/L); the U.S. EPA regulatory limit for the two radionuclides is 5.0 pCi/L (U.S. EPA 1991, 2009). The source of the radium in the aquifers is thought to be fine-grained materials such as the shale layers that form the bounds of the sandstone aquifers.

Conclusion

The quality of groundwater in Illinois changes with depth and location of the aquifer. Shallow surficial aquifers, such as glacially deposited sand and gravel or bedrock units near the land surface in the northern third of the state, contain relatively dilute groundwater compared with groundwater from deeper bedrock aquifers in the central and southern two-thirds of the state. Most of the aquifers in Illinois are made up of carbonate rock or contain considerable amounts of carbonate rock fragments, resulting in an almost ubiquitous problem with hard water. Many of the unconsolidated sand and gravel aquifers are deposited within fine-grained glacial tills and are confined aquifers that are under reducing conditions. The reducing conditions result in considerable amounts of dissolved iron and manganese and, in some cases, methane (drift gas). Most private wells in rural areas of Illinois use water softeners to extract iron and decrease the hardness of the groundwater. Groundwater pumped from wells in the central and southern parts of the state quickly become more saline as depths of wells increase and penetrate into the Pennsylvanian and deeper Paleozoic aquifers. Sodium and chloride concentrations tend to increase as depth increases.

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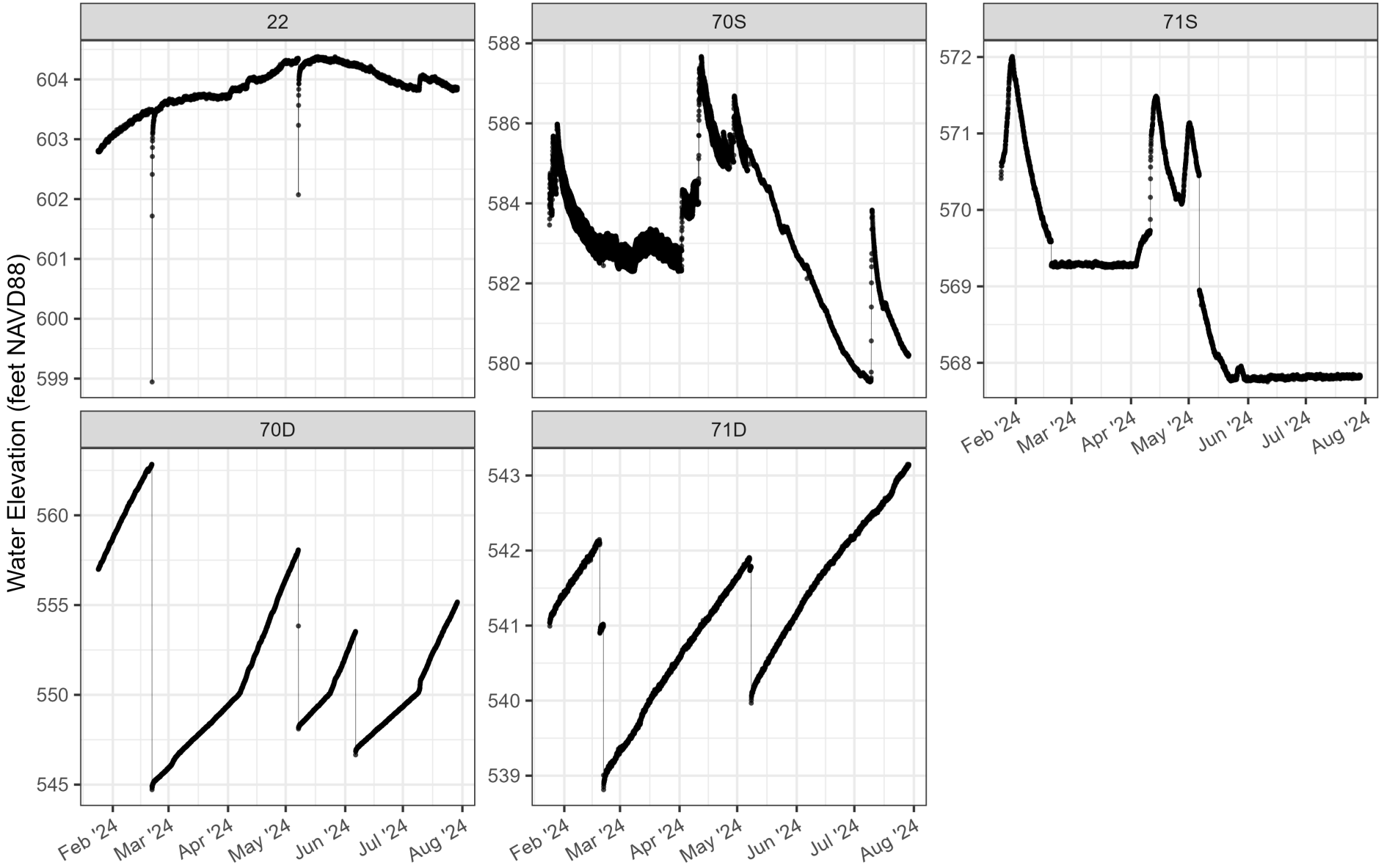
APPENDIX B
Plots of Groundwater Elevation Data from Pressure Transducers Installed in Monitoring Wells 22, 70S, 70D, 71S, and 71D



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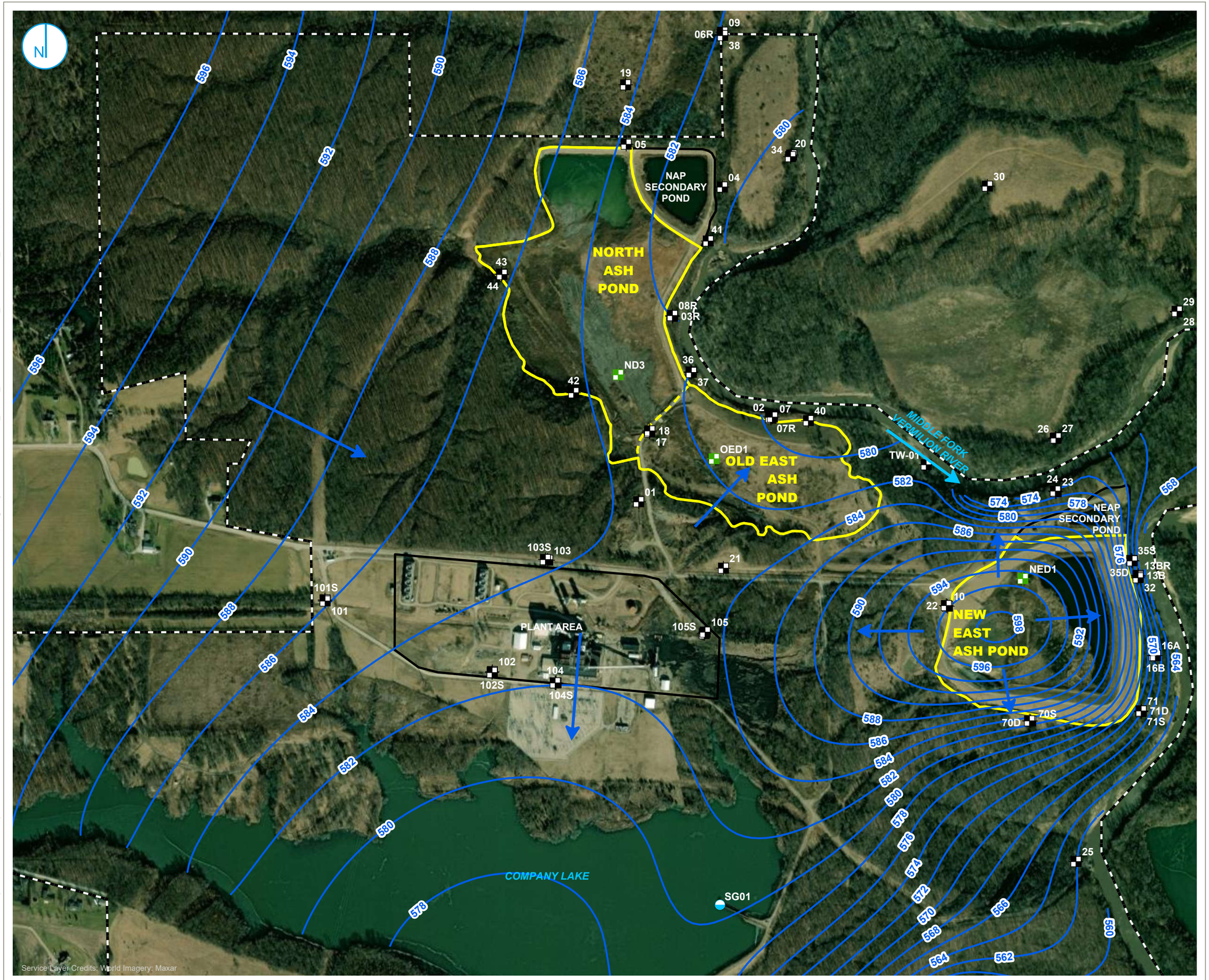
DRAFTED BY: AO | 12/19/2024

Hydrographs for Wells 22, 70S, 71S, 70D, and 71D
Alternative Source Demonstration
New East Ash Pond
Vermilion Power Plant
Oakwood, IL

Appendix C

APPENDIX C
Simulated Bedrock Confining Unit Potentiometric Surface Contours from the January 2022 Construction Permit Application for the North Ash Pond and Old East Ash Pond



- MONITORING WELL
- PORE WATER WELL
- STAFF GAGE, LAKE
- SIMULATED POTENTIOMETRIC SURFACE ELEVATION (FEET)
- GROUNDWATER FLOW DIRECTION
- REGULATED UNIT (SUBJECT UNIT)
- SITE FEATURE
- PROPERTY BOUNDARY

NOTES:
1. ELEVATION CONTOURS SHOWN IN FEET, NORTH AMERICAN VERTICAL DATUM OF 1988 (NAVD88).

0 300 600 Feet

SIMULATED BEDROCK CONFINING UNIT POTENTIOMETRIC SURFACE CONTOURS FROM THE CONSTRUCTION PERMIT APPLICATION FOR THE NORTH ASH POND AND OLD EAST ASH POND

ALTERNATIVE SOURCE DEMONSTRATION
NEW EAST ASH POND
VERMILION POWER PLANT
OAKWOOD, ILLINOIS

APPENDIX C

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Y:\Mapping\Projects\222285\MXD\Alt_Source_Dem\Vermilion\NEAP_912\E006\ASD_E006.aprx\Appendix D. Simulated BCU Contours VER NAP OEAP GMR

PROJECT: 169000XXXX | DATED: 12/10/2024 | DESIGNER: GALARNMC

APPENDIX D
Geosyntec Consultants, 2024. Technical Memorandum: Evaluation of Alternative Sources for Lithium and Chloride within Bedrock Aquifer Solids, Vermilion Power Plant – New East Ash Pond. December 20, 2024.

Geosyntec consultants

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TECHNICAL MEMORANDUM

Date:	December 19, 2024
To:	Brian Voelker, Dynegy Midwest Generation, LLC
Copies to:	Stu Cravens and Phil Morris, Dynegy Midwest Generation, LLC Eric Tlachac and Brian Hennings, Ramboll
From:	Allison Kreinberg, Geosyntec Consultants
Subject:	Evaluation of Alternative Sources for Chloride and Lithium within Bedrock Solids Vermilion Power Plant – New East Ash Pond

This document serves as an Appendix to the December 20, 2024, Alternative Source Demonstration (ASD) for the Vermilion Power Plant New East Ash Pond (NEAP) (Site) for the Quarter 3 2024 sampling event completed pursuant to Title 35 of the Illinois Administrative Code (35 I.A.C.) § 845.650(e) (VER NEAP E006 ASD). All documents referenced in this ASD may be referenced as indicated in the References section.

The Q3 2024 sampling event identified potential exceedances of the GWPSs for chloride and lithium at monitoring well 71D (Ramboll 2024a). Geosyntec Consultants, Inc. (Geosyntec) has completed a review of geochemical and geologic conditions at the Site to evaluate the elevated chloride and lithium values observed in groundwater at compliance monitoring well 71D. Using evidence from laboratory analyses, statistical evaluations, and the depositional history of the geologic units at the Site, this technical memorandum demonstrates that the NEAP is not the source of the chloride or lithium potential exceedances in Site groundwater and supports the conclusion that natural variation in groundwater quality due to interactions with bedrock caused the elevated lithium and chloride concentrations observed at well 71D during the E006 sampling event and the VERM NEAP, Old East Ash Pond, and North Ash Pond did not contribute to the elevated concentrations.

SITE CONDITIONS

Site geology consists primarily of unlithified alluvial and glacial deposits overlying shale bedrock that contains a major coal seam mined in the region. The alluvial deposits consist of the Cahokia Alluvium composed primarily of sand with occasional layers of silty clay and the Upper Till Unit (Wedron Formation and Glasford Formation Till) consisting of clay and silty clay with occasional sand lenses. The Cahokia Alluvium comprises the Upper Unit (UU) at the NEAP and is generally 10 to 25 feet thick. Below this unit is the Upper Confining Unit (UCU) that is comprised of the lower permeability Wedron and Glasford Formations. The UCU is of variable thickness, ranging from up to 100 feet west of the NEAP and absent east of the NEAP (Ramboll 2021).

The Bedrock Confining Unit (BCU), which is typically greater than 80 feet thick, consists of the Pennsylvanian-age Shelburn Formation, which is primarily a low permeability shale with thin limestone, sandstone, and coal beds. The top of the shale unit in the vicinity of the NEAP is described as highly weathered and decomposed. This unit contains the Danville (No. 7) Coal, which was encountered near the NEAP at approximately 80 to 100 feet below ground surface (ft bgs). Well 71D is screened within the BCU.

Additional information regarding Site hydrogeology and stratigraphy is provided in the ASD prepared by Ramboll.

NATURAL VARIABILITY ASSOCIATED WITH BEDROCK SOLIDS

Geosyntec reviewed the results of analyses completed on solid phase samples collected from the Site near well 71D to evaluate if elevated chloride and lithium concentrations at well 71D could be derived from the native weathered shale bedrock lithology.

Samples were collected from soil borings advanced in June 2023 near two locations: compliance well 35D and compliance well 70D (**Figure 1**). Due to access limitations and health and safety considerations at the Site, the boring locations were adjusted in the field and are approximately 200-250 feet offset from the original well locations. Differences in ground surface elevations and bedrock dip were considered during drilling and sample selection so that the sampled intervals correspond with the well screen interval. Documentation for solid phase analyses is attached and referenced in the text. Soil borings were advanced using a sonic drill rig. Borings were advanced and samples were collected in general accordance with USEPA Soil Sampling Operating Procedure LSASDPROC-300-R5 (USEPA 2023). Boring locations and well screen intervals are shown in the cross sections provided in **Attachment 1**. The field boring log for these soil borings are provided as **Attachment 2**.

Two samples were collected from the boring near well 35D (VER-35), and three samples were collected from the boring near well 70D (VER-70) at various depths. While samples were not collected from the immediate vicinity of 71D, the screened lithology at 71D is expected to be similar to the conditions at 35D and 70D based on the boring logs provided in **Attachment 3**. The material sampled for geochemical characterization is consistent with the material present in the well screens at well 71D (gray weathered shale). Additional information regarding solids sampling at 71D at the time of well installation can be found in the Initial Operating Permit Application for the NEAP (Geosyntec, 2021).

Evaluation of Geogenic Lithium

Two samples from VER-35 (55-60 ft bgs and 60-63 ft bgs) and one sample from well VER-70 (75-80 ft bgs) were submitted for analyses of total lithium and lithium distribution within the bedrock using sequential extraction procedure (SEP). SEP is an analytical technique that uses progressively stronger reagents to solubilize metals from specific phases within the solid matrix and is used to infer associations between constituents and different classes of solids (Tessier et al. 1979). These classes of solids are identified based on their solubility under different reagents; the reagents are identified in **Table 1** and the analytical laboratory report provided in **Attachment 4**.

Results for total and SEP analyses of lithium in these samples are presented in **Table 1**. As a first step to evaluate data quality in an SEP analysis, the sum of individual extraction steps from the SEP was compared to the total lithium concentration. The sum of the SEP procedure is not expected to be exactly equal to the total metals analysis but should generally be consistent with the total metals analysis. The total lithium concentrations ranged from 39 micrograms per gram of material (µg/g) to 42 µg/g in the shale samples. The summed concentrations of lithium from the SEP analyses ranged from 45.3 to 50.8 µg/g. The results were generally consistent between the total metals analyses and the summed SEP steps, indicating good metals recovery and data quality. These results are also consistent with previous samples collected at the Site (31.1-33.3 mg/kg, Ramboll 2021) and within the Danville coal (5.5-89 mg/kg, USGS 2002).

The results presented in **Table 1** demonstrate that lithium is associated with multiple solid phase components. The majority of the lithium was released via leaching steps associated with two reactive solid phase components: metal oxides (between 24 and 28%) and sulfides (between 28 and 31%). Lithium associated with oxides and sulfides may be mobilized via desorption or dissolution of these phases in the event of geochemical changes to the system due to the relative instability of oxide and sulfide minerals.

The SEP results also identified an abundance of iron in the leaching step associated with non-crystalline oxides (Step 3; **Attachment 4**). Non-crystalline materials cannot be identified via X-

ray Diffraction (XRD); however, the thermodynamic stability of some of these phases can be assessed using Eh-pH diagrams. An Eh-pH diagram generated using well 71D groundwater data (**Figure 2**) indicates that the groundwater chemistry at 71D generally favors the thermodynamic stability of ferrihydrite ($Fe(OH)_3$(ppd)), a common amorphous iron oxide phase. However, some samples plot along the solid-aqueous phase boundary indicating a component of dynamic equilibrium in the system. Under these observed conditions, minor geochemical shifts could cause dissolution of crystalline and non-crystalline iron oxide phases, resulting in mobilization of associated lithium to groundwater. Iron sulfide mineral pyrite is not predicted to be stable at 71D; therefore, sulfidic minerals within the bedrock which were present in SEP results (**Table 1**) would be expected to undergo oxidative dissolution. Lithium associated with the sulfide solid phase component would then be mobilized due to dissolution/desorption processes, resulting in aqueous lithium groundwater concentration increases.

Mineralogical analyses were completed on all samples using XRD to evaluate whole rock mineralogy and determine the presence of oxide minerals, sulfide minerals, clay minerals, and micas within the bedrock solids. Whole rock mineralogy results are provided in **Table 2**. The analytical laboratory report for XRD is provided as **Attachment 5**. Sample mineralogy consists predominantly of quartz, mica (muscovite), feldspars (albite and microcline), and clay minerals (illite, chlorite, and kaolinite) (**Table 2**). Of these minerals, muscovite and clays are known hosts of natural lithium within their crystal structures and comprise natural sources of lithium in the system (Starkey 1982). These minerals are present at large abundances in samples from well 35D and well 70D (between 43.0 to 47.4%, **Table 2**), indicating that these lithium-host minerals occur in the BCU and constitute a geogenic source of aqueous lithium which could potentially mobilize to groundwater. This is supported by SEP results which contain notable abundances (31 to 37%) of lithium associated with the final extraction of the analysis, which is typically considered to be associated with residual metals which are not readily soluble (i.e., primary mineral phases like clays and micas). Further, field lithologic descriptions of the samples from VER-35 and VER-70 indicate that the samples collected from these two locations consist of weathered shale, which is comprised primarily of mica and clay minerals that are known to be hosts of natural lithium.

Lithium is known to leach from lithium-hosting igneous rocks and micas through weathering processes. Mineral weathering reactions occurring in micas may result in lithium-rich micas transforming directly to illitic clays, and then to mixed-layer and smectite clays. The lithium within these primary minerals either becomes incorporated directly into the crystal structures of the clay minerals or is mobilized to groundwater and later concentrated through evaporation (Cannon et al. 1975).

Clay minerals are known to be common sorbents for naturally occurring lithium (Starkey 1982) and are able to host lithium within vacant sites in the octahedral layers comprising part of their

crystal structures (Schultz 1969). Lithium association with clays comes in part from the weathering reactions discussed above. In addition to mineral alteration reactions, clays can be enriched in lithium from saline depositional waters. Monitoring well 71D is screened within the shale of the Shelburn Formation. The Shelburn Formation, like many of the Pennsylvanian-age deposits within the Illinois Basin, represents marine cyclic depositional sequences which feature transgressive and regressive periods that cause the deposition of interbedded sequences of sandstone, shale, and limestone (Weller 1930). These depositional environments provide both the clay mineral component and the saline marine depositional water component of the lithium enrichment process mentioned above.

The weathered nature of the shale bedrock which was documented in field boring logs suggests that physical and chemical weathering processes are likely occurring, which supports the occurrence of weathering reactions involving metal oxide and sulfide minerals as well as alteration reactions between mica and clay minerals and between different types of clay minerals. These reactions all represent processes by which lithium associated with the native geologic materials may become mobilized, contributing aqueous lithium to groundwater.

Evaluation of Geogenic Chloride

As previously mentioned, monitoring well 71D is screened within shale of the Shelburn formation, which contains marine cyclic depositional sequences. These sequences result in deposition of fine grained shales which are cyclically exposed to high ionic strength marine waters. These marine waters are saline and ubiquitously concentrated in chloride. Fine-grained marine shales specifically are known to retain this chloride for long periods, resulting in elevated concentrations in formation water (Hem 1985). Further, transgression-regression cycling creates sequences in which saline marine waters saturate open pore space in these sediments, which are then retained due to the subsequent deposition of and burial by additional fine-grained sediment, trapping the marine water at the time of deposition. While the original water within the pore space is typically replaced by meteoric recharge early after deposition, the dissolved ions (i.e., chloride) in the water are typically retained by membrane filtration as an effect of the phyllosilicate (clay/mica) mineralogy of the shales (Drever 1988). These clay and mica minerals are observed in all shale samples from the Site at notable quantities discussed above (**Table 2**), suggesting that this mechanism is applicable to groundwater at this Site. In addition to the retention of marine water within the pore space of fine-grained sedimentary rocks, deposited sediment in cyclic marine environments also may become impregnated with soluble salts like halite (crystalline sodium chloride, NaCl) or sylvite (crystalline potassium chloride, KCl), which contain chloride in the crystal structure (Hem 1985). These evaporites are known to be highly soluble and subject to dissolution during pore fluid evolution. Dissolution of these salts results in further increases in the

concentrations of aqueous chloride in pore fluid from rocks of coastal marine origin, regardless of whether the evaporite minerals are still present currently.

Studies within the region have found that groundwater chloride concentrations comparable to or higher than those observed at well 71D are often found within the Pennsylvanian-aged shale bedrock due to the depositional environment mentioned above. The mean chloride concentration in Pennsylvanian bedrock aquifers in the area reported by the Illinois State Geological Survey is 1,689 mg/L and a chloride maximum concentration of 30,269 mg/L was reported (Mehnert and Dreher 2002). The chloride concentration observed in well 71D for the Q3 2024 sampling event is 680 mg/L, well below the referenced mean value.

Furthermore, seeps with high naturally occurring salinity (i.e., brines) are known to occur in southern Illinois. Samples of seeps and shallow wells affected by brine in Illinois had highly variable chloride concentrations ranging from ~100 mg/L up to more than 30,000 mg/L at the Vermilion Salines in Kickapoo Creek State Park (Kelly et al, 2012). These observed concentrations further support the prominence of elevated naturally occurring chloride within groundwater from Pennsylvanian aquifer units in the region due to the depositional history of these units.

STATISTICAL EVALUATION OF GROUNDWATER COMPOSITION

Advanced statistical analyses were employed to evaluate the similarity or dissimilarity among different groundwater samples or groups based on a broad suite of analytes. Dimensional reduction techniques, such as principal component analysis (PCA), are especially effective in identifying the analytes responsible for statistical differences between samples and revealing underlying patterns related to environmental factors, contamination sources, or other natural characteristics of the Site (Mumford et al. 2007). Clustering methods were further utilized to group samples based on their combined chemical composition through maximizing intra-group similarity.

PCA is often used to simplify large datasets with multiple variables by creating new uncorrelated variables known as principal components (PCs). The PCs are linear combinations of the original variables; the first few PCs typically capture most of the variation within the dataset. Factor loadings are calculated based on the correlation between PCs and the original variables. As such, variables with notably higher positive or negative factor loadings are main drivers of similarity or dissimilarity and clustering of samples. Factor scores are calculated based on the correlation between the chemical composition of each sample and the PCs. Samples with similar chemical compositions show similar factor scores and tend to cluster together on a PCA plot.

In this study, the dataset used for PCA included 106 groundwater samples collected from the NEAP in 2021, 2023 and 2024 from upgradient wells (10 and 22), downgradient wells (70S, 71S,

70D, 71D, 16A, and 35D), and porewater wells NED1, ND3 and OED1.[1] While the NED1 sampling location is associated with the NEAP, samples were included from two porewater wells associated with the Old East Ash Pond/North Ash Pond (OEAP/NAP) CCR unit (ND3, OED1) to evaluate the potential influence of the OEAP/NAP on groundwater composition at NEAP downgradient well 71D. Most groundwater and porewater data used in the following analyses were submitted quarterly to IEPA in accordance with 35 I.A.C. § 845.610(b)(3)(D) (Ramboll 2023a, 2023b, and 2024b, c, and d,) and are incorporated by reference in this ASD. Laboratory electronic data deliverables (EDDs) for additional groundwater data not included in the quarterly reports or previously provided to IEPA have been transmitted electronically.

The CCR porewater chemistry from both the NEAP and OEAP/NAP is significantly different from that of the monitoring wells (e.g., boron concentration in porewater was 29.66 ± 12.29 mg/L compared to 0.79 ± 0.64 mg/L in the rest of the wells). Therefore, the total variability in the dataset is expected to be dominated by the greater variance of CCR signatures between pore water and the rest of the wells, potentially obscuring the variabilities in samples from monitoring wells. As such, two parallel scenarios – one with and one without porewater samples - were evaluated. PCA requires that input variables have similar scales of measurement and variances. As such, data were standardized by mean-centering and scaling to unit variance prior to performing PCA. Data were further square transformed to reduce the skewness of dataset.

The results from the evaluation with porewater are discussed first and shown in **Figures 3 to 5**. The fraction of total variation explained by each PC is shown in **Figure 3a**, with the first two PCs accounting for approximately 83% of the total variation in the datasets. Additionally, the quality of representation of each variable by the first two PCs is presented in **Figure 3b**. As illustrated in the figure, the first dimension is dominated by calcium, total alkalinity, and boron, while the second dimension is influenced by chloride and barium.

PCA results are often visualized using biplots where samples are projected on the first two PCs (i.e., factor scores), and factor loadings are represented as vectors. The closer the data points are on the graph, the greater the similarity in their chemical composition. The result from this study is shown on **Figure 4**, where the samples acquired from the BCU are orange, UCU and UU samples are shades of blue, and the porewater samples are gray. The biplot suggests that porewater samples cluster separately from the groundwater samples in all hydrostratigraphic units (i.e., BCU, UCU, and UU samples). The factor loadings, represented as vectors on the biplot, suggest that

[1] Analytes included in this PCA include total alkalinity, boron, calcium, pH, barium, chloride, and fluoride. The complete dataset used for PCA analysis is provided with this submission as **Attachment 6**.

constituents such as boron and calcium are responsible for the chemical signature of the porewater cluster.

Clustering was further explored using Ward's hierarchical clustering method, a distance measure employed in agglomerative algorithms and commonly applied in hydrogeochemical studies. The analysis was performed on a scaled and centered dataset. The results from clustering (**Figure 5**), align with findings from the PCA (**Figure 4**). Both PCA and clustering analysis supported the distinction between porewater samples and groundwater samples from both downgradient and upgradient locations.

The results of the evaluation without porewater samples included are shown in **Figures 6 to 8**. In this scenario, the first two principal components captured approximately 75% of total variance (**Figure 6a**), with fluoride and chloride dominating the first dimension and total alkalinity and pH dominating the second dimension (**Figure 6b**). The biplot is presented on **Figure 7**, which shows that the BCU samples are clustered separately from the combined UCU and UU samples. Clustering was also performed for this second analysis, as shown in **Figure 8**, with the results indicating that samples from the BCU cluster separately from the combined UCU and UU samples. This PCA analysis and clustering suggests that lithology is the main driver for the chemistry of groundwater samples. Overall, the results of the PCA and clustering analyses from different scenarios support the conclusion that the elevated concentrations of lithium and chloride at 71D are not attributable to the NEAP CCR unit and instead the groundwater geochemistry is influenced primarily by the native lithology.

Due to anomalously high sulfate concentrations in well 35D (Ramboll 2023c), sulfate and TDS were excluded from both multivariate analyses described above. Two additional scenarios which included sulfate and TDS but exclude 35D samples are presented in **Attachment 7**. As before, the evaluation included one analysis with porewater samples and one without porewater samples included. The findings were consistent with the multivariate analyses described above, in that groundwater composition is influenced by native lithology.

CONCLUSION

Naturally occurring lithium associated with minerals in the BCU at the Site was identified as the alternative source of lithium to Site groundwater. Solid-phase samples collected near compliance wells 35D and 70D contained lithium, and SEP analyses demonstrated that much of the lithium in the solid phase is associated with the fractions which correlate to primary minerals such as micas and clay minerals, as well as the reactive fractions associated with sulfides and oxide minerals. XRD confirmed the presence of abundant micas and clay minerals hosted in the shale bedrock that are probable sources of lithium in Site groundwater due to the weathering of bedrock. Naturally

occurring chloride associated with saline formation water at the time of deposition was identified as the alternative source of chloride. Evidence of comparable or greater chloride concentrations in regional groundwater from similar-aged strata suggests that chloride groundwater concentrations are naturally variable within Pennsylvanian aquifers in Illinois at concentrations greater than the 35 I.A.C. § 845.600(a) GWPS.

Advanced statistical methods also demonstrate that groundwater geochemical signatures from the BCU, the UCU, and the UU are distinctly different from that of the porewater based on a combination of parameters.

Based on the facts and evidence included and referenced herein, a source other than the VER NEAP (naturally occurring major ion concentrations associated with bedrock underlying the Site) caused the chloride and lithium potential exceedances observed at well 71D during the E006 sampling event and the VER NEAP did not contribute to the elevated chloride and lithium. This information serves as the written demonstration of an alternative source for the potential exceedances of chloride and lithium at well 71D and that the NEAP CCR Unit did not contribute to elevated chloride and lithium concentrations.

REFERENCES

Data presented in documents referenced herein are considered incorporated by references and may be found in **Attachment 8** or at publicly accessible internet addresses provided following each reference below.

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TABLES

Table 1 - Lithium SEP Results Summary
Vermilion Power Plant - New East Ash Pond

Geosyntec Consultants, Inc.

Soil Boring Location		**VER-35**		**VER-35**		**VER-70**	
Sample Depth (ft bgs)		**(55-60)**		**(60-63)**		**(75-80)**	
Location		**Downgradient**		**Downgradient**		**Downgradient**	
Field Boring Log Description		**Weathered Shale**		**Highly Weathered Shale**		**Highly Weathered Shale**	
Total Lithium		42		39		42	
SEP Results							
SEP Fraction	**SEP Reagent**	**Concentration**	**% of Total**	**Concentration**	**% of Total**	**Concentration**	**% of Total**
Exchangeable Metals Fraction	$MgSO_4$	<10	--	<10	--	<11	--
Metals Bound to Carbonates Fraction	Sodium acetate, acetic acid	0.56 J	1%	0.62 J	1%	<8.3	--
Non-crystalline Materials Fraction	Ammonium oxalate (pH 3)	0.52 J	1%	0.74 J	2%	0.41 J	1%
Metals Bound to Metal Hydroxide Fraction	Hydroxylamine HCl and acetic acid	13	28%	12	27%	12	24%
Bound to Organic Material Fraction	5% sodium hypochlorite (pH 9.5)	4.1 J	9%	3.9 J	9%	4.4 J	9%
Metals Bound to Acid/Sulfide Fraction	HNO_3, HCl, and H_2O	13	28%	14	31%	15	30%
Residual Metals Fraction	HF, HNO_3, HCL, and H_3BO_3	15	33%	14	31%	19	37%
SEP Total		46.2	100%	45.3	100%	50.8	100%

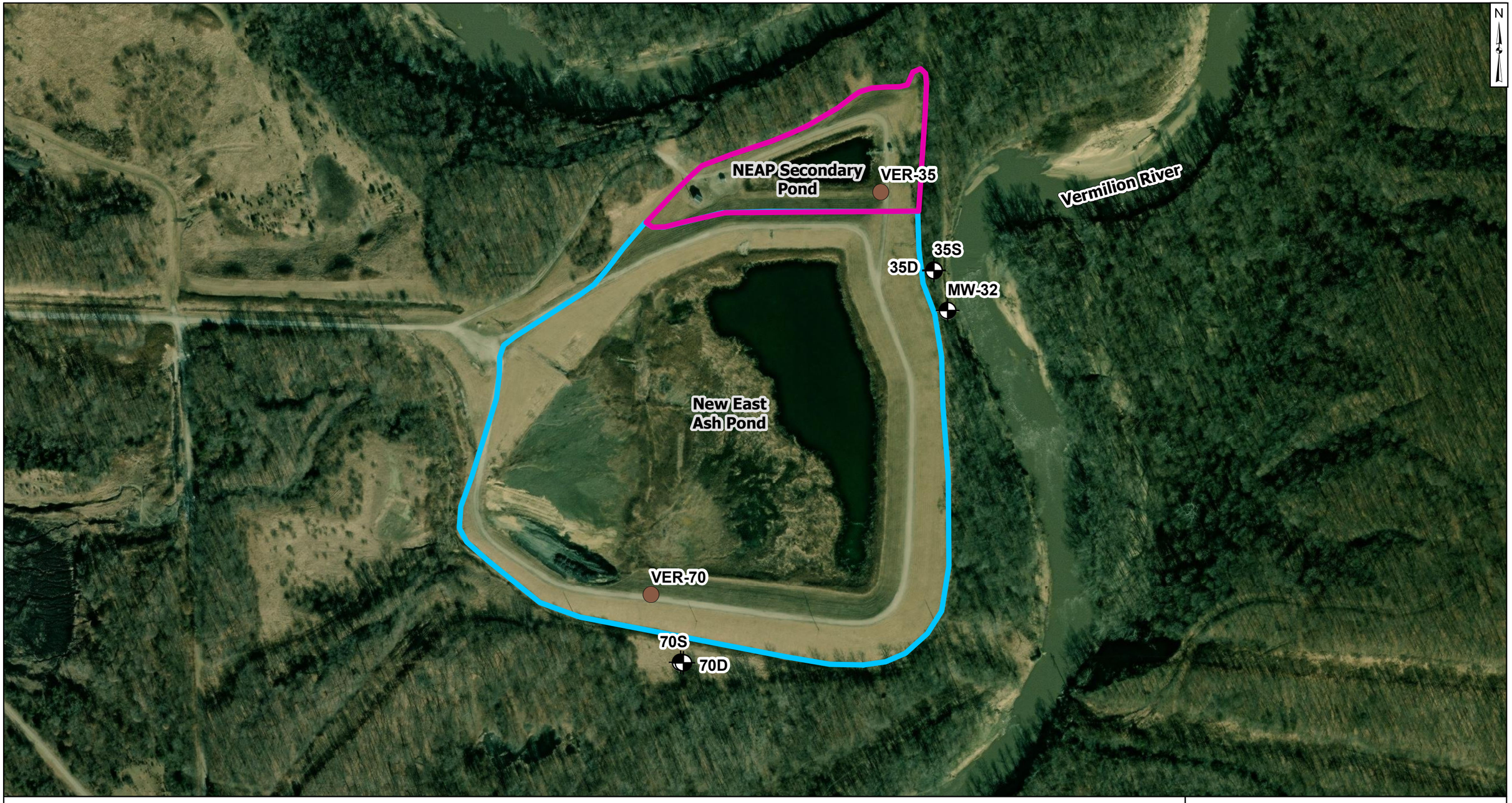
Notes:
SEP - sequential extraction procedure
ft bgs - feet below ground surface
All results shown in microgram of lithium per gram of soil (µg/g).
Total lithium was analyzed using aqua regia digest, ICP-MS
Non-detect values are shown as less than the reporting limit.
The lithium fraction associated with each SEP phase is shown.
% of total lithium is calculated from the sum of the SEP fractions.

Table 2 - Summary of X-Ray Diffraction Analysis
Vermillion Power Plant - New East Ash Pond

Field Boring Location			VER-35	VER-35	VER-70
Sample Depth (ft bgs)			(55-60)	(60-63)	(75-80)
Location			Downgradient	Downgradient	Downgradient
Field Boring Log Description			Weathered Shale	Highly Weathered Shale	Highly Weathered Shale
Mineral/Compound	**Formula**	**Mineral Type**	**(wt %)**	**(wt %)**	**(wt %)**
Quartz	SiO_2	Silicate	38.5	38.1	35.0
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	Mica	23.4	23.0	27.0
Albite	$NaAlSi_3O_8$	Feldspar	12.6	12.6	11.5
Illite	$K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$	Clay	7.1	8.0	5.2
Chlorite	$(Fe,(Mg,Mn)_5,Al)(Si_3Al)O_{10}(OH)_8$	Clay	6.9	6.8	7.7
Kaolinite	$Al_2Si_2O_5(OH)_4$	Clay	5.6	5.4	7.5
Siderite	$FeCO_3$	Carbonate	4.9	5.0	5.4
Microcline	$KAlSi_3O_8$	Feldspar	1.0	1.1	0.70
Clay Minerals Total			19.6	20.2	20.4
Clays + Muscovite Total			43.0	43.2	47.4

Notes
Sample depth is shown in feet below ground surface (ft bgs).
wt %: percentage by weight

FIGURES



Legend

- Monitoring Well
- Boring Location
- New East Ash Pond (NEAP)
- NEAP Secondary Pond

Notes

- Soil boring locations are approximate.
- Only select monitoring well locations are shown.
- Ash pond boundaries are approximate.

250 125 0 250 Feet

Boring Locations

Dynegy Midwest Generation
Vermilion Site
Oakwood, Illinois

Geosyntec consultants

Columbus, Ohio | December 2024

Figure 1

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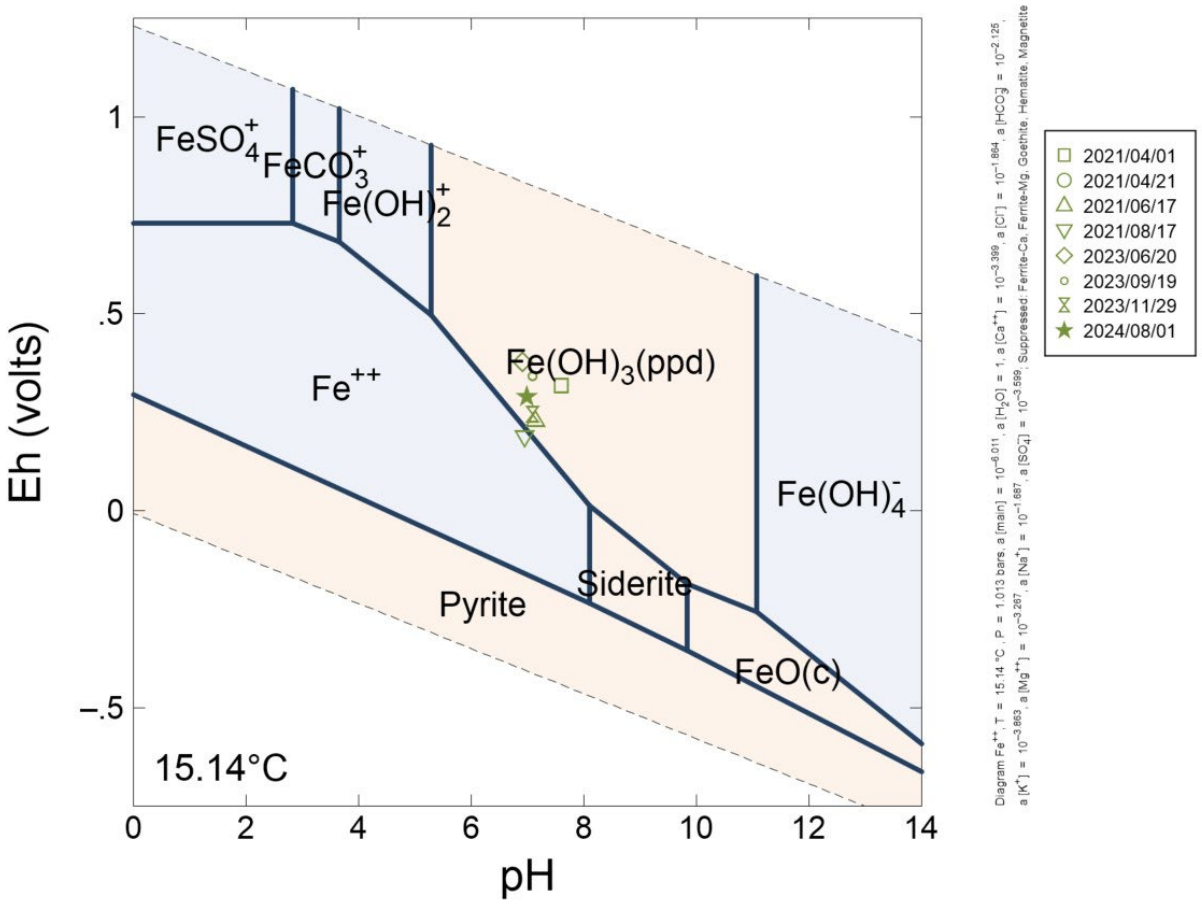

Notes:

1. Activities of constituents were calculated from average values for well 71D groundwater.

Fe – iron, pyrite – FeS2, siderite – FeCO3, Fe(OH)3(ppd) – precipitated ferrihydrite, Eh – oxidation reduction potential (converted from field measurements using + 0.2 volts)

Well 71D Iron Stability Diagram
Vermilion Power Plant – New East Ash Pond

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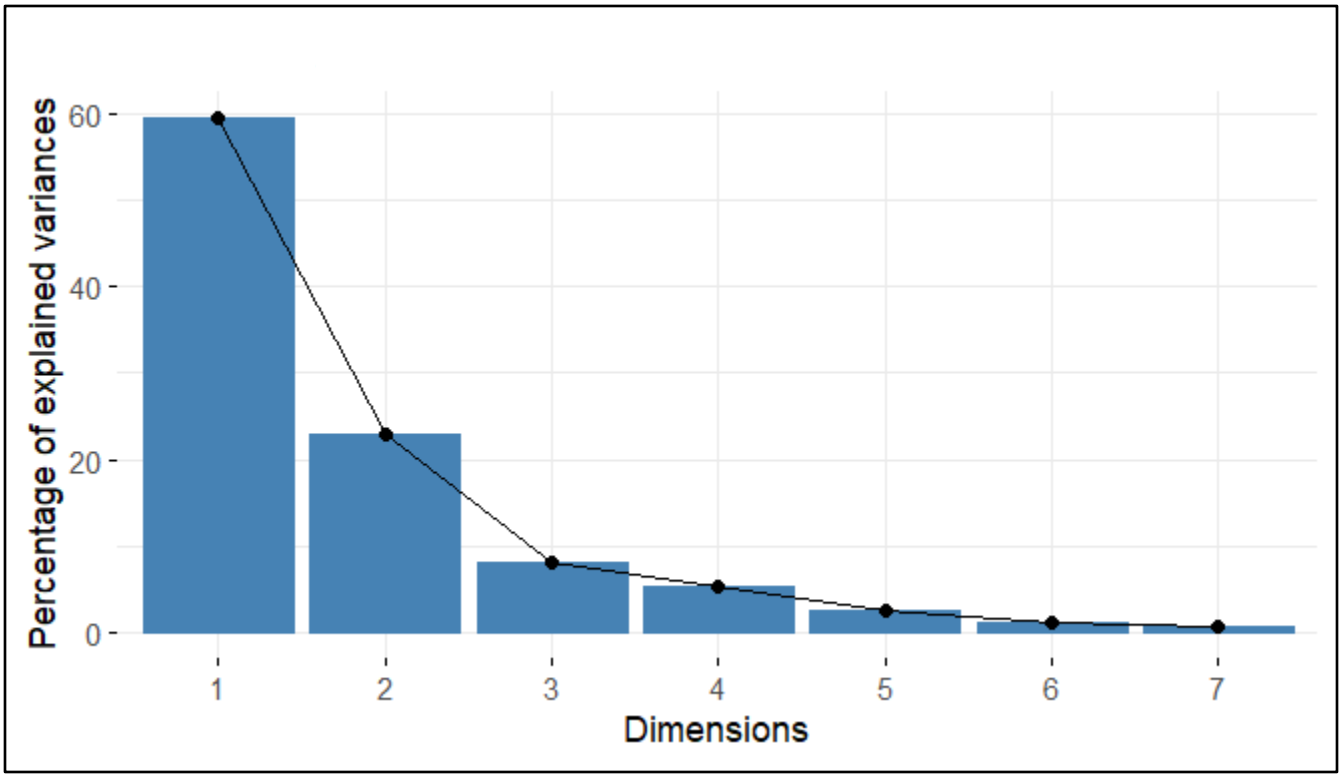
Figure **2**



Notes:
1. Samples collected from upgradient wells 10 and 22, downgradient wells 70S, 71S, 16A, 35D, 70D, and 71D, and porewater wells NED1, ND3 and OED1 were included in the evaluation.

PCA Analysis - Quality of Representation of Principal Components
Vermilion Power Plant – New East Ash Pond

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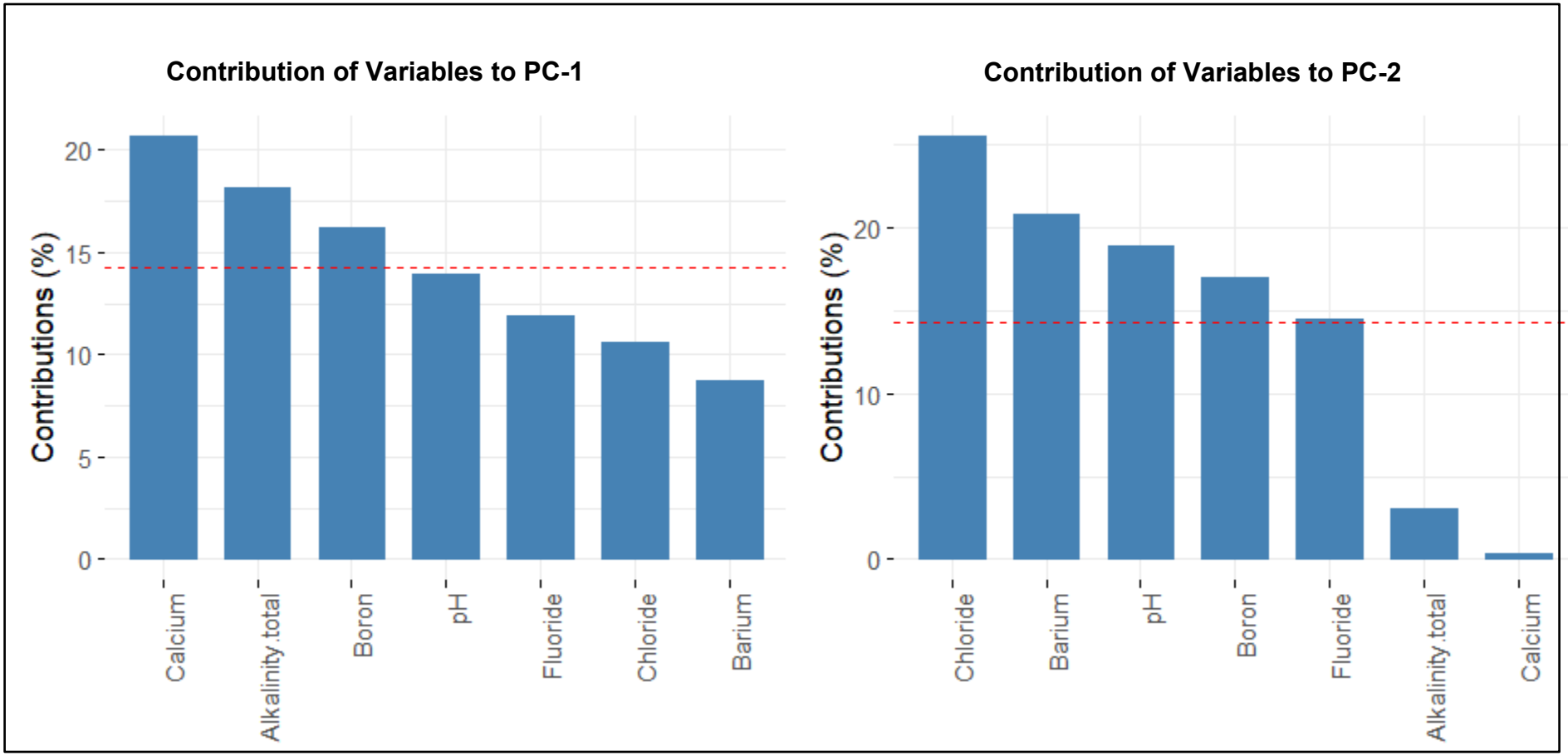
Figure **3a**



Notes:
1. The dashed red line represents the anticipated value for uniform contribution. The constituents with a contribution exceeding the reference line are considered significant in its contribution to each PC (principal component).

Contribution of Variables to First Two Principal Components

Vermilion Power Plant – New East Ash Pond

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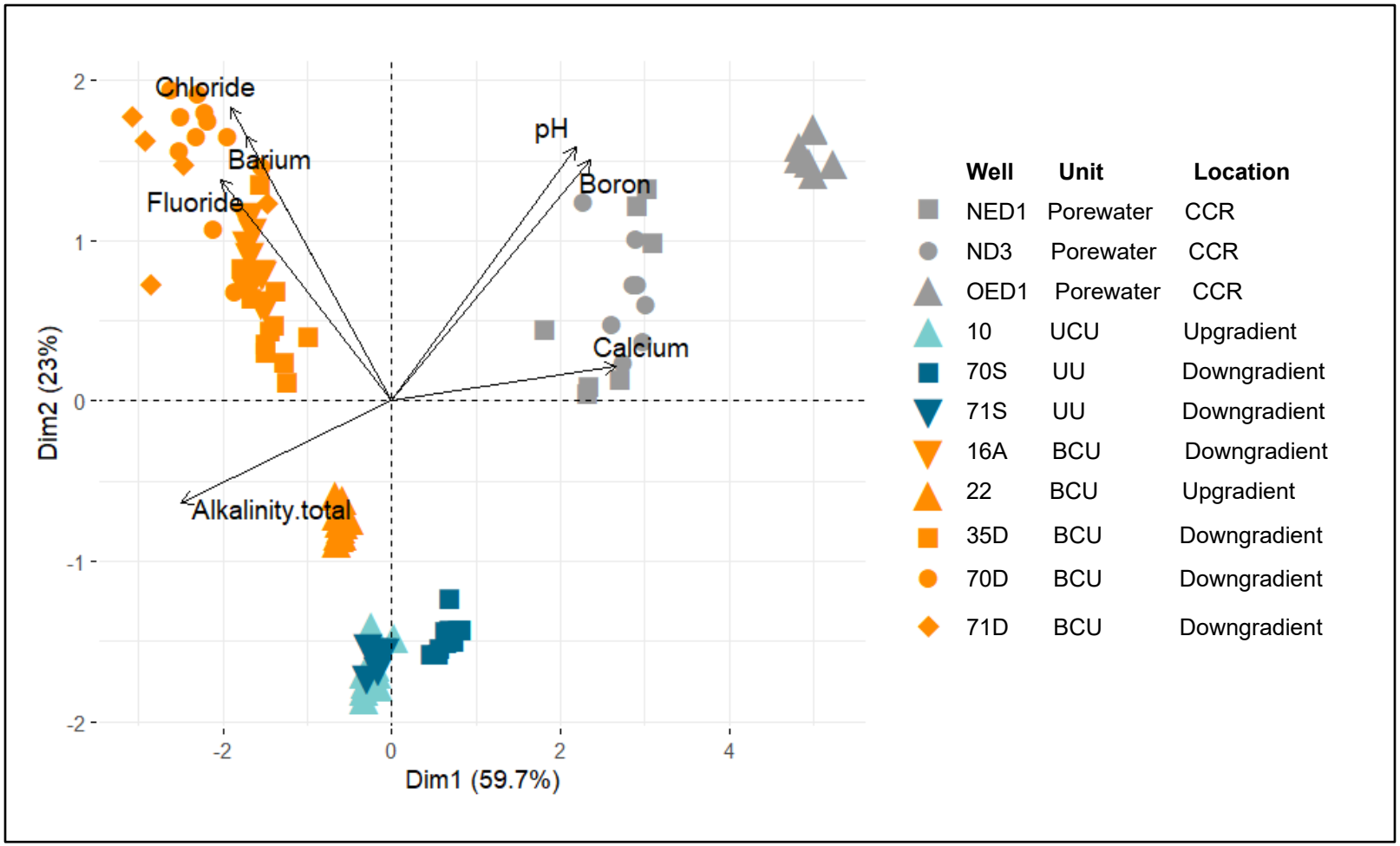
Figure **3b**



Notes:
1. The arrows signify the correlations between the constituents and the principal components.
2. Datapoints are colored based on hydrostratigraphic unit of sampling locations as follows:
   - Bedrock Confining Unit (BCU) wells: 16A, 22, 35D, 70D, 71D.
   - Upper Confining Unit (UCU) well: 10.
   - Upper Unit (UU) wells: 70S, 71S.
   - Coal Combustion Residual (CCR) wells: NED1, ND3, OED1.
3. Dim: Dimension

Principal Components Analysis Biplot

Vermilion Power Plant – New East Ash Pond

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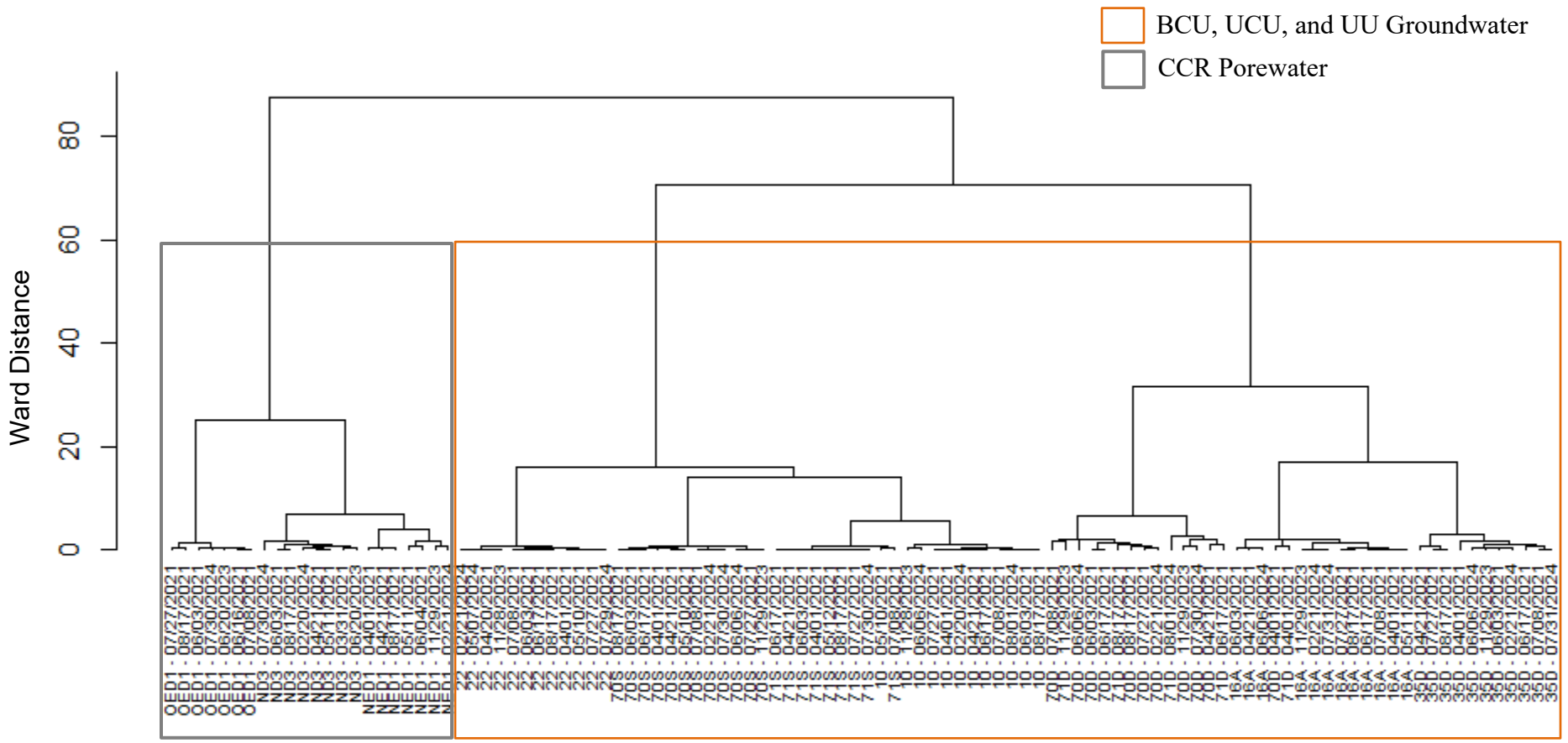
Figure **4**



Notes:
1. The cluster analysis used Euclidean distances, and Ward's method as the clustering algorithm.
2. In the dendrogram, samples on the same branch are more similar to each other. The samples with the highest similarity are on the closest branches.
3. The boxes around the branches represent the two clusters into which samples from each source grouped.
4. BCU, CCR, UCU and UU refer to Bedrock Confining Unit, Coal Combustion Residual, Upper Confining Unit, and Upper Unit, respectively.

Dendrogram Graph from Cluster Analysis

Vermilion Power Plant – New East Ash Pond

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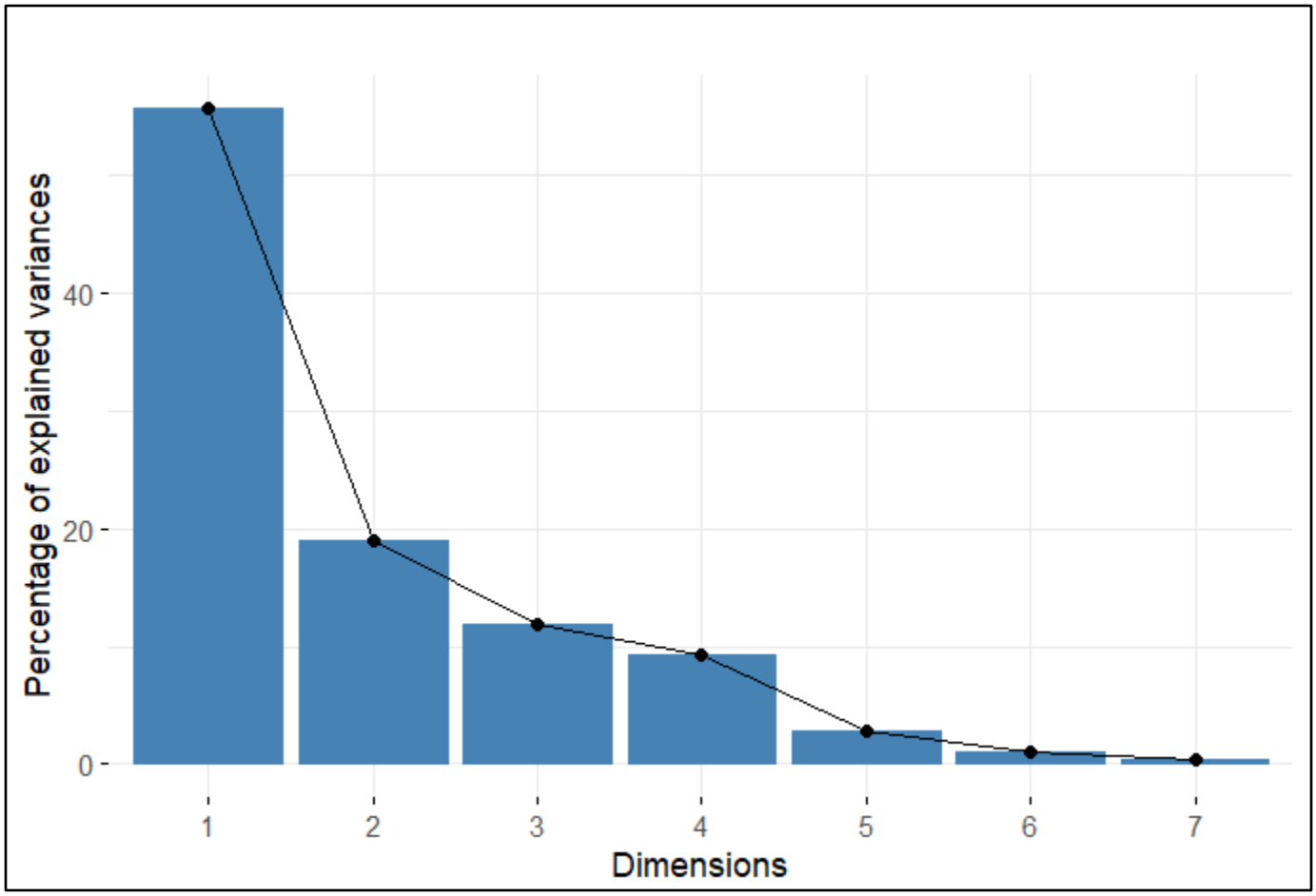
Figure **5**



Notes:
1. Samples collected from upgradient wells 10 and 22 and downgradient wells 70S, 71S, 16, 35D, 70D, and 71D were included in the evaluation.

PCA Analysis - Quality of Representation of Principal Components (Porewater Excluded)
Vermilion Power Plant – New East Ash Pond

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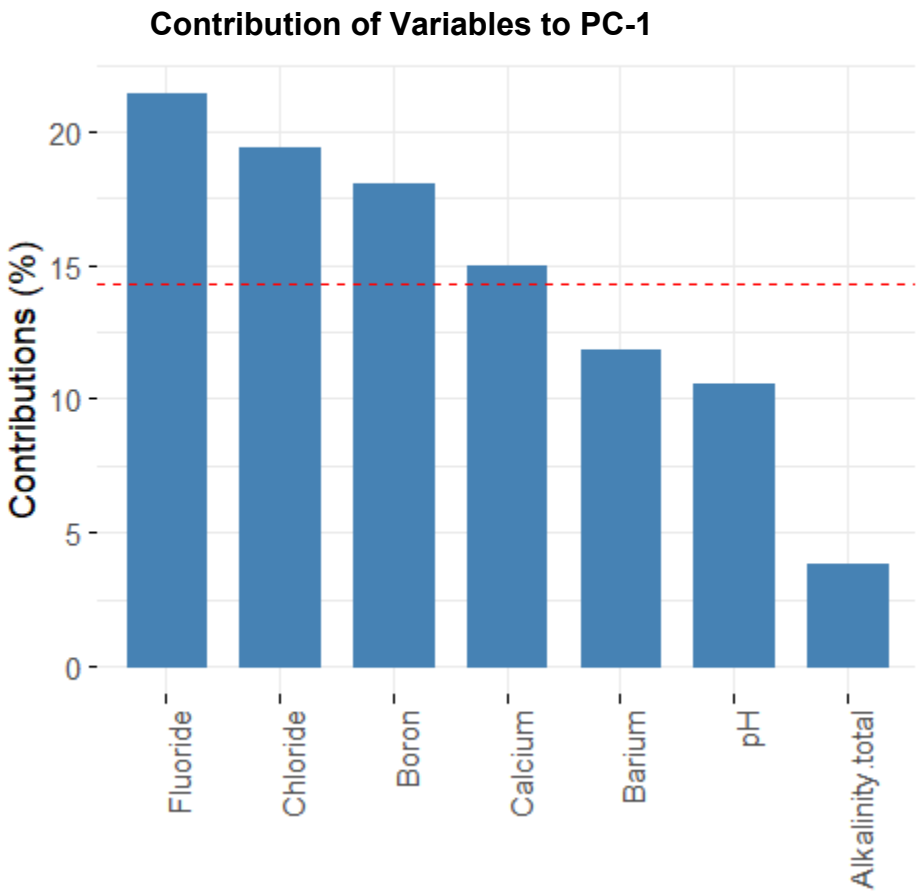
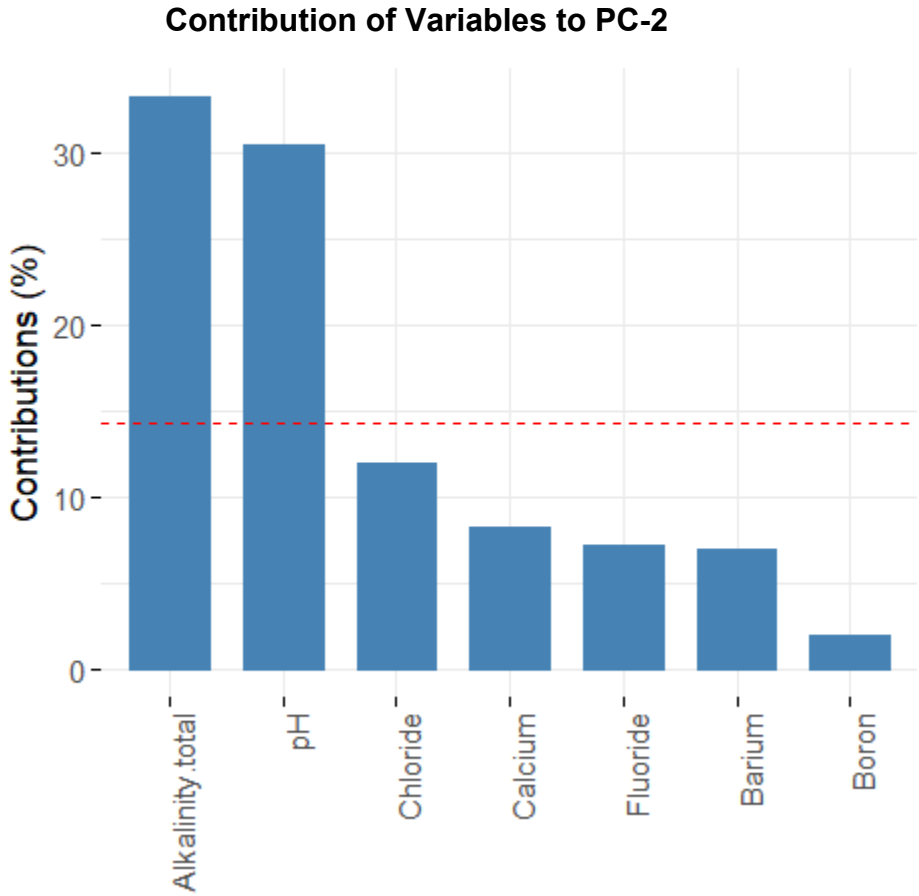
Figure **6a**





Notes:
1. The dashed red line represents the anticipated value for uniform contribution. The constituents with a contribution exceeding the reference line are considered significant in its contribution to each PC (principal component).

Contribution of Variables to First Two Principal Components (Porewater Excluded)

Vermilion Power Plant – New East Ash Pond

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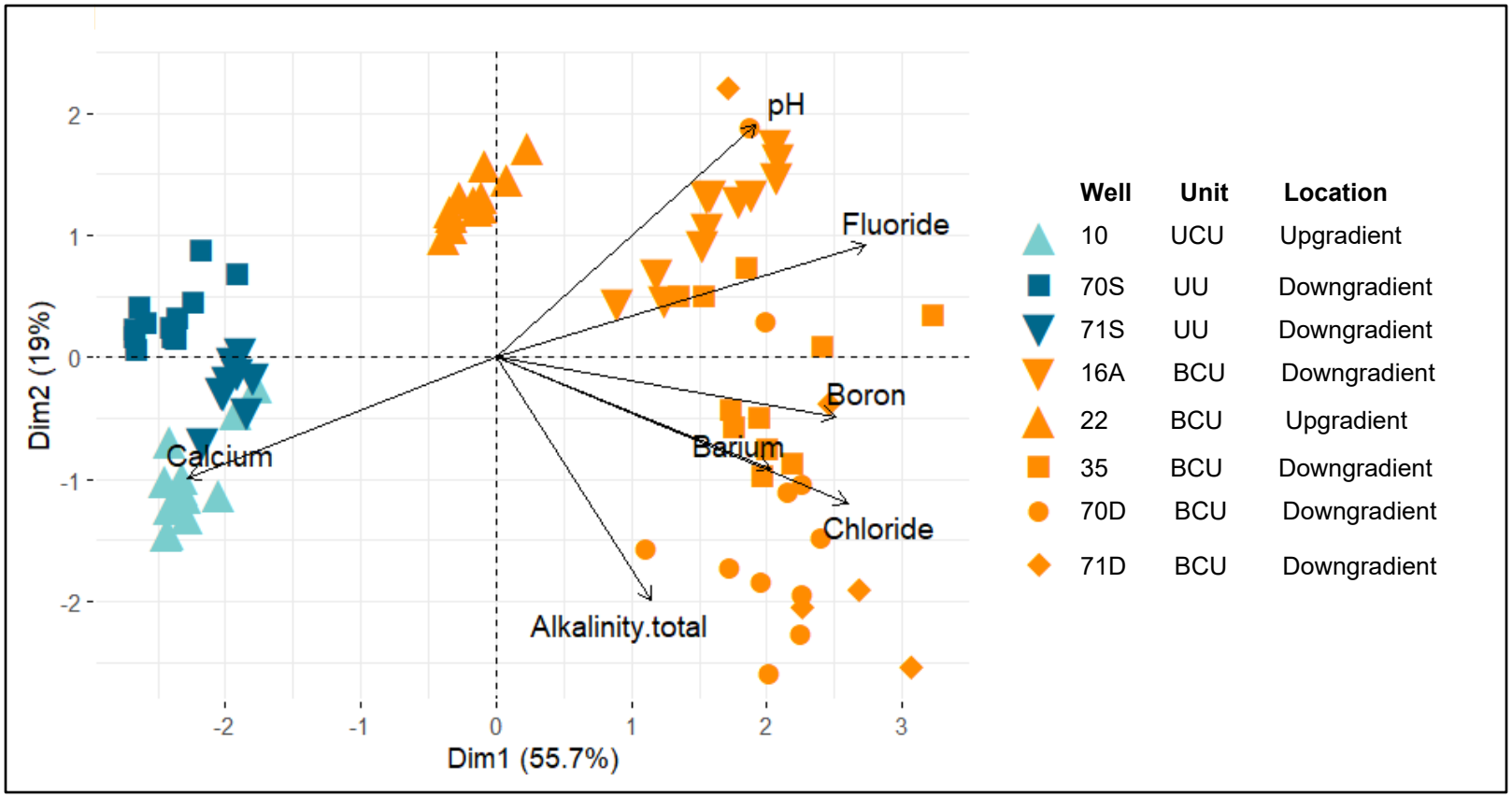
Figure **6b**



Notes:
1. The arrows signify the correlations between the constituents and the principal components.
2. Datapoints are colored based on hydrostratigraphic unit of sampling locations as follows:
   - Bedrock Confining Unit (BCU) wells: 16A, 22, 35D, 70D, 71D.
   - Upper Confining Unit (UCU) well: 10.
   - Upper Unit (UU) wells: 70S, 71S.
3. Dim: Dimension

Principal Components Analysis Biplot
(Porewater Excluded)
Vermilion Power Plant – New East Ash Pond

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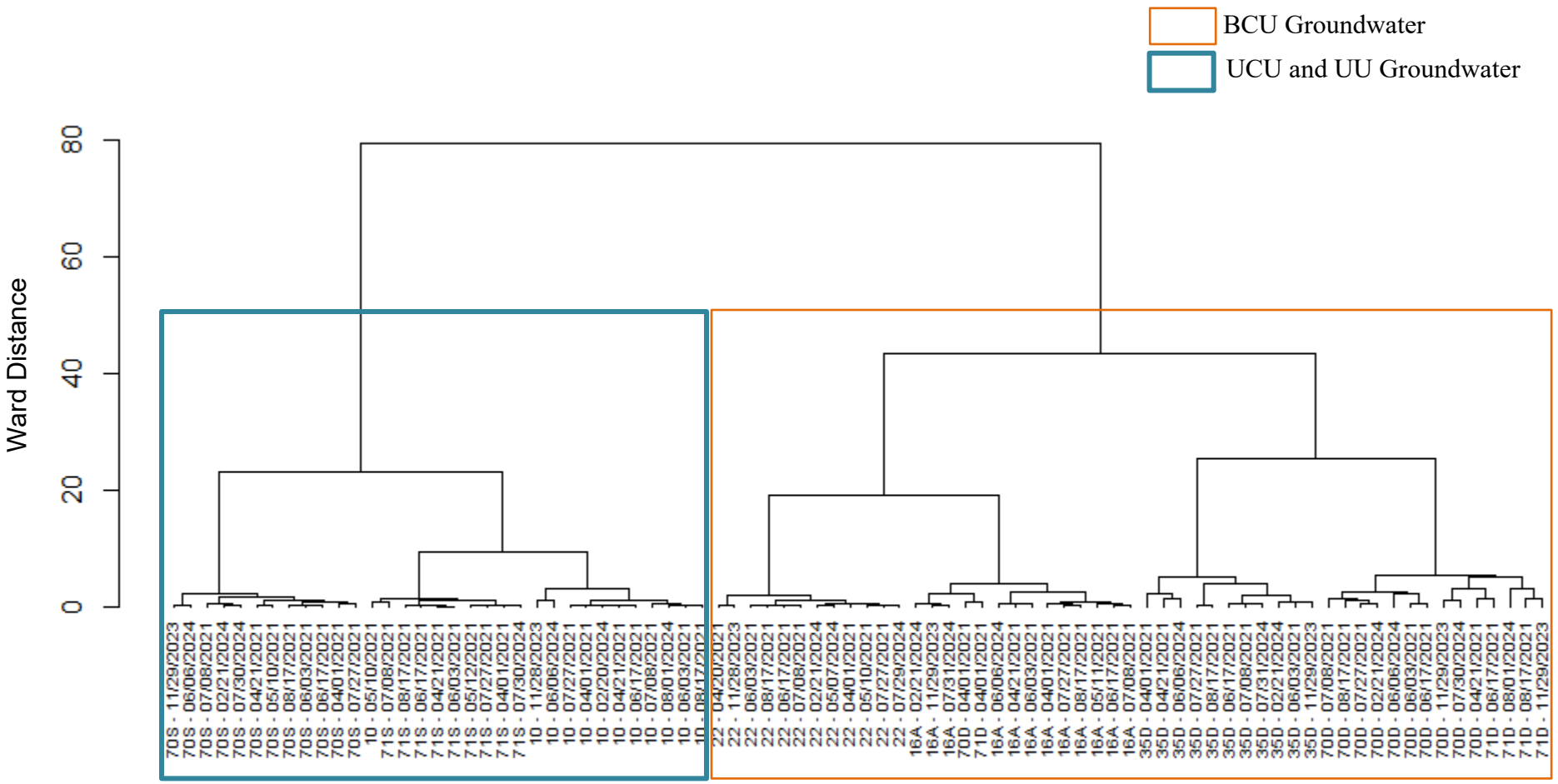
Figure **7**



Notes:
1. The cluster analysis used Euclidean distances, and Ward's method as the clustering algorithm.
2. In the dendrogram, samples on the same branch are more similar to each other. The samples with the highest similarity are on the closest branches.
3. The boxes around the branches represent the two clusters into which samples from each source grouped.
4. BCU, UCU and UU refer to Bedrock Confining Unit, Upper Confining Unit, and Upper Unit, respectively.

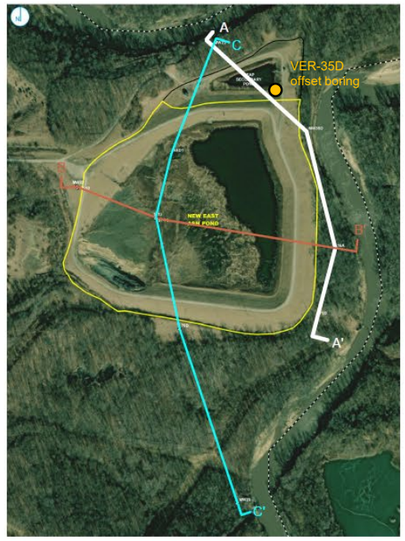
Dendrogram Graph from Cluster Analysis
(Porewater Excluded)
Vermilion Power Plant – New East Ash Pond

Geosyntec consultants

Columbus, Ohio | December 2024

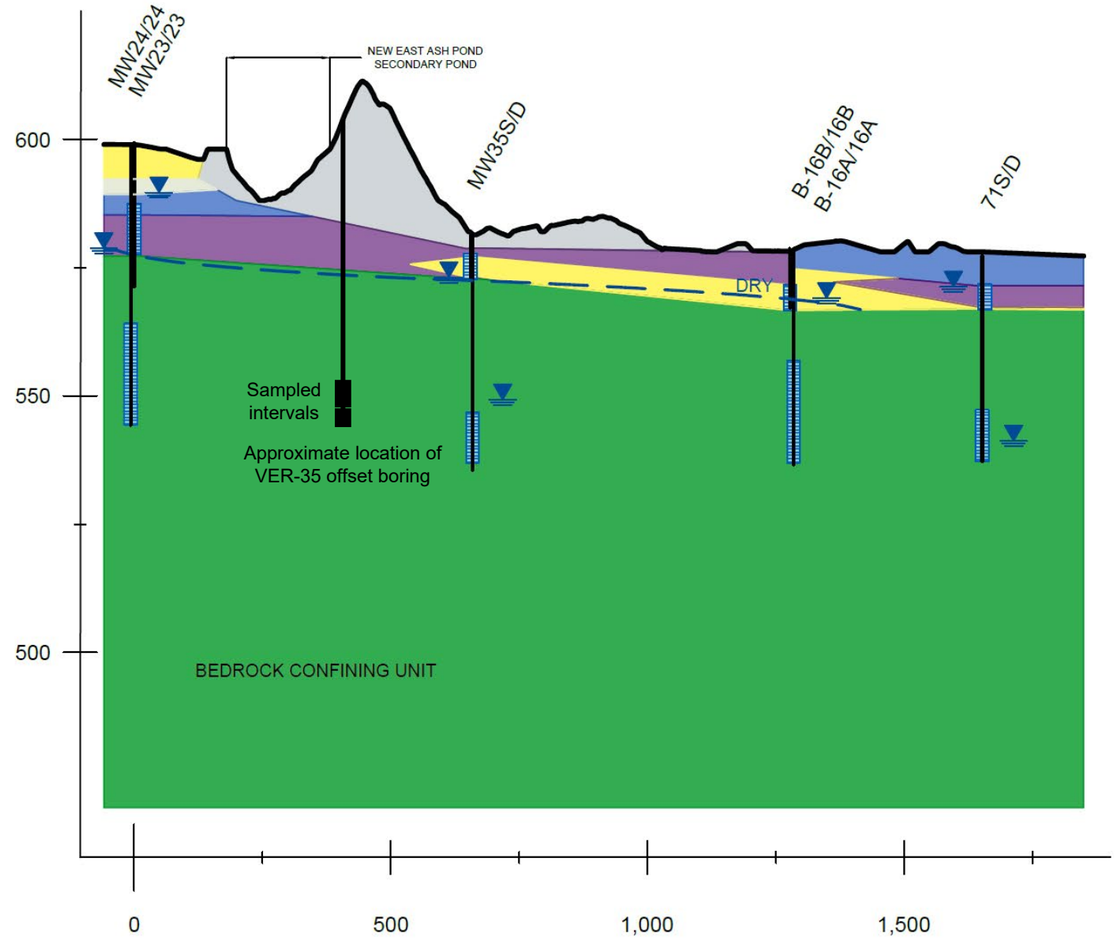
Figure **8**

ATTACHMENT 1
Geologic Cross Sections



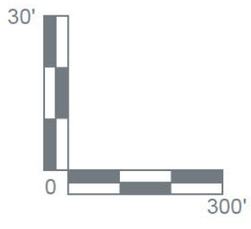
A
(NORTH)

A'
(SOUTH)



NOTES

1. This profile was developed by interpolation between widely spaced boreholes. Only at the borehole location should it be considered as an approximately accurate representation and then only to the degree implied by the notes on the borehole logs.
2. Scale is approximate.
3. Vertical scale is exaggerated 10X.
4. Groundwater elevations measured on March 29, 2021.
5. PMP = Potential Migration Pathway



LEGEND

- FILL
- CLAY (CL/CH)
- TILL (CL/CH)
- SILT (ML)
- SAND (SP/SM/SW)
- GRAVEL (GP/GW)
- BEDROCK / WEATHERED BEDROCK (INTERBEDDED SHALE, LIMESTONE, SANDSTONE, V. LITTLE SS)

- WELL SCREEN INTERVAL
- BEDROCK CONFINING UNT POTENTIOMETRIC SURFACE
- BEDROCK CONFINING UNIT / PMP GROUNDWATER / OTHER GROUNDWATER / SURFACE WATER ELEVATION(S)

GEOLOGIC CROSS SECTION
A-A'

HYDROGEOLOGIC SITE CHARACTERIZATION REPORT
NEW EAST ASH POND
VERMILION POWER PLANT
OAKWOOD, ILLINOIS

FIGURE 2-9

RAMBOLL AMERICAS
ENGINEERING SOLUTIONS, INC.

RAMBOLL

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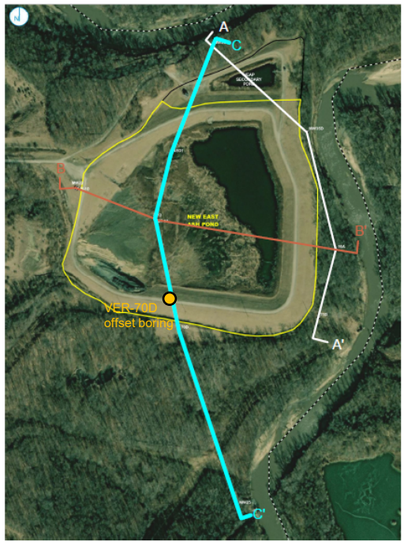
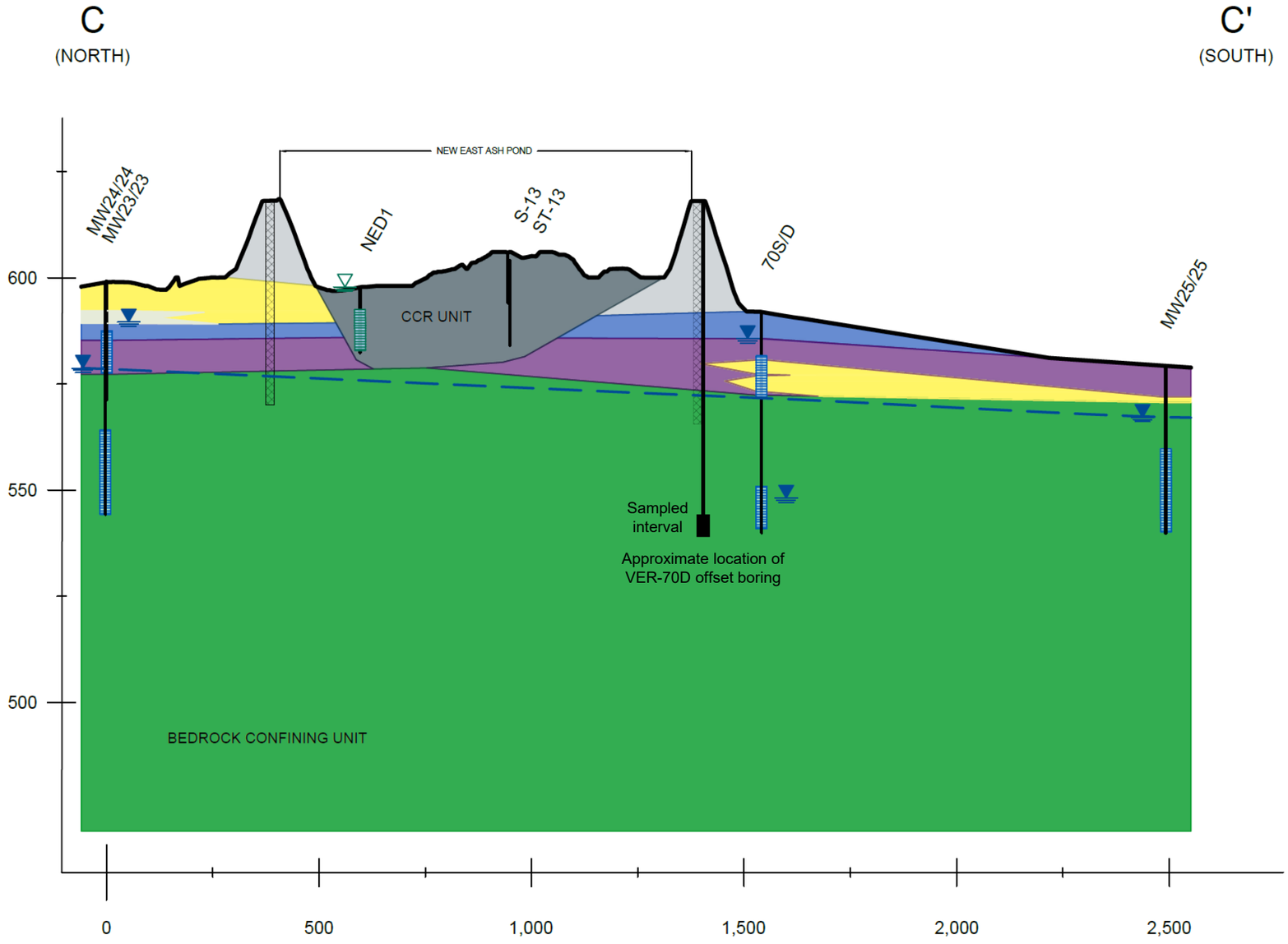
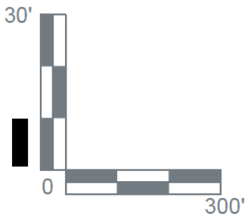




NOTES

1. This profile was developed by interpolation between widely spaced boreholes. Only at the borehole location should it be considered as an approximately accurate representation and then only to the degree implied by the notes on the borehole logs.
2. Scale is approximate.
3. Vertical scale is exaggerated 10X.
4. Groundwater elevations measured on March 29, 2021.
5. PMP = Potential Migration Pathway



LEGEND

- COAL COMBUSTION RESIDUALS (CCR)
- FILL
- CLAY (CL/CH)
- TILL (CL/CH)
- SILT (ML)
- SAND (SP/SM/SW)
- GRAVEL (GP/GW)
- BEDROCK / WEATHERED BEDROCK (INTERBEDDED SHALE, LIMESTONE, SANDSTONE, V. LITTLE SS)
- WELL SCREEN INTERVAL
- BEDROCK CONFINING UNT POTENTIOMETRIC SURFACE
- POREWATER ELEVATION
- BEDROCK CONFINING UNIT / PMP GROUNDWATER / OTHER GROUNDWATER / SURFACE WATER ELEVATION(S)
- CLAY CORE KEYED 8-FT INTO BEDROCK

GEOLOGIC CROSS SECTION
C-C'

HYDROGEOLOGIC SITE CHARACTERIZATION REPORT
NEW EAST ASH POND
VERMILION POWER PLANT
OAKWOOD, ILLINOIS

FIGURE 2-11

RAMBOLL AMERICAS
ENGINEERING SOLUTIONS, INC.

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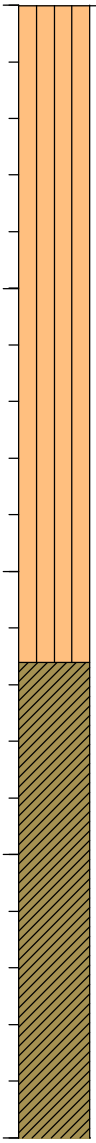
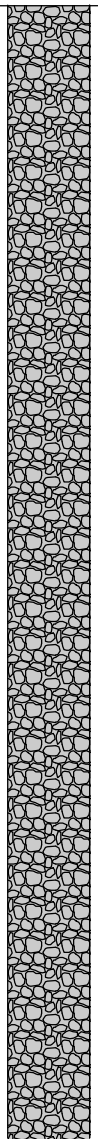
ATTACHMENT 2
Field Boring Logs

Geosyntec consultants
engineers | scientists | innovators

Client: Vistra
Project: Vermilion Power Plant New East Ash Pond
Address: 10188 East 2150 North Road, Oakwood, IL

BORING LOG
Boring No. VER-35
Page: 1 of 4

Drilling Start Date:	**06/24/2023**	Boring Depth (ft):	**63**
Drilling End Date:	**06/24/2023**	Boring Diameter (in):	**6**
Drilling Company:	**Cascade Drilling**	Ground Surface Elev. (ft):	**Not surveyed**
Drilling Method:	**Sonic**	Boring was advanced adjacent to well 35D. Samples collected from 55-60 ft bgs and 60-63 ft bgs	
Drilling Equipment:	**Geoprobe**		
Driller:	**Jeff Jehn**		
Logged By:	**Andrew Kelley**		

DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT: Sample Type	COLLECT: Date & Time	COLLECT: Blow Counts	COLLECT: Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
0					10:35	NA	5.1/10	(0') GRAVELLY SILT (ML); light gray to brown (darkens downward), dry, loose, little sand, minor concretions.
								(3') CLAYEY SILT (ML); dark reddish brown, moist, firm, some black organics staining, few gravel, minor iron oxide stains.
5								
10					10:45		2.5/10	(10') As above.
								(10.6') GRAVELLY SILT (ML); light gray to brown, moist, loose, fine to coarse gravel, little sand.
								(11.6') SILTY CLAY (CL); dark grayish brown, moist, stiff, medium plasticity.
15								
20								

NOTES:

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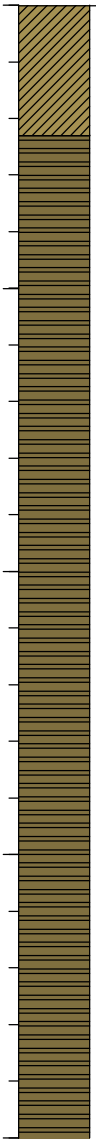
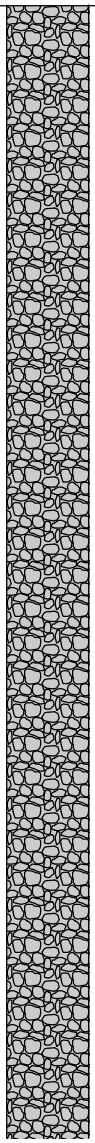
Client: Vistra
Project: Vermilion Power Plant New East Ash Pond
Address: 10188 East 2150 North Road, Oakwood, IL

BORING LOG
Boring No. VER-35
Page: 2 of 4

Drilling Start Date:	**06/24/2023**	Boring Depth (ft):	**63**
Drilling End Date:	**06/24/2023**	Boring Diameter (in):	**6**
Drilling Company:	**Cascade Drilling**	Ground Surface Elev. (ft):	**Not surveyed**
Drilling Method:	**Sonic**	Boring was advanced adjacent to well 35D. Samples collected from 55-60 ft bgs and 60-63 ft bgs	
Drilling Equipment:	**Geoprobe**		
Driller:	**Jeff Jehn**		
Logged By:	**Andrew Kelley**		

DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT: Sample Type	COLLECT: Date & Time	COLLECT: Blow Counts	COLLECT: Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
20					10:55	NA	8/8	(20') CLAY (CL); gray to light brown, moist, very soft, trace coarse gravel, high plasticity.
								(22.3') WEATHERED SHALE, gray, moist, highly decomposed, moderately disintegrated.
25								
							2/2	(28') As above.
30					11:55		8/10	(30') SHALE, gray, wet, highly decomposed, slightly disintegrated.
35								(35.3') WEATHERED SHALE, gray, moist, highly decomposed, highly disintegrated.
40								

NOTES:

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Client: Vistra
Project: Vermilion Power Plant New East Ash Pond
Address: 10188 East 2150 North Road, Oakwood, IL

BORING LOG
Boring No. VER-35
Page: 3 of 4

Drilling Start Date:	**06/24/2023**	Boring Depth (ft):	**63**
Drilling End Date:	**06/24/2023**	Boring Diameter (in):	**6**
Drilling Company:	**Cascade Drilling**	Ground Surface Elev. (ft):	**Not surveyed**
Drilling Method:	**Sonic**	Boring was advanced adjacent to well 35D. Samples collected from 55-60 ft bgs and 60-63 ft bgs	
Drilling Equipment:	**Geoprobe**		
Driller:	**Jeff Jehn**		
Logged By:	**Andrew Kelley**		

DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT: Sample Type	Date & Time	Blow Counts	Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
40					12:10	NA	2/2	(40') As above.
					13:20		4/5	(42') WEATHERED SHALE, gray, moist, highly decomposed, highly disintegrated.
45								
					13:40		3.3/4	(47') As above.
50								
					14:05		3/4	(51') As above: slightly decomposed, competent at 1.5-1.6 ft.
55								
					14:20		4/5	(55') As above: slightly less weathered.
60								

NOTES:

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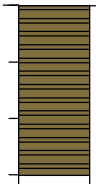
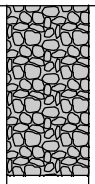
Client: Vistra
Project: Vermilion Power Plant New East Ash Pond
Address: 10188 East 2150 North Road, Oakwood, IL

BORING LOG
Boring No. VER-35
Page: 4 of 4

Drilling Start Date:	**06/24/2023**	Boring Depth (ft):	**63**
Drilling End Date:	**06/24/2023**	Boring Diameter (in):	**6**
Drilling Company:	**Cascade Drilling**	Ground Surface Elev. (ft):	**Not surveyed**
Drilling Method:	**Sonic**	Boring was advanced adjacent to well 35D. Samples collected from 55-60 ft bgs and 60-63 ft bgs	
Drilling Equipment:	**Geoprobe**		
Driller:	**Jeff Jehn**		
Logged By:	**Andrew Kelley**		

DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT: Sample Type	COLLECT: Date & Time	COLLECT: Blow Counts	COLLECT: Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
60					14:50	NA	2/3	(60') As above: gray, moist, highly decomposed, highly disintegrated, few fragments are slightly more competent.
								(63') End of Boring.
65								

NOTES:

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Client: Vistra
Project: Vermilion Power Plant New East Ash Pond
Address: 10188 East 2150 North Road, Oakwood, IL

BORING LOG
Boring No. VER-70
Page: 1 of 4

Drilling Start Date:	**06/23/2023**	Boring Depth (ft):	**80**
Drilling End Date:	**06/23/2023**	Boring Diameter (in):	**6**
Drilling Company:	**Cascade Drilling**	Ground Surface Elev. (ft):	**Not surveyed**
Drilling Method:	**Sonic**	Boring was advanced adjacent to well 70D. Samples collected from 30-40 ft bgs, 41-42 ft bgs and 75-80 ft bgs	
Drilling Equipment:	**Geoprobe**		
Driller:	**Jeff Jehn**		
Logged By:	**Andrew Kelley**		

DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT: Sample Type	COLLECT: Date & Time	COLLECT: Blow Counts	COLLECT: Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
0					10:40	NA	6/10	(0') SILT WITH GRAVEL (ML); light brown, dry, loose, fine to coarse gravel.
								(1') SILT (ML); brown to tan, dry, firm, moderate concretions, little gravel, few clay.
5								(3.6') SILT (ML); gray to dark gray with little brown, dry, firm, few fine sand, few fine gravel, coarsens downwards, moderate concretions.
10					10:55		4/10	(10') SILTY GRAVEL (GM); gray to dark gray, moist, loose, some fine to coarse sand.
								(10.5') SILTY GRAVEL (GM); light gray, moist, loose, fines downward.
								(12') SANDY SILT (ML); brown, moist, medium dense, firm, little clay, little fine gravel.
15								
20								

NOTES:

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Client: Vistra
Project: Vermilion Power Plant New East Ash Pond
Address: 10188 East 2150 North Road, Oakwood, IL

BORING LOG
Boring No. VER-70
Page: 2 of 4

Drilling Start Date:	**06/23/2023**	Boring Depth (ft):	**80**
Drilling End Date:	**06/23/2023**	Boring Diameter (in):	**6**
Drilling Company:	**Cascade Drilling**	Ground Surface Elev. (ft):	**Not surveyed**
Drilling Method:	**Sonic**	Boring was advanced adjacent to well 70D. Samples collected from 30-40 ft bgs, 41-42 ft bgs and 75-80 ft bgs	
Drilling Equipment:	**Geoprobe**		
Driller:	**Jeff Jehn**		
Logged By:	**Andrew Kelley**		

DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT: Sample Type	COLLECT: Date & Time	COLLECT: Blow Counts	COLLECT: Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
20					13:00	NA	3/10	(20') CLAY WITH SILT (CL); grayish brown, wet, stiff, little sand, little fine to coarse gravel.
								(21') SILTY CLAY (CL); grayish brown, wet, soft, little fine gravel, few sand.
								(21.3') SANDY CLAY (CL); grayish brown, wet, very stiff, some gravel.
25								
30							3/10	(30') GRAVELLY CLAY WITH SAND (CL); grayish brown, wet, firm, sand coarsens downward.
								(31.8') CLAY (CL); dark gray to black, wet, firm, little gravel, few roots observed, dark organics.
35								
40								

NOTES:

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Client: Vistra
Project: Vermilion Power Plant New East Ash Pond
Address: 10188 East 2150 North Road, Oakwood, IL

BORING LOG
Boring No. VER-70
Page: 3 of 4

Drilling Start Date:	**06/23/2023**	Boring Depth (ft):	**80**
Drilling End Date:	**06/23/2023**	Boring Diameter (in):	**6**
Drilling Company:	**Cascade Drilling**	Ground Surface Elev. (ft):	**Not surveyed**
Drilling Method:	**Sonic**	Boring was advanced adjacent to well 70D. Samples collected from 30-40 ft bgs, 41-42 ft bgs and 75-80 ft bgs	
Drilling Equipment:	**Geoprobe**		
Driller:	**Jeff Jehn**		
Logged By:	**Andrew Kelley**		

DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT: Sample Type	COLLECT: Date & Time	COLLECT: Blow Counts	COLLECT: Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
40					13:50	NA	8/10	(40') POORLY GRADED SAND (SP); brown with hint of gray, wet, medium dense, fine grained.
								(41.7') CLAY (CL); brownish gray, moist, very stiff, few coarse gravel, some sand.
								(42.4') SHALE, gray, moist, laminated, highly decomposed, moderately disintegrated.
45								
50					14:30		5/10	(50') As above.
55								
60								

NOTES:

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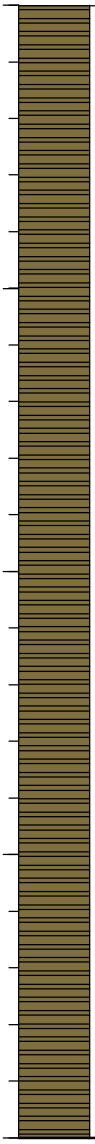
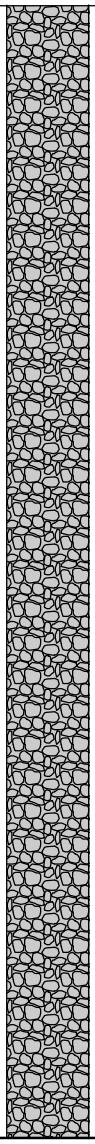
Client: Vistra
Project: Vermilion Power Plant New East Ash Pond
Address: 10188 East 2150 North Road, Oakwood, IL

BORING LOG
Boring No. VER-70
Page: 4 of 4

Drilling Start Date:	**06/23/2023**	Boring Depth (ft):	**80**
Drilling End Date:	**06/23/2023**	Boring Diameter (in):	**6**
Drilling Company:	**Cascade Drilling**	Ground Surface Elev. (ft):	**Not surveyed**
Drilling Method:	**Sonic**	Boring was advanced adjacent to well 70D. Samples collected from 30-40 ft bgs, 41-42 ft bgs and 75-80 ft bgs	
Drilling Equipment:	**Geoprobe**		
Driller:	**Jeff Jehn**		
Logged By:	**Andrew Kelley**		

DEPTH (ft)	LITHOLOGY	WATER LEVEL	BORING COMPLETION	COLLECT: Sample Type	COLLECT: Date & Time	COLLECT: Blow Counts	COLLECT: Recovery (ft)	SOIL/ROCK VISUAL DESCRIPTION
60					15:15	NA	1/10	(60') SHALE, gray to dark gray, wet (driller water), foliated, highly decomposed, slightly disintegrated, weaker and more highly disintegrated shale likely washed out by driller fluids.
65								
70					17:00		10/10	(70') SHALE, gray to dark gray, wet, highly decomposed, moderately disintegrated, coated in wet clay (likely slough).
75								(75') SHALE, gray to dark gray, moist, highly decomposed, slightly disintegrated.
80								(80') End of Boring.

NOTES:

ATTACHMENT 3

Boring Logs and Well Construction Logs

RAMBOLL

SOIL BORING LOG INFORMATION

Facility/Project Name	License/Permit/Monitoring Number	Boring Number
Vermilion Power Station		71D

Boring Drilled By: Name of crew chief (first, last) and Firm	Date Drilling Started	Date Drilling Completed	Drilling Method
Jason Greer Cascade Drilling	3/3/2021	3/3/2021	Mini Sonic

Common Well Name	Final Static Water Level	Surface Elevation	Borehole Diameter
71D	Feet (NAVD88)	577.18 Feet (NAVD88)	6.0 inches

Local Grid Origin ☐ (estimated: ☐) or Boring Location ☐
State Plane 1,278,992.96 N, 1,151,334.05 E Ⓔ/ W
1/4 of 1/4 of Section , T N, R
Lat ° ' "
Long ° ' "
Local Grid Location
Feet ☐N ☐S Feet ☐E ☐W

Facility ID	County	State	Civil Town/City/ or Village
	Vermilion	Illinois	Oakwood

Sample Number and Type	Sample Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	USCS	Graphic Log	Well Diagram	PID 10.6 eV Lamp	Soil Properties: Compressive Strength (tsf)	Moisture Content	Liquid Limit	Plasticity Index	P 200	RQD/ Comments
1 CS	120 / 110		1.5	0 - 5.8' **SILT WITH SAND:** (ML)s, dark brown (10YR 3/3) to brown (10YR 4/3), sand (15-25%), clay (5-10%), organic material (0-10%), firm, slow dilatancy, low toughness, low plasticity, moist.	(ML)s				0.75					CS= Core Sample
			3.0						0.75					
			4.5						0.75					SH= Shelby Tube
			6.0	5.8 - 9.9' **LEAN CLAY:** CL, brown (10YR 4/3), silt (15-25%), sand (0-5%), gravel (0-5%), firm, slow dilatancy, low toughness, medium plasticity, moist.	CL				0.75					
			7.5						0.75					
			9.0						0.75					
2 CS	96 / 96		10.5	9.9 - 10.3' **POORLY-GRADED SAND:** SP, dark grayish brown (10YR 4/2), subrounded to rounded, medium to coarse sand, clay (0-10%), loose, wet.	SP				2.5					
			12.0	10.3 - 20' **Weathered SHALE Bedrock** BDX (SH), gray (10YR 5/1), dry.	BDX (SH)									
			13.5											
			15.0											
			16.5											
3 SH	24 / 24		18.0											
			19.5											

I hereby certify that the information on this form is true and correct to the best of my knowledge.

Signature

Firm Ramboll
234 W. Florida Street, Milwaukee,WI 53204
Tel: (414) 837-3607
Fax: (414) 837-3608

Boring Number 71D

Sample Number and Type	Sample Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	U S C S	Graphic Log	Well Diagram	PID 10.6 eV Lamp	Soil Properties: Compressive Strength (tsf)	Soil Properties: Moisture Content	Soil Properties: Liquid Limit	Soil Properties: Plasticity Index	Soil Properties: P 200	RQD/ Comments
4 CS	120 81		21.0	20 - 40' **SHALE:** BDX (SH), dark gray (10YR 4/1).										
			22.5											
			24.0											
			25.5											
			27.0											
			28.5											
5 CS	120 120		30.0		BDX (SH)									
			31.5											
			33.0											
			34.5											
			36.0											
			37.5											
			39.0											
				40' End of Boring.										

RAMBOLL

MONITORING WELL CONSTRUCTION

Facility/Project Name: Vermilion Power Station	Local Grid Location of Well: ____ ft. ☐ N. ☐ S. ____ ft. ☐ E. ☐ W.	Well Name: 71D
Facility License, Permit or Monitoring No.	Local Grid Origin ☐ (estimated: ☐) or Well Location ☐ Lat. ° ' " Long. ° ' " or St. Plane 1,278,993 ft. N, 1,151,334 ft. E. Ⓔ/W	
Facility ID		Date Well Installed: 03/03/2021
Type of Well: Well Code 12/pz	Section Location of Waste/Source: ____ 1/4 of ____ 1/4 of Sec. ____, T. ____ N, R. ____ ☐ E ☐ W	Well Installed By: (Person's Name and Firm): Jason Greer; Cascade Drilling
Distance from Waste/Source ft. / State: Illinois	Location of Well Relative to Waste/Source: u ☐ Upgradient s ☐ Sidegradient d ☒ Downgradient n ☐ Not Known	Gov. Lot Number

A. Protective pipe, top elevation: 580.25 ft. MSL
B. Well casing, top elevation: 579.89 ft. MSL
C. Land surface elevation: 577.2 ft. MSL
D. Surface seal, bottom: 576.2 ft. MSL or 1.0 ft.

12. USCS classification of soil near screen:
GP ☐ GM ☐ GC ☐ GW ☐ SW ☐ SP ☐
SM ☐ SC ☐ ML ☐ MH ☐ CL ☐ CH ☐
Bedrock ☒

13. Sieve analysis attached? ☐ Yes ☒ No

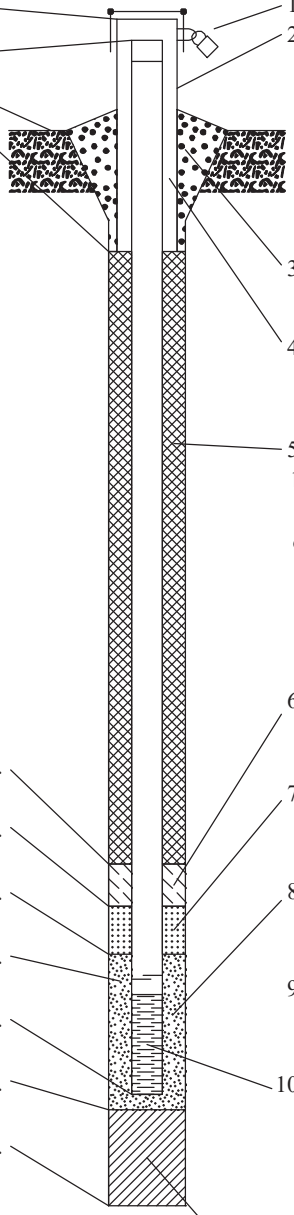
14. Drilling method used: Rotary ☐ Hollow Stem Auger ☐ Sonic Other ☒

15. Drilling fluid used: Water ☒ 0 2 Air ☐ Drilling Mud ☐ 0 3 None ☐

16. Drilling additives used? ☐ Yes ☒ No
Describe ____

17. Source of water (attach analysis, if required): Potable City Water

E. Bentonite seal, top: 551.2 ft. MSL or 26.0 ft.
F. Fine sand, top: ____ ft. MSL or ____ ft.
G. Filter pack, top: 549.2 ft. MSL or 28.0 ft.
H. Screen joint, top: 547.2 ft. MSL or 30.0 ft.
I. Well bottom: 537.2 ft. MSL or 40.0 ft.
J. Filter pack, bottom: 537.2 ft. MSL or 40.0 ft.
K. Borehole, bottom: 537.2 ft. MSL or 40.0 ft.
L. Borehole, diameter: 6.0 in.
M. O.D. well casing: 2.38 in.
N. I.D. well casing: 2.07 in.



1. Cap and lock? ☒ Yes ☐ No
2. Protective cover pipe:
a. Inside diameter: 4.0 in.
b. Length: 5.0 ft.
c. Material: Steel ☒ Other ☐
d. Additional protection? ☒ Yes ☐ No
If yes, describe: 4 Steel Bollards
3. Surface seal: Bentonite ☐ Concrete ☒ Other ☐
4. Material between well casing and protective pipe: Bentonite ☐ Sand Other ☒
5. Annular space seal: a. Granular/Chipped Bentonite ☐
b. ____ Lbs/gal mud weight . . . Bentonite-sand slurry ☐
c. 9.5 Lbs/gal mud weight . . . Bentonite slurry ☒
d. ____ % Bentonite . . . Bentonite-cement grout ☐
e. ____ Ft^3 volume added for any of the above
f. How installed: Tremie ☐ Tremie pumped ☒ Gravity ☐
6. Bentonite seal: a. Bentonite granules ☐
b. ☐ 1/4 in. ☒ 3/8 in. ☐ 1/2 in. Bentonite chips ☒
c. ____ Other ☐
7. Fine sand material: Manufacturer, product name & mesh size
a. NA
b. Volume added 0 ft^3
8. Filter pack material: Manufacturer, product name & mesh size
a. FILTERSIL 0.85
b. Volume added ____ ft^3
9. Well casing: Flush threaded PVC schedule 40 ☒ Flush threaded PVC schedule 80 ☐ Other ☐
10. Screen material: Schedule 40 PVC
a. Screen Type: Factory cut ☒ Continuous slot ☐ Other ☐
b. Manufacturer Johnson Screens
c. Slot size: 0.010 in.
d. Slotted length: 10.0 ft.
11. Backfill material (below filter pack): None ☒ Other ☐

I hereby certify that the information on this form is true and correct to the best of my knowledge.

Date Modified: 3/31/2021

Signature: ____

Firm: Ramboll
234 W. Florida Street, Milwaukee,WI 53204
Tel: (414) 837-3607
Fax: (414) 837-3608

NATURAL RESOURCE TECHNOLOGY

SOIL BORING LOG INFORMATION

Facility/Project Name	License/Permit/Monitoring Number	Boring Number
Vermilion Power Station		MW35D

Boring Drilled By: Name of crew chief (first, last) and Firm	Date Drilling Started	Date Drilling Completed	Drilling Method
Bruno Williamson Ramsey Geotechnical Engineering	3/1/2017	3/3/2017	rotary/auger

Common Well Name	Final Static Water Level	Surface Elevation	Borehole Diameter
MW35D	Feet (NAVD88)	581.25 Feet (NAVD88)	7.3 inches

Local Grid Origin ☐ (estimated: ☐) or Boring Location ☒
State Plane 1,279,955.58 N, 1,151,276.17 E Ⓔ/W
1/4 of 1/4 of Section , T N, R
Lat 40° 10'47.14212"
Long 87° 44' 8.06652"
Local Grid Location
Feet ☐N ☐S Feet ☐E ☐W

Facility ID	County	State	Civil Town/City/ or Village
	Vermilion	IL	Danville

Sample Number and Type	Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	USCS	Graphic Log	Well Diagram	Compressive Strength (tsf)	Moisture Content	Liquid Limit	Plasticity Index	P 200	RQD/ Comments
1 SS	24 / 16.5	2 2 3 3	0	0 - 2.5' **FILL, SILT:** ML, very dark grayish brown (10YR 3/2), 15-30% silt, trace wood and roots, cohesive, low plasticity, moist.	(FILL) ML								
2 SS	24 / 19	1 3 3 3	2	2.5 - 4.3' **SANDY LEAN CLAY:** s(CL), weak red (2.5YR 4/2), 5-15% fine sand, sand content increasing with depth, low plasticity, moist.	s(CL)								
3 SS	24 / 21	2 3 4 3	4	4.3 - 8' **POORLY-GRADED SAND:** SP, yellowish brown (10YR 5/6), fine sand, 15-30% clay, moist. 5.1' trace clay.	SP								
4 SS	24 / 18	3 3 3 3	6	7.5' trace gravel and cobbles.									Auger bringing up cobbles on flights.
5 SS	24 / 10	3 4 4 22	8	8 - 8.5' **FAT CLAY:** CH, very dark grayish brown (10YR 3/2), trace silt, high plasticity, moist.	CH			0.5					
			9	8.5 - 10' **Weathered SHALE Bedrock** BDX (SH), very dark grayish brown (10YR 3/2) to very dark greenish gray (GLEY 1 3/10Y), highly weathered, red (7.5YR 4/6) discoloration, fissile, moist.	BDX (SH)								
6 SS	15 / 15	20 34 50 for 3"	10	10 - 15.6' **Weathered SHALE Bedrock** to **SHALE:** BDX (SH), gray (GLEY 1 6/N), weak, fissile, intensely fractured, red (7.5YR 4/6) discoloration, dry.	BDX (SH)								
			11										
			12										

I hereby certify that the information on this form is true and correct to the best of my knowledge.

Signature

Firm Natural Resource Technology
234 W. Florida St., Fifth Floor, Milwaukee, WI 53204
Tel: (414) 837-3607
Fax: (414) 837-3608

NATURAL RESOURCE TECHNOLOGY

Boring Number MW35D

Sample Number and Type	Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	USCS	Graphic Log	Well Diagram	Soil Properties: Compressive Strength (tsf)	Moisture Content	Liquid Limit	Plasticity Index	P 200	RQD/ Comments
7 SS	8 9	45 50 for 2"	13	10 - 15.6' **Weathered SHALE Bedrock** to **SHALE**: BDX (SH), gray (GLEY 1 6/N), weak, fissile, intensely fractured, red (7.5YR 4/6) discoloration, dry. *(continued)*									
8 SS	9 7	31 50 for 3"	14		BDX (SH)								
			15										
9 CORE	120 120		16	15.6 - 45.8' **SHALE**: BDX (SH), dark reddish gray (10YR 4/1) to gray (2.5Y 5/1), microcrystalline, thinly bedded to laminated, weak, slightly decomposed (very dark gray (10YR 3/1) to black (10YR 2/1) discoloration in partly healed fractures), competent, dry to moist in fractures.									Core 9, RQD = 89%. Light brown gray return water. 4" diameter outer casing set from 0-16 ft bgs.
			17										
			18										
			19										
			20										
			21										
			22										
			23										
			24		BDX (SH)								
			25										
10 CORE	131.3 120		26	25.6' partly to totally healed fractures.									Core 10, RQD = 89%. Light gray return water.
			27										
			28										
			29										
			30										
			31										
			32										

NATURAL RESOURCE TECHNOLOGY

Boring Number MW35D

Sample Number and Type	Sample Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	U S C S	Graphic Log	Well Diagram	Soil Properties: Compressive Strength (tsf)	Moisture Content	Liquid Limit	Plasticity Index	P 200	RQD/ Comments
			33	15.6 - 45.8' **SHALE**: BDX (SH), dark reddish gray (10YR 4/1) to gray (2.5Y 5/1), microcrystalline, thinly bedded to laminated, weak, slightly decomposed (very dark gray (10YR 3/1) to black (10YR 2/1) discoloration in partly healed fractures), competent, dry to moist in fractures. *(continued)*									
			34										
			35										
			36										
11 CORE	111.1 120		37										Core 11, RQD = 93%. Gray return water.
			38										
			39		BDX (SH)								
			40										
			41										
			42	41.9' - 43' crossbedding.									
			43										
			44										
			45										
				45.8' End of Boring.									

NATURAL RESOURCE TECHNOLOGY

MONITORING WELL CONSTRUCTION

Facility/Project Name: Vermilion Power Station	Local Grid Location of Well: ____ ft. ☐ N. ☐ S. ____ ft. ☐ E. ☐ W.	Well Name: MW35D
Facility License, Permit or Monitoring No.	Local Grid Origin ☐ (estimated: ☐) or Well Location ☒ Lat. 40° 10' 47.142" Long. 87° 44' 8.067" or St. Plane 1,279,955.58 ft. N, 1,151,276.17 ft. E. Ⓔ/W	Date Well Installed: 03/03/2017
Facility ID	Section Location of Waste/Source: ____ 1/4 of ____ 1/4 of Sec. ____, T. ____ N, R. ____ ☐ E ☐ W	Well Installed By: (Person's Name and Firm): Bruno Williamson, Ramsey Geotechnical Engineering
Type of Well: mw	Location of Well Relative to Waste/Source: u ☐ Upgradient s ☐ Sidegradient d ☐ Downgradient n ☐ Not Known	Gov. Lot Number:
Distance from Waste/Source: ft. / State: IL		

A. Protective pipe, top elevation ____ ft. MSL

B. Well casing, top elevation 584.15 ft. MSL

C. Land surface elevation 581.25 ft. MSL

D. Surface seal, bottom 579.3 ft. MSL or 2.0 ft.

12. USCS classification of soil near screen:
GP ☐ GM ☐ GC ☐ GW ☐ SW ☐ SP ☐
SM ☐ SC ☐ ML ☐ MH ☐ CL ☐ CH ☐
Bedrock ☒

13. Sieve analysis attached? ☐ Yes ☒ No

14. Drilling method used: Rotary ☐
Hollow Stem Auger ☐
HSA / Rotary Other ☒

15. Drilling fluid used: Water ☒ 0 2 Air ☐
Drilling Mud ☐ 0 3 None ☐

16. Drilling additives used? ☐ Yes ☒ No

Describe ____

17. Source of water (attach analysis, if required):
City of Champaign

E. Bentonite seal, top 551.3 ft. MSL or 30.0 ft.

F. Fine sand, top ____ ft. MSL or ____ ft.

G. Filter pack, top 548.3 ft. MSL or 33.0 ft.

H. Screen joint, top 546.3 ft. MSL or 35.0 ft.

I. Well bottom 536.3 ft. MSL or 45.0 ft.

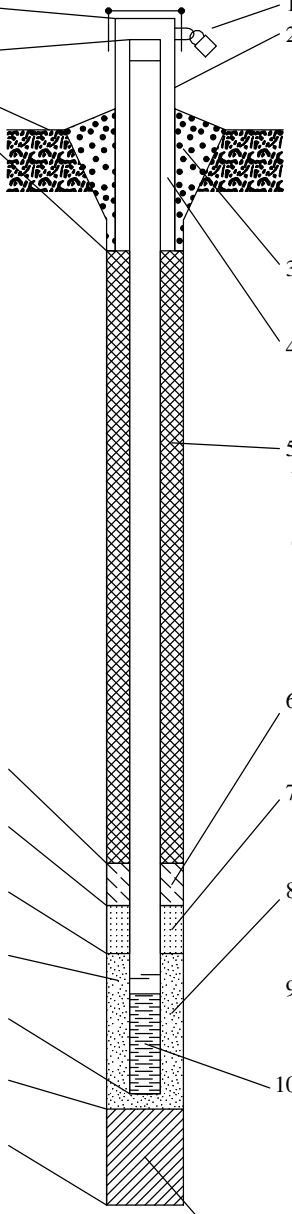
J. Filter pack, bottom 535.5 ft. MSL or 45.8 ft.

K. Borehole, bottom 535.5 ft. MSL or 45.8 ft.

L. Borehole, diameter 7.3 in.

M. O.D. well casing 2.38 in.

N. I.D. well casing 1.99 in.



1. Cap and lock? ☒ Yes ☐ No
2. Protective cover pipe:
a. Inside diameter: 6.0 in.
b. Length: 6.0 ft.
c. Material: Steel ☒ Other ☐
d. Additional protection? ☒ Yes ☐ No
If yes, describe: 4" diameter protective PVC casing
3. Surface seal: Bentonite ☐ Concrete ☒ Other ☐
4. Material between well casing and protective pipe: Bentonite ☒ Sand Other ☒
5. Annular space seal: a. Granular/Chipped Bentonite ☐
b. ____Lbs/gal mud weight . . . Bentonite-sand slurry ☐
c. ____Lbs/gal mud weight . . . Bentonite slurry ☐
d. 30 % Bentonite . . . Bentonite-cement grout ☒
e. ____ Ft^3 volume added for any of the above
f. How installed: Tremie ☒ Tremie pumped ☐ Gravity ☐
6. Bentonite seal: a. Bentonite granules ☐
b. ☐ 1/4 in. ☒ 3/8 in. ☐ 1/2 in. Bentonite chips ☒
c. ____ Other ☐
7. Fine sand material: Manufacturer, product name & mesh size
a. ____
b. Volume added ____ ft^3
8. Filter pack material: Manufacturer, product name & mesh size
a. NSF Quartz Sand #10-20
b. Volume added ____ ft^3
9. Well casing: Flush threaded PVC schedule 40 ☒ Flush threaded PVC schedule 80 ☐ Other ☐
10. Screen material: Schedule 40 PVC
a. Screen Type: Factory cut ☒ Continuous slot ☐ Other ☐
b. Manufacturer ____
c. Slot size: 0.100 in.
d. Slotted length: 10.0 ft.
11. Backfill material (below filter pack): None ☒ Other ☐

I hereby certify that the information on this form is true and correct to the best of my knowledge. Date Modified: 4/6/2017

Signature ____ Firm Natural Resource Technology, 234 W. Florida Street, Floor 5, Milwaukee, WI 53204 Tel: (414) 837-3607 Fax: (414) 837-3608

RAMBOLL

SOIL BORING LOG INFORMATION

Facility/Project Name	License/Permit/Monitoring Number	Boring Number
Vermilion Power Station		70D

Boring Drilled By: Name of crew chief (first, last) and Firm	Date Drilling Started	Date Drilling Completed	Drilling Method
Jason Greer Cascade Drilling	3/4/2021	3/4/2021	Mini Sonic

Common Well Name	Final Static Water Level	Surface Elevation	Borehole Diameter
70D	Feet (NAVD88)	591.90 Feet (NAVD88)	6.0 inches

Local Grid Origin ☐ (estimated: ☐) or Boring Location ☐
State Plane 1,278,929.46 N, 1,150,617.15 E Ⓔ/W
1/4 of 1/4 of Section , T N, R
Lat ° ' "
Long ° ' "
Local Grid Location
Feet ☐N ☐S Feet ☐E ☐W

Facility ID	County	State	Civil Town/City/ or Village
	Vermilion	Illinois	Oakwood

Sample Number and Type	Sample Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	USCS	Graphic Log	Well Diagram	PID 10.6 eV Lamp	Soil Properties: Compressive Strength (tsf)	Moisture Content	Liquid Limit	Plasticity Index	P 200	RQD/ Comments
1 CS	60 47		1	0 - 6.3' **SILT:** ML, dark brown (10YR 3/3) to brown (10YR 4/3), clay (15-25%), sand, (0-5%), roots (0-5%), stiff, slow dilatancy, low toughness, low plasticity, moist.	ML				1.5					CS= Core Sample
			2											
			3						1.5					
			4											
2 CS	60 60		5						1.5					
			6											
			7	6.3 - 11.3' **SILTY CLAY:** CL/ML, brown (10YR 4/3), sand (0-10%), gravel (0-5%), firm, slow dilatancy, low toughness, medium plasticity, moist.	CL/ML				0.75					
			8											
			9						0.75					
			10	9.4' color change to yellowish brown (10YR 5/4).										
3 CS	120 120		11											
			12	11.3 - 14.7' **CLAYEY SAND:** SC, yellowish brown (10YR 5/6), rounded fine sand, silt (5-10%), gravel (0-5%), loose, wet.	SC									
			13											
			14											
			15											

I hereby certify that the information on this form is true and correct to the best of my knowledge.

Signature

Firm Ramboll
234 W. Florida Street, Milwaukee,WI 53204
Tel: (414) 837-3607
Fax: (414) 837-3608

Boring Number 70D

Sample Number and Type	Sample Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	USCS	Graphic Log	Well Diagram	PID 10.6 eV Lamp	Soil Properties: Compressive Strength (tsf)	Soil Properties: Moisture Content	Soil Properties: Liquid Limit	Soil Properties: Plasticity Index	Soil Properties: P 200	RQD/ Comments
			16	14.7 - 15' **SILTY CLAY:** CL/ML, yellowish brown (10YR 5/6), soft, slow dilatancy, low toughness, medium plasticity.	CL/ML									
			16	15 - 16.2' **CLAYEY SAND:** SC, yellowish brown (10YR 5/6), rounded fine sand, silt (5-10%), gravel (0-5%), loose, wet.	SC									
			17	16.2 - 18.8' **POORLY-GRADED SAND WITH CLAY:** SP-SC, ???, subrounded to rounded, fine to medium sand, loose, wet.	SP-SC									
			18											
			19	18.8 - 19.6' **LEAN CLAY:** CL, dark gray (10YR 4/1), gravel, (0-5%), sand (0-5%), stiff, no dilatancy, low toughness, medium plasticity, moist.	CL				2.5					
4 CS	120 97		20	19.6 - 20.3' **Weathered SHALE Bedrock** BDX (SH), gray (10YR 5/1), dry.	BDX (SH)									
			21	20.3 - 52' **SHALE:** BDX (SH), gray (10YR 5/1).										
			22											
			23											
			24											
			25											
			26											
			27											
			28											
			29											
5 CS	132 132		30		BDX (SH)									
			31											
			32											
			33											
			34											
			35											
			36											
			37											
			38											
			39											
			40											

Boring Number 70D

Sample Number and Type	Sample Length Att. & Recovered (in)	Blow Counts	Depth In Feet	Soil/Rock Description And Geologic Origin For Each Major Unit	USCS	Graphic Log	Well Diagram	PID 10.6 eV Lamp	Soil Properties: Compressive Strength (tsf)	Soil Properties: Moisture Content	Soil Properties: Liquid Limit	Soil Properties: Plasticity Index	Soil Properties: P 200	RQD/ Comments
6 CS	132 132		41	20.3 - 52' **SHALE:** BDX (SH), gray (10YR 5/1). *(continued)*	BDX (SH)									
			42											
			43											
			44											
			45											
			46											
			47											
			48											
			49											
			50											
			51											
			52	52' End of Boring.										

RAMBOLL

MONITORING WELL CONSTRUCTION

Facility/Project Name: Vermilion Power Station	Local Grid Location of Well: ____ ft. ☐ N. ☐ S. ____ ft. ☐ E. ☐ W.	Well Name: 70D
Facility License, Permit or Monitoring No.	Local Grid Origin ☐ (estimated: ☐) or Well Location ☐ Lat. ° ' " Long. ° ' " or St. Plane 1,278,929 ft. N, 1,150,617 ft. E. Ⓔ/W	
Facility ID		Date Well Installed: 03/04/2021
Type of Well: Well Code 12/pz	Section Location of Waste/Source: ____ 1/4 of ____ 1/4 of Sec. ____, T. ____ N, R. ____ ☐ E ☐ W	Well Installed By: (Person's Name and Firm): Jason Greer; Cascade Drilling
Distance from Waste/Source ft. / State: Illinois	Location of Well Relative to Waste/Source: u ☐ Upgradient s ☐ Sidegradient d ☒ Downgradient n ☐ Not Known	Gov. Lot Number

A. Protective pipe, top elevation: 595.10 ft. MSL
B. Well casing, top elevation: 594.52 ft. MSL
C. Land surface elevation: 591.9 ft. MSL
D. Surface seal, bottom: 590.9 ft. MSL or 1.0 ft.

12. USCS classification of soil near screen:
GP ☐ GM ☐ GC ☐ GW ☐ SW ☐ SP ☐
SM ☐ SC ☐ ML ☐ MH ☐ CL ☐ CH ☐
Bedrock ☒

13. Sieve analysis attached? ☐ Yes ☒ No

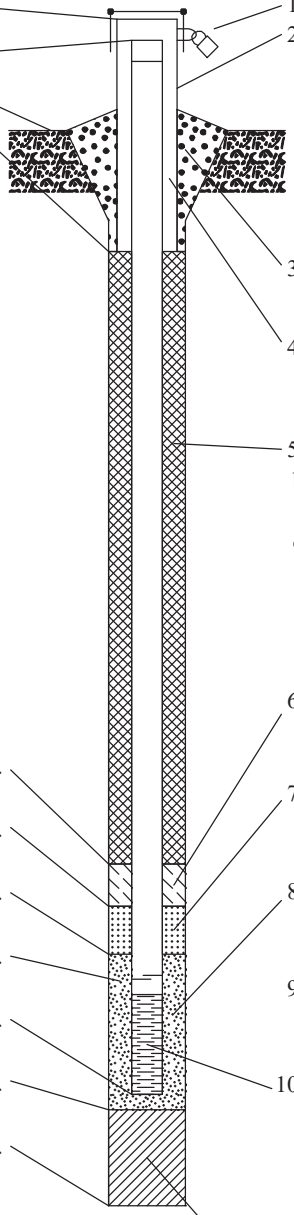
14. Drilling method used: Rotary ☐ Hollow Stem Auger ☐ Sonic Other ☒

15. Drilling fluid used: Water ☒ 0 2 Air ☐ Drilling Mud ☐ 0 3 None ☐

16. Drilling additives used? ☐ Yes ☒ No
Describe ____

17. Source of water (attach analysis, if required): Potable City Water

E. Bentonite seal, top: 557.9 ft. MSL or 34.0 ft.
F. Fine sand, top: ____ ft. MSL or ____ ft.
G. Filter pack, top: 552.9 ft. MSL or 39.0 ft.
H. Screen joint, top: 550.9 ft. MSL or 41.0 ft.
I. Well bottom: 540.9 ft. MSL or 51.0 ft.
J. Filter pack, bottom: 540.9 ft. MSL or 51.0 ft.
K. Borehole, bottom: 539.9 ft. MSL or 52.0 ft.
L. Borehole, diameter: 6.0 in.
M. O.D. well casing: 2.38 in.
N. I.D. well casing: 2.07 in.



1. Cap and lock? ☒ Yes ☐ No
2. Protective cover pipe:
a. Inside diameter: 4.0 in.
b. Length: 5.0 ft.
c. Material: Steel ☒ Other ☐
d. Additional protection? ☒ Yes ☐ No
If yes, describe: 4 Steel Bollards
3. Surface seal: Bentonite ☐ Concrete ☒ Other ☐
4. Material between well casing and protective pipe: Bentonite ☐ Sand Other ☒
5. Annular space seal: a. Granular/Chipped Bentonite ☐
b. ____ Lbs/gal mud weight . . . Bentonite-sand slurry ☐
c. 9.2 Lbs/gal mud weight . . . Bentonite slurry ☒
d. ____ % Bentonite . . . Bentonite-cement grout ☐
e. ____ Ft^3 volume added for any of the above
f. How installed: Tremie ☐ Tremie pumped ☒ Gravity ☐
6. Bentonite seal: a. Bentonite granules ☐
b. ☐ 1/4 in. ☒ 3/8 in. ☐ 1/2 in. Bentonite chips ☒
c. ____ Other ☐
7. Fine sand material: Manufacturer, product name & mesh size
a. NA
b. Volume added 0 ft^3
8. Filter pack material: Manufacturer, product name & mesh size
a. FILTERSIL 0.85
b. Volume added ____ ft^3
9. Well casing: Flush threaded PVC schedule 40 ☒ Flush threaded PVC schedule 80 ☐ Other ☐
10. Screen material: Schedule 40 PVC
a. Screen Type: Factory cut ☒ Continuous slot ☐ Other ☐
b. Manufacturer Johnson Screens
c. Slot size: 0.010 in.
d. Slotted length: 10.0 ft.
11. Backfill material (below filter pack): None ☐ Formation Materials Other ☒

I hereby certify that the information on this form is true and correct to the best of my knowledge. Date Modified: 3/31/2021

Signature ____ Firm Ramboll, 234 W. Florida Street, Milwaukee,WI 53204 Tel: (414) 837-3607 Fax: (414) 837-3608

ATTACHMENT 4
Sequential Extraction Procedure Analytical Report

eurofins | Environment Testing

ANALYTICAL REPORT

PREPARED FOR

Attn: Allison Kreinberg
Geosyntec Consultants Inc
941 Chatham Lane
Suite 103
Columbus, Ohio 43221

Generated 8/3/2023 11:56:48 AM

JOB DESCRIPTION

Vermilion SEP

JOB NUMBER

140-32513-1

Eurofins Knoxville
5815 Middlebrook Pike
Knoxville TN 37921

See page two for job notes and contact information.

my EOL

Job Notes

This report may not be reproduced except in full, and with written approval from the laboratory. The results relate only to the samples tested. For questions please contact the Project Manager at the e-mail address or telephone number listed on this page.

The test results in this report relate only to the samples as received by the laboratory and will meet all requirements of the methodology, with any exceptions noted. This report shall not be reproduced except in full, without the express written approval of the laboratory. All questions should be directed to the Eurofins TestAmerica Project Manager.

Authorization

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Authorized for release by
Ryan Henry, Project Manager I
WilliamR.Henry@et.eurofinsus.com
(865)291-3006

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Definitions/Glossary

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Qualifiers

Metals

Qualifier	Qualifier Description
B	Compound was found in the blank and sample.
J	Result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value.

Glossary

Abbreviation	These commonly used abbreviations may or may not be present in this report.
¤	Listed under the "D" column to designate that the result is reported on a dry weight basis
%R	Percent Recovery
CFL	Contains Free Liquid
CFU	Colony Forming Unit
CNF	Contains No Free Liquid
DER	Duplicate Error Ratio (normalized absolute difference)
Dil Fac	Dilution Factor
DL	Detection Limit (DoD/DOE)
DL, RA, RE, IN	Indicates a Dilution, Re-analysis, Re-extraction, or additional Initial metals/anion analysis of the sample
DLC	Decision Level Concentration (Radiochemistry)
EDL	Estimated Detection Limit (Dioxin)
LOD	Limit of Detection (DoD/DOE)
LOQ	Limit of Quantitation (DoD/DOE)
MCL	EPA recommended "Maximum Contaminant Level"
MDA	Minimum Detectable Activity (Radiochemistry)
MDC	Minimum Detectable Concentration (Radiochemistry)
MDL	Method Detection Limit
ML	Minimum Level (Dioxin)
MPN	Most Probable Number
MQL	Method Quantitation Limit
NC	Not Calculated
ND	Not Detected at the reporting limit (or MDL or EDL if shown)
NEG	Negative / Absent
POS	Positive / Present
PQL	Practical Quantitation Limit
PRES	Presumptive
QC	Quality Control
RER	Relative Error Ratio (Radiochemistry)
RL	Reporting Limit or Requested Limit (Radiochemistry)
RPD	Relative Percent Difference, a measure of the relative difference between two points
TEF	Toxicity Equivalent Factor (Dioxin)
TEQ	Toxicity Equivalent Quotient (Dioxin)
TNTC	Too Numerous To Count

Job ID: 140-32513-1

Laboratory: Eurofins Knoxville

Narrative

Job Narrative
140-32513-1

Receipt
The samples were received on 7/3/2023 at 11:15am and arrived in good condition, and where required, properly preserved and on ice. The temperature of the cooler at receipt was 20.3º C.

Receipt Exceptions
The Field Sampler was not listed on the Chain of Custody.

Metals
7 Step Sequential Extraction Procedure

These soil samples were prepared and analyzed using Eurofins TestAmerica Knoxville standard operating procedure KNOX-MT-0008, "7 Step Sequential Extraction Procedure". SW-846 Method 6010B as incorporated in Eurofins TestAmerica Knoxville standard operating procedure KNOX-MT-0007 was used to perform the final instrument analyses.

An aliquot of each sample was sequentially extracted using the steps listed below:

· Step 1 - Exchangeable Fraction: A 5 gram aliquot of sample was extracted with 25 mL of 1M magnesium sulfate (MgSO4), centrifuged and filtered. 5 mL of the resulting leachate was digested using method 3010A and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
· Step 2 - Carbonate Fraction: The sample residue from step 1 was extracted with 25 mL of 1M sodium acetate/acetic acid (NaOAc/HOAc) at pH 5, centrifuged and filtered. 5 mL of the resulting leachate was digested using method 3010A and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
· Step 3 - Non-crystalline Materials Fraction: The sample residue from step 2 was extracted with 25 mL of 0.2M ammonium oxalate (pH 3), centrifuged and filtered. 5 mL of the resulting leachate was digested using method 3010A and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
· Step 4 - Metal Hydroxide Fraction: The sample residue from step 3 was extracted with 25 mL of 1M hydroxylamine hydrochloride solution in 25% v/v acetic acid, centrifuged and filtered. 5 mL of the resulting leachate was digested using method 3010A and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
· Step 5 - Organic-bound Fraction: The sample residue from step 4 was extracted three times with 25 mL of 5% sodium hypochlorite (NaClO) at pH 9.5, centrifuged and filtered. The resulting leachates were combined and 5 mL were digested using method 3010A and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
· Step 6 - Acid/Sulfide Fraction: The sample residue from step 5 was extracted with 25 mL of a 3:1:2 v/v solution of HCl-HNO3-H2O, centrifuged and filtered. 5 mL of the resulting leachate was diluted to 50 mL with reagent water and analyzed by method 6010B. Results are reported in mg/kg on a dry weight basis.
· Step 7 - Residual Fraction: A 1.0 g aliquot of the sample residue from step 6 was digested using HF, HNO3, HCl and H3BO3. The digestate was analyzed by ICP using method 6010B. Results are reported in mg/kg on a dry weight basis.

In addition, a 1.0 g aliquot of the original sample was digested using HF, HNO3, HCl and H3BO3. The digestate was analyzed by ICP using method 6010B. Total metal results are reported in mg/kg on a dry weight basis.

Results were calculated using the following equation:

Result, µg/g or mg/Kg, dry weight = (C × V × V1 × D) / (W × S × V2)

Where:
C = Concentration from instrument readout, µg/mL
V = Final volume of digestate, mL
D = Instrument dilution factor
V1 = Total volume of leachate, mL
V2 = Volume of leachate digested, mL
W = Wet weight of sample, g

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Laboratory: Eurofins Knoxville (Continued)

S = Percent solids/100

A method blank, laboratory control sample and laboratory control sample duplicate were prepared and analyzed with each SEP step in order to provide information about both the presence of elements of interest in the extraction solutions, and the recovery of elements of interest from the extraction solutions. Results outside of laboratory QC limits do not reflect out of control performance, but rather the effect of the extraction solution upon the analyte.

A laboratory sample duplicate was prepared and analyzed with each batch of samples in order to provide information regarding the reproducibility of the procedure.

SEP Report Notes:

The final report lists the results for each step, the result for the total digestion of the sample, and a sum of the results of steps 1 through 7 by element.

Magnesium was not reported for step 1 because the extraction solution for this step (magnesium sulfate) contains high levels of magnesium.

Sodium was not reported for steps 2 and 5 since the extraction solution for these steps contain high levels of sodium.

The sum of steps 1 through 7 is much higher than the total result for sodium and magnesium due to the magnesium and sodium introduced by the extraction solutions.

The digestates for steps 1, 2 and 5 were analyzed at a dilution due to instrument problems caused by the high solids content of the digestates. The reporting limits were adjusted accordingly.

The serial diilution is analyzed at an additional 5 fold dilution using the dilution factors applied to the duplicate and the associated original sample. Due to a limitation of the expanded deliverable forms, the dilutions of the duplicate and serial dilution in the expanded deliverable are not expressed on a per analyte basis.

Please refer to the summary section of the report for the duplicate information as it contains the dilution factors at which the sample was analyzed.

Method 6010B: The serial dilution performed for the following samples associated with batch 140-75976 were outside control limits: VER-35 55-60 20230624 (140-32513-1), (140-32513-A-1-C SD ^10) and (140-32513-A-1-C SD ^5)

Method 6010B: The following samples were diluted to bring the concentration of target analyte, Iron, within the calibration range: VER-35 55-60 20230624 (140-32513-1), VER-35 60-63 20230624 (140-32513-2) and VER-70 75-80 20230623 (140-32513-3). Elevated reporting limits (RLs) are provided.

Method 6010B SEP: The serial dilution performed for the following samples associated with batch 140-75894 was outside control limits: VER-35 55-60 20230624 (140-32513-1), (140-32513-A-1-S SD ^5) and (140-32513-A-1-W SD ^5)

No additional analytical or quality issues were noted, other than those described above or in the Definitions/Glossary page.

General Chemistry
% Moisture: The samples were analyzed for percent moisture using SOP number KNOX-WC-0012 (based on Modified MCAWW 160.3 and SM2540B and on the percent moisture determinations described in methods 3540C and 3550B).

No additional analytical or quality issues were noted, other than those described above or in the Definitions/Glossary page.

Sample Summary

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Lab Sample ID	Client Sample ID	Matrix	Collected	Received
140-32513-1	VER-35 55-60 20230624	Solid	06/24/23 14:20	07/03/23 11:15
140-32513-2	VER-35 60-63 20230624	Solid	06/24/23 14:50	07/03/23 11:15
140-32513-3	VER-70 75-80 20230623	Solid	06/23/23 17:00	07/03/23 11:15

Client Sample ID: VER-35 55-60 20230624
Date Collected: 06/24/23 14:20
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-1
Matrix: Solid
Percent Solids: 95.4

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 1

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		21	12	mg/Kg	☼	07/11/23 08:00	07/27/23 13:01	4
Lithium	ND		10	0.63	mg/Kg	☼	07/11/23 08:00	07/27/23 13:01	4
Manganese	7.6		3.1	0.13	mg/Kg	☼	07/11/23 08:00	07/27/23 13:01	4

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 2

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	560		16	9.1	mg/Kg	☼	07/12/23 08:00	07/27/23 13:51	3
Lithium	0.56	J	7.9	0.47	mg/Kg	☼	07/12/23 08:00	07/27/23 13:51	3
Manganese	29		2.4	0.88	mg/Kg	☼	07/12/23 08:00	07/27/23 13:51	3

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 3

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	4300		5.2	3.0	mg/Kg	☼	07/13/23 08:00	07/27/23 14:40	1
Lithium	0.52	J	2.6	0.16	mg/Kg	☼	07/13/23 08:00	07/27/23 14:40	1
Manganese	110	B	0.79	0.028	mg/Kg	☼	07/13/23 08:00	07/27/23 14:40	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 4

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	20000		5.2	3.0	mg/Kg	☼	07/17/23 08:00	07/28/23 12:49	1
Lithium	13		2.6	0.16	mg/Kg	☼	07/17/23 08:00	07/28/23 12:49	1
Manganese	430		0.79	0.14	mg/Kg	☼	07/17/23 08:00	07/28/23 12:49	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 5

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		79	46	mg/Kg	☼	07/19/23 08:00	07/28/23 13:39	5
Lithium	4.1	J	39	2.3	mg/Kg	☼	07/19/23 08:00	07/28/23 13:39	5
Manganese	46		12	1.9	mg/Kg	☼	07/19/23 08:00	07/28/23 13:39	5

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 6

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	11000		5.2	3.0	mg/Kg	☼	07/19/23 08:00	07/28/23 14:29	1
Lithium	13		2.6	0.16	mg/Kg	☼	07/19/23 08:00	07/28/23 14:29	1
Manganese	130		0.79	0.26	mg/Kg	☼	07/19/23 08:00	07/28/23 14:29	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	4300		5.2	4.3	mg/Kg	☼	07/20/23 08:00	07/31/23 12:46	1
Lithium	15		2.6	0.16	mg/Kg	☼	07/20/23 08:00	07/31/23 12:46	1
Manganese	31		0.79	0.32	mg/Kg	☼	07/20/23 08:00	07/31/23 12:46	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Sum of Steps 1-7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	41000		5.0	4.1	mg/Kg			08/02/23 14:24	1
Lithium	46		2.5	0.15	mg/Kg			08/02/23 14:24	1
Manganese	780		0.75	0.052	mg/Kg			08/02/23 14:24	1

Method: SW846 6010B - SEP Metals (ICP) - Total

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	38000		10	8.6	mg/Kg	☼	07/21/23 08:00	07/31/23 14:12	2
Lithium	42		2.6	0.16	mg/Kg	☼	07/21/23 08:00	07/31/23 13:22	1
Manganese	610		0.79	0.32	mg/Kg	☼	07/21/23 08:00	07/31/23 13:22	1

Client Sample ID: VER-35 60-63 20230624
Date Collected: 06/24/23 14:50
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-2
Matrix: Solid
Percent Solids: 95.4

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 1

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		21	12	mg/Kg	☼	07/11/23 08:00	07/27/23 13:11	4
Lithium	ND		10	0.63	mg/Kg	☼	07/11/23 08:00	07/27/23 13:11	4
Manganese	**7.9**		3.1	0.13	mg/Kg	☼	07/11/23 08:00	07/27/23 13:11	4

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 2

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**570**		16	9.1	mg/Kg	☼	07/12/23 08:00	07/27/23 14:01	3
Lithium	**0.62**	**J**	7.9	0.47	mg/Kg	☼	07/12/23 08:00	07/27/23 14:01	3
Manganese	**29**		2.4	0.88	mg/Kg	☼	07/12/23 08:00	07/27/23 14:01	3

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 3

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**4200**		5.2	3.0	mg/Kg	☼	07/13/23 08:00	07/27/23 14:50	1
Lithium	**0.74**	**J**	2.6	0.16	mg/Kg	☼	07/13/23 08:00	07/27/23 14:50	1
Manganese	**110**	**B**	0.79	0.028	mg/Kg	☼	07/13/23 08:00	07/27/23 14:50	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 4

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**18000**		5.2	3.0	mg/Kg	☼	07/17/23 08:00	07/28/23 12:59	1
Lithium	**12**		2.6	0.16	mg/Kg	☼	07/17/23 08:00	07/28/23 12:59	1
Manganese	**380**		0.79	0.14	mg/Kg	☼	07/17/23 08:00	07/28/23 12:59	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 5

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		79	46	mg/Kg	☼	07/19/23 08:00	07/28/23 13:49	5
Lithium	**3.9**	**J**	39	2.3	mg/Kg	☼	07/19/23 08:00	07/28/23 13:49	5
Manganese	**35**		12	1.9	mg/Kg	☼	07/19/23 08:00	07/28/23 13:49	5

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 6

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**11000**		5.2	3.0	mg/Kg	☼	07/19/23 08:00	07/28/23 14:39	1
Lithium	**14**		2.6	0.16	mg/Kg	☼	07/19/23 08:00	07/28/23 14:39	1
Manganese	**140**		0.79	0.26	mg/Kg	☼	07/19/23 08:00	07/28/23 14:39	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**4200**		5.2	4.3	mg/Kg	☼	07/20/23 08:00	07/31/23 12:57	1
Lithium	**14**		2.6	0.16	mg/Kg	☼	07/20/23 08:00	07/31/23 12:57	1
Manganese	**30**		0.79	0.33	mg/Kg	☼	07/20/23 08:00	07/31/23 12:57	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Sum of Steps 1-7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**38000**		5.0	4.1	mg/Kg			08/02/23 14:24	1
Lithium	**45**		2.5	0.15	mg/Kg			08/02/23 14:24	1
Manganese	**730**		0.75	0.052	mg/Kg			08/02/23 14:24	1

Method: SW846 6010B - SEP Metals (ICP) - Total

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**37000**		10	8.6	mg/Kg	☼	07/21/23 08:00	07/31/23 14:22	2
Lithium	**39**		2.6	0.16	mg/Kg	☼	07/21/23 08:00	07/31/23 13:33	1
Manganese	**520**		0.79	0.33	mg/Kg	☼	07/21/23 08:00	07/31/23 13:33	1

Client Sample ID: VER-70 75-80 20230623
Date Collected: 06/23/23 17:00
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-3
Matrix: Solid
Percent Solids: 90.0

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 1

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		22	13	mg/Kg	☼	07/11/23 08:00	07/27/23 13:16	4
Lithium	ND		11	0.67	mg/Kg	☼	07/11/23 08:00	07/27/23 13:16	4
Manganese	**7.6**		3.3	0.14	mg/Kg	☼	07/11/23 08:00	07/27/23 13:16	4

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 2

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**730**		17	9.7	mg/Kg	☼	07/12/23 08:00	07/27/23 14:06	3
Lithium	ND		8.3	0.50	mg/Kg	☼	07/12/23 08:00	07/27/23 14:06	3
Manganese	**36**		2.5	0.93	mg/Kg	☼	07/12/23 08:00	07/27/23 14:06	3

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 3

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**5500**		5.6	3.2	mg/Kg	☼	07/13/23 08:00	07/27/23 14:55	1
Lithium	**0.41**	**J**	2.8	0.17	mg/Kg	☼	07/13/23 08:00	07/27/23 14:55	1
Manganese	**130**	**B**	0.83	0.030	mg/Kg	☼	07/13/23 08:00	07/27/23 14:55	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 4

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**31000**		11	6.4	mg/Kg	☼	07/17/23 08:00	07/28/23 14:55	2
Lithium	**12**		2.8	0.17	mg/Kg	☼	07/17/23 08:00	07/28/23 13:04	1
Manganese	**510**		0.83	0.14	mg/Kg	☼	07/17/23 08:00	07/28/23 13:04	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 5

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**61**	**J**	83	49	mg/Kg	☼	07/19/23 08:00	07/28/23 13:54	5
Lithium	**4.4**	**J**	42	2.4	mg/Kg	☼	07/19/23 08:00	07/28/23 13:54	5
Manganese	**54**		12	2.1	mg/Kg	☼	07/19/23 08:00	07/28/23 13:54	5

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 6

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**14000**		5.6	3.2	mg/Kg	☼	07/19/23 08:00	07/28/23 14:44	1
Lithium	**15**		2.8	0.17	mg/Kg	☼	07/19/23 08:00	07/28/23 14:44	1
Manganese	**160**		0.83	0.28	mg/Kg	☼	07/19/23 08:00	07/28/23 14:44	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Step 7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**5500**		5.6	4.6	mg/Kg	☼	07/20/23 08:00	07/31/23 13:17	1
Lithium	**19**		2.8	0.17	mg/Kg	☼	07/20/23 08:00	07/31/23 13:17	1
Manganese	**39**		0.83	0.34	mg/Kg	☼	07/20/23 08:00	07/31/23 13:17	1

Method: SW846 6010B SEP - SEP Metals (ICP) - Sum of Steps 1-7

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**57000**		5.0	4.1	mg/Kg			08/02/23 14:24	1
Lithium	**51**		2.5	0.15	mg/Kg			08/02/23 14:24	1
Manganese	**940**		0.75	0.052	mg/Kg			08/02/23 14:24	1

Method: SW846 6010B - SEP Metals (ICP) - Total

Analyte	Result	Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	**66000**		28	23	mg/Kg	☼	07/21/23 08:00	07/31/23 15:08	5
Lithium	**42**		2.8	0.17	mg/Kg	☼	07/21/23 08:00	07/31/23 13:39	1
Manganese	**720**		0.83	0.34	mg/Kg	☼	07/21/23 08:00	07/31/23 13:39	1

Default Detection Limits

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Method: 6010B SEP - SEP Metals (ICP) - Step 1
Prep: 3010A
SEP: Exchangeable

Analyte	RL	MDL	Units
Iron	5.0	2.9	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.031	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 2
Prep: 3010A
SEP: Carbonate

Analyte	RL	MDL	Units
Iron	5.0	2.9	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.28	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 3
Prep: 3010A
SEP: Non-Crystalline

Analyte	RL	MDL	Units
Iron	5.0	2.9	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.027	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 4
Prep: 3010A
SEP: Metal Hydroxide

Analyte	RL	MDL	Units
Iron	5.0	2.9	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.13	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 5
Prep: 3010A
SEP: Organic-Bound

Analyte	RL	MDL	Units
Iron	15	8.8	mg/Kg
Lithium	7.5	0.44	mg/Kg
Manganese	2.3	0.37	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 6
SEP: Acid/Sulfide

Analyte	RL	MDL	Units
Iron	5.0	2.9	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.25	mg/Kg

Method: 6010B SEP - SEP Metals (ICP) - Step 7
Prep: Residual

Analyte	RL	MDL	Units
Iron	5.0	4.1	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.31	mg/Kg

Default Detection Limits

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Method: 6010B SEP - SEP Metals (ICP) - Sum of Steps 1-7

Analyte	RL	MDL	Units
Iron	5.0	4.1	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.052	mg/Kg

Method: 6010B - SEP Metals (ICP) - Total

Prep: Total

Analyte	RL	MDL	Units
Iron	5.0	4.1	mg/Kg
Lithium	2.5	0.15	mg/Kg
Manganese	0.75	0.31	mg/Kg

Method: 6010B - SEP Metals (ICP) - Total

Lab Sample ID: MB 140-75187/5-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Method Blank
Prep Type: Total/NA
Prep Batch: 75187

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		5.0	4.1	mg/Kg		07/21/23 08:00	07/31/23 12:31	1
Lithium	ND		2.5	0.15	mg/Kg		07/21/23 08:00	07/31/23 12:31	1
Manganese	ND		0.75	0.31	mg/Kg		07/21/23 08:00	07/31/23 12:31	1

Lab Sample ID: LCS 140-75187/6-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Lab Control Sample
Prep Type: Total/NA
Prep Batch: 75187

Analyte	Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits
Iron	50.0	53.2		mg/Kg		106	80 - 120
Lithium	5.00	5.23		mg/Kg		105	80 - 120
Manganese	5.00	5.21		mg/Kg		104	80 - 120

Lab Sample ID: LCSD 140-75187/7-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Lab Control Sample Dup
Prep Type: Total/NA
Prep Batch: 75187

Analyte	Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron	50.0	54.5		mg/Kg		109	80 - 120	2	30
Lithium	5.00	5.14		mg/Kg		103	80 - 120	2	30
Manganese	5.00	5.27		mg/Kg		105	80 - 120	1	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: VER-35 55-60 20230624
Prep Type: Total/NA
Prep Batch: 75187

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Lithium	42		42.1		mg/Kg	☼	0	30
Manganese	610		613		mg/Kg	☼	0.8	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: VER-35 55-60 20230624
Prep Type: Total/NA
Prep Batch: 75187

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	38000		39200		mg/Kg	☼	2	30

Method: 6010B SEP - SEP Metals (ICP)

Lab Sample ID: MB 140-75184/5-B ^4
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Method Blank
Prep Type: Step 1
Prep Batch: 75207

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		20	12	mg/Kg		07/11/23 08:00	07/27/23 12:47	4
Lithium	ND		10	0.60	mg/Kg		07/11/23 08:00	07/27/23 12:47	4
Manganese	ND		3.0	0.12	mg/Kg		07/11/23 08:00	07/27/23 12:47	4

Method: 6010B SEP - SEP Metals (ICP) (Continued)

Lab Sample ID: LCS 140-75184/6-B ^5
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample
Prep Type: Step 1
Prep Batch: 75207

Analyte			Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits		
Iron			50.0	54.4		mg/Kg		109	80 - 120		
Lithium			5.00	5.66	J	mg/Kg		113	80 - 120		
Manganese			5.00	5.54		mg/Kg		111	80 - 120		

Lab Sample ID: LCSD 140-75184/7-B ^5
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 1
Prep Batch: 75207

Analyte			Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron			50.0	54.2		mg/Kg		108	80 - 120	0	30
Lithium			5.00	5.44	J	mg/Kg		109	80 - 120	4	30
Manganese			5.00	5.51		mg/Kg		110	80 - 120	1	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 1
Prep Batch: 75207

Analyte	Sample Result	Sample Qualifier		DU Result	DU Qualifier	Unit	D			RPD	RPD Limit
Iron	ND			ND		mg/Kg	☼			NC	30
Lithium	ND			ND		mg/Kg	☼			NC	30
Manganese	7.6			7.29		mg/Kg	☼			4	30

Lab Sample ID: MB 140-75227/5-B ^3
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Method Blank
Prep Type: Step 2
Prep Batch: 75260

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		15	8.7	mg/Kg		07/12/23 08:00	07/27/23 13:36	3
Lithium	ND		7.5	0.45	mg/Kg		07/12/23 08:00	07/27/23 13:36	3
Manganese	ND		2.3	0.84	mg/Kg		07/12/23 08:00	07/27/23 13:36	3

Lab Sample ID: LCS 140-75227/6-B ^5
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample
Prep Type: Step 2
Prep Batch: 75260

Analyte			Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits		
Iron			50.0	ND		mg/Kg		3			
Lithium			5.00	5.13	J	mg/Kg		103	80 - 120		
Manganese			5.00	5.01		mg/Kg		100	80 - 120		

Lab Sample ID: LCSD 140-75227/7-B ^5
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 2
Prep Batch: 75260

Analyte			Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron			50.0	ND		mg/Kg		3		28	
Lithium			5.00	4.95	J	mg/Kg		99	80 - 120	4	30
Manganese			5.00	4.96		mg/Kg		99	80 - 120	1	30

Method: 6010B SEP - SEP Metals (ICP) (Continued)

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 2
Prep Batch: 75260

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	560		531		mg/Kg	☼	5	
Lithium	0.56	J	ND		mg/Kg	☼	NC	30
Manganese	29		27.9		mg/Kg	☼	4	30

Lab Sample ID: MB 140-75274/5-B
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Method Blank
Prep Type: Step 3
Prep Batch: 75294

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		5.0	2.9	mg/Kg		07/13/23 08:00	07/27/23 14:26	1
Lithium	ND		2.5	0.15	mg/Kg		07/13/23 08:00	07/27/23 14:26	1
Manganese	0.0935	J	0.75	0.027	mg/Kg		07/13/23 08:00	07/27/23 14:26	1

Lab Sample ID: LCS 140-75274/6-B
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample
Prep Type: Step 3
Prep Batch: 75294

Analyte	Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits
Iron	50.0	51.9		mg/Kg		104	80 - 120
Lithium	5.00	4.98		mg/Kg		100	80 - 120
Manganese	5.00	5.04		mg/Kg		101	80 - 120

Lab Sample ID: LCSD 140-75274/7-B
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 3
Prep Batch: 75294

Analyte	Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron	50.0	49.5		mg/Kg		99	80 - 120	5	30
Lithium	5.00	4.82		mg/Kg		96	80 - 120	3	30
Manganese	5.00	4.89		mg/Kg		98	80 - 120	3	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75871

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 3
Prep Batch: 75294

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	4300		4280		mg/Kg	☼	1	30
Lithium	0.52	J	0.516	J	mg/Kg	☼	1	30
Manganese	110	B	114		mg/Kg	☼	2	30

Lab Sample ID: MB 140-75320/5-B
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Method Blank
Prep Type: Step 4
Prep Batch: 75407

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		5.0	2.9	mg/Kg		07/17/23 08:00	07/28/23 12:35	1
Lithium	ND		2.5	0.15	mg/Kg		07/17/23 08:00	07/28/23 12:35	1
Manganese	ND		0.75	0.13	mg/Kg		07/17/23 08:00	07/28/23 12:35	1

Method: 6010B SEP - SEP Metals (ICP) (Continued)

Lab Sample ID: LCS 140-75320/6-B
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample
Prep Type: Step 4
Prep Batch: 75407

Analyte			Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits		
Iron			50.0	55.0		mg/Kg		110	80 - 120		
Lithium			5.00	5.38		mg/Kg		108	80 - 120		
Manganese			5.00	5.49		mg/Kg		110	80 - 120		

Lab Sample ID: LCSD 140-75320/7-B
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 4
Prep Batch: 75407

Analyte			Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron			50.0	54.6		mg/Kg		109	80 - 120	1	30
Lithium			5.00	5.41		mg/Kg		108	80 - 120	0	30
Manganese			5.00	5.45		mg/Kg		109	80 - 120	1	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 4
Prep Batch: 75407

Analyte	Sample Result	Sample Qualifier		DU Result	DU Qualifier	Unit	D			RPD	RPD Limit
Iron	20000			19600		mg/Kg	☼			4	30
Lithium	13			12.6		mg/Kg	☼			3	30
Manganese	430			406		mg/Kg	☼			5	30

Lab Sample ID: MB 140-75406/5-B ^5
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Method Blank
Prep Type: Step 5
Prep Batch: 75487

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		75	44	mg/Kg		07/19/23 08:00	07/28/23 13:24	5
Lithium	ND		38	2.2	mg/Kg		07/19/23 08:00	07/28/23 13:24	5
Manganese	ND		11	1.9	mg/Kg		07/19/23 08:00	07/28/23 13:24	5

Lab Sample ID: LCS 140-75406/6-B ^5
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample
Prep Type: Step 5
Prep Batch: 75487

Analyte			Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits		
Iron			150	ND		mg/Kg		-0.07			
Lithium			15.0	16.9	J	mg/Kg		112	80 - 150		
Manganese			15.0	3.96	J	mg/Kg		26	1 - 60		

Lab Sample ID: LCSD 140-75406/7-B ^5
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 5
Prep Batch: 75487

Analyte			Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron			150	ND		mg/Kg		-0.5		156	
Lithium			15.0	16.7	J	mg/Kg		111	80 - 150	1	30
Manganese			15.0	4.01	J	mg/Kg		27	1 - 60	1	30

Method: 6010B SEP - SEP Metals (ICP) (Continued)

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 5
Prep Batch: 75487

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	ND		ND		mg/Kg	☼	NC	
Lithium	4.1	J	4.21	J	mg/Kg	☼	2	30
Manganese	46		40.0		mg/Kg	☼	14	30

Lab Sample ID: MB 140-75511/5-A
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Method Blank
Prep Type: Step 6
Prep Batch: 75511

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		5.0	2.9	mg/Kg		07/19/23 08:00	07/28/23 14:14	1
Lithium	ND		2.5	0.15	mg/Kg		07/19/23 08:00	07/28/23 14:14	1
Manganese	ND		0.75	0.25	mg/Kg		07/19/23 08:00	07/28/23 14:14	1

Lab Sample ID: LCS 140-75511/6-A
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample
Prep Type: Step 6
Prep Batch: 75511

Analyte	Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits
Iron	50.0	54.8		mg/Kg		110	80 - 120
Lithium	5.00	5.27		mg/Kg		105	80 - 120
Manganese	5.00	5.47		mg/Kg		109	80 - 120

Lab Sample ID: LCSD 140-75511/7-A
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 6
Prep Batch: 75511

Analyte	Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron	50.0	50.7		mg/Kg		101	80 - 120	8	30
Lithium	5.00	4.89		mg/Kg		98	80 - 120	7	30
Manganese	5.00	5.06		mg/Kg		101	80 - 120	8	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75894

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 6
Prep Batch: 75511

Analyte	Sample Result	Sample Qualifier	DU Result	DU Qualifier	Unit	D	RPD	RPD Limit
Iron	11000		10600		mg/Kg	☼	4	30
Lithium	13		12.7		mg/Kg	☼	4	30
Manganese	130		127		mg/Kg	☼	2	30

Lab Sample ID: MB 140-75565/5-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Method Blank
Prep Type: Step 7
Prep Batch: 75565

Analyte	MB Result	MB Qualifier	RL	MDL	Unit	D	Prepared	Analyzed	Dil Fac
Iron	ND		5.0	4.1	mg/Kg		07/20/23 08:00	07/31/23 12:16	1
Lithium	ND		2.5	0.15	mg/Kg		07/20/23 08:00	07/31/23 12:16	1
Manganese	ND		0.75	0.31	mg/Kg		07/20/23 08:00	07/31/23 12:16	1

Method: 6010B SEP - SEP Metals (ICP) (Continued)

Lab Sample ID: LCS 140-75565/6-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Lab Control Sample
Prep Type: Step 7
Prep Batch: 75565

Analyte			Spike Added	LCS Result	LCS Qualifier	Unit	D	%Rec	%Rec Limits		
Iron			50.0	54.2		mg/Kg		108	80 - 120		
Lithium			5.00	5.37		mg/Kg		107	80 - 120		
Manganese			5.00	5.35		mg/Kg		107	80 - 120		

Lab Sample ID: LCSD 140-75565/7-A
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: Lab Control Sample Dup
Prep Type: Step 7
Prep Batch: 75565

Analyte			Spike Added	LCSD Result	LCSD Qualifier	Unit	D	%Rec	%Rec Limits	RPD	RPD Limit
Iron			50.0	54.0		mg/Kg		108	80 - 120	0	30
Lithium			5.00	5.29		mg/Kg		106	80 - 120	2	30
Manganese			5.00	5.30		mg/Kg		106	80 - 120	1	30

Lab Sample ID: 140-32513-1 DU
Matrix: Solid
Analysis Batch: 75976

Client Sample ID: VER-35 55-60 20230624
Prep Type: Step 7
Prep Batch: 75565

Analyte	Sample Result	Sample Qualifier		DU Result	DU Qualifier	Unit	D			RPD	RPD Limit
Iron	4300			4610		mg/Kg	☼			6	30
Lithium	15			16.0		mg/Kg	☼			9	30
Manganese	31			32.3		mg/Kg	☼			3	30

Metals

SEP Batch: 75184

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 1	Solid	Exchangeable	
140-32513-2	VER-35 60-63 20230624	Step 1	Solid	Exchangeable	
140-32513-3	VER-70 75-80 20230623	Step 1	Solid	Exchangeable	
MB 140-75184/5-B ^4	Method Blank	Step 1	Solid	Exchangeable	
LCS 140-75184/6-B ^5	Lab Control Sample	Step 1	Solid	Exchangeable	
LCSD 140-75184/7-B ^5	Lab Control Sample Dup	Step 1	Solid	Exchangeable	
140-32513-1 DU	VER-35 55-60 20230624	Step 1	Solid	Exchangeable	

Prep Batch: 75187

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Total/NA	Solid	Total	
140-32513-2	VER-35 60-63 20230624	Total/NA	Solid	Total	
140-32513-3	VER-70 75-80 20230623	Total/NA	Solid	Total	
MB 140-75187/5-A	Method Blank	Total/NA	Solid	Total	
LCS 140-75187/6-A	Lab Control Sample	Total/NA	Solid	Total	
LCSD 140-75187/7-A	Lab Control Sample Dup	Total/NA	Solid	Total	
140-32513-1 DU	VER-35 55-60 20230624	Total/NA	Solid	Total	

Prep Batch: 75207

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 1	Solid	3010A	75184
140-32513-2	VER-35 60-63 20230624	Step 1	Solid	3010A	75184
140-32513-3	VER-70 75-80 20230623	Step 1	Solid	3010A	75184
MB 140-75184/5-B ^4	Method Blank	Step 1	Solid	3010A	75184
LCS 140-75184/6-B ^5	Lab Control Sample	Step 1	Solid	3010A	75184
LCSD 140-75184/7-B ^5	Lab Control Sample Dup	Step 1	Solid	3010A	75184
140-32513-1 DU	VER-35 55-60 20230624	Step 1	Solid	3010A	75184

SEP Batch: 75227

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 2	Solid	Carbonate	
140-32513-2	VER-35 60-63 20230624	Step 2	Solid	Carbonate	
140-32513-3	VER-70 75-80 20230623	Step 2	Solid	Carbonate	
MB 140-75227/5-B ^3	Method Blank	Step 2	Solid	Carbonate	
LCS 140-75227/6-B ^5	Lab Control Sample	Step 2	Solid	Carbonate	
LCSD 140-75227/7-B ^5	Lab Control Sample Dup	Step 2	Solid	Carbonate	
140-32513-1 DU	VER-35 55-60 20230624	Step 2	Solid	Carbonate	

Prep Batch: 75260

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 2	Solid	3010A	75227
140-32513-2	VER-35 60-63 20230624	Step 2	Solid	3010A	75227
140-32513-3	VER-70 75-80 20230623	Step 2	Solid	3010A	75227
MB 140-75227/5-B ^3	Method Blank	Step 2	Solid	3010A	75227
LCS 140-75227/6-B ^5	Lab Control Sample	Step 2	Solid	3010A	75227
LCSD 140-75227/7-B ^5	Lab Control Sample Dup	Step 2	Solid	3010A	75227
140-32513-1 DU	VER-35 55-60 20230624	Step 2	Solid	3010A	75227

SEP Batch: 75274

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 3	Solid	Non-Crystalline	

Metals (Continued)

SEP Batch: 75274 (Continued)

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-2	VER-35 60-63 20230624	Step 3	Solid	Non-Crystalline	
140-32513-3	VER-70 75-80 20230623	Step 3	Solid	Non-Crystalline	
MB 140-75274/5-B	Method Blank	Step 3	Solid	Non-Crystalline	
LCS 140-75274/6-B	Lab Control Sample	Step 3	Solid	Non-Crystalline	
LCSD 140-75274/7-B	Lab Control Sample Dup	Step 3	Solid	Non-Crystalline	
140-32513-1 DU	VER-35 55-60 20230624	Step 3	Solid	Non-Crystalline	

Prep Batch: 75294

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 3	Solid	3010A	75274
140-32513-2	VER-35 60-63 20230624	Step 3	Solid	3010A	75274
140-32513-3	VER-70 75-80 20230623	Step 3	Solid	3010A	75274
MB 140-75274/5-B	Method Blank	Step 3	Solid	3010A	75274
LCS 140-75274/6-B	Lab Control Sample	Step 3	Solid	3010A	75274
LCSD 140-75274/7-B	Lab Control Sample Dup	Step 3	Solid	3010A	75274
140-32513-1 DU	VER-35 55-60 20230624	Step 3	Solid	3010A	75274

SEP Batch: 75320

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 4	Solid	Metal Hydroxide	
140-32513-2	VER-35 60-63 20230624	Step 4	Solid	Metal Hydroxide	
140-32513-3	VER-70 75-80 20230623	Step 4	Solid	Metal Hydroxide	
MB 140-75320/5-B	Method Blank	Step 4	Solid	Metal Hydroxide	
LCS 140-75320/6-B	Lab Control Sample	Step 4	Solid	Metal Hydroxide	
LCSD 140-75320/7-B	Lab Control Sample Dup	Step 4	Solid	Metal Hydroxide	
140-32513-1 DU	VER-35 55-60 20230624	Step 4	Solid	Metal Hydroxide	

SEP Batch: 75406

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 5	Solid	Organic-Bound	
140-32513-2	VER-35 60-63 20230624	Step 5	Solid	Organic-Bound	
140-32513-3	VER-70 75-80 20230623	Step 5	Solid	Organic-Bound	
MB 140-75406/5-B ^5	Method Blank	Step 5	Solid	Organic-Bound	
LCS 140-75406/6-B ^5	Lab Control Sample	Step 5	Solid	Organic-Bound	
LCSD 140-75406/7-B ^5	Lab Control Sample Dup	Step 5	Solid	Organic-Bound	
140-32513-1 DU	VER-35 55-60 20230624	Step 5	Solid	Organic-Bound	

Prep Batch: 75407

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 4	Solid	3010A	75320
140-32513-2	VER-35 60-63 20230624	Step 4	Solid	3010A	75320
140-32513-3	VER-70 75-80 20230623	Step 4	Solid	3010A	75320
MB 140-75320/5-B	Method Blank	Step 4	Solid	3010A	75320
LCS 140-75320/6-B	Lab Control Sample	Step 4	Solid	3010A	75320
LCSD 140-75320/7-B	Lab Control Sample Dup	Step 4	Solid	3010A	75320
140-32513-1 DU	VER-35 55-60 20230624	Step 4	Solid	3010A	75320

Prep Batch: 75487

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 5	Solid	3010A	75406
140-32513-2	VER-35 60-63 20230624	Step 5	Solid	3010A	75406

Metals (Continued)

Prep Batch: 75487 (Continued)

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-3	VER-70 75-80 20230623	Step 5	Solid	3010A	75406
MB 140-75406/5-B ^5	Method Blank	Step 5	Solid	3010A	75406
LCS 140-75406/6-B ^5	Lab Control Sample	Step 5	Solid	3010A	75406
LCSD 140-75406/7-B ^5	Lab Control Sample Dup	Step 5	Solid	3010A	75406
140-32513-1 DU	VER-35 55-60 20230624	Step 5	Solid	3010A	75406

SEP Batch: 75511

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 6	Solid	Acid/Sulfide	
140-32513-2	VER-35 60-63 20230624	Step 6	Solid	Acid/Sulfide	
140-32513-3	VER-70 75-80 20230623	Step 6	Solid	Acid/Sulfide	
MB 140-75511/5-A	Method Blank	Step 6	Solid	Acid/Sulfide	
LCS 140-75511/6-A	Lab Control Sample	Step 6	Solid	Acid/Sulfide	
LCSD 140-75511/7-A	Lab Control Sample Dup	Step 6	Solid	Acid/Sulfide	
140-32513-1 DU	VER-35 55-60 20230624	Step 6	Solid	Acid/Sulfide	

Prep Batch: 75565

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 7	Solid	Residual	
140-32513-2	VER-35 60-63 20230624	Step 7	Solid	Residual	
140-32513-3	VER-70 75-80 20230623	Step 7	Solid	Residual	
MB 140-75565/5-A	Method Blank	Step 7	Solid	Residual	
LCS 140-75565/6-A	Lab Control Sample	Step 7	Solid	Residual	
LCSD 140-75565/7-A	Lab Control Sample Dup	Step 7	Solid	Residual	
140-32513-1 DU	VER-35 55-60 20230624	Step 7	Solid	Residual	

Analysis Batch: 75871

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 1	Solid	6010B SEP	75207
140-32513-1	VER-35 55-60 20230624	Step 2	Solid	6010B SEP	75260
140-32513-1	VER-35 55-60 20230624	Step 3	Solid	6010B SEP	75294
140-32513-2	VER-35 60-63 20230624	Step 1	Solid	6010B SEP	75207
140-32513-2	VER-35 60-63 20230624	Step 2	Solid	6010B SEP	75260
140-32513-2	VER-35 60-63 20230624	Step 3	Solid	6010B SEP	75294
140-32513-3	VER-70 75-80 20230623	Step 1	Solid	6010B SEP	75207
140-32513-3	VER-70 75-80 20230623	Step 2	Solid	6010B SEP	75260
140-32513-3	VER-70 75-80 20230623	Step 3	Solid	6010B SEP	75294
MB 140-75184/5-B ^4	Method Blank	Step 1	Solid	6010B SEP	75207
MB 140-75227/5-B ^3	Method Blank	Step 2	Solid	6010B SEP	75260
MB 140-75274/5-B	Method Blank	Step 3	Solid	6010B SEP	75294
LCS 140-75184/6-B ^5	Lab Control Sample	Step 1	Solid	6010B SEP	75207
LCS 140-75227/6-B ^5	Lab Control Sample	Step 2	Solid	6010B SEP	75260
LCS 140-75274/6-B	Lab Control Sample	Step 3	Solid	6010B SEP	75294
LCSD 140-75184/7-B ^5	Lab Control Sample Dup	Step 1	Solid	6010B SEP	75207
LCSD 140-75227/7-B ^5	Lab Control Sample Dup	Step 2	Solid	6010B SEP	75260
LCSD 140-75274/7-B	Lab Control Sample Dup	Step 3	Solid	6010B SEP	75294
140-32513-1 DU	VER-35 55-60 20230624	Step 1	Solid	6010B SEP	75207
140-32513-1 DU	VER-35 55-60 20230624	Step 2	Solid	6010B SEP	75260
140-32513-1 DU	VER-35 55-60 20230624	Step 3	Solid	6010B SEP	75294

Metals

Analysis Batch: 75894

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 4	Solid	6010B SEP	75407
140-32513-1	VER-35 55-60 20230624	Step 5	Solid	6010B SEP	75487
140-32513-1	VER-35 55-60 20230624	Step 6	Solid	6010B SEP	75511
140-32513-2	VER-35 60-63 20230624	Step 4	Solid	6010B SEP	75407
140-32513-2	VER-35 60-63 20230624	Step 5	Solid	6010B SEP	75487
140-32513-2	VER-35 60-63 20230624	Step 6	Solid	6010B SEP	75511
140-32513-3	VER-70 75-80 20230623	Step 4	Solid	6010B SEP	75407
140-32513-3	VER-70 75-80 20230623	Step 4	Solid	6010B SEP	75407
140-32513-3	VER-70 75-80 20230623	Step 5	Solid	6010B SEP	75487
140-32513-3	VER-70 75-80 20230623	Step 6	Solid	6010B SEP	75511
MB 140-75320/5-B	Method Blank	Step 4	Solid	6010B SEP	75407
MB 140-75406/5-B ^5	Method Blank	Step 5	Solid	6010B SEP	75487
MB 140-75511/5-A	Method Blank	Step 6	Solid	6010B SEP	75511
LCS 140-75320/6-B	Lab Control Sample	Step 4	Solid	6010B SEP	75407
LCS 140-75406/6-B ^5	Lab Control Sample	Step 5	Solid	6010B SEP	75487
LCS 140-75511/6-A	Lab Control Sample	Step 6	Solid	6010B SEP	75511
LCSD 140-75320/7-B	Lab Control Sample Dup	Step 4	Solid	6010B SEP	75407
LCSD 140-75406/7-B ^5	Lab Control Sample Dup	Step 5	Solid	6010B SEP	75487
LCSD 140-75511/7-A	Lab Control Sample Dup	Step 6	Solid	6010B SEP	75511
140-32513-1 DU	VER-35 55-60 20230624	Step 4	Solid	6010B SEP	75407
140-32513-1 DU	VER-35 55-60 20230624	Step 5	Solid	6010B SEP	75487
140-32513-1 DU	VER-35 55-60 20230624	Step 6	Solid	6010B SEP	75511

Analysis Batch: 75976

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Step 7	Solid	6010B SEP	75565
140-32513-1	VER-35 55-60 20230624	Total/NA	Solid	6010B	75187
140-32513-1	VER-35 55-60 20230624	Total/NA	Solid	6010B	75187
140-32513-2	VER-35 60-63 20230624	Step 7	Solid	6010B SEP	75565
140-32513-2	VER-35 60-63 20230624	Total/NA	Solid	6010B	75187
140-32513-2	VER-35 60-63 20230624	Total/NA	Solid	6010B	75187
140-32513-3	VER-70 75-80 20230623	Step 7	Solid	6010B SEP	75565
140-32513-3	VER-70 75-80 20230623	Total/NA	Solid	6010B	75187
140-32513-3	VER-70 75-80 20230623	Total/NA	Solid	6010B	75187
MB 140-75187/5-A	Method Blank	Total/NA	Solid	6010B	75187
MB 140-75565/5-A	Method Blank	Step 7	Solid	6010B SEP	75565
LCS 140-75187/6-A	Lab Control Sample	Total/NA	Solid	6010B	75187
LCS 140-75565/6-A	Lab Control Sample	Step 7	Solid	6010B SEP	75565
LCSD 140-75187/7-A	Lab Control Sample Dup	Total/NA	Solid	6010B	75187
LCSD 140-75565/7-A	Lab Control Sample Dup	Step 7	Solid	6010B SEP	75565
140-32513-1 DU	VER-35 55-60 20230624	Step 7	Solid	6010B SEP	75565
140-32513-1 DU	VER-35 55-60 20230624	Total/NA	Solid	6010B	75187
140-32513-1 DU	VER-35 55-60 20230624	Total/NA	Solid	6010B	75187

Analysis Batch: 76083

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Sum of Steps 1-7	Solid	6010B SEP	
140-32513-2	VER-35 60-63 20230624	Sum of Steps 1-7	Solid	6010B SEP	
140-32513-3	VER-70 75-80 20230623	Sum of Steps 1-7	Solid	6010B SEP	

General Chemistry

Analysis Batch: 75814

Lab Sample ID	Client Sample ID	Prep Type	Matrix	Method	Prep Batch
140-32513-1	VER-35 55-60 20230624	Total/NA	Solid	Moisture	
140-32513-2	VER-35 60-63 20230624	Total/NA	Solid	Moisture	
140-32513-3	VER-70 75-80 20230623	Total/NA	Solid	Moisture	
140-32513-1 DU	VER-35 55-60 20230624	Total/NA	Solid	Moisture	

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: VER-35 55-60 20230624
Date Collected: 06/24/23 14:20
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-1
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Sum of Steps 1-7	Analysis	6010B SEP		1			76083	08/02/23 14:24	KNC	EET KNX
	Instrument ID: NOEQUIP									
Total/NA	Analysis	Moisture		1			75814	07/26/23 15:29	ACW	EET KNX
	Instrument ID: NOEQUIP									

Client Sample ID: VER-35 55-60 20230624
Date Collected: 06/24/23 14:20
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-1
Matrix: Solid
Percent Solids: 95.4

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 13:22	KNC	EET KNX
	Instrument ID: DUO									
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		2			75976	07/31/23 14:12	KNC	EET KNX
	Instrument ID: DUO									
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		4			75871	07/27/23 13:01	KNC	EET KNX
	Instrument ID: DUO									
Step 2	SEP	Carbonate			5.00 g	25 mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EET KNX
Step 2	Analysis	6010B SEP		3			75871	07/27/23 13:51	KNC	EET KNX
	Instrument ID: DUO									
Step 3	SEP	Non-Crystalline			5.00 g	25 mL	75274	07/12/23 08:00	LAH	EET KNX
Step 3	Prep	3010A			5 mL	50 mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:40	KNC	EET KNX
	Instrument ID: DUO									
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:49	KNC	EET KNX
	Instrument ID: DUO									
Step 5	SEP	Organic-Bound			5.00 g	75 mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50 mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:39	KNC	EET KNX
	Instrument ID: DUO									
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:29	KNC	EET KNX
	Instrument ID: DUO									
Step 7	Prep	Residual			1.00 g	50 mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:46	KNC	EET KNX
	Instrument ID: DUO									

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: VER-35 60-63 20230624

Date Collected: 06/24/23 14:50
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-2

Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Sum of Steps 1-7	Analysis	6010B SEP		1			76083	08/02/23 14:24	KNC	EET KNX
	Instrument ID: NOEQUIP									
Total/NA	Analysis	Moisture		1			75814	07/26/23 15:29	ACW	EET KNX
	Instrument ID: NOEQUIP									

Client Sample ID: VER-35 60-63 20230624

Date Collected: 06/24/23 14:50
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-2

Matrix: Solid
Percent Solids: 95.4

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 13:33	KNC	EET KNX
	Instrument ID: DUO									
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		2			75976	07/31/23 14:22	KNC	EET KNX
	Instrument ID: DUO									
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		4			75871	07/27/23 13:11	KNC	EET KNX
	Instrument ID: DUO									
Step 2	SEP	Carbonate			5.00 g	25 mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EET KNX
Step 2	Analysis	6010B SEP		3			75871	07/27/23 14:01	KNC	EET KNX
	Instrument ID: DUO									
Step 3	SEP	Non-Crystalline			5.00 g	25 mL	75274	07/12/23 08:00	LAH	EET KNX
Step 3	Prep	3010A			5 mL	50 mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:50	KNC	EET KNX
	Instrument ID: DUO									
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:59	KNC	EET KNX
	Instrument ID: DUO									
Step 5	SEP	Organic-Bound			5.00 g	75 mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50 mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:49	KNC	EET KNX
	Instrument ID: DUO									
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:39	KNC	EET KNX
	Instrument ID: DUO									
Step 7	Prep	Residual			1.00 g	50 mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:57	KNC	EET KNX
	Instrument ID: DUO									

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: VER-70 75-80 20230623
Date Collected: 06/23/23 17:00
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-3
Matrix: Solid

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Sum of Steps 1-7	Analysis	6010B SEP		1			76083	08/02/23 14:24	KNC	EET KNX
	Instrument ID: NOEQUIP									
Total/NA	Analysis	Moisture		1			75814	07/26/23 15:29	ACW	EET KNX
	Instrument ID: NOEQUIP									

Client Sample ID: VER-70 75-80 20230623
Date Collected: 06/23/23 17:00
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-3
Matrix: Solid
Percent Solids: 90.0

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 13:39	KNC	EET KNX
	Instrument ID: DUO									
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		5			75976	07/31/23 15:08	KNC	EET KNX
	Instrument ID: DUO									
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		4			75871	07/27/23 13:16	KNC	EET KNX
	Instrument ID: DUO									
Step 2	SEP	Carbonate			5.00 g	25 mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EET KNX
Step 2	Analysis	6010B SEP		3			75871	07/27/23 14:06	KNC	EET KNX
	Instrument ID: DUO									
Step 3	SEP	Non-Crystalline			5.00 g	25 mL	75274	07/12/23 08:00	LAH	EET KNX
Step 3	Prep	3010A			5 mL	50 mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:55	KNC	EET KNX
	Instrument ID: DUO									
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 13:04	KNC	EET KNX
	Instrument ID: DUO									
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		2			75894	07/28/23 14:55	KNC	EET KNX
	Instrument ID: DUO									
Step 5	SEP	Organic-Bound			5.00 g	75 mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50 mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:54	KNC	EET KNX
	Instrument ID: DUO									
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:44	KNC	EET KNX
	Instrument ID: DUO									
Step 7	Prep	Residual			1.00 g	50 mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 13:17	KNC	EET KNX
	Instrument ID: DUO									

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: Method Blank
Lab Sample ID: MB 140-75184/5-B ^4
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		4			75871	07/27/23 12:47	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Method Blank
Lab Sample ID: MB 140-75187/5-A
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 12:31	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Method Blank
Lab Sample ID: MB 140-75227/5-B ^3
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 2	SEP	Carbonate			5.00 g	25 mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EET KNX
Step 2	Analysis	6010B SEP		3			75871	07/27/23 13:36	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Method Blank
Lab Sample ID: MB 140-75274/5-B
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 3	SEP	Non-Crystalline			5.00 g	25 mL	75274	07/12/23 08:00	LAH	EET KNX
Step 3	Prep	3010A			5 mL	50 mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:26	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Method Blank
Lab Sample ID: MB 140-75320/5-B
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:35	KNC	EET KNX
	Instrument ID: DUO									

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: Method Blank
Lab Sample ID: MB 140-75406/5-B ^5

Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 5	SEP	Organic-Bound			5.00 g	75 mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50 mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:24	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Method Blank
Lab Sample ID: MB 140-75511/5-A

Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:14	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Method Blank
Lab Sample ID: MB 140-75565/5-A

Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 7	Prep	Residual			1.00 g	50 mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:16	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample
Lab Sample ID: LCS 140-75184/6-B ^5

Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		5			75871	07/27/23 12:52	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample
Lab Sample ID: LCS 140-75187/6-A

Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 12:36	KNC	EET KNX
	Instrument ID: DUO									

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: Lab Control Sample
Lab Sample ID: LCS 140-75227/6-B ^5
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 2	SEP	Carbonate			5.00 g	25 mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EET KNX
Step 2	Analysis	6010B SEP		5			75871	07/27/23 13:41	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample
Lab Sample ID: LCS 140-75274/6-B
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 3	SEP	Non-Crystalline			5.00 g	25 mL	75274	07/12/23 08:00	LAH	EET KNX
Step 3	Prep	3010A			5 mL	50 mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:31	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample
Lab Sample ID: LCS 140-75320/6-B
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:40	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample
Lab Sample ID: LCS 140-75406/6-B ^5
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 5	SEP	Organic-Bound			5.00 g	75 mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50 mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:29	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample
Lab Sample ID: LCS 140-75511/6-A
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:19	KNC	EET KNX
	Instrument ID: DUO									

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: Lab Control Sample
Lab Sample ID: LCS 140-75565/6-A
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 7	Prep	Residual			1.00 g	50 mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:21	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup
Lab Sample ID: LCSD 140-75184/7-B ^5
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		5			75871	07/27/23 12:57	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup
Lab Sample ID: LCSD 140-75187/7-A
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 12:41	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup
Lab Sample ID: LCSD 140-75227/7-B ^5
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 2	SEP	Carbonate			5.00 g	25 mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EET KNX
Step 2	Analysis	6010B SEP		5			75871	07/27/23 13:46	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup
Lab Sample ID: LCSD 140-75274/7-B
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 3	SEP	Non-Crystalline			5.00 g	25 mL	75274	07/12/23 08:00	LAH	EET KNX
Step 3	Prep	3010A			5 mL	50 mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:36	KNC	EET KNX
	Instrument ID: DUO									

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: Lab Control Sample Dup
Lab Sample ID: LCSD 140-75320/7-B
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:44	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup
Lab Sample ID: LCSD 140-75406/7-B ^5
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 5	SEP	Organic-Bound			5.00 g	75 mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50 mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:34	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup
Lab Sample ID: LCSD 140-75511/7-A
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:24	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: Lab Control Sample Dup
Lab Sample ID: LCSD 140-75565/7-A
Date Collected: N/A
Matrix: Solid
Date Received: N/A

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Step 7	Prep	Residual			1.00 g	50 mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:26	KNC	EET KNX
	Instrument ID: DUO									

Client Sample ID: VER-35 55-60 20230624
Lab Sample ID: 140-32513-1 DU
Date Collected: 06/24/23 14:20
Matrix: Solid
Date Received: 07/03/23 11:15

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Analysis	Moisture		1			75814	07/26/23 15:29	ACW	EET KNX
	Instrument ID: NOEQUIP									

Lab Chronicle

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Client Sample ID: VER-35 55-60 20230624

Date Collected: 06/24/23 14:20
Date Received: 07/03/23 11:15

Lab Sample ID: 140-32513-1 DU

Matrix: Solid
Percent Solids: 95.4

Prep Type	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		1			75976	07/31/23 13:28	KNC	EET KNX
	Instrument ID: DUO									
Total/NA	Prep	Total			1.00 g	50 mL	75187	07/21/23 08:00	LAH	EET KNX
Total/NA	Analysis	6010B		2			75976	07/31/23 14:17	KNC	EET KNX
	Instrument ID: DUO									
Step 1	SEP	Exchangeable			5.00 g	25 mL	75184	07/10/23 12:30	LAH	EET KNX
Step 1	Prep	3010A			5 mL	50 mL	75207	07/11/23 08:00	LAH	EET KNX
Step 1	Analysis	6010B SEP		4			75871	07/27/23 13:06	KNC	EET KNX
	Instrument ID: DUO									
Step 2	SEP	Carbonate			5.00 g	25 mL	75227	07/11/23 08:00	LAH	EET KNX
Step 2	Prep	3010A			5 mL	50 mL	75260	07/12/23 08:00	LAH	EET KNX
Step 2	Analysis	6010B SEP		3			75871	07/27/23 13:56	KNC	EET KNX
	Instrument ID: DUO									
Step 3	SEP	Non-Crystalline			5.00 g	25 mL	75274	07/12/23 08:00	LAH	EET KNX
Step 3	Prep	3010A			5 mL	50 mL	75294	07/13/23 08:00	LAH	EET KNX
Step 3	Analysis	6010B SEP		1			75871	07/27/23 14:45	KNC	EET KNX
	Instrument ID: DUO									
Step 4	SEP	Metal Hydroxide			5.00 g	25 mL	75320	07/13/23 08:00	LAH	EET KNX
Step 4	Prep	3010A			5 mL	50 mL	75407	07/17/23 08:00	LAH	EET KNX
Step 4	Analysis	6010B SEP		1			75894	07/28/23 12:54	KNC	EET KNX
	Instrument ID: DUO									
Step 5	SEP	Organic-Bound			5.00 g	75 mL	75406	07/17/23 08:00	LAH	EET KNX
Step 5	Prep	3010A			5 mL	50 mL	75487	07/19/23 08:00	LAH	EET KNX
Step 5	Analysis	6010B SEP		5			75894	07/28/23 13:44	KNC	EET KNX
	Instrument ID: DUO									
Step 6	SEP	Acid/Sulfide			5.00 g	250 mL	75511	07/19/23 08:00	LAH	EET KNX
Step 6	Analysis	6010B SEP		1			75894	07/28/23 14:34	KNC	EET KNX
	Instrument ID: DUO									
Step 7	Prep	Residual			1.00 g	50 mL	75565	07/20/23 08:00	LAH	EET KNX
Step 7	Analysis	6010B SEP		1			75976	07/31/23 12:51	KNC	EET KNX
	Instrument ID: DUO									

Laboratory References:
EET KNX = Eurofins Knoxville, 5815 Middlebrook Pike, Knoxville, TN 37921, TEL (865)291-3000

Accreditation/Certification Summary

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Laboratory: Eurofins Knoxville

All accreditations/certifications held by this laboratory are listed. Not all accreditations/certifications are applicable to this report.

Authority	Program	Identification Number	Expiration Date
	AFCEE	N/A	
ANAB	Dept. of Defense ELAP	L2311	02-13-25
ANAB	Dept. of Energy	L2311.01	02-13-25
ANAB	ISO/IEC 17025	L2311	02-13-25
Arkansas DEQ	State	88-0688	06-16-24
Colorado	State	TN00009	02-29-24
Connecticut	State	PH-0223	09-30-23
Florida	NELAP	E87177	06-30-24
Georgia (DW)	State	906	07-27-25
Hawaii	State	NA	07-27-23 *
Kansas	NELAP	E-10349	10-31-23
Kentucky (DW)	State	90101	12-31-23
Louisiana (All)	NELAP	83979	06-30-24
Louisiana (DW)	State	LA019	12-31-23
Maryland	State	277	03-31-24
Michigan	State	9933	07-27-25
Nevada	State	TN00009	07-31-23 *
New Hampshire	NELAP	2999	01-17-24
New Jersey	NELAP	TN001	07-01-24
New York	NELAP	10781	03-31-24
North Carolina (DW)	State	21705	07-31-24
North Carolina (WW/SW)	State	64	12-31-23
Oklahoma	State	9415	08-31-23
Oregon	NELAP	TNI0189	01-01-24
Pennsylvania	NELAP	68-00576	12-01-23
Tennessee	State	02014	07-27-25
Texas	NELAP	T104704380-22-17	08-31-23
US Fish & Wildlife	US Federal Programs	058448	07-31-24
USDA	US Federal Programs	525-22-279-18762	10-06-25
Utah	NELAP	TN00009	07-31-24
Virginia	NELAP	460176	09-14-23
Washington	State	C593	01-19-24
West Virginia (DW)	State	9955C	12-31-23
West Virginia DEP	State	345	04-30-24
Wisconsin	State	998044300	08-31-23

* Accreditation/Certification renewal pending - accreditation/certification considered valid.

Method Summary

Client: Geosyntec Consultants Inc
Project/Site: Vermilion SEP

Job ID: 140-32513-1

Method	Method Description	Protocol	Laboratory
6010B	SEP Metals (ICP) - Total	SW846	EET KNX
6010B SEP	SEP Metals (ICP)	SW846	EET KNX
Moisture	Percent Moisture	EPA	EET KNX
3010A	Preparation, Total Metals	SW846	EET KNX
Acid/Sulfide	Sequential Extraction Procedure, Acid/Sulfide Fraction	TAL-KNOX	EET KNX
Carbonate	Sequential Extraction Procedure, Carbonate Fraction	TAL-KNOX	EET KNX
Exchangeable	Sequential Extraction Procedure, Exchangeable Fraction	TAL-KNOX	EET KNX
Metal Hydroxide	Sequential Extraction Procedure, Metal Hydroxide Fraction	TAL-KNOX	EET KNX
Non-Crystalline	Sequential Extraction Procedure, Non-crystalline Materials	TAL-KNOX	EET KNX
Organic-Bound	Sequential Extraction Procedure, Organic Bound Fraction	TAL-KNOX	EET KNX
Residual	Sequential Extraction Procedure, Residual Fraction	TAL-KNOX	EET KNX
Total	Preparation, Total Material	TAL-KNOX	EET KNX

Protocol References:

EPA = US Environmental Protection Agency

SW846 = "Test Methods For Evaluating Solid Waste, Physical/Chemical Methods", Third Edition, November 1986 And Its Updates.

TAL-KNOX = TestAmerica Laboratories, Knoxville, Facility Standard Operating Procedure.

Laboratory References:

EET KNX = Eurofins Knoxville, 5815 Middlebrook Pike, Knoxville, TN 37921, TEL (865)291-3000

Eurofins TestAmerica, Knoxville
5815 Middlebrook Pike

Knoxville, TN 37921-5947
phone 865.291.3000 fax 865.584.4315

Chain of Custody Record

eurofins Environment Testing TestAmerica

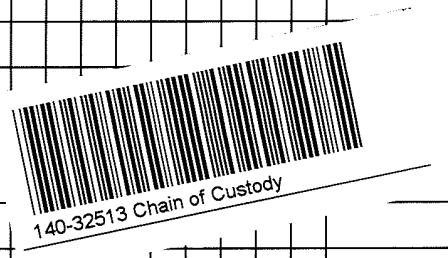
Regulatory Program: ☐ DW ☐ NPDES ☐ RCRA ☑ Other:

TestAmerica Laboratories, Inc. d/b/a Eurofins TestAmerica

Client Contact	Project Manager: Allison Kreinberg	Site Contact: NA	Date:	COC No:
Geosyntec Consultants, Inc.	Tel/Fax:	Lab Contact: Ryan Henry	Carrier:	___1___ of ___1___ COCs
941 Chatham Lane, Suite 103	Analysis Turnaround Time			Sampler:
Columbus, OH 43221	☐ CALENDAR DAYS ☐ WORKING DAYS			For Lab Use Only:
(614) 468-0421 Phone	TAT if different from Below _____			Walk-in Client:
	☒ 2 weeks			Lab Sampling:
Project Name: Vistra	☐ 1 week			
Site: Vermilion	☐ 2 days			Job / SDG No.:
P O #	☐ 1 day			

Sample Identification	Sample Date	Sample Time	Sample Type (C=Comp, G=Grab)	Matrix	# of Cont.	Filtered Sample (Y / N)	Perform MS / MSD (Y / N)	6010B SEP (Li, Fe, Mn)	Sample Specific Notes:
VER-35 55-60 20230624	6/24/2023	1420	G	Solid	1	N	N	X	
VER-35 60-63 20230624	6/24/2023	1450	G	Solid	1	N	N	X	
VER-70 75-80 20230623	6/23/2023	1700	G	Solid	1	N	N	X	

No Custody Seal
Received Ambient AT: 20.0/CT: 20.3C
DH 7/3/23
1 Box FedEx 7804 7929 1869 G



Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other _____

Possible Hazard Identification:
Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample.

☑ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)

☐ Return to Client ☐ Disposal by Lab ☑ Archive for _____ Months

Special Instructions/QC Requirements & Comments:

Custody Seals Intact: ☐ Yes ☐ No	Custody Seal No.:		Cooler Temp. (°C): Obs'd: _____ Corr'd: _____		Therm ID No.: _____	
Relinquished by: Graham Kelley	Company: GEOSYNTEC	Date/Time: 6/28/23	Received by: Dean Hick	Company: ETA KNX	Date/Time: 7/3/23 11:15	7/3/23
Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:	
Relinquished by:	Company:	Date/Time:	Received in Laboratory by:	Company:	Date/Time:	

Form No. CA-C-WI-002, Rev. 4.21, dated 4/4/2019

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7/3/2023

Loc: 140
32513

EUROFINS/TESTAMERICA KNOXVILLE SAMPLE RECEIPT/CONDITION UPON RECEIPT ANOMALY CHECKLIST **Log In Number:**

Review Items	Yes	No	NA	If No, what was the problem?
1. Are the shipping containers intact?	✓			☐ **Containers, Broken**
2. Were ambient air containers received intact?			✓	☐ Checked in lab
3. The coolers/containers custody seal if present, is it intact?			✓	☐ Yes ☐ NA
4. Is the cooler temperature within limits? (> freezing temp. of water to 6 °C, VOST: 10°C) Thermometer ID : SC73 Correction factor: +0.3°C			✓	☐ **Cooler Out of Temp, Client Contacted, Proceed/Cancel** ☐ **Cooler Out of Temp, Same Day Receipt**
5. Were all of the sample containers received intact?	✓			☐ **Containers, Broken**
6. Were samples received in appropriate containers?			✓	☐ **Containers, Improper; Client Contacted; Proceed/Cancel**
7. Do sample container labels match COC? (IDs, Dates, Times)	✓			☐ **COC & Samples Do Not Match** ☐ **COC Incorrect/Incomplete** ☐ **COC Not Received**
8. Were all of the samples listed on the COC received?	✓			☐ **Sample Received, Not on COC** ☐ **Sample on COC, Not Received**
9. Is the date/time of sample collection noted?	✓			☐ **COC; No Date/Time; Client Contacted**
10. Was the sampler identified on the COC?		✓		☐ **Sampler Not Listed on COC**
11. Is the client and project name/# identified?	✓			☐ **COC Incorrect/Incomplete**
12. Are tests/parameters listed for each sample?	✓			☐ **COC No tests on COC**
13. Is the matrix of the samples noted?	✓			☐ **COC Incorrect/Incomplete**
14. Was COC relinquished? (Signed/Dated/Timed)	✓			☐ **COC Incorrect/Incomplete**
15. Were samples received within holding time?	✓			☐ **Holding Time - Receipt**
16. Were samples received with correct chemical preservative (excluding Encore)?			✓	☐ **pH Adjusted, pH Included (See box 16A)** ☐ **Incorrect Preservative**
17. Were VOA samples received without headspace?			✓	☐ **Headspace (VOA only)**
18. Did you check for residual chlorine, if necessary? (e.g. 1613B, 1668) Chlorine test strip lot number:			✓	☐ **Residual Chlorine**
19. For 1613B water samples is pH<9?			✓	☐ If no, notify lab to adjust
20. For rad samples was sample activity info. Provided?			✓	☐ Project missing info

Comments/Actions Taken

10,

Labeling Verified by: **Date:**

pH test strip lot number:

	Box 16A: pH Preservation	Box 18A: Residual Chlorine
Preservative:		
Lot Number:		
Exp Date:		
Analyst:		
Date:		
Time:		

Project #: 14006199 PM Instructions:

Sample Receiving Associate: Dean Hicks Date: 7/3/23

QA026R32.doc, 062719

ATTACHMENT 5
X-Ray Diffraction
Laboratory Analytical Report

Quantitative X-Ray Diffraction by Rietveld Refinement

Report Prepared for:	*Environmental Services*
Project Number/ LIMS No.	*Custom XRD/MI4526-AUG23*
Sample Receipt:	*August 10, 2023*
Sample Analysis:	*August 31, 2023*
Reporting Date:	*September 13, 2023*

Instrument:	BRUKER AXS D8 Advance Diffractometer
Test Conditions:	Co radiation, 35 kV, 40 mA; Detector: LYNXEYE Regular Scanning: Step: 0.02°, Step time: 0.75s, 2θ range: 6-80° Clay Section Scanning: Step: 0.01°, Step time:0.2s, 2θ range: 3-40°
Interpretations :	PDF2/PDF4 powder diffraction databases issued by the International Center for Diffraction Data (ICDD). DiffracPlus Eva and Topas software.
Detection Limit :	0.5-2%. Strongly dependent on crystallinity.

Contents:

1) Method Summary
2) Quantitative XRD Results
3) XRD Pattern(s)

Zhihai (Adrian) Zhang, Ph.D
Mineralogist

Kim Gibbs, H.B.Sc., P.Geo.
Senior Mineralogist

ACCREDITATION: SGS Natural Resources Lakefield is accredited to the requirements of ISO/IEC 17025 for specific tests as listed on our scope of accreditation, including geochemical, mineralogical and trade mineral tests. To view a list of the accredited methods, please visit the following website and search SGS Canada Inc. - Minerals: https://www.scc.ca/en/search/palcan.

Method Summary

The Rietveld Method of Mineral Identification by XRD (ME-LR-MIN-MET-MN-D05) method used by SGS Natural Resources is accredited to the requirements of ISO/IEC 17025.

Mineral Identification and Interpretation:

Mineral identification and interpretation involves matching the diffraction pattern of an unknown material to patterns of single-phase reference materials. The reference patterns are compiled by the Joint Committee on Powder Diffraction Standards - International Center for Diffraction Data (JCPDS-ICDD) database and released on software as Powder Diffraction Files (PDF).

Interpretations do not reflect the presence of non-crystalline and/or amorphous compounds, except when internal standards have been added by request. Mineral proportions may be strongly influenced by crystallinity, crystal structure and preferred orientations. Mineral or compound identification and quantitative analysis results should be accompanied by supporting chemical assay data or other additional tests.

Clay Mineral Separation and Identification:

Clay minerals are typically fine-grained (<2 µm) phyllosilicates in sedimentary rock. Due to the poor crystallinity and fine size of clay minerals, separation of the clay fraction from bulk samples by centrifuge is required. A slide of the oriented clay fraction is prepared and scanned followed by a series of procedures (the addition of ethylene glycol and high temperature heating). Clay minerals are identified by their individual diffraction patterns and changes in their diffraction pattern after different treatments. Clay speciation and mineral identification of the bulk sample are performed using DIFFRACplus EVA (Bruker AXS).

Quantitative Rietveld Analysis:

Quantitative Rietveld Analysis is performed by using Topas 4.2 (Bruker AXS), a graphics based profile analysis program built around a non-linear least squares fitting system, to determine the amount of different phases present in a multicomponent sample. Whole pattern analyses are predicated by the fact that the X-ray diffraction pattern is a total sum of both instrumental and specimen factors. Unlike other peak intensity-based methods, the Rietveld method uses a least squares approach to refine a theoretical line profile until it matches the obtained experimental patterns.

Rietveld refinement is completed with a set of minerals specifically identified for the sample. Zero values indicate that the mineral was included in the refinement calculations, but the calculated concentration was less than 0.05wt%. Minerals not identified by the analyst are not included in refinement calculations for specific samples and are indicated with a dash.

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WARNING: The sample(s) to which the findings recorded herein (the "Findings") relate was(were) drawn and / or provided by the Client or by a third party acting at the Client's direction. The Findings constitute no warranty of the sample's representativeness of any goods and strictly relate to the sample(s). The Company accepts no liability with regard to the origin or source from which the sample(s) is/are said to be extracted.

Summary of Rietveld Quantitative Analysis X-Ray Diffraction Results

Mineral/Compound	VER-35 55-60 20230624 AUG4526-01 (wt %)	VER-35 60-63 20230624 AUG4526-02 (wt %)	VER-70 30-40 20230623 AUG4526-03 (wt %)	VER-70 41-42 20230623 AUG4526-04 (wt %)	VER-70 75-80 20230623 AUG4526-05 (wt %)
Quartz	38.5	38.1	48.6	48.2	35.0
Chlorite	6.9	6.8	1.2	3.6	7.7
Muscovite	23.4	23.0	13.5	15.2	27.0
Albite	12.6	12.6	10.6	10.8	11.5
Microcline	1.0	1.1	1.3	1.1	0.7
Siderite	4.9	5.0	0.9	0.1	5.4
Actinolite	-	-	0.8	-	-
Dolomite	-	-	11.7	11.7	-
Clays					
Illite	7.1	8.0	7.4	5.6	5.2
Kaolinite	5.6	5.4	3.2	3.7	7.5
Montmorillonite	-	-	0.8	-	-
TOTAL	100	100	100	100	100

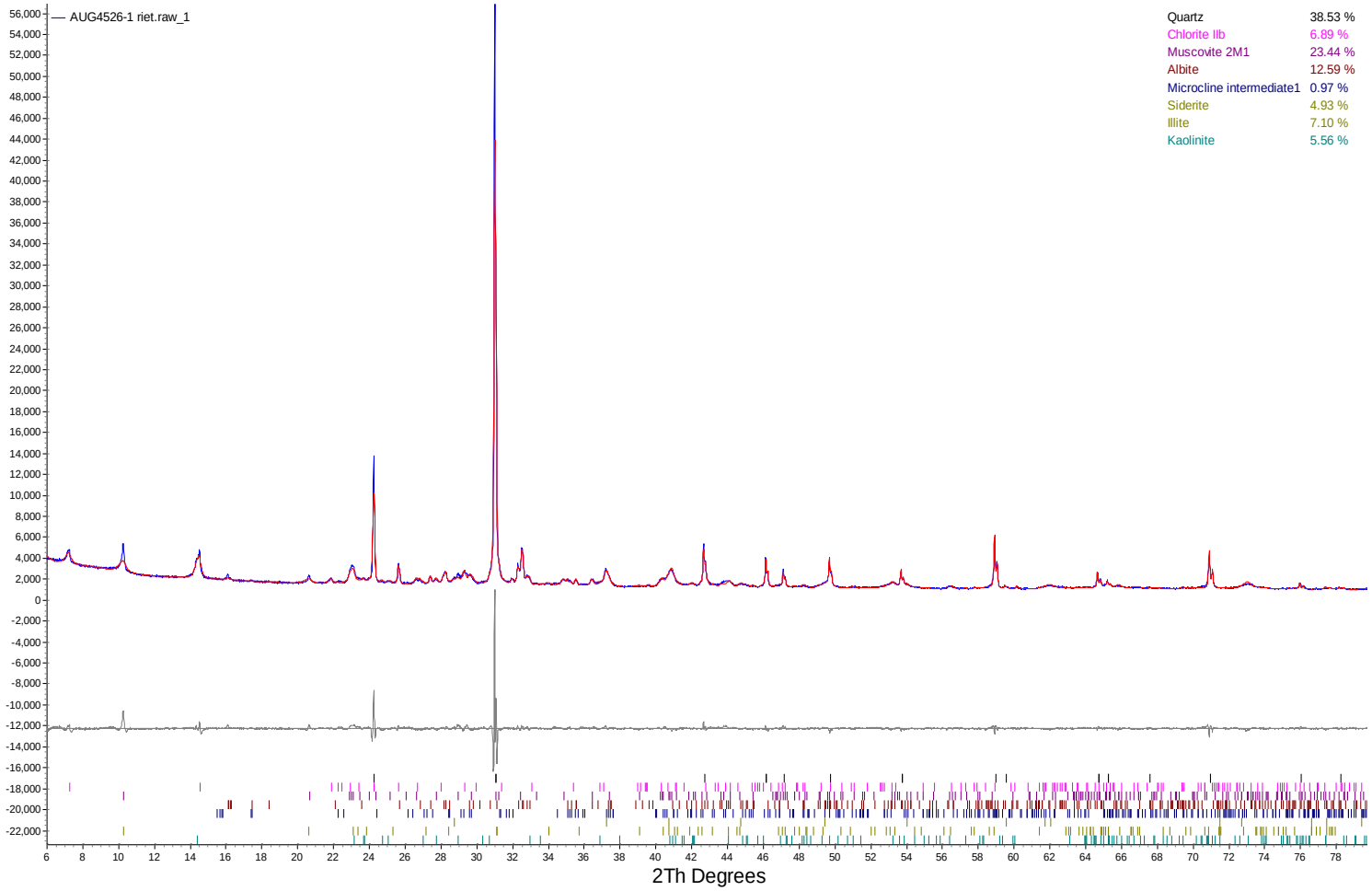
Zero values indicate that the mineral was included in the refinement, but the calculated concentration is below a measurable value.

Dashes indicate that the mineral was not identified by the analyst and not included in the refinement calculation for the sample.

The weight percent quantities indicated have been normalized to a sum of 100%. The quantity of amorphous material has not been determined.

Mineral/Compound	Formula
Quartz	SiO_2
Chlorite	$(Fe,(Mg,Mn)_5,Al)(Si_3Al)O_{10}(OH)_8$
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$
Albite	$NaAlSi_3O_8$
Microcline	$KAlSi_3O_8$
Siderite	$FeCO_3$
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
Dolomite	$CaMg(CO_3)_2$
Montmorillonite	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot 10H_2O$

VER-35 55-60 20230624



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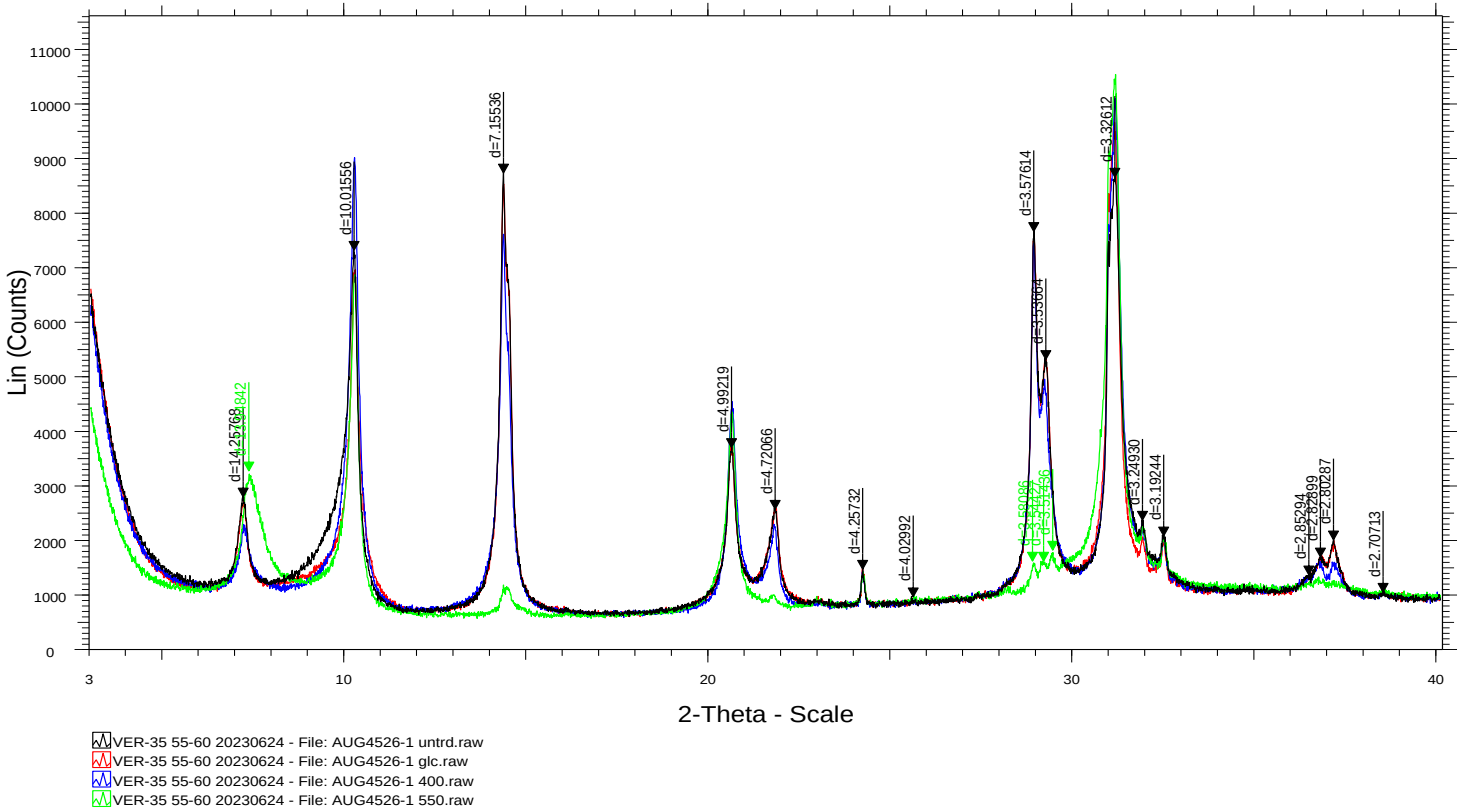

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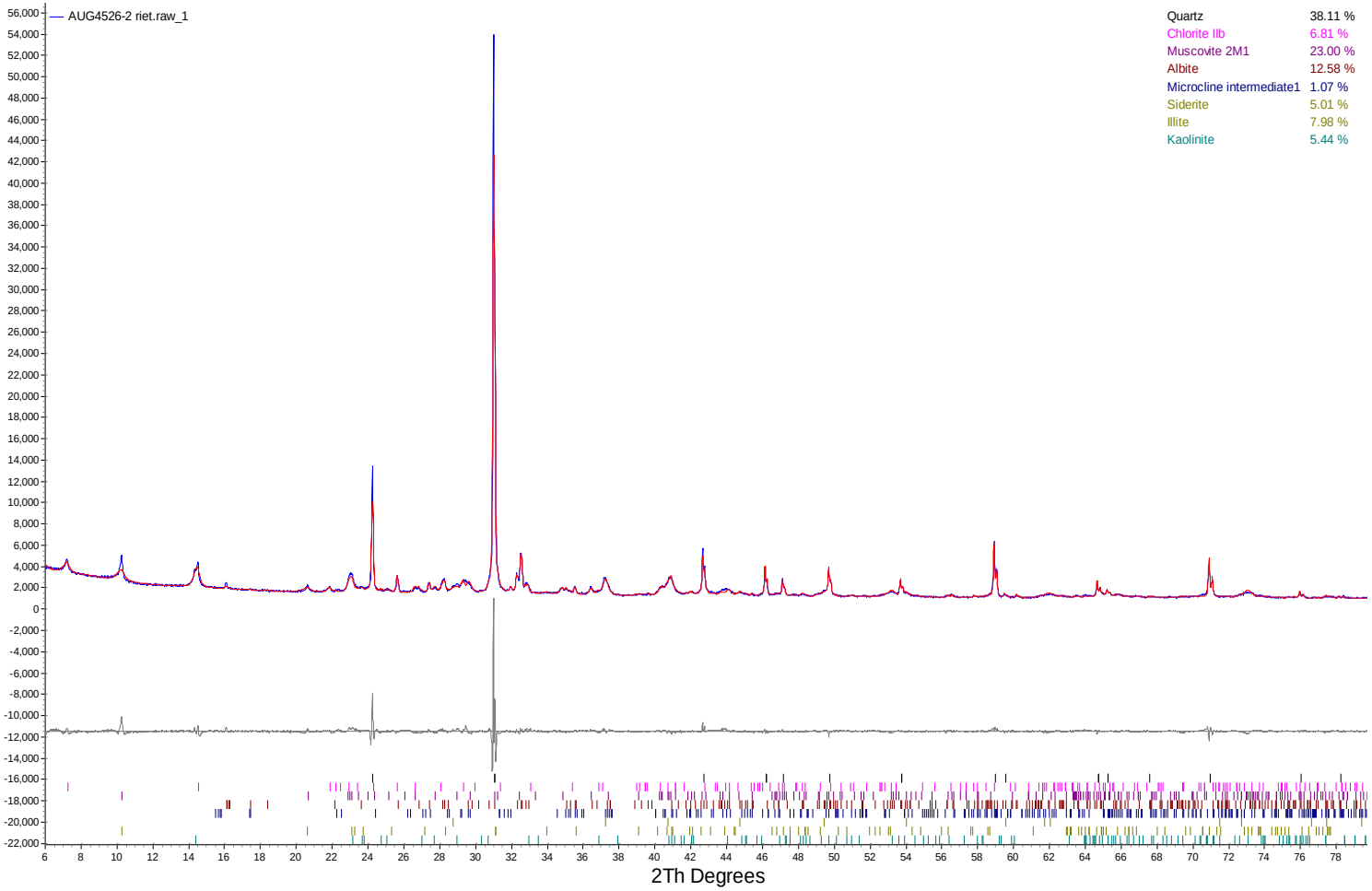

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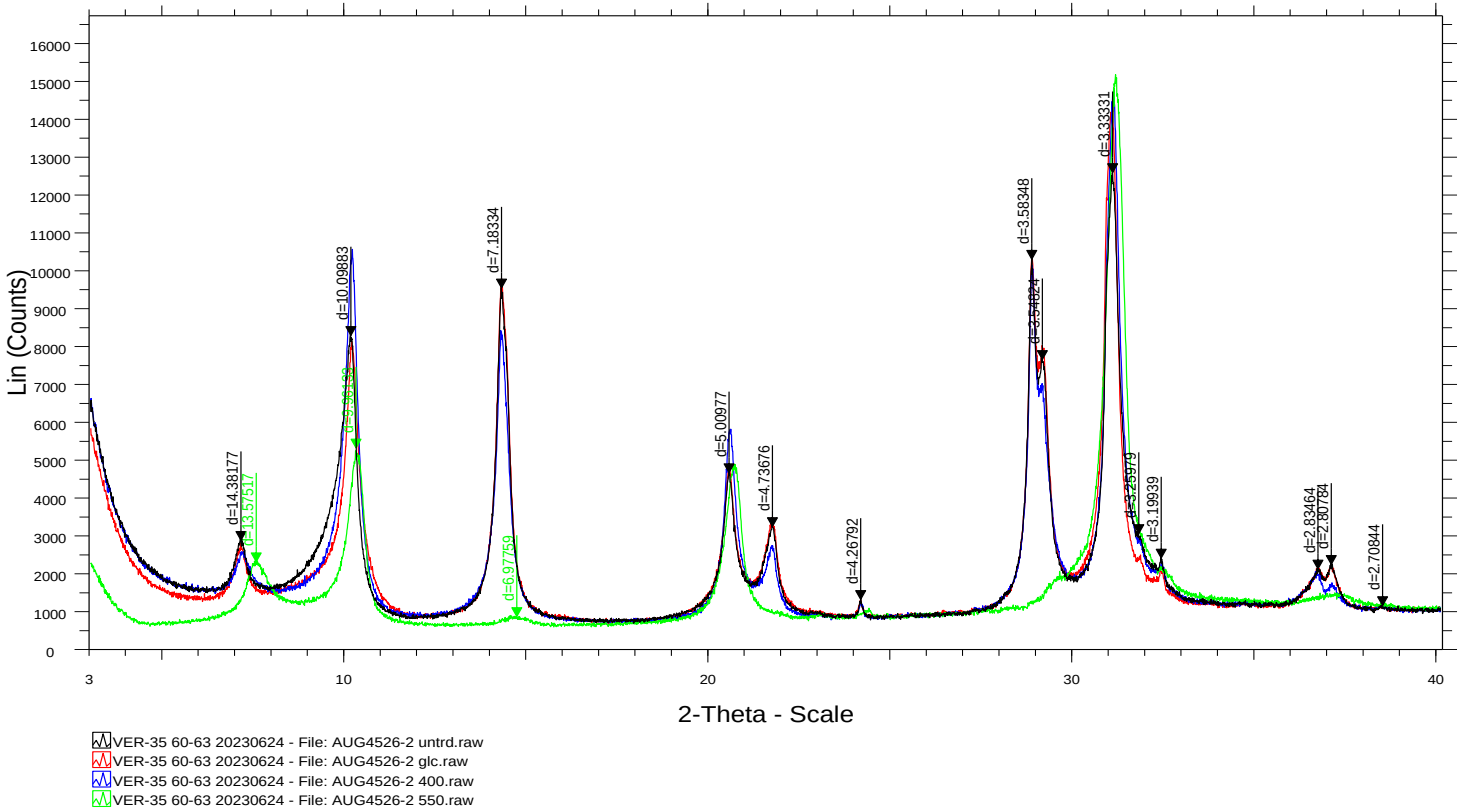

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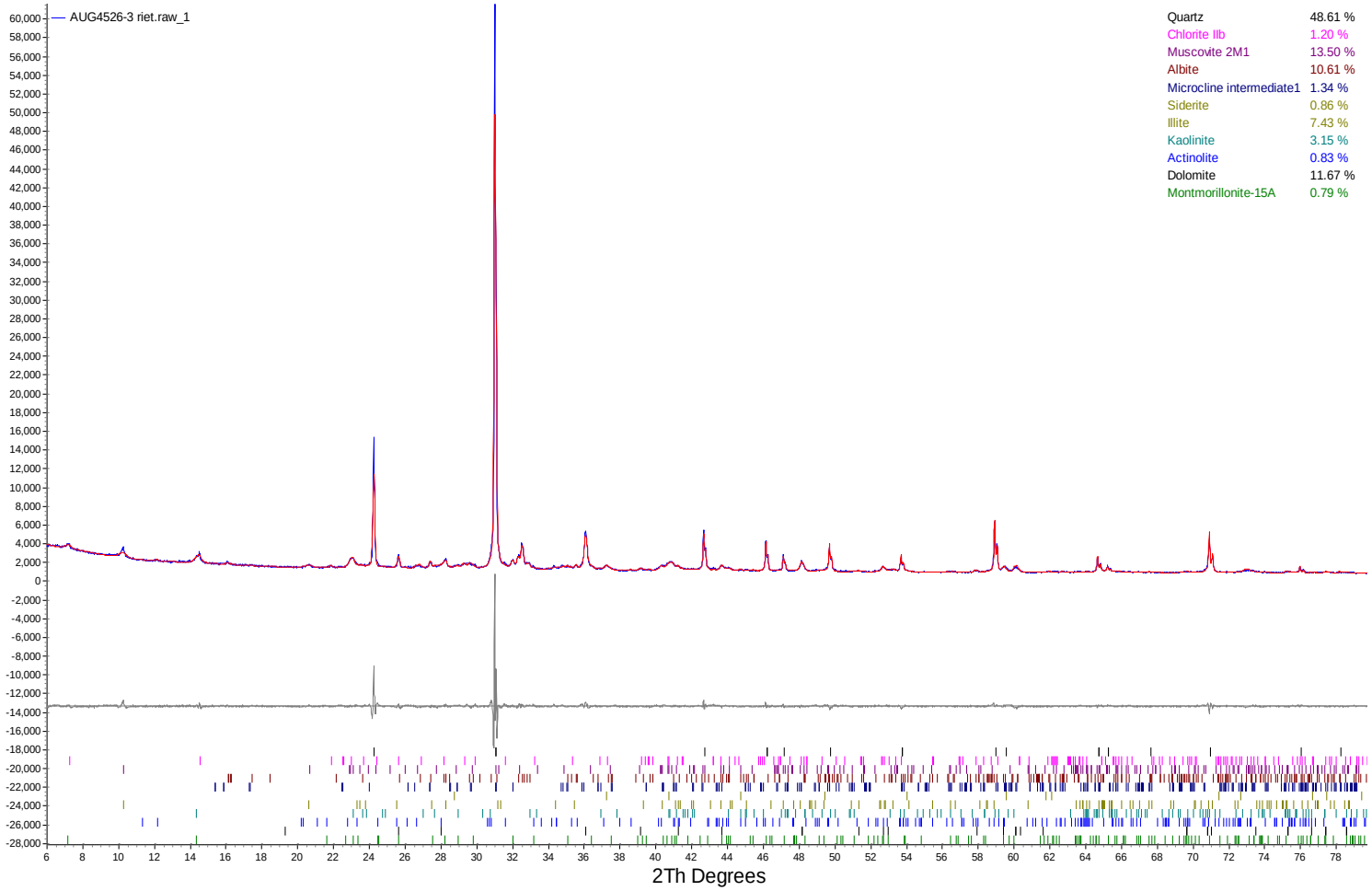

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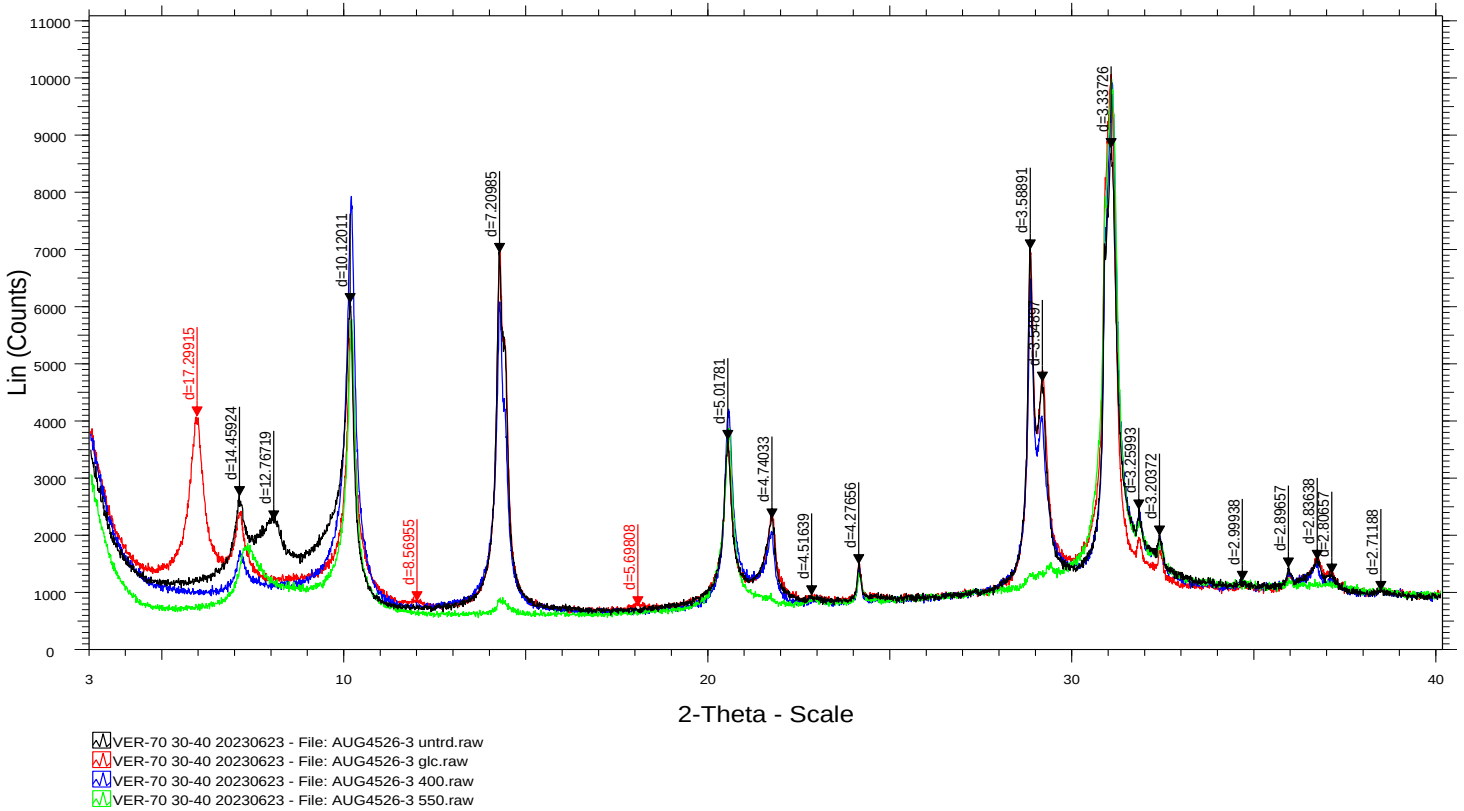

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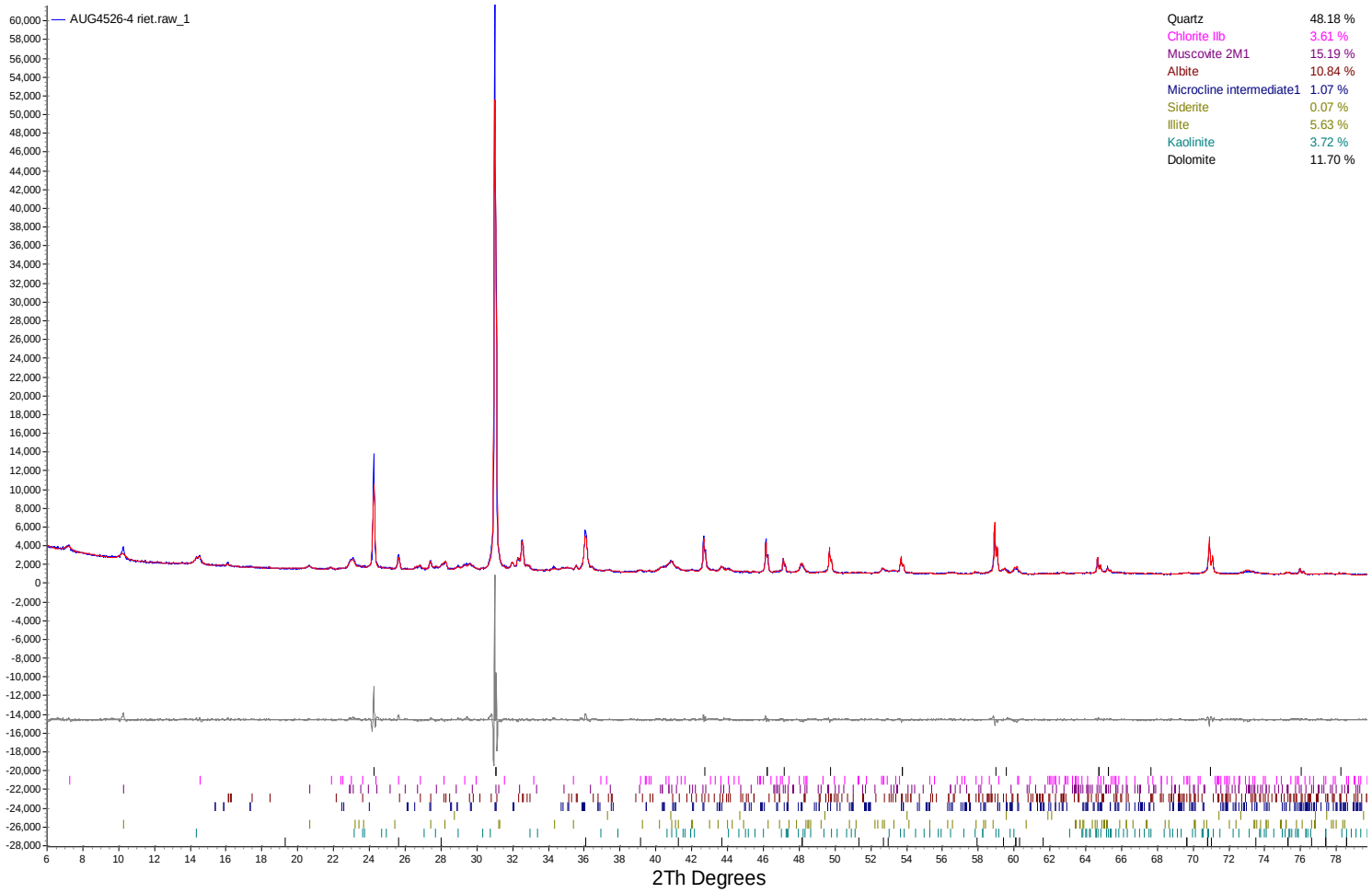

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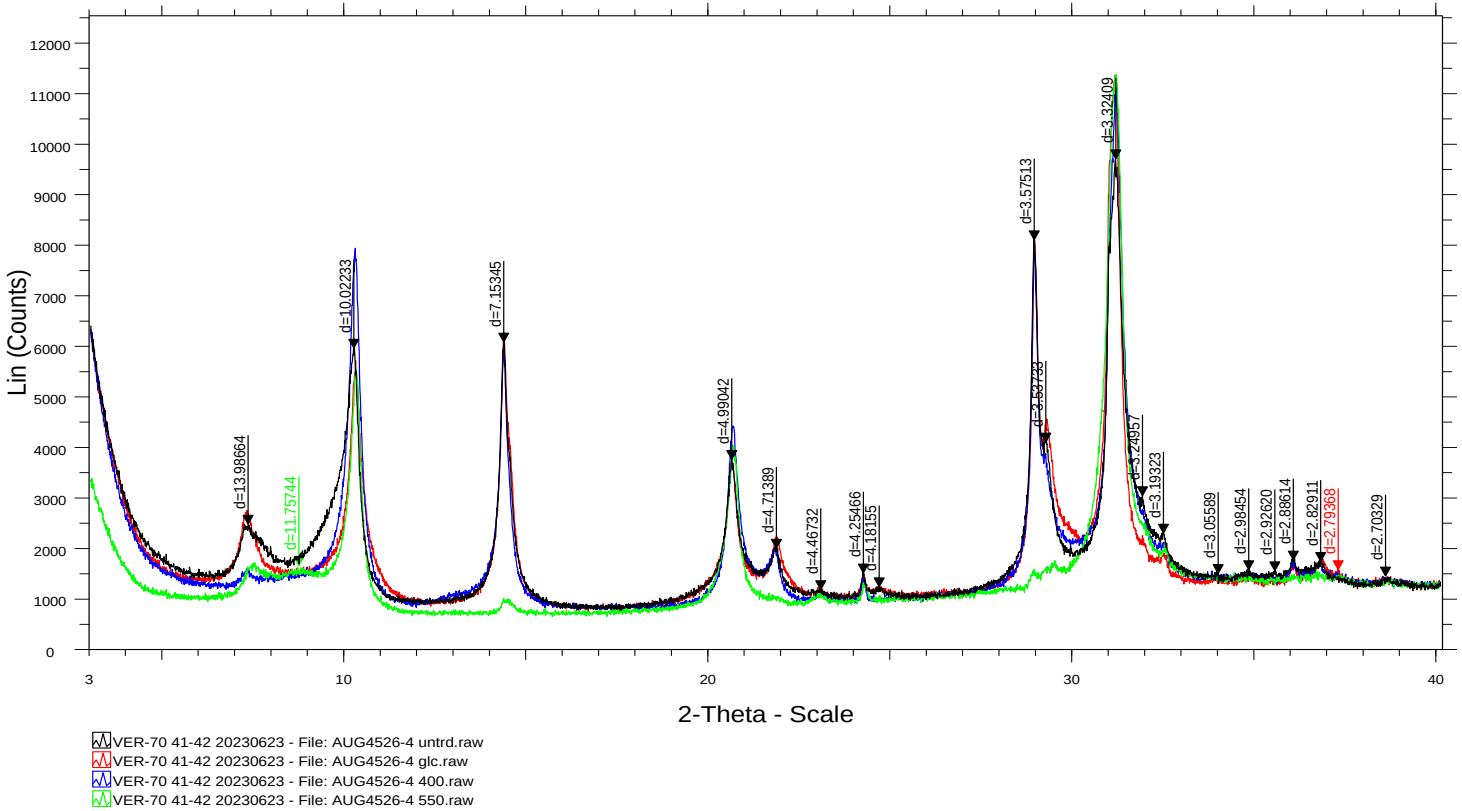

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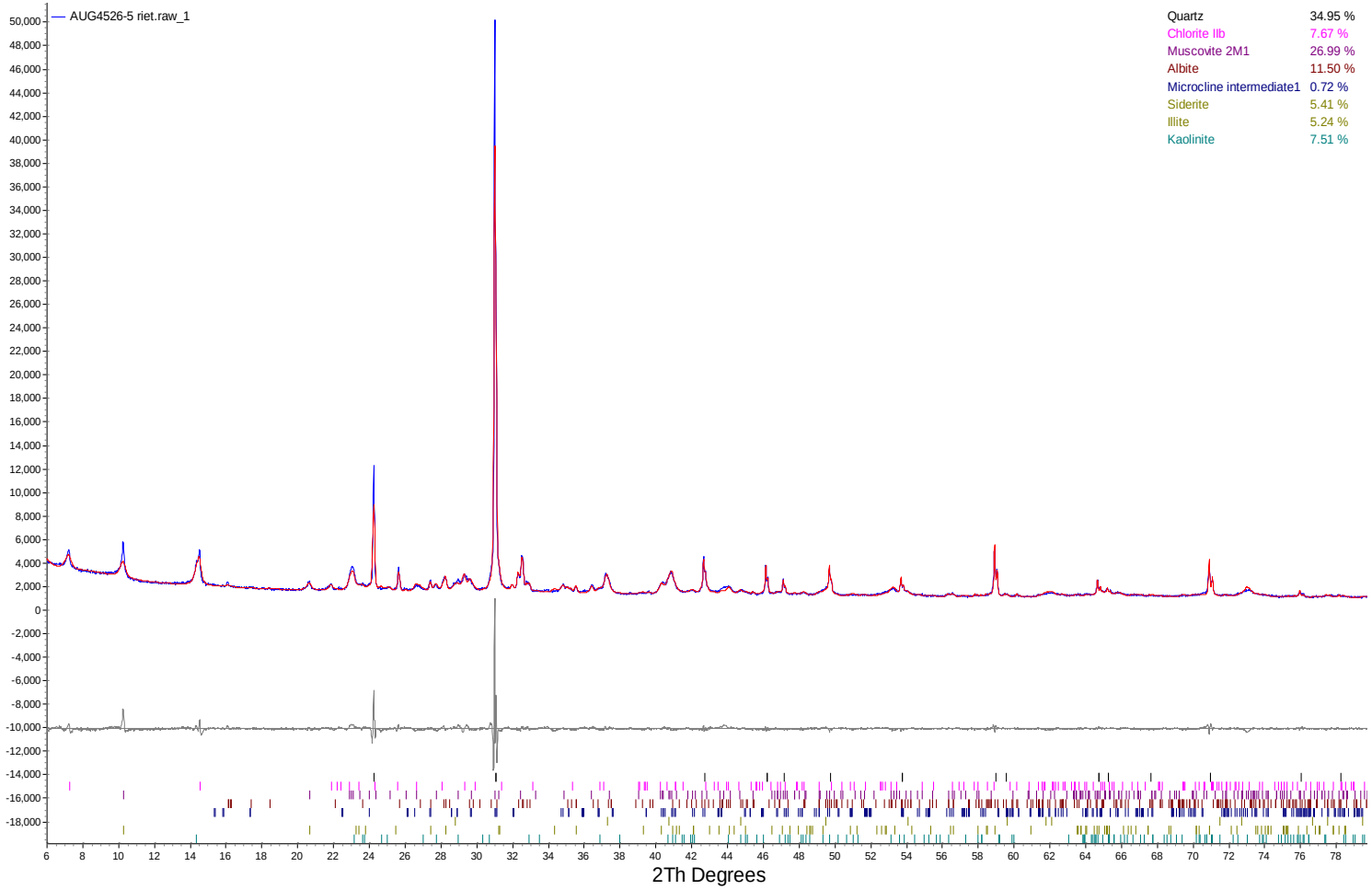

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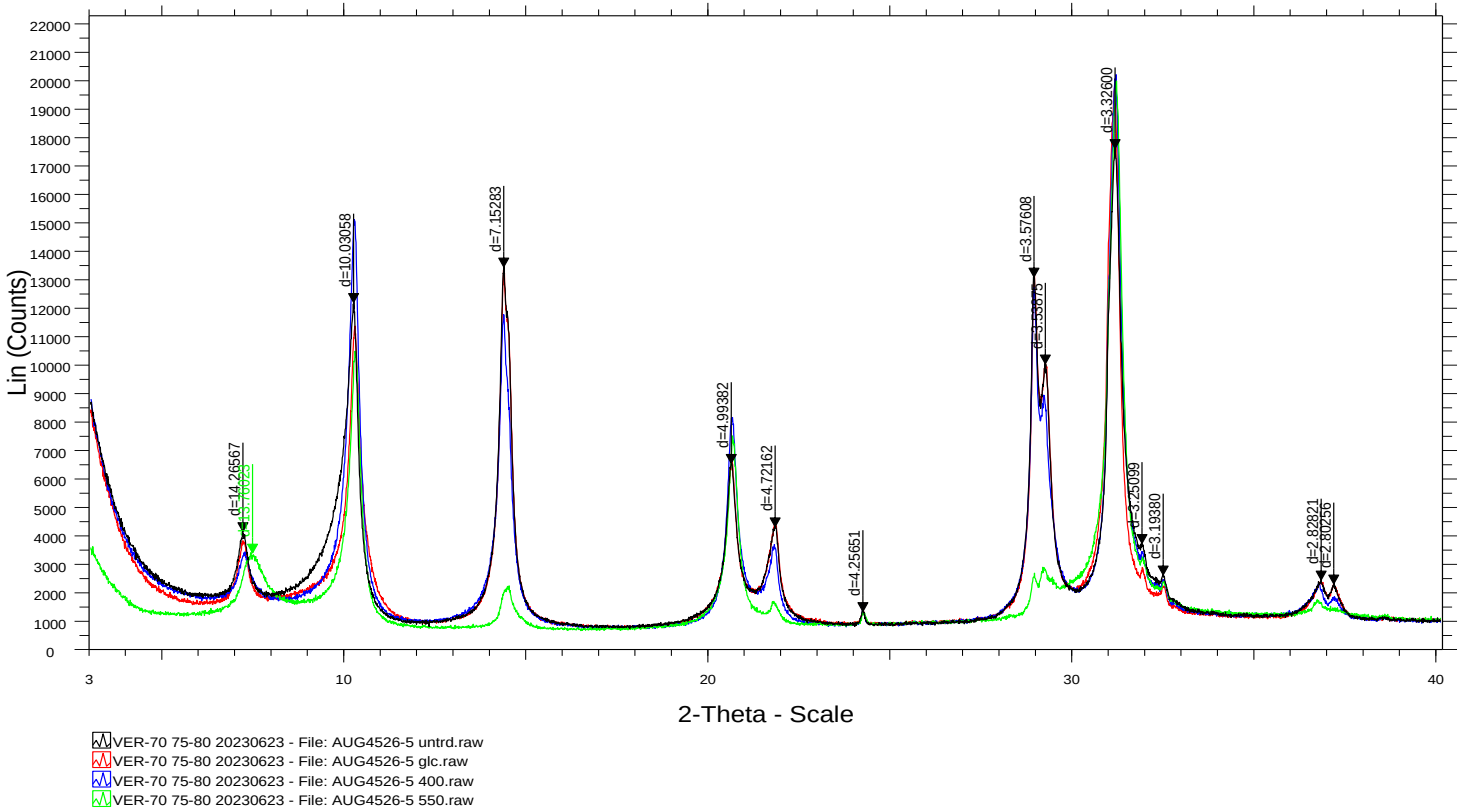


ATTACHMENT 6

PCA Data Input

Summary

ELECTRONIC PCA DATA FOR ATTACHMENT 6
35 I.A.C. § 845: ALTERNATIVE SOURCE DEMONSTRATION
VERMILION POWER PLANT
NEW EAST ASH POND
OAKWOOD, IL

Well	HSU	Date	Well Type	pH (SU)	Alkalinity, total (mg/L)	Barium (mg/L)	Boron (mg/L)	Calcium (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Sulfate (mg/L)	TDS (mg/L)
16A	BCU	04/01/2021	Downgradient	7.50	391.5	0.261	0.675	40.8	131	0.77	31	662
16A	BCU	04/21/2021	Downgradient	7.20	408.5	0.335	0.613	71.1	106	0.64	78	692
16A	BCU	05/11/2021	Downgradient	7.40	362.5	0.245	0.807	36.6	139	0.78	16	582
16A	BCU	06/03/2021	Downgradient	7.26	406.5	0.272	0.716	51.6	128	0.68	47	680
16A	BCU	06/17/2021	Downgradient	7.40	407.5	0.251	0.746	42.2	144	0.78	30	630
16A	BCU	07/08/2021	Downgradient	7.31	405.5	0.249	0.768	38	151	0.77	24	688
16A	BCU	07/27/2021	Downgradient	7.45	391.5	0.248	0.794	35.3	163	0.84	16	662
16A	BCU	08/17/2021	Downgradient	7.50	394.5	0.261	0.755	33.3	176	0.84	11	654
16A	BCU	11/29/2023	Downgradient	7.66	403.7	0.33	0.76	37	160	0.82	4.1	770
16A	BCU	02/21/2024	Downgradient	7.68	383.7	0.34	0.62	30	140	0.87	5.2	650
16A	BCU	06/06/2024	Downgradient	7.12	403.7	0.35	0.8	46	110	0.72	37	700
16A	BCU	07/31/2024	Downgradient	7.65	393.7	0.3	0.8	33	130	0.86	2.9	640
35D	BCU	04/01/2021	Downgradient	8.20	708.5	0.111	2.0	112	529	0.76	1640	3830
35D	BCU	04/21/2021	Downgradient	7.76	534.5	0.0294	1.8	93.6	281	0.65	1220	2920
35D	BCU	06/03/2021	Downgradient	7.25	638.5	0.0546	2.5	98	461	0.75	1300	3240
35D	BCU	06/17/2021	Downgradient	7.25	604.5	0.1400	1.8	99.4	393	0.75	1320	3170
35D	BCU	07/08/2021	Downgradient	7.22	583.5	0.0297	1.93	86	372	0.74	1230	2910
35D	BCU	07/27/2021	Downgradient	7.37	508.5	0.0263	1.46	70	234	0.79	981	2320
35D	BCU	08/17/2021	Downgradient	7.30	492.5	0.0269	1.41	66	199	0.76	895	2090
35D	BCU	11/29/2023	Downgradient	7.34	683.7	0.029	2.4	120	470	0.65	1700	4300
35D	BCU	02/21/2024	Downgradient	7.42	633.7	0.0260	2.1	110	440	0.7	1600	3900
35D	BCU	06/06/2024	Downgradient	7.77	653.7	0.025	2	100	470	0.73	1500	3500
35D	BCU	07/31/2024	Downgradient	7.27	633.7	0.023	1.9	95.0	380	0.73	1400	3500
70D	BCU	04/01/2021	Downgradient	7.60	263.5	0.336	0.712	39.6	317	0.76	53	792
70D	BCU	04/21/2021	Downgradient	7.28	335.5	0.521	1.01	48.1	517	0.57	48	1150
70D	BCU	06/03/2021	Downgradient	7.03	417.5	0.687	1.56	68.6	665	0.47	48	1570
70D	BCU	06/17/2021	Downgradient	7.14	444.5	0.726	1.33	73	680	0.5	49	1600
70D	BCU	07/08/2021	Downgradient	6.85	528.5	0.954	1.58	83	735	0.41	49	1770
70D	BCU	07/27/2021	Downgradient	6.96	541.5	0.734	1.54	78.1	745	0.44	48	1830
70D	BCU	08/17/2021	Downgradient	6.84	611.5	0.761	1.5	91.5	716	0.36	50	1940
70D	BCU	11/29/2023	Downgradient	6.98	583.7	0.42	1.4	84	550	0.43	47	1800
70D	BCU	02/21/2024	Downgradient	6.91	493.7	0.6800	1.5	84	730	0.40	43	1900
70D	BCU	06/06/2024	Downgradient	7.24	543.7	0.48	1.7	96	890	0.45	41	1800
70D	BCU	07/30/2024	Downgradient	6.79	523.7	0.32	1.3	91	410	0.45	61	1400
71D	BCU	04/01/2021	Downgradient	7.60	259.5	0.299	0.58	37.7	172	0.92	44	896
71D	BCU	06/17/2021	Downgradient	7.15	476.5	0.4	1.1	28.7	563	0.73	72	1640
71D	BCU	08/17/2021	Downgradient	6.95	629.5	0.677	1.3	34.9	674	0.56	63	1900
71D	BCU	11/29/2023	Downgradient	7.09	773.7	0.78	1.5	45	800	0.47	53	2400
71D	BCU	08/01/2024	Downgradient	6.99	833.7	0.25	0.78	22	680	0.52	42	2300
22	BCU	04/01/2021	Upgradient	7.40	391.5	0.0723	0.41	41.5	23	0.43	34	484
22	BCU	04/20/2021	Upgradient	7.58	408.5	0.0798	0.4	38	11	0.4	27	476
22	BCU	05/10/2021	Upgradient	7.29	396.5	0.0795	0.4	46	11	0.42	30	494
22	BCU	06/03/2021	Upgradient	7.26	391.5	0.0787	0.361	48	7	0.38	29	450
22	BCU	06/17/2021	Upgradient	7.23	407.5	0.0791	0.377	50	7	0.39	30	468
22	BCU	07/08/2021	Upgradient	7.20	413.5	0.082	0.348	48	7	0.37	30	476
22	BCU	07/27/2021	Upgradient	7.34	402.5	0.0795	0.311	48	7	0.39	30	486
22	BCU	08/17/2021	Upgradient	7.26	403.5	0.0785	0.34	47	7	0.38	29	474
22	BCU	11/28/2023	Upgradient	7.51	403.7	0.084	0.34	44	6.4	0.36	26	490
22	BCU	02/21/2024	Upgradient	7.40	413.7	0.084	0.4	46	7.7	0.37	29	490
22	BCU	05/07/2024	Upgradient	7.36	423.7	0.078	0.4	45	6.9	0.37	29	460
22	BCU	07/29/2024	Upgradient	7.33	403.7	0.08	0.38	46	7.4	0.4	29	460
10	UCU	04/01/2021	Upgradient	6.80	82.5	0.079	0.0587	182	6	0.13	292	942
10	UCU	04/21/2021	Upgradient	6.80	66	0.047	0.0587	193	6	0.14	309	1080
10	UCU	05/10/2021	Upgradient	6.76	133.5	0.0678	0.053	160	4	0.14	224	850
10	UCU	06/03/2021	Upgradient	6.74	118.5	0.0795	0.0835	186	5	0.14	317	980
10	UCU	06/17/2021	Upgradient	6.76	59	0.06	0.11	186	6	0.14	272	946
10	UCU	07/08/2021	Upgradient	6.69	214	0.07	0.05	166	5	0.13	328	988
10	UCU	07/27/2021	Upgradient	6.80	104	0.07	0.24	182	4	0.14	338	1010
10	UCU	08/17/2021	Upgradient	6.69	552	0.08	0.07	192	5	0.13	296	970
10	UCU	11/28/2023	Upgradient	7.03	548	0.11	0.06	160	5	0.15	230	890
10	UCU	02/20/2024	Upgradient	6.82	478	0.08	0.07	180	4	0.13	300	1100
10	UCU	06/06/2024	Upgradient	7.33	581	0.07	0.10	190	5	0.13	320	990
10	UCU	08/01/2024	Upgradient	6.66	552	0.07	0.07	180	3	0.13	280	1000
70S	UU	04/01/2021	Downgradient	7.00	562.5	0.0175	0.457	253	19	0.14	760	1450
70S	UU	04/21/2021	Downgradient	6.94	551.5	0.021	0.403	281	17	0.14	840	1580
70S	UU	05/10/2021	Downgradient	6.99	583.5	0.019	0.382	270	16	0.14	779	1480
70S	UU	06/03/2021	Downgradient	6.91	513.7	0.0165	0.424	245	15	0.14	673	1350
70S	UU	06/17/2021	Downgradient	6.85	543.7	0.0187	0.363	250	15	0.15	730	1340
70S	UU	07/08/2021	Downgradient	6.80	563.7	0.017	0.253	220	14	0.16	589	1220
70S	UU	07/27/2021	Downgradient	7.01	593.7	0.015	0.556	229	11	0.17	541	1140
70S	UU	08/17/2021	Downgradient	6.87	311.5	0.020	0.538	232	15	0.16	638	1250
70S	UU	11/29/2023	Downgradient	7.16	271.5	0.020	0.63	220	20	0.17	670	1500
70S	UU	02/21/2024	Downgradient	6.93	263.5	0.024	0.43	210	11	0.13	600	1200
70S	UU	06/06/2024	Downgradient	7.20	273.5	0.016	0.47	210	10	0.13	560	1100
70S	UU	07/30/2024	Downgradient	6.88	279.5	0.015	0.45	190	9.8	0.15	510	1200
71S	UU	04/01/2021	Downgradient	6.90	306.5	0.048	0.179	115	2	0.18	68	486
71S	UU	04/21/2021	Downgradient	6.73	288.5	0.053	0.215	116	3	0.17	68	500
71S	UU	05/12/2021	Downgradient	6.84	273.5	0.049	0.227	124	3	0.18	69	474
71S	UU	06/03/2021	Downgradient	6.71	283.7	0.045	0.229	116	2	0.18	60	484
71S	UU	06/17/2021	Downgradient	6.76	313.7	0.042	0.219	117	2	0.19	65	502
71S	UU	07/08/2021	Downgradient	6.60	273.7	0.049	0.173	128	2	0.19	46	490
71S	UU	07/27/2021	Downgradient	6.83	293.7	0.046	0.251	132	2	0.2	60	538
71S	UU	08/17/2021	Downgradient	6.73	423.5	0.067	0.272	122	3	0.19	69	534
71S	UU	07/30/2024	Downgradient	6.83	420.5	0.049	0.24	120	1.5	0.21	62	560
NED1	CCR	04/01/2021	Porewater	9.20	404.5	0.032	18.6	497	44	0.32	1340	2340
NED1	CCR	04/21/2021	Porewater	8.86	420.5	0.03	19.3	472	32	0.38	1230	2130
NED1	CCR	05/11/2021	Porewater	7.88	423.5	0.0289	14	674	18	0.2	1300	2170
NED1	CCR	06/04/2021	Porewater	7.55	463.5	0.0319	13.5	532	18	0.24	1400	2340
NED1	CCR	08/17/2021	Porewater	8.73	422.5	0.0314	18.3	531	25	0.29	1510	2350
NED1	CCR	11/29/2023	Porewater	8.04	443.5	0.23	10	470	11	0.15	1300	2500
NED1	CCR	02/21/2024	Porewater	7.78	443.7	0.13	10	470	13	0.099	1300	2200
ND3	CCR	03/31/2021	Porewater	8.70	100.5	0.060	32	291	10	0.2	953	1680
ND3	CCR	04/21/2021	Porewater	8.38	98	0.059	30.3	310	9	0.16	984	1740
ND3	CCR	05/11/2021	Porewater	8.35	94	0.038	31	332	8	0.15	970	1720
ND3	CCR	06/03/2021	Porewater	7.93	116.5	0.027	28.5	333	7	0.15	1040	1790
ND3	CCR	08/17/2021	Porewater	7.94	121.5	0.064	29.4	344	6	0.17	1050	1680
ND3	CCR	06/20/2023	Porewater	8.40	72.5	0.023	29	303	9	0.24	933	1500
ND3	CCR	02/20/2024	Porewater	8.25	96.7	0.025	28	330	6.5	0.14	1100	1700
ND3	CCR	07/30/2024	Porewater	8.16	99.7	0.270	30	290	3.7	0.21	990	1700
OED1	CCR	06/03/2021	Porewater	10.00	109.5	0.039	45.5	886	5	0.1	1890	3240
OED1	CCR	06/16/2021	Porewater	10.20	85.5	0.034	46.7	838	4	0.1	1930	3170
OED1	CCR	07/08/2021	Porewater	10.30	93.5	0.031	46.7	810	3	0.1	1960	3170
OED1	CCR	07/27/2021	Porewater	10.30	86.5	0.026	35	886	3	0.1	1950	3220
OED1	CCR	08/17/2021	Porewater	10.10	89.5	0.039	39.5	828	2	0.1	1910	3060
OED1	CCR	06/20/2023	Porewater	10.10	76.5	0.038	49.2	834	2	0.04	1860	3130
OED1	CCR	07/30/2024	Porewater	10.24	123.7	0.029	48	760	0.58	0.056	1800	3100

Notes:
mg/L = milligrams per liter
TDS= Total Dissolved Solids
SU= standard units
HSU = hydrostratigraphic unit
CCR = coal combustion residual
BCU = Bedrock Confining Unit
UCU = Upper Confining Unit
UU = Upper Unit
Non-detect values were replaced with half of detection limit.

ATTACHMENT 7

PCA Analyses - Well 35D Results Excluded

ATTACHMENT 7 – ADDITIONAL PCA ANALYSES

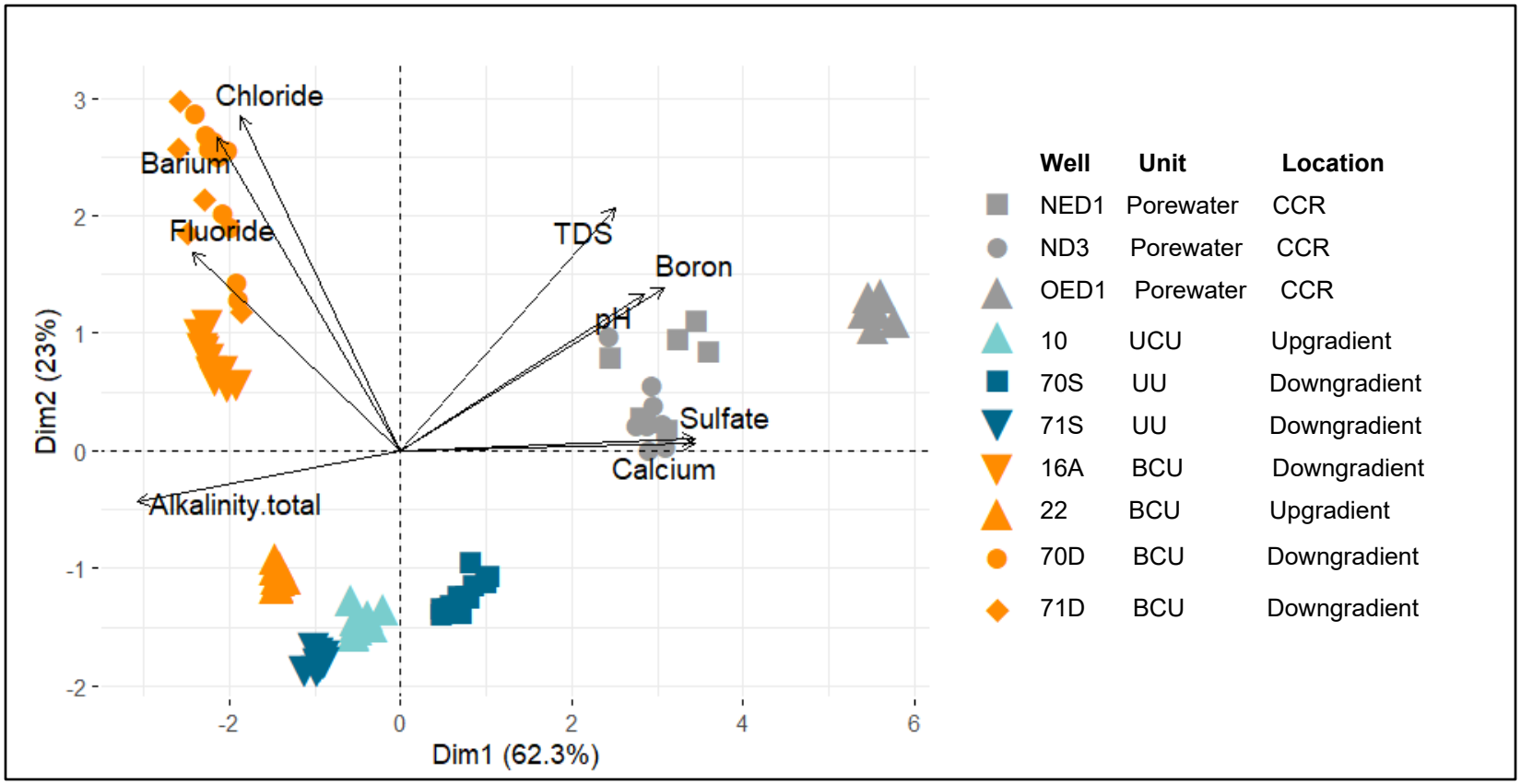
Due to anomalously high sulfate concentrations in well 35D[1], sulfate and TDS were excluded from both multivariate analyses described in the December 2024 *Evaluation of Alternative Sources for Chloride and Lithium within Bedrock Solids* technical memorandum prepared by Geosyntec. Two additional scenarios which included sulfate and TDS but exclude 35D samples are presented herein. The evaluation included one analysis with porewater samples and one without porewater samples included.

The biplot for the scenario with porewater samples included is shown on **Attachment 7a** indicating that the porewater samples are clustered separately from the BCU, UCU, and UU samples. This finding is consistent with the scenario where both 35D and porewater samples were included (**Figure 3** of main text). As before, constituents such as boron and sulfate are responsible for the chemical signature of the porewater samples. The results of clustering analysis confirmed one cluster of porewater samples distinct from the combined BCU, UCU and UU groundwater sample cluster (**Attachment 7b**).

The biplot for the scenario without porewater samples is shown on **Attachment 7c** indicating that BCU samples cluster separately from the combined UCU and UU samples. This finding is consistent with the previous scenario where 35D samples were included and porewater was excluded (**Figure 6** of main text). Clustering, as shown in **Attachment 7d**, also confirmed distinct clustering of BCU samples from the UCU and UU samples.

These findings are consistent with the scenarios described in the main document, in which lithology is the main driver for the chemistry of the groundwater samples.

[1] Ramboll. 2023. *35 I.A.C. § 845.650(E): Alternative Source Demonstration – New East Ash Pond*. Vermilion Power Plant, Oakwood, Illinois. Ramboll Americas Engineering Solutions, Inc. December.



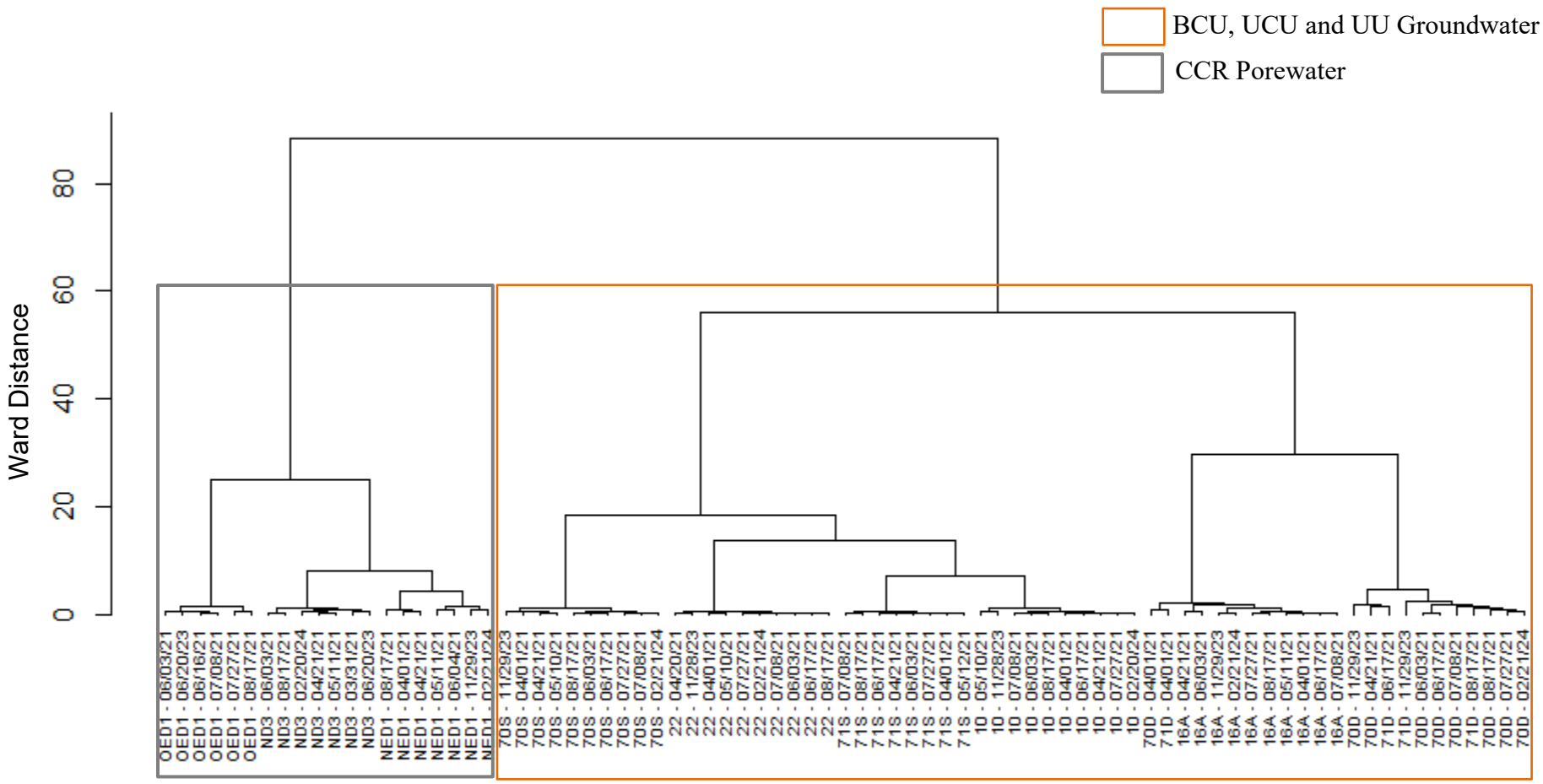
Notes:
1. The arrows signify the correlations between the constituents and the principal components.
2. Datapoints are colored based on hydrostratigraphic unit of sampling locations as follows:
   - Bedrock Confining Unit (BCU) wells: 16A, 22, 70D, 71D.
   - Upper Confining Unit (UCU) well: 10.
   - Upper Unit (UU) wells: 70S, 71S.
   - Coal Combustion Residual (CCR) well: NED1, ND3, OED1.
3. Dim: Dimension

Principal Components Analysis Biplot
(35D Excluded)
Vermilion Power Plant – New East Ash Pond

Geosyntec consultants

Columbus, Ohio | November 2024

Attachment **7a**



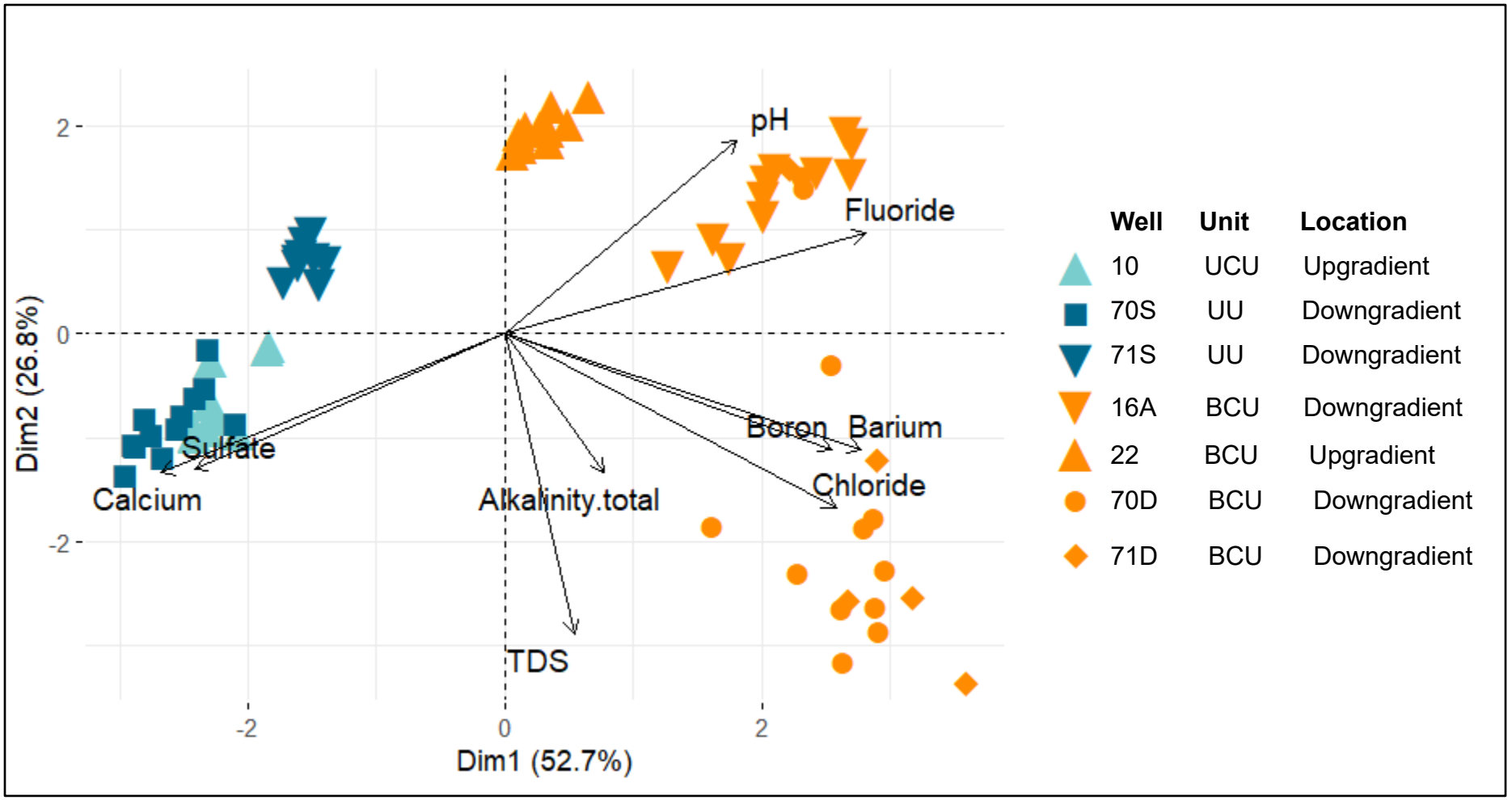
Notes:
1. The cluster analysis used Euclidean distances, and Ward's method as the clustering algorithm.
2. In the dendrogram, samples on the same branch are more similar to each other. The samples with the highest similarity are on the closest branches.
3. The boxes around the branches represent the two clusters into which samples from each source grouped.
4. BCU, UCU, UU and CCR refer to Bedrock Confining Unit, Upper Confining Unit, Upper Unit, and Coal Combustion Residual, respectively.

Dendrogram Graph from Cluster Analysis (35D Excluded)
Vermilion Power Plant – New East Ash Pond

Geosyntec consultants

Columbus, Ohio | November 2024

Attachment **7b**



Notes:
1. The arrows signify the correlations between the constituents and the principal components.
2. Datapoints are colored based on hydrostratigraphic unit of sampling locations as follows:
   - Bedrock Confining Unit (BCU) wells: 16A, 22, 70D, 71D.
   - Upper Confining Unit (UCU) well: 10.
   - Upper Unit (UU) wells: 70S, 71S.
3. Dim: Dimension

Principal Components Analysis Biplot
(Porewater Wells and 35D are Excluded)
Vermilion Power Plant – New East Ash Pond

Geosyntec consultants

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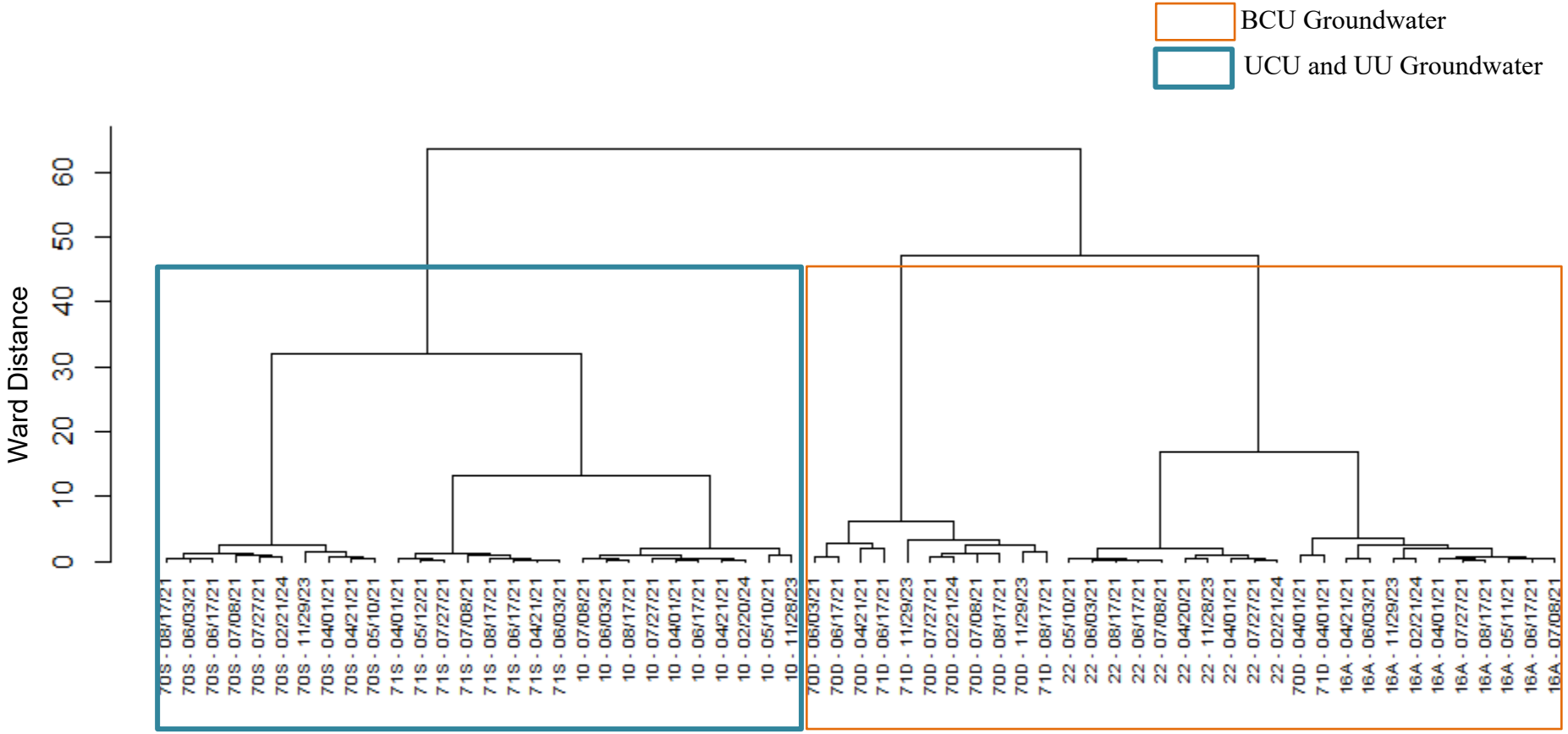
Attachment **7c**



Notes:
1. The cluster analysis used Euclidean distances, and Ward's method as the clustering algorithm.
2. In the dendrogram, samples on the same branch are more similar to each other. The samples with the highest similarity are on the closest branches.
3. The boxes around the branches represent the two clusters into which samples from each source grouped.
4. BCU, UCU and UU refer to Bedrock Confining Unit, Upper Confining Unit, and Upper Unit, respectively.

Dendrogram Graph from Cluster Analysis
(Porewater Wells and 35D Excluded)
Vermilion Power Plant – New East Ash Pond

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Columbus, Ohio | November 2024

Attachment
7d

ATTACHMENT 8
References

VOLUME XXXVIII NUMBER 2

THE

JOURNAL OF GEOLOGY

February-March 1930

CYCLICAL SEDIMENTATION OF THE PENNSYLVANIAN PERIOD AND ITS SIGNIFICANCE[1]

J. MARVIN WELLER
Illinois State Geological Survey

ABSTRACT

The Pennsylvanian strata of western Illinois exhibit a cyclical repetition of beds as follows: (1) sandstone and sandy shales, (2) underclay, (3) coal, and (4) marine limestones and shales. Each cycle was initiated by uplift which was reflected first by erosion and later by continental deposition of clastic materials. This was followed by a long period of stability during which weathering developed a typical poorly drained profile of weathering, now represented by underclay. Then peat, later transformed to coal, accumulated in more or less extensive swamps. These conditions were terminated by subsidence so that the area was inundated by a shallow sea in which marine strata were deposited until uplift brought the cycle to a close.

The cyclical repetition of beds is regional rather than local, and analysis of the conditions necessary for the formation and preservation of such strata over broad areas furnishes the basis for a reconstruction of the physiography of the Pennsylvanian period. The conception of widespread sedimentary cycles provides new criteria for correlation in Pennsylvanian areas, as a definite succession of strata not dependent upon certain key horizons is established. It also furnishes a new basis for paleontologic studies, since faunules restricted to different habitats may be grouped with regard to definite marine invasions and an approximation of the total marine fauna of each invasion may be obtained.

INTRODUCTION

Detailed geologic investigations in western Illinois, which have been conducted during the last few years by various members of the State Geological Survey, and reconnaissance studies in other areas, have revealed many facts concerning the relationships which commonly exist between the various strata in the Pennsylvanian system. Generalizations based upon these facts have led to the

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development of a working hypothesis by which the stratigraphic succession may be explained and the physiography of the Pennsylvanian period interpreted. Although most of these facts have been noted by previous workers and although most of the inferences derived from them have been previously stated, still they have never been treated before in a comprehensive manner nor followed to a logical conclusion.

Like most hypotheses, this will inevitably be amended in the light of future investigations, but the new conceptions concerning Pennsylvanian conditions which it entails promise achievement and refinement in stratigraphic interpretation and correlation far beyond that which has resulted up to this time. The hypothesis of cyclical sedimentation has already proved its value in the detailed stratigraphic studies conducted in western Illinois. The extent to which it is applicable is not fully known, but with slight modifications it may be possibly extended to apply to the Pennsylvanian deposits in the entire interior of North America. With these points in view, the hypothesis is presented in the hope that geologists working in other areas of Pennsylvanian strata will consider their problems in its light and will observe and record the data which are significant and essential to the study of the Pennsylvanian problem in its broadest aspects.

I. THE CYCLE—ITS NATURE

PREVIOUS RECOGNITION

In 1912 Udden[1] subdivided the Pennsylvanian strata exposed in the Peoria quadrangle, Illinois, into four series of beds each of which included "four successive stages, namely: (1) accumulation of vegetation; (2) deposition of calcareous material; (3) sand importation; and (4) aggradation to sea level and soil making" (Fig. 1). This clear exposition of cyclical sedimentation and its possible significance in the field of correlation and interpretation of Pennsylvanian stratigraphy has received practically no attention from geologists.

Stout[2] has recognized that in Ohio certain types of strata, notably

[1] J. A. Udden, "Geology and Mineral Resources of the Peoria Quadrangle," *U.S. Geol. Survey Bull. 506* (1912), pp. 47–50.

[2] W. Stout, "Coal Formation Clays of Ohio," *Ohio Geol. Survey*, Ser. 4, *Bull. 26*, chap. vii (1923), pp. 533–68.

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underclays, coals, and limestones, bear consistent relationships to each other, and he has developed a cyclical theory for the formation of underclays. Again, the possible stratigraphic importance of the repetition of beds has not been realized, and this consideration has not been carried to a logical paleophysiographic conclusion.

OTHER GEOLOGICAL CYCLES

The cycles (or rhythms)[1] which punctuated geologic time have been considered in some detail by Barrell,[2] who wrote,

> Nature vibrates with rhythms, climatic and diastrophic, those finding stratigraphic expression ranging in period from the rapid oscillation of surface waters, recorded in ripple-mark, to those long deferred stirrings of the deep imprisoned titans which have divided earth history into periods and eras.

Many examples of cyclical change might be drawn from geologic history. Among the most conspicuous are the Pliocene-Pleistocene diastrophic cycles which resulted in sedimentation upon the Atlantic coastal plain and erosion along the adjoining river systems, and the climatic cycles of the Pleistocene, which caused the alternate extension and recession of the great continental glaciers.

UNCONFORMITIES WITHIN THE PENNSYLVANIAN

Another equally important fact, which has been greatly neglected, is the occurrence of unconformities within the Pennsylvanian deposits. Such an unconformity in Illinois was first recognized by Worthen[3] in the Peoria district where coal No. 5 is cut by channels filled with sandstone. Subsequent observers have reported similar unconformities at other Pennsylvanian horizons in different parts of the state, and Savage[4] has proposed to utilize such breaks in the sedimentary series as more natural boundaries between the Pottsville, Carbondale, and McLeansboro formations than the coal beds which have been so long employed for this purpose.

[1] *Cycle* seems to be the better term, as it implies simply recurrence, repetition, or a return to the starting-point, while *rhythm* includes also a time consideration, such as regular or measured movements. Geological phenomena were repeated at more or less irregular intervals.

[2] J. Barrell, "Rhythms and the Measurements of Geologic Time," *Bull. Geol. Soc. Am.*, Vol. XXVIII (1917), pp. 745–904.

[3] A. H. Worthen, "Geology of Peoria County," *Geol. Survey Ill.*, Vol. V (1873), p. 242.

[4] T. E. Savage, "Significant Breaks and Overlaps in the Pennsylvanian Rocks of Illinois," *Am. Jour. Sci.*, Ser. 5, Vol. XIV (1927), pp. 307–16.

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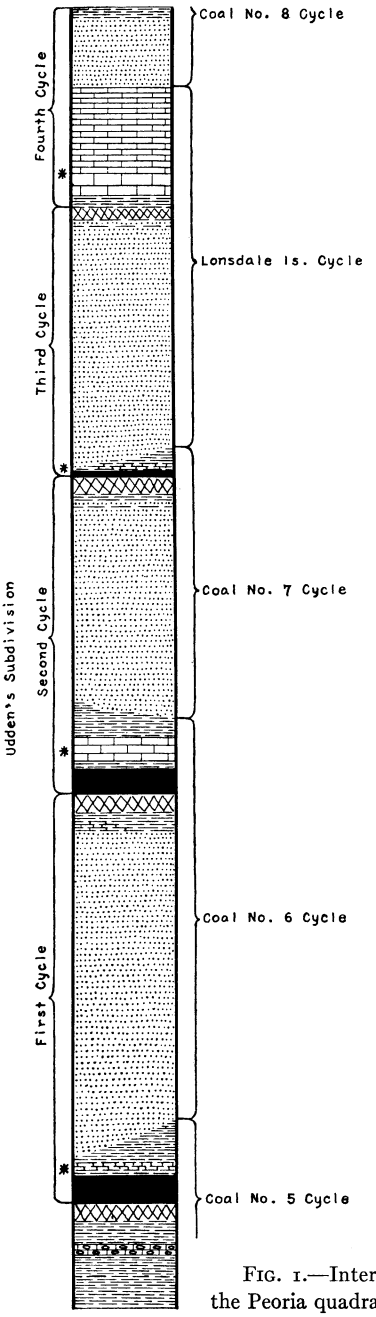

FIG. 1.—Interpretation of Udden's generalized section for the Peoria quadrangle. Scale 1 inch to 40 feet.

Similar unconformities have been noted in other states. In Missouri, the Moberly and Warrensburg channels are outstanding examples.[1] They occur abundantly also in the Coal Measures of the Appalachian basin and are casually mentioned in many reports: "The sandstone [Morgantown] reaches the Ames horizon and replaces the limestone over limited areas. In such instances there is a basal conglomerate";[2] "The disconformity at the base of the Lower Massillon sandstone at many places is marked as it replaces many feet of other strata [coals, clays, limestones, and shales] in a short distance";[3] "It [Mahoning sandstone] immediately overlies the Upper Freeport coal and often cuts out that seam";[4] "It [Freeport sandstone] may in some instances replace the coal [Upper Kittanning]. . . . . It has indeed

[1] H. Hinds and F. C. Greene, "The Stratigraphy of the Pennsylvanian Series in Missouri," *Missouri Bur. Geol.*, Ser. 2, Vol. XVIII (1915), pp. 91–106.

[2] D. D. Condit, "Conemaugh Formation in Ohio," *Ohio Geol. Survey*, Ser. 4, *Bulletin 7* (1912), p. 25.

[3] W. Stout, "Geology of Muskingum County," *ibid.*, *Bulletin 21* (1918), p. 60.

[4] C. Butts, "Economic Geology of the Kittanning and Rural Valley Quadrangles, Pennsylvania," *U.S. Geol. Survey Bulletin 279* (1906), p. 39.

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been observed to begin even below the Darlington coal."[1] Similar unconformities are not uncommon in the English coal fields, as "large areas have been proved to exist, where the coal has been removed by wash-outs which have occurred at various horizons in the Middle and Lower Coal-Measures."[2]

Recent observations in Illinois indicate that unconformities within the Pennsylvanian system are more numerous than has been suspected. Detailed areal studies reveal that most massive sandstones lie unconformably upon subjacent beds, although this relation is rarely apparent in single outcrops. The evidence is so abundant that the generalization naturally follows that every massive sandstone lies unconformably upon the beds below.

FORMATIONS AND FORMATION BOUNDARIES

It has long been the custom to subdivide the strata of the Pennsylvanian system at prominent coal beds, because such beds are comparatively easy to trace and correlate. Udden[3] accordingly divided his section in the Peoria district at the coals. However, according to the accepted practice of stratigraphy, subdivisions of geologic time are separated by periods of instability, and as there is no evidence that any marked diastrophism occurred between the deposition of the beds below the coal and the development of the underclay, nor between the development of the underclay and the accumulation of peat, it does not seem advisable to use either the base of the underclay or the base of the coal as a series or formation boundary.

It is now proposed that each cyclical repetition of beds be considered a formation of the Pennsylvanian system. In each cycle there were two times when diastrophism was active: namely, (1) at the close of the period of peat accumulation when subsidence resulted in extensive transgression by the sea, and (2) before the development of the unconformity beneath the sandstone when uplift occurred and the sea withdrew from its shallow basin. The first probably represents the greater amount of local vertical movement, because in an

[1] L. H. Woolsey, "Economic Geology of the Beaver Quadrangle, Pennsylvania," *U.S. Geol. Survey Bulletin 286* (1906), p. 13.

[2] F. E. Middleton, "On the Wash-outs in the Middle Coal-Measures of South Yorkshire," *Quart. Jour. Geol. Soc. London*, Vol. LXI (1905), pp. 339–44 (illustrated).

[3] J. A. Udden, *op. cit.*

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area of deposition subsidence must exceed uplift, but this horizon is unsuitable for a formation boundary, because marine beds do not succeed all of the coals in most areas. On the other hand, the unconformities—although more or less local in development—may be present and conspicuous even in areas not subjected to marine submergence. Also, as they are uneven surfaces, mapping of them reveals many interesting and significant features that would otherwise escape notice.

THE TYPICAL FORMATION

If Udden's section in the Peoria district[1] be subdivided at the bases of the sandstones, each series of beds starts with an unconformable sandstone below, contains an underclay and coal horizon in the middle, and continues above with limestone and shale. Such a series of beds is considered to be a typical Pennsylvanian formation, whose counterpart may be observed in almost every section from the bottom to the top of the system as developed in western Illinois.

In detail, the typical Pennsylvanian formation is composed of the following members:

Marine	8. Shale, containing "ironstone" bands in upper part and thin limestone layers in lower part
	7. Limestone
	6. Calcareous shale
	5. Black "fissile" shale
Continental	4. Coal
	3. Underclay, not uncommonly containing concretionary or bedded fresh-water limestone
	2. Sandy and micaceous shale
	1. Sandstone
	Unconformity

The succession of beds at any particular locality may be incomplete, or some members may be poorly developed owing to more or less local conditions. In most of such cases the absent or underdeveloped member appears at its proper position in the formation at other places. Such deviations from the typical formation as well as the rare introduction of additional members are not considered here, as they do not vitiate the essential principle and probably they can be logically explained when more detailed observations have

[1] *Ibid.*

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been made. These irregularities in the formations are commonly confusing, but when the essential principle that the strata occur in a definite order, which is repeated many times, is once understood, almost any Pennsylvanian section may be readily subdivided into its component formations.

THE OHIO SECTION

Formations exhibiting cyclical repetition of beds similar to those which are so well developed in Illinois may be recognized readily in other states. In the generalized geologic sections for the Pottsville, Allegheny, and most of the Conemaugh series published in certain of the more recent *Bulletins* of the Ohio Survey,[1] the formations are distinct and easily separated (Fig. 2). However, distinctive marine horizons are lacking in the upper Conemaugh and Monongahela series, and it is difficult to interpret the published descriptions of this part of the section which is made up almost entirely of continental deposits. Of the forty-two formations indicated, a few, such as that including the Lower Kittanning coal, may be composite. Apparently the fossiliferous beds of the Brush Creek horizon fall within two formations (Nos. 22 and 23), but these are not very sharply differentiated.

This interpretation of the Ohio section is only tentative, as workers familiar with this area will probably find it necessary to make numerous alterations. It is presented here in order to establish the remarkable similarity of the Pennsylvanian sections in Ohio and Illinois and because the various members have been traced more consistently throughout Ohio than in Illinois. Most of the members in Ohio are very widely distributed, and there can be little doubt that nearly all of the Ohio formations are characteristically developed through the entire southeastern part of that state.

INADEQUACY OF MANY PUBLISHED SECTIONS

Many published geologic sections of Pennsylvanian strata are inadequate for subdivision into their component cyclical formations.

[1] D. D. Condit, "Conemaugh Formation in Ohio," *Ohio Geol. Survey*, Ser. 2, *Bulletin 17* (1912); W. Stout, "Geology of Southern Ohio," *Bulletin 20* (1916); "Geology of Muskingum County," *Bulletin 21* (1918); H. Morningstar, "Pottsville Fauna of Ohio," *Bulletin 25* (1922); W. Stout, and R. E. Lamborn, "Geology of Columbiana County," *Bulletin 28* (1924); W. Stout, "Geology of Vinton County," *Bulletin 31* (1927).

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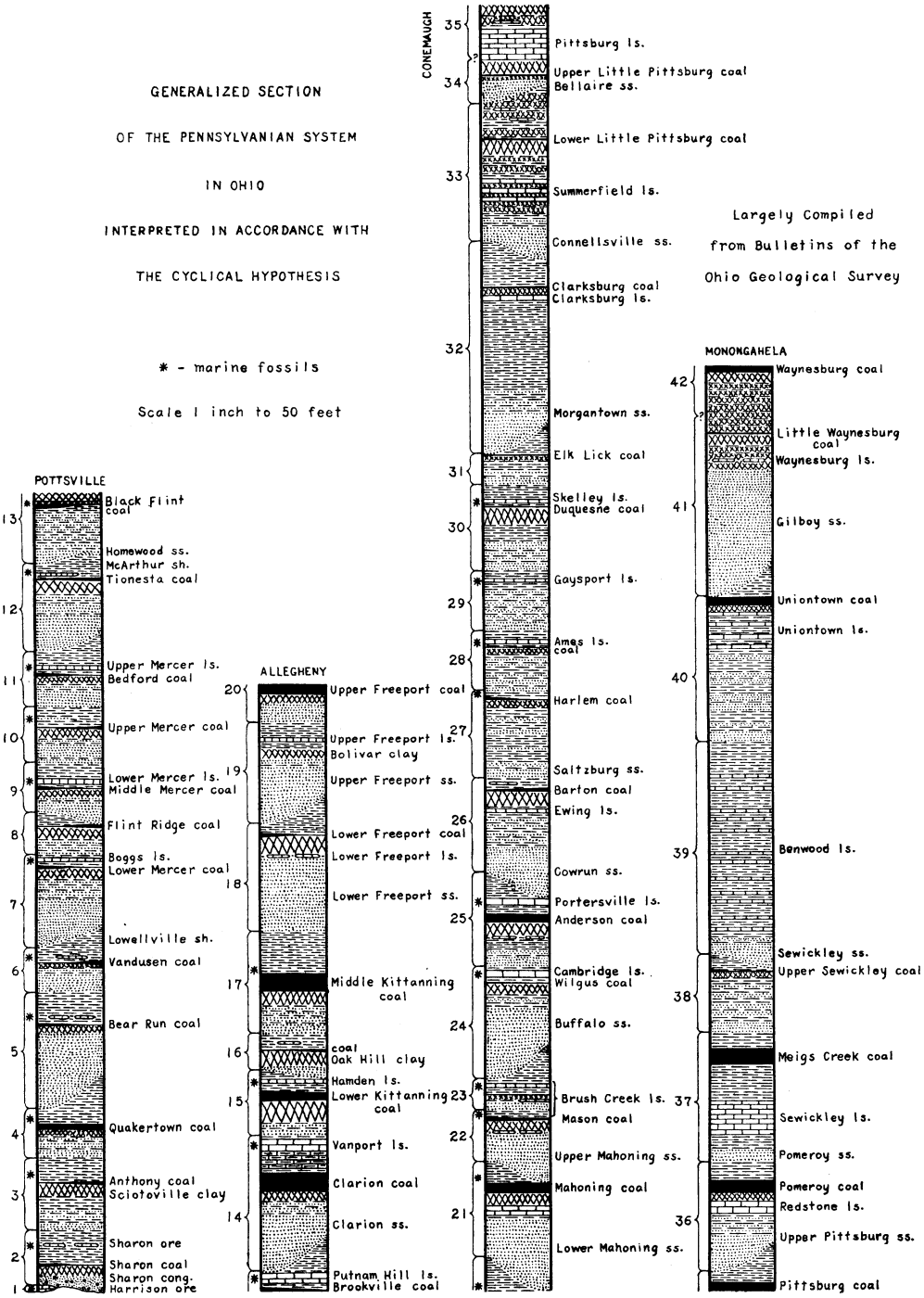

FIG. 2

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In most cases this is due to the fact that they are not presented in sufficient detail. The grouping of a considerable thickness of strata as "sandstones and shales including thin coals and limestones" has been a common practice. Extreme variation, both vertical and lateral, has been considered a feature of general prevalence in Pennsylvanian deposits, but recent detailed studies prove that the formations as a whole remain remarkably uniform over wide areas, although individual members may thicken or thin and change greatly in character.

COMPARISON WITH CHESTER SERIES

The cyclical sedimentation which took place during the Pennsylvanian period is comparable to that which occurred in Chester time. In Illinois, the Chester series (Upper Mississippian) has been divided into sixteen alternating arenaceous and calcareous formations. A pair of these consisting of sandstone below and calcareous beds above constitutes a cycle. In one case,[1] a thin coal is widely present between the arenaceous and calcareous beds at a position precisely comparable to that occupied by the widespread Pennsylvanian coals.

The Chester series is transitional between the dominant limestone sedimentation of the earlier Paleozoic in the Mississippi and lower Ohio Valleys and the dominantly clastic sediments of the Pennsylvanian. A cyclical alternation between sandy and calcareous beds is well developed in the Chester and most of these units have been traced continuously from southwestern Missouri, across southern Illinois, and into western Kentucky, and it is probable that additional investigation will show that some of these are sharply differentiated and practically continuous as far south as Alabama. It is not unlikely that the cycles of the succeeding Pennsylvanian period were produced by similar changes in conditions which were likewise effective throughout extensive areas.

EXTENT OF CYCLES

It is obvious that the repetition of a certain series of beds reflects a similar repetition of a certain series of conditions. It is important to ascertain whether these conditions were prevalent contemporaneously throughout wide areas or were only local, as upon this de-

[1] J. M. Weller, "The Geology of Edmonson County," *Kentucky Geol. Survey*, Ser. 6, Vol. XXVIII (1927), pp. 121–22.

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pends entirely the usefulness of the conception of cyclical sedimentation.

Extent of coal beds.—It has been long known that certain individual coal beds are continuous over extensive areas. The Pittsburg coal has been commonly cited as an outstanding example, estimates of its proved extent ranging from 6,000 to 8,000 square miles.[1] In the southern half of Illinois, a workable thickness of the Herrin (No. 6) coal is known to be present throughout an area of about 8,000 square miles, in addition to which a considerable territory remains unexplored. In the northwestern part of the Illinois basin, a coal that is probably the equivalent of this bed is extensively developed, so that an estimate of 10,000 square miles for a single seam in Illinois is considered conservative.[2] There is also little doubt that this same seam is extensively developed in Indiana and western Kentucky, which accordingly increases its estimated area. Less imposing figures might be quoted for other coal beds.

The thickness or quality of a coal is immaterial in the study of the stratigraphic succession; it is the position or horizon of the seam that is important. The figures given in the foregoing apply only to continuous developments of workable coal. If the areas in which coal of unworkable thickness is present, and those in which its horizon is indicated only by an underclay and dark shale be included, the figure for the areal extent of its horizon would be much larger. The facts that the Pittsburg coal is mined at widely distant localities in Pennsylvania, Ohio, West Virginia, and Maryland and that a thinner development of it has been recognized in outcrops and well records at many intervening places makes it fairly certain that the *horizon* of this coal is practically continuous throughout the Appalachian basin except where it has been cut out by intra-Pennsylvanian or by more recent erosion.

Extent of limestones.—The limestones of the Coal Measures constitute some of the most conspicuous and important horizons. Recent *Bulletins* published by the Ohio Survey[3] report in some detail

[1] I. C. White, "Report on Coal," Vol. II, *West Virginia Geol. Survey* (1903), pp. 166, 384.

[2] Estimates by G. H. Cady.

[3] D. D. Condit, "Conemaugh Formation in Ohio," *Ohio Geol. Survey*, Ser. 4, *Bulletin 17* (1912); H. Morningstar, "Pottsville Fauna of Ohio," *Ohio Geol. Survey* Ser. 4, *Bulletin 25* (1922).

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on the occurrences of the Pottsville and Conemaugh limestones throughout that state. These beds occupy definite positions in the geologic section and some of them are widely distributed in West Virginia, and extend into Pennsylvania, Maryland, and eastern Kentucky. One of the most important is the Ames limestone (middle Conemaugh), which is not only widespread in Ohio but is also extensively developed in West Virginia and Pennsylvania and even continues as a marine bed into Maryland.[1] The Upper and Lower Mercer limestones of the Pottsville are very persistent and occur almost uninterruptedly along the whole length of the Pennsylvanian outcrop in Ohio as well as extending into neighboring states.

It seems probable that the rare limestones observed in Tennessee[2] and Alabama[3] may be the exact equivalents of certain of the lower Pottsville limestones in Ohio, and other fossiliferous horizons (five in Tennessee[4] and four in Alabama[5]) may also represent southern continuations of marine stages which are better known farther to the north.

Owing to low relief and thick glacial drift, the details of the Pennsylvanian section in Illinois are not so well known as they are in the northern portion of the Appalachian basin. Some of the limestone beds in Illinois, however, are known to be very persistent, as, for example, the "Fusulina limestone" cap-rock of the Herrin (No. 6) coal, which overlies this seam quite uniformly throughout the wide area in which it is known to occur.

In the Western Interior basin, where the marine beds are even more important than they are farther east, the lateral extension of various comparatively thin strata is still more striking and "there is increasing evidence of remarkable lateral persistence of various stratigraphic units."[6] For example, the beds assigned to the Hen-

[1] C. K. Swartz, W. A. Price, and H. Bassler, "Coal Measures of Maryland," *Bull. Geol. Soc. Amer.*, Vol. XXX (1919), pp. 567–96.

[2] J. M. Safford, *Geology of Tennessee* (1869), p. 367.

[3] J. Square, "Report on the Cahaba Coal Field," *Alabama Geol. Survey* (1890), p. 4.

[4] L. C. Glenn, "The Northern Tennessee Coal Field," *Tennessee Div. Geol. Bulletin 33B* (1925), pp. 23, 28, 34–36, 60, 134–36, 167, 227, 311, 316, 319, 330–32, 373, 426.

[5] C. Butts, "Geology of Alabama: The Paleozoic Rocks," *Alabama Geol. Survey Special Report 14* (1926), p. 213.

[6] R. C. Moore, "Environment of Pennsylvanian Life in North America," *Bulletin Amer. Assoc. Pet. Geol.*, Vol. XIII (1929), p. 479.

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rietta formation have been traced with little modification from Oklahoma northeastward across Kansas and Missouri into Iowa, and a recent reconnaissance by Mr. J. B. Knight and the writer has served to indicate that these beds are probably exactly equivalent to certain strata in western Illinois (Fig. 3). This group of beds is easily identified by one of the most characteristic faunal assemblages in the Pennsylvanian system. Numerous other Pennsylvanian horizons are extensively persistent.[1]

Thin horizons in Illinois.—Recent work in the western part of Illinois by members of the State Geological Survey, of whom Dr. H. R. Wanless deserves particular mention, has proved that many individual horizons, some of which are only a few inches thick, are remarkably persistent. Such beds are not only easily recognized at scattered outcrops by lithologic and faunal peculiarities but also have been actually traced for long distances.

Conclusion.—The great lateral extent of many horizons in the Pennsylvanian system strongly supports the expectation that the cyclical formations of which these horizons are members may retain their individuality throughout areas of equal extent.

CORRELATION

Stratigraphic possibilities.—The problem of Pennsylvanian correlation has always been difficult. Dependence usually has been placed on certain lithologic characters of one or two closely associated beds. Coals and limestones have been relied upon, but coals thicken and thin, change in character, and not uncommonly pinch out entirely, and many limestones vary greatly within small areas, grade into calcareous shales, or perhaps are cut out by unconformities, so that uncertainty is introduced. However, if the hypothesis of widely extensive cyclical sedimentation is established, a *group* of beds may be used for correlation. Its thickness makes it easier to trace and the change in character, or complete absence of any particular member, creates no great perplexity.

Paleontologic possibilities.—As each cycle includes an advance and retreat of the sea, as will be set forth in some detail later,

[1] E. Haworth and J. Bennett, "Special Report on Oil and Gas," chap. iii, "General Stratigraphy," *Univ. Geol. Survey Kansas*, Vol. IX (1908), pp. 57–77; H. Hinds and F. C. Greene, "The Stratigraphy of the Pennsylvanian Series in Missouri," *Missouri Bur. Geol.*, Ser. 2, Vol. XIII (1915); G. E. Condra, "The Stratigraphy of the Pennsylvanian System in Nebraska," *Nebraska Geol. Survey*, Ser. 2, *Bulletin 1* (1927).

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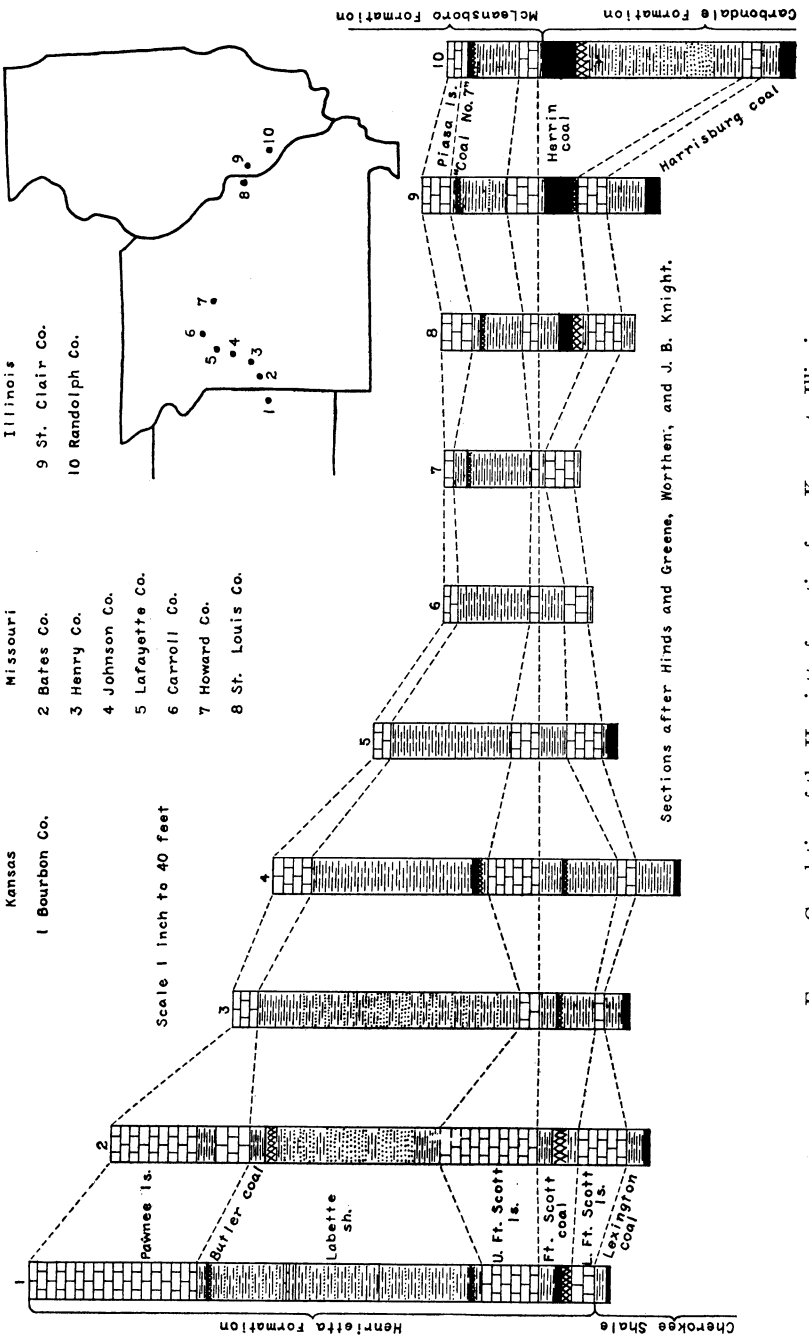

FIG. 3.—Correlation of the Henrietta formation from Kansas to Illinois

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paleontologic studies may be logically based upon the cyclical formations. Heretofore, invertebrate fossils have given little aid in the precise correlation of Pennsylvanian strata. Many species were so restricted to certain habitats that few collections of Pennsylvanian fossils furnish a representative fauna. On the other hand, the more adaptable forms which are found associated with various types of sediments are nearly all long-range species and consequently are of little value to the stratigrapher. Therefore, the faunules which are obtained from beds lithologically similar, even though widely separated stratigraphically, are likely to resemble each other more closely than do practically contemporaneous faunules from different types of sediment.

However, if the various faunules of a single cycle are determined and combined, an approximation of the total marine fauna inhabiting the sea at the time of a single advance may be obtained. When such information for the various cycles has been gathered and is compared, it will probably reveal that certain species, varieties, or assemblages can be relied upon as guide fossils for the different formations.

Conclusion.—If the hypothesis of regional cycles be established, it will be possible to set up, in various widely separated Pennsylvanian areas, general geologic sections each of which is subdivided into a succession of comparable formations, and with the aid of paleontology these should be subject to precise correlation. Thus it should be possible to make definite, detailed correlations between the Pennsylvanian strata in Missouri-Kansas, Illinois, and Ohio, an accomplishment which has been heretofore impossible.

II. THE CYCLE—ITS INTERPRETATION

PHYSICAL ASPECTS OF NORTH AMERICA

The basin in which the Pennsylvanian sediments were deposited was bounded on the east and south by Appalachia and Llanoris, a newly upraised belt of highlands, and by the relatively low Canadian positive area upon the north. This broad basin was interrupted by the Cincinnati anticline, which was not a very important structural feature at the time, and by the Ozark dome which was not high enough to contribute any considerable amount of sediment, but which stood sufficiently above the basin of deposition that little

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sediment was laid down upon it, at least during the first half of the Pennsylvanian period. The conditions to the west cannot be satisfactorily determined because the Pennsylvanian beds are buried beneath younger sediments. There is no evidence of any marine connection to the northwest or north, but it is clear that an unobstructed passage existed to the southwest, and it is probable that the later marine invasions which periodically submerged the interior of the continent advanced from this direction.

FORMER EXTENT AND SOURCE OF SEDIMENTS

Prevailing opinion.—There is a tendency to associate the original depositional limits of a geologic formation with the boundaries of its present occurrence, but such an idea is untenable unless there is definite evidence to substantiate it. Perhaps the dominantly clastic nature of Pennsylvanian strata, which does not indicate typical marine conditions, has led so many workers to assume that the present boundaries of the Pennsylvanian strata have been eroded back only a short distance from the original limits of their extent and as a result continental sedimentation has been generally mistaken for littoral.

Paleontologic evidence.—The Pennsylvanian strata of the interior of North America are confined to four structural basins, each of which is entirely separated from all of the others. Yet certain beds in each of these areas carry marine fossils. This proves that all of the basins were connected with the sea at various times during the Pennsylvanian period. The fossils of each area are similar and for the most part specifically identical, which shows that they were derived from the same source. Therefore, there can be no doubt that all of these areas were formerly connected.

Petrographic evidence.—In the literature are many references to the source of the Pennsylvanian sediments, but apparently this matter has never been especially investigated. Petrographic studies of certain Pennsylvanian sandstones in western Illinois by R. S. Poor and H. B. Willman has revealed the presence of unaltered feldspars and ferromagnesian minerals in greater or less abundance. These minerals show that the Pennsylvanian sands were derived from areas of igneous rock which were undergoing erosion sufficiently rapid that such minerals were not completely decomposed. Grains

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of characteristic metamorphic minerals, except garnet, are absent or very rare.

The area of Pennsylvanian sedimentation was bounded by regions of crystalline rocks upon the north, east, and south. It is improbable that the Canadian Shield, during the Pennsylvanian period, was a mountainous area such as would have produced sands containing undecomposed feldspars, etc. Therefore, the petrographic character of the Pennsylvanian sandstones points strongly toward Appalachia and Llanoris as their source. Other evidence supports this conclusion. Many writers have pointed out that the various divisions of the Pennsylvanian system east of the Mississippi River increase in thickness as Appalachia is approached. The quartz pebble conglomerates, which are so common in the Pottsville of the Appalachian, and the southeastern part of the Eastern Interior basins, are similar to those which were deposited in the Appalachian trough in the Devonian and Mississippi periods, but it was not until Pennsylvanian time that they were carried out into the interior of the continent as far as western Kentucky and southern Illinois. It is also significant that, in general, the size of the pebbles increases eastwardly. A careful study of the cross-bedding and current-ripple marks of the Pennsylvanian sandstones should reveal the direction of the currents from which the sands were deposited.

Conclusions.—These facts indicate that the clastic Pennsylvanian sediments, at least as far west as Illinois, were derived from the highland regions of Appalachia and that the areas of Pennsylvanian strata, now isolated, were originally connected. It is probable that the structural basins in which the Pennsylvanian sediments of the interior now exist are very largely the result of warping which occurred at the close of the Paleozoic era, and that Pennsylvanian strata originally extended as an unbroken blanket far beyond their present limits. Subsequent to post-Paleozoic warping, erosion removed all or a large portion of these beds over wide areas, and they are preserved only in the down-warped basins.

Although small quantities of sedimentary material were undoubtedly derived from other sources, by far the greatest part of the Pennsylvanian sediments, at least those as far west as Illinois, was derived from Appalachia. This highland region included at least the

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area of the present Piedmont Plateau and the adjoining belt eastward to the outer edge of the continental shelf (Fig. 4). It is significant that this area is widest at the south, where the lower Pennsylvanian sediments are thickest.

PENNSYLVANIAN SEDIMENTATION

In early Pennsylvanian time it is possible that periodic invasion of the sea extended up the Appalachian Valley from the south, reaching Illinois later than areas to the east, as the lower marine horizons of Ohio are believed to be older than any known in Illinois. It is very unlikely that marine connection with the Gulf of Mexico, by way of the Mississippi Valley, was cut off early in the Pennsylvanian period, because the only other possible connection was the trough lying between Llanoris and Ozarkia, and the sediments in it do not indicate that it was a seaway at this time, as they are clastic and almost entirely barren of marine fossils, except for the Morrow fauna (lowest Pottsville), which is older than any of the faunas that are known to the east or north.

The oldest conspicuous marine horizon of western Illinois is the limestone cap-rock above the Rock Island (No. 1) coal. It occurs at a horizon which is approximately equivalent to the Lower Mercer limestone of Ohio. The deposition of this bed appears to mark the first possible extensive marine connection between Illinois and the Western Interior basin. Direct connection between the Illinois basin and the Gulf of Mexico probably existed until this time, but subsequent marine invasions may have entered Illinois from the west rather than the south. The close similarity of fauna in higher horizons in Illinois and in Missouri, Iowa, Kansas, Oklahoma, and even Texas is evidence that in Allegheny and subsequent Pennsylvanian times the main invasions of the epicontinental seas were from the west and a direct connection with the gulf by way of the Mississippi Valley was no longer required.

If the Mississippi Valley connection was blocked in late Pottsville time, as seems likely, this was probably accomplished by sedimentation rather than by diastrophism. Erosion in southern Appalachia was very rapid, as shown by the coarse and unweathered sands which were derived from it to form a great delta and alluvial-plain

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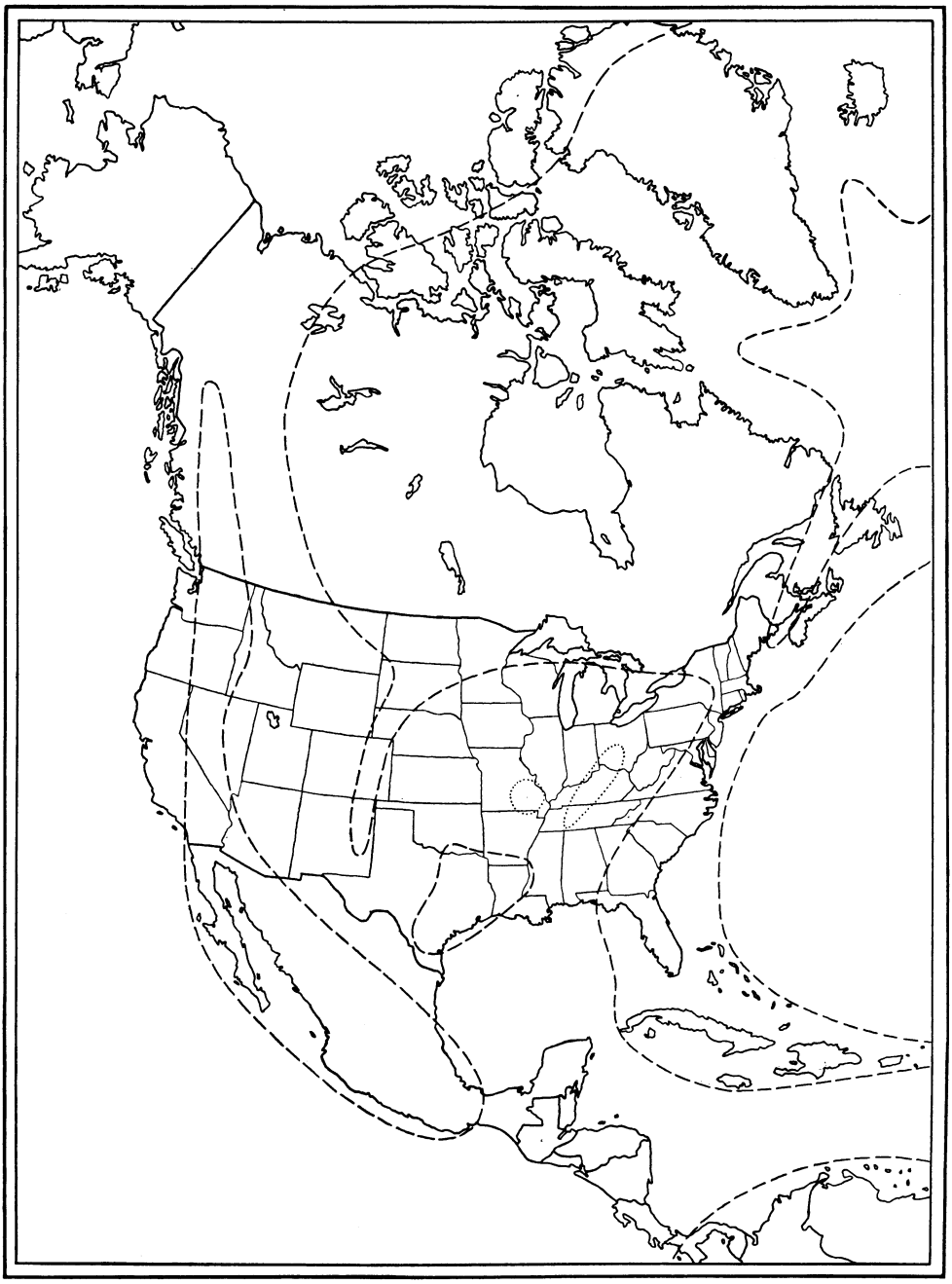

FIG. 4.—Paleogeographic map of North America, showing the total area submerged at one time or another by the Pennsylvanian seas. The Ozark Dome and Cincinnati Anticline, which were formerly covered by Pennsylvanian sediments, are outlined with dots.

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deposit.[1] Similar processes operating on a grand scale in northern Llanoris produced the enormously thick Pennsylvanian clastics in Arkansas, filling the trough between Llanoris and Ozarkia, and probably spreading out eastward to connect with the southern Appalachian deposits. Possibly thus the Mississippi embayment was cut off.

The physical conditions which prevailed during the Pennsylvanian period in Eastern North America—a broad, interior lowland bordered by highlands undergoing rapid erosion—were ideal for the development of a series of confluent alluvial fans which later merged into a great alluvial plain stretching far westward from Appalachia. These continental deposits and the marine beds that record the periodic flooding of this area by the sea make up the strata of the Pennsylvanian period.

THE CYCLE OF DEPOSITION

The physiographic cycle of erosion is a concept familiar to all geologists and its effects are readily discerned on many land surfaces, but the material removed during the course of these cycles of erosion was deposited rarely in such positions that its connection with them may be observed. On the other hand, the older clastic sediments have been uplifted, deformed, and dissected so that they may be studied at many places, but the areas of erosion from which these sediments were derived are no longer preserved. In neither case can the intimate but variable relations which undoubtedly exist between an area of erosion and its corresponding area of deposition be studied directly. However, for each cycle of erosion in the uplands there should be a cycle of deposition in the basin. The two types of cycles are antithetical but complementary. They are similar only in that each is controlled by baselevel, the erosion cycle cutting downward to baselevel and the depositional cycle building up to it.[2]

Cycles of deposition may be best observed in ancient delta or

[1] D. White, "Deposition of the Appalachian Pottsville," *Bulletin Geol. Soc. Amer.*, Vol. XV (1904), pp. 267–82.

[2] J. Barrell, "Rhythms and Measurements of Geologic Time," *Bulletin Geol. Soc. Amer.*, Vol. XXVIII (1927), pp. 746–809; J. E. Eaton, "The By-passing and Discontinuous Deposition of Sedimentary Materials," *Bulletin Amer. Assoc. Petrol. Geol.*, Vol. XIII (1929), pp. 713–61.

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alluvial-plain deposits, where strata were laid down partly under continental and partly under marine environments. Barrell[1] wrote

> to simply determine in some regions some formations as fluviatile and others as marine does not complete the conceptions of the larger relations of each to the other, which is given by the theory of the growth and retreat of deltas.
>
> When such a conception is attained, the mind may look back at the complete geosyncline and view it as made of beds laid down on the one side by the land and on the other by the sea, each advancing into the other and dovetailing in intricate fashion, though one or the other may much of the time be absent, and when present seldom of equal development. Looking down through the depths of the solid rocks the surface of separation is seen to be generated by the ascent of the strand-line through the geologic ages, oscillating back and forth and often completely across the zone of sedimentation.

These remarks are particularly applicable to the Pennsylvanian system, which over large areas is made up of alternating continental and marine strata. A careful consideration of the various types of sediments which occur at remarkably consistent positions in the various Pennsylvanian formations and the conditions which were required for their formation and preservation leads to a clear picture of the physiographic history of the Pennsylvanian period. It is possible that with this knowledge the stratigraphic sections in other areas where the succession of events is less apparent may be deciphered.

UNCONFORMITIES

The typical cyclical formation, as previously outlined, begins with an unconformity which separates the new formation from subjacent strata. This unconformity, which followed a period of marine sedimentation, was caused by regional uplift. The evidence for this conclusion will be presented later. Into this newly upraised plain, streams intrenched valleys, some of which have been traced long distances as, for example, the Moberly and Warrensburg channels in Missouri. In western Illinois channels from 80 to 100 feet deep were developed at at least two of these erosional stages. Such channels are not uncommonly several miles in width, and the sides of many of them are very steep. Small tributary channels have rarely been observed. It is highly improbable that such channels could have been eroded in the bottom of a shallow epicontinental sea, because

[1] J. Barrell, "Criteria for the Recognition of Ancient Delta Deposits," *Bulletin Geol. Soc. Amer.*, Vol. XXIII (1912), pp. 413–14.

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upon the modern sea bottom even small channels are absent except in localities where current rather than wave action is unusually effective.[1]

The channels are now filled with sand or sandy shale and locally bear conglomerates in the lower portions. Some writers have explained such channel sandstones as being due only to lateral variation in sedimentation, but their true character is clearly apparent wherever the margins of the channels are exposed.

The erosion which produced these unconformities was fairly rapid and most of it in Illinois and adjacent areas was probably accomplished by streams whose waters were derived from distant sources. There was only slight weathering of the land surface either in or adjacent to the channels or upon the uplands where erosion was not active. Evidently the land surface was not exposed long enough for the development of a weathering profile.

One feature of many of the unconformities deserves particular mention. The sandstones which now fill the old channels not uncommonly rest more or less evenly upon the underlying coal beds. The channels were, therefore, cut downward not only through a considerable thickness of shale but also, in most cases, through a conspicuous limestone bed. The erosion which was capable of cutting through shale and limestone was checked at the coal bed, which was probably compressed peat at this time. Such occurrences, which are too numerous to be due to chance, indicate that the peat beds must have offered more resistance to erosion than the shales and limestones. This conclusion is verified by observations of an existing English peat bed which resists erosive action by a river so that it projects as a promontory.[2]

CONTINENTAL DEPOSITION

Causes.—The erosional unconformity was followed by aggradation. This reversal in the physiographic process was caused either by decreased gradient or overloading of the streams at their sources. There may have been (1) subsidence in the area of aggradation, (2)

[1] J. Barrell, "Criteria for the Recognition of Ancient Delta Deposits," *Bulletin Geol. Soc. Amer.*, Vol. XXIII (1912), pp. 427–28.

[2] E. W. Prevost and T. M. Reade, "The Peat and Forest Bed at Westbury-on-Severn," *Cotteswold Nat. Club Proc.*, Vol. XIV (1901).

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uplift in the region from which the sediments were derived, (3) change in climatic conditions, or (4) a combination of these causes.

Climatic change,[1] especially affecting the amount or seasonal distribution of rainfall, must not be disregarded throughout this discussion. Its effect, however, is very difficult to evaluate. Additional rainfall might result in a greater amount of erosion or it might favor more luxuriant vegetable growth, which would serve as a protection against erosion. Also climatic change may have been purely cyclical and independent of changes in the physical features of the continent, or it may have resulted from such changes.

Without disregarding the possibility of climatic change, the reversal of the physiographic process from erosion to sedimentation may be satisfactorily explained by diastrophic movements. Thus the uplift which resulted in erosion may have been followed by continued uplift of considerable magnitude in Appalachia but less pronounced to the west. Erosion in the uplands would be accelerated, the streams would be overloaded and their excess sediments would be deposited upon the plains where erosion had been formerly active.

Nature of deposits.—Under such conditions the channels were quickly filled with sand and silt, after which the sediments were spread irregularly over practically the entire plain. The courses of the streams continually shifted. Temporary lagoons were first formed and later filled with sandy and micaceous silts. Aggradation continued until the surface of the plain had been built more or less uniformly up to baselevel.

This alluvial plain may be compared in a general way to the basin of the Ob River and its tributaries in Western Siberia,[2] which has an areal extent of over half a million square miles and is one of the largest unbroken lowland regions on the earth. It is almost entirely composed of alluvial materials brought down from the highlands of Central Asia and spread out to form a practically level plain, whose regional slope throughout wide areas is less than 1 foot per mile. However, alluviation is no longer taking place. The rivers

[1] J. Barrell, "Relations between Climate and Terrestrial Deposits," *Jour. Geol.*, Vol. XVI (1908), pp. 159–90, 255–95, 363–84.

[2] T. Belt, "The Steppes of Siberia," *Quart. Jour. Geol. Soc. London*, Vol. XIII (1874), pp. 490–98; *Encyclopedia Britannica*, 14th ed. (1929), Vol. XIX, p. 684.

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have been rejuvenated, probably since glacial times, and are now flowing in intrenched valleys.

The arenaceous strata that comprise the lower portions of the Pennsylvanian cyclical formations are widespread but thin. In Illinois they rarely achieve a thickness of 100 feet even in the channel zones, and elsewhere they are commonly from 5 to 10 feet thick. These figures indicate that the baselevel of deposition was not greatly displaced upward. For the most part these strata have the character of top-set delta beds.

The clastic materials deposited upon the great Pennsylvanian alluvial plain are coarsest nearest Appalachia and become finer westward. Many of the arenaceous beds in Illinois appear to be typical sandstone but are composed largely of silt-sized grains.

It is probable that in most of the Pennsylvanian cycles aggradation was almost universal from Appalachia to the withdrawn epicontinental sea. Material not deposited upon the alluvial plain was carried into the sea and the coarser part spread out along the shore, while the finer settled far and wide upon its shallow bottom. Thus, although most of the arenaceous beds are believed to have been deposited under subaerial conditions, some similar material was probably also laid down under a truly marine but littoral environment.

Continental character.—The continental character of most Pennsylvanian sandstones and sandy shales is plainly written upon them. Their cross-bedded and current-rippled structure, their occasional mud cracks, and the abundant vegetable impressions and fragments are among their most conspicuous features, and their poorly sorted nature and rapid lateral variation are impressive on closer examination. The pebbles which are so common in some parts of the Pottsville series must have required fairly strong currents for their transportation. Littoral currents might have carried them long distances, but their wide distribution at certain horizons and their occurrence in erosional channels is strong evidence of their having been transported by streams.

Marine fossils rarely occur in the Pennsylvanian sandstones of the Eastern Interior or Appalachian basins, but thin films or lenses of coal are not uncommon. The absence of marine fossils is negative evidence; the coaly material might have been formed from vegeta-

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tion washed into the sea, but still they strongly point toward a continental origin for the sandstones. Those rare arenaceous beds which contain marine fossils are possibly the shoreward facies of marine deposits contemporaneous with the aggradation of the alluvial plain.

CESSATION OF CONTINENTAL SEDIMENTATION

Causes.—The deposition of sands and sandy silts over the interior of the continent ceased, not only because the alluvial plain was aggraded to baselevel but also because the supply of clastic material from Appalachia was cut off. The lack of sediment may be attributed to (1) peneplanation of Appalachia, (2) subsidence of Appalachia, or (3) change of climate.

Peneplanation.—The peneplanation of Appalachia would satisfactorily explain the lack of sediments. However, very long periods of time are generally considered necessary for the development of peneplains, and it is improbable that forty-two or more successive peneplanations should have occurred during the Pennsylvanian period alone.

Subsidence of Appalachia.—Subsidence of Appalachia would also terminate continental sedimentation upon the alluvial plain by reducing the gradient of the streams. It is not unusual for a rapid uplift of a positive area to be followed by a slighter, more gradual, compensating subsidence, and such reactions might have followed the periodic elevations of Appalachia during Pennsylvanian time. This possibility is supported by the not uncommon occurrence of lenticular non-marine limestones closely underlying coal beds of the upper part of the Pennsylvanian system in Ohio and also at numerous horizons in Illinois. Such limestones were probably deposited in local and shallow depressions ponded by a slight subsidence of Appalachia.

Change in climate.—It has been stated previously that the probable consequences of climatic changes are not known, but their possibilities cannot be ignored. A careful study and comparison of the plant remains found in the clastic continental sediments and the overlying carbonaceous beds might throw considerable light upon this phase of the problem.

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UNDERCLAY FORMATION

Previous opinions.—The intimate association of Carboniferous coals and underclays is almost universal. This association, the character of the underclay, and the not uncommon occurrence of root markings in it have been considered, for many years, evidence that the underclay represents the soil in which the coal plants grew. More recently Stout[1] has shown that the thicknesses of associated coals and underclays bear no relationship to each other, and that the chemical compositions of underclays and coal ashes are strikingly similar. On the basis of these facts he contends that the underclay is not merely an old soil but that it is composed of insoluble sediments which slowly accumulated under conditions very similar to those which prevailed during the time of peat formation, except that the vegetable material decayed completely, instead of being preserved and later transformed into coal. Therefore, he considers that "the clay represents the accumulation of terriginous sediments and minerals from the plant ash, and the coals these with the addition of preserved carbon."

Recent observations.—In 1928 Drs. M. M. Leighton, H. R. Wanless, and A. C. Bevan observed an exposure of the underclay beneath the Herrin (No. 6) coal of the Peoria district, in which there were exhibited all zones of a characteristic poorly drained weathering profile,[2] as follows:

Coal
Underclay
1. Dark, humus-bearing clay, more or less laminated
2. Light, bleached, very plastic clay
3. Irregularly iron-stained clay
4. Calcareous clay, containing impure limestone nodules grading into
5. Unaltered silty, calcareous, shale

More recently Wanless has carefully examined many Pennsylvanian sections in western Illinois in which the underclays beneath a large number of different coal beds are exposed. He reports that in almost every case a poorly drained profile of weathering is at least suggested, and that in many places it is well developed.

[1] W. Stout, "Coal Formation Clays," *Ohio Geol. Survey*, Ser. 4, *Bulletin 26*, chap. vii (1923).

[2] M. M. Leighton and Paul MacClintock, "Weathered Zones of the Drift-sheets of Illinois," *Jour. Geol.*, Vol. XXXVIII (1930), pp. 28 ff.

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Interpretation.[1]—These observations supply very suggestive evidence that the underclays represent weathering profiles produced by long-continued exposure to atmospheric agents. The time required for their development, judged in the light of recent observations on the weathering profiles of the earlier Pleistocene drift-sheets to which they are comparable, was very great. Horizon 2 of the gumbotil profile on the Illinoian drift, which corresponds to the plastic clay horizon of the underclay, commonly attains a thickness of from $3\frac{1}{2}$ to 5 feet and is considered to have required from 100,000 to 200,000 years for its development.[2] The Pennsylvanian underclays, which rarely achieve greater thickness, were probably produced somewhat more rapidly as they were derived from more homogeneous and permeable materials without pebbles or boulders, and as the climate of the Carboniferous was probably such that ground-water circulation was not interrupted during certain seasons by freezing. The time required for the formation of an underclay, however, may have nearly equaled that during which all the sediments of the complete cycle accumulated.

The presence of an underclay in every cyclical formation is perhaps the most convincing evidence that the cycle of conditions was regional rather than local. It is highly improbable that the long periods of stability necessary for the development of weathering profiles with precisely identical relations to certain stages of sedimentation could have occurred at unsynchronized intervals in numerous local areas. Theoretically, therefore, the underclays should be the most important, most significant, and most persistent members of the cyclical formations. This is substantiated by field observation as the underclays persist more or less uniformly far beyond their accompanying coals and over areas in which the other members of the formations change markedly in character and thickness.

The land surface upon which the underclay developed was practically free from either erosion or deposition, although some

[1] Further studies of the underclays are planned by the Illinois State Geological Survey. These will include additional field observations and chemical and petrographic investigations.

[2] M. M. Leighton, personal communication.

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local transference of the surface materials probably occurred. The shallow, local depressions in which fresh-water limestones had previously been deposited were partially filled by the inwash of small amounts of material from closely adjacent, slightly higher areas. At a few localities a persistent coal rests unconformably upon lower beds without an underclay. Such situations prove that at a few places local erosion actually occurred either during or after development of the underclay.

The local unconformities below certain persistent coals are more significant in that they show the underclay was not a soil developed by the action of the plants whose remains were later transformed into the coal. Apparently, the underclay was fully developed before peat accumulation began. This conclusion is substantiated by the fact that the roots of Lepidodendron and Sigillaria stumps, which have been preserved *in situ*, spread out laterally along or close to the surface of the peat bog as it existed at the time they lived,[1] instead of penetrating downward into the peat or underlying material. The laminated structure of most coals and the undisturbed clay partings that are common in them plainly indicate that the peat was undisturbed by the roots of plants growing above. Conditions in the lower layers of the peat were probably such that even the roots of the coal plants could not endure them.

The not uncommon occurrence of Pennsylvanian underclays without overlying coal beds is evidence that peat-bog conditions were not necessary for the development of underclays, nor were they produced later by sulphuric acid bearing solutions derived from the oxidation of pyrite in an overlying coal bed. On the other hand, the occurrence of coal seams without underclays, rare in the case of Pennsylvanian coals in Illinois, but of general prevalence in the post-Paleozoic coal fields of the Book Cliffs region in Utah[2] and probably elsewhere, proves that underclays are not necessarily developed below peat bogs. The fact that coals and underclays are not genetically related is shown also by the nature of the underclay itself and by the conditions necessary for the existence of a peat bog. The

[1] D. White, "The Origin of Coal," *U.S. Bureau Mines, Bulletin 38* (1913), p. 56.

[2] D. J. Fisher, personal communication.

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weathering profile of the underclay was produced by the leaching and oxidizing action of descending ground waters, while stagnation of drainage and lack of oxidation are required for the occurrence of peat bogs. Finally, no profiles of weathering are known to have developed beneath either Pleistocene or recent peat bogs.[1]

COAL FORMATION

A great deal has been written on the formation of coal, particularly with regard to whether the vegetable matter from which it was produced grew in place or was transported. Practically everyone in this country, however, now agrees that the evidence is conclusive that the American Carboniferous coals were formed in place. Therefore, it is necessary only to consider the physical conditions which prevailed throughout the interior of the continent during the accumulation of the vegetable material which has been subsequently transformed into coal.

Plants undoubtedly grew upon the alluvial plain since the beginning of the cycle, but rapid sedimentation or adverse climatic conditions during its early part prevented any extensive or thick accumulations of peat. Coal partings or lenses occur in the sandstones at many places, but such deposits are thin and local. The humus-bearing layer in the upper part of the underclay indicates that vegetation grew during the long period while the weathering profile was being developed, but evidently conditions were still unfavorable for accumulation and preservation of peat.

The development of coal swamps was caused either by slight subsidence of the alluvial plain, still further reducing its gradient, or by increased rainfall which caused a luxuriant jungle growth to spring up. Certain areas were so situated that the very sluggish surface drainage was trapped by this tangled mass of vegetation, and they became extensive swamps in which peat accumulated. In other areas, more easily drained, conditions were changed little, the vegetation was more sparse, and as it died it decomposed, either producing only a layer of humus or leaving not even material of this nature Here and there in the swamps were more or less open bodies of stagnant water in which spore cases and pollen settled and were later transformed into cannel coal. Although peat did not accumu-

[1] M. M. Leighton, personal communication.

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late over the whole of the alluvial plain, this surface represents an important coal horizon which is now marked by coal, black shale, or humus almost invariably present above the underclay.

Such a picture of enormous, discontinuous, but contemporaneous coal swamps extending from Kansas to Pennsylvania may be startling to one who has always considered them to have occupied a rather narrow belt along a shore line which gradually retreated owing to the filling up of the inland sea. However, this view is perfectly consistent with the cyclical hypothesis and satisfactorily explains the great extent of many important coal beds.

Extensive modern swampy areas comparable to those which existed during Pennsylvanian time are found in the circumpolar tundra, of which Alaska offers excellent examples.[1] The tundra is a more or less level but slightly undulatory region. It is carpeted with dense, luxuriant, dwarf vegetation as saturated with water as a sponge even on the steeper slopes. It is swampy, drainage is very poor, and many small lakes and ponds without outlets or inlets dot its surface, occurring not only in depressions but also on the hillsides. A layer of peat or humus is constantly accumulating by the death and decay of the vegetation, while other plants continue to grow above. This layer may attain considerable thickness; from 12 to 15 feet is not unusual and from 150 to 300 feet has been reported as exposed in a sea cliff on Eschscholtz Bay.

Russell was much impressed by the peat deposits of the tundra and wrote:

> So vast is the amount of vegetable material now imprisoned in the tundra of the North, that I venture to suggest that possibly some coal seams may have had a similar origin.
>
> This suggestion does not seem so very unreasonable when one remembers that except in the circum-polar tundra, deposits of vegetable matter are nowhere accumulating at the present day to anything like the extent or thickness required for the formation of coal fields like the one, for example, of which Pennsylvania still remains a remnant. Botanists will say at once, in opposition to this suggestion, that the flora of most of our coal fields, and especially those of Paleozoic age, indicate tropical or sub-tropical conditions. The flora of the tundra, however, like the plants of the Carboniferous, is essentially and characteristically cryptogamic. Two species of Equisetum, which may be con-

[1] I. C. Russell, "Notes on the Surface Geology of Alaska," *Bulletin Geol. Soc. Amer.*, Vol. I (1890), pp. 125–28.

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sidered as representing the Calamites of former time, flourish with rank luxuriance over great areas along the Yukon.

If the tundra-fringed coast of Alaska should subside, the peaty layer with which it is covered would become buried beneath sands and clays, and form a stratum in every way favorable for transformation into lignite and coal.[1]

SUBMERGENCE

The period of emergence was brought to a close by rapid subsidence of the coal swamps, which resulted in a great transgression by the inland sea. The marine waters extended widely throughout the interior of the continent and opened a vast area for the colonization of marine organisms. These migrated from the southwest in great numbers and variety. The sea was shallow, as shown by the sediments which accumulated in it and the animals which lived upon its bottom. Conditions of turbidity and salinity varied greatly from place to place and the migrating marine organisms sought those habitats to which they were adapted. Thus faunules of quite different character existed contemporaneously in adjoining areas.

It is significant that, over broad areas not only in North America but also in other lands, the periods of peat accumulation were commonly brought to a close by marine inundation. In England marine conditions directly succeeded the formation of many peat beds,[2] and marine limestones are generously distributed throughout the Coal Measures of the Donetz basin in southern Russia. In regions where characteristically marine faunas are lacking, brackish water molluscs (commonly termed "non-marine") are in many cases to be found in the roof shales of the coal seams.[3] Such a parallelism between American and European Coal Measures stratigraphy suggests that the conditions and processes which prevailed throughout Upper Carboniferous time were essentially similar over large portions of the globe.

Black "fissile" shale.—The Pennsylvanian coal beds are commonly overlain by black "fissile" shale, termed "slate" by the

[1] *Ibid.*, pp. 127–28.

[2] G. Wild, "Lower Coal Measures of Lancashire," *Manchester Geol. Soc. Trans.*, Vol. II (1892), pp. 364 ff.

[3] J. H. Davis, "Zoning of the Coal Measures by Non-marine Lamellibranchs," *Congrès pour l'avancement des études de Stratigraphie Carbonifère (Heerlen, 1927) Compte rendu* (1928), p. 219.

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miners. The formation of black shale of this kind has attracted the attention of numerous writers, but little is known concerning the conditions under which it accumulated. The Pennsylvanian black shales are marine, but the fossils which occur in them show that conditions were peculiar and almost invariably inhospitable to normal marine faunas.

As the black shales were the first deposits in the transgressing sea, it seems probable that they were laid down in very shallow water, but their finely laminated structure shows conclusively that the sea bottom was not subject to any great stirring by wave action. Unless the waves, which even gentle winds are capable of producing, were damped in some manner, this structure could not have been developed and preserved. Possibly lowly organized plants, such as marine algae, may have been present in sufficient abundance to prevent the development of waves, and when they died they left no other trace than the carbonaceous content of the shales. This carbonaceous matter cannot have been obtained by reworking of the upper portion of the peat bed as some of the black shales attain a considerable thickness without apparent decrease in carbon content above, and others are separated from the underlying coals by as much as from 40 to 50 feet of light gray, plant-bearing shales.

Calcareous shale and limestone.—The black shale is followed by lighter-colored, calcareous shale, which in most cases grades upward into limestone. This limestone and its associated calcareous shale ordinarily contain a varied fauna and indicate that normal, shallow marine conditions prevailed during their deposition. The Pennsylvanian limestones vary greatly in character. Some of them are earthy, shaly, or impure, but others are quite pure and dense and were largely produced by bacterial or chemical precipitation in clear water. Other beds are dominantly algal, but very few of them, except some thin layers in the shales, are composed largely of shells or shell fragments, corals, bryozoa, etc. It is evident that during the time of limestone deposition, comparatively little clastic material was being contributed by the land.

A number of limestones that are generally considered to be of fresh-water origin occur in the upper part of the Pennsylvanian system in Ohio and adjoining states of the northern Appalachian

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region. These beds contain ostracods, worm tubes, and a few species of minute molluscs, but lack the remains of characteristic marine invertebrates. In general they should probably be considered to occupy positions corresponding to the non-marine limestones, which normally occur a short distance beneath the coal beds in the lower part of the system in that region and in Illinois. However, fish remains, which appear to be identical with some of those found in the marine limestones of Illinois,[1] occur in several of these beds, showing that brief marine connections did exist. Periodic marine extensions as far east as Ohio persisted even in Dunkard time, as a species of *Lingula* has been collected from shale overlying the Washington coal.[2]

Shales.—The Pennsylvanian limestones grade upward through highly calcareous shales to more or less silty shales in which there are thin layers of limestone, "ironstone," or sideritic concretions. These shales are commonly bluish or grayish in color, and vary from finely laminated to massive in structure. Some of them are micaceous, but few are arenaceous. Although fossils occur in great numbers in the lower part of these shales at some localities, most of the beds are entirely barren of remains of both animals and plants. A few marine fossils, chiefly molluscs, occur in the upper parts of such shales at a few places and an occasional limy or sideritic layer contains a varied fauna. Well-preserved leaf impressions are also rarely present in concretionary nodules. The few molluscan fossils which are contained in these beds indicate that they were deposited in the sea, but normal marine conditions were probably lacking during most of the time that they were accumulating.

The fact that such shales follow the limestones shows that for some cause clastic material was again being contributed by the land. This might have been due to slight uplift of Appalachia or to climatic change. During all of the time that had been required for the development of underclay and the accumulation of coal and limestone in the interior, Appalachia had been subject to weathering, and it is probable that the crystalline rocks exposed there were more or less

[1] J. J. Stevenson, "The Formation of Coal Beds, III," *Amer. Philo. Soc. Proc.*, Vol. LI (1912), p. 504.

[2] C. R. Stauffer and C. R. Schroyer, "The Dunkard Series of Ohio," *Ohio Geol. Survey*, Ser. 4, *Bulletin 22* (1920), p. 143.

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decomposed to considerable depth. An uplift would have enabled erosion to act upon this material, which was prepared for easy removal, and if the uplift were slight, only the finest material would have been transported to the sea and spread out upon its bottom while the sands remained in place, or at most were removed no farther than the sea shore.

Similar results may have been achieved by climatic change, but the nature of the changes required is intangible and uncertain.

Nature of Pennsylvanian seas.—The extensive, shallow, landlocked seas of the Pennsylvanian period were probably almost tideless, as are modern landlocked seas, such as the Baltic and Mediterranean, to which they may be roughly compared, and consequently tidal currents or scour could not have been effective. Other currents, however, produced by rotation of the earth, winds, differences in temperature, and the inflow of terrestrial waters undoubtedly were present, but it is improbable that they achieved more than moderate velocity and therefore served merely for the transportation and dispersal of sediments over the sea bottom.

Wave action undoubtedly played an important part in molding the character of some of the Pennsylvanian beds. Many of the purer limestones are somewhat brecciated or conglomeratic. This texture is probably the result of wave action on the partially consolidated lime muds of the sea floor. Some of the shales are thick bedded and almost structureless, possibly owing to repeated stirring up by waves. As a whole, however, the results of wave action upon the marine beds of the Pennsylvanian system are not as conspicuous as might be expected in sediments deposited in such shallow seas. The climate of the Pennsylvanian period was equable over practically the whole world, so that meteorological conditions were probably rather uniform and violent winds and storms which characterize the modern world were absent. Consequently, wave action was probably not as effective at that time as it is today.

Under the conditions which existed in the epicontinental Pennsylvanian seas, the fresh terrestrial waters would not have been mixed readily with the saline waters of the embayment but would have gradually pushed the salt water backward away from the shore. Thus, fresh or only slightly brackish conditions probably prevailed

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along the shore, merging through a transitional zone with the normal saline waters of the sea. In just this way the salinity of the modern ocean is greatly reduced near the mouth of a large river, such as the Mississippi or the Amazon. Under such circumstances a normal marine fauna should not be expected in the deposits of the fresh or brackish waters adjacent to the shore. An example of faunal changes resulting from such conditions may be seen in the Cambridge horizon of Maryland,[1] which contains marine species in the western outcrops, but to the eastward the fauna becomes meager, brackish-water forms appear, and finally the marine species disappear entirely. Such an explanation may also account for the few indications of marine life which have been observed in the upper Pennsylvanian beds in Ohio and West Virginia.

It seems likely that the fresh or brackish-water conditions which existed only adjacent to the shores during the time of limestone deposition were more widespread later while the overlying shales accumulated. Under these circumstances, the sea waters would not have been notably saline and therefore not capable of rapid flocculation, and the fine sediment would have been spread far and wide in the shallow waters. Such conditions also satisfactorily explain why the seas were largely inhospitable to normal marine life at these times.

UPLIFT

The cycle was brought to a close by uplift, and the whole sequence of events outlined in the foregoing was repeated.

At the beginning of this discussion, the presentation of evidence indicating that the various cycles were separated by times of uplift was deferred, but now this may be considered. The unconformities which are locally well developed, and which have been employed to separate the formations, have been described, and as these were produced by subaerial erosion it follows that the sea no longer covered this area. However, the questions might be raised whether all of these upper shales, which are commonly unfossiliferous, are actually marine, and whether in this case it might not be possible to explain the unconformities without appealing to uplift. Consequently, it is significant that locally many of these surfaces of unconformity cut

[1] C. K. Swartz, W. A. Price, and H. Bassler, "Coal Measures of Maryland," *Bulletin Geol. Soc. Amer.*, Vol. XXX (1919), p. 580.

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down completely across the upper shales through the characteristically marine limestones and calcareous shales and even through the coals themselves. The limestones which certainly were deposited beneath the sea must have been upraised, or erosion of this type could not have reached them beneath their fairly thick covering of shales.

The recognition at many horizons of unconformities which are the result of uplift is of considerable importance because the widely accepted interpretation of Pennsylvanian sedimentation has been that the sea was silted up, coal plants grew upon this low surface, subsidence brought back the sea, which was again silted up, etc. Although few writers have commented upon it, the sedimentary cycle is generally so well exhibited that many must have observed it, but it has not been recognized as the result of diastrophic cycles.

DIASTROPHISM

Before concluding the consideration of cyclical Pennsylvanian sedimentation, it is necessary to consider briefly the nature of the diastrophism which controlled it. Although climatic change may have been an important factor, evidence of its influence has not been recognized and therefore it may be ignored at this time, as diastrophism alone is capable of providing an adequate explanation for the cycle.

At that stage of the cycle just before the cessation of clastic sedimentation, the extensive alluvial plain must have sloped sufficiently to allow streams to carry fine sands, that is about 6 inches or more per mile,[1] and if the plain was 1,000 miles wide its piedmont edge must have been 500 or more feet above sea-level. However, the shallow-water faunas and the variable nature of the marine sediments, including brecciated limestone, show that the subsidence which resulted in marine submergence as far east as Pennsylvania did not produce, in the Mississippi Valley, seas 500 feet or more in depth. Consequently, the uplifts and subsidences must have been of a hinge type, greatest in Appalachia and decreasing in magnitude westward. Appalachia, the area of erosion, moved dominantly up-

[1] The grade of the Mississippi River between St. Louis and Cairo is about 7 inches per mile; the fall of the Nile from Assuan to Cairo, a distance of more than 700 miles, is less than 5 inches to the mile; the Amazon over considerable stretches descends at a rate of less than 2 inches in a mile; and the Yangtse River is said to fall about 1 inch per mile in the last 200 miles of its course. Most large rivers, however, carry only fine muds in their lower course.

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ward while the interior, the area of sedimentation, moved dominantly downward (Figs. 5 and 6).

In the last few years, comprehensive studies of the Carboniferous stratigraphy of the mid-continent area by geologists in the employ of numerous oil companies have produced much information concerning the geologic history of that region. These data, which recently have been summarized,[1] reveal that diastrophism was more or less active in Llanoris and adjacent areas throughout Pennsylvanian time. It is not unlikely that future studies will make it possible to correlate these movements with the diastrophism of Appalachia, which resulted in the sedimentary cycles of the northern and eastern coal fields.

INTERBASIN CORRELATION

The diastrophic movements of the Pennsylvanian period were not all of uniform degree. As a result, the areas of emergence and submergence within the cycles were not of equal extent. The strand line oscillated backward and forward unevenly, extending much farther to the east during some cycles and withdrawing a greater distance to the west at some of the intercyclical stages. Therefore, the deposits in the various seas and upon the different land surfaces were of unequal extent. However, as the transgressions of the sea after lower Pottsville time probably always came from the west and southwest, each marine invasion of Illinois should be represented in Missouri by marine beds also, but marine beds in Missouri laid down in less extensive transgressions would have no counterpart in Illinois. Likewise, after lower Pottsville time, there might have been more marine horizons deposited during a given period in Illinois than in Ohio.

In the same manner, each underclay and coal horizon in Illinois should be represented by an equivalent underclay and coal horizon in Ohio, although it is conceivable that in Ohio there might be additional ones representing land surfaces that did not extend as far west as Illinois. Similarly, each underclay and coal horizon in Missouri should have its counterpart in Illinois but not all of the Illinois horizons may have extended as far west as Missouri.

[1] S. Powers, "Age of the Folding of the Oklahoma Mountains," *Bulletin Geol. Soc. Amer.*, Vol. XXXIX (1928), pp. 1031–72; M. G. Cheney, "History of the Carboniferous Sediments of the Mid-continent Oil Field," *Bulletin Amer. Assoc. Petrol. Geol.*, Vol. XIII (1929), pp. 557–94.

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During the first part of each cycle, when land conditions prevailed extensively throughout the interior of the continent, there not uncommonly occurred local accumulations of peat now transformed

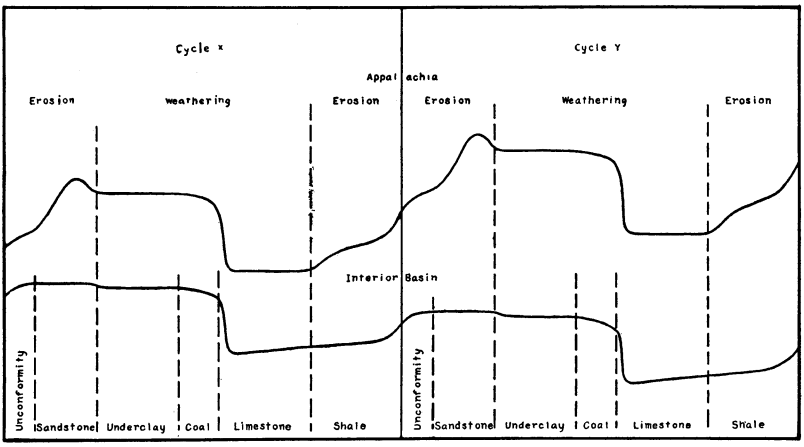

FIG. 5.—Diagram showing relative uplifts and depressions in Appalachia and the Interior Basin during the course of two typical cycles.

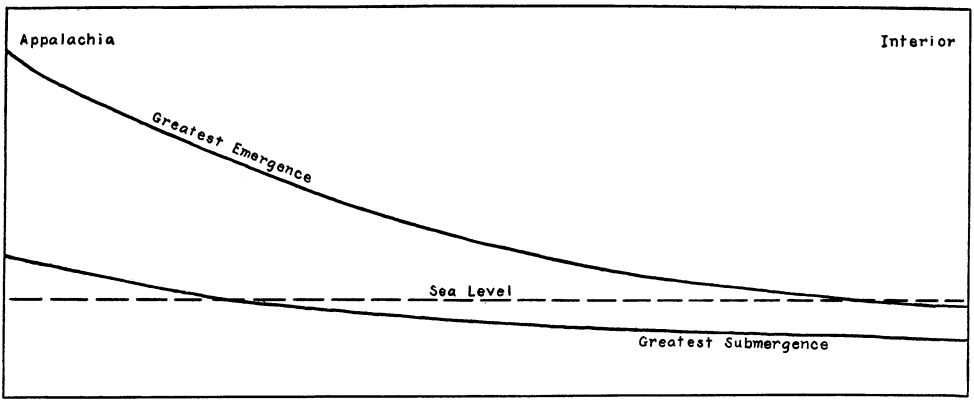

FIG. 6.—Diagram illustrating the hinge action of the Pennsylvanian diastrophism and the extremes of uplift and subsidence in Appalachia and the Interior Basin.

to thin layers or lenses of coal. Such coals are without underclays and do not represent extensive coal horizons so that they are of no significance in correlation. On the other hand, there can be no local or "stray" marine horizons, as all marine beds must have been connected with more extensive marine deposits to the west or south.

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It is possible that difficulties may arise in the interpretation of the Missouri and Kansas sections because the diastrophism of Llanoris may have been imperfectly synchronized with that of Appalachia. If the uplifts and depressions of these two highland areas were not always contemporaneous but conflicted with each other, the strata in Missouri and Kansas, which may be composed of sediments derived from both of them, would be a complicated sequence of beds. However, there should be no such difficulty in the correlation of the Illinois and Ohio sections.

ESTIMATES OF TIME

Barrell has estimated that the Pennsylvanian period was from 35,000,000 to 50,000,000 years in duration.[1] If an intermediate figure of 40,000,000 be divided by two in order to make allowance for the Mississippian-Pennsylvanian unconformity and the early Pennsylvanian beds which are absent from Illinois and Ohio, the Pennsylvanian strata in these states represent about 20,000,000 years. If, for convenience, the forty-two cycles recognized in the Ohio section be increased to fifty, the time that might be assigned to an average Pennsylvanian cycle would be 400,000 years.

Each cycle includes two intervals during which deposition did not occur; namely, (1) that represented by the unconformity beneath the sandstone, and (2) that represented by the underclay. If it be assumed that deposition took place during 75 per cent of the time assigned to the average cycle, 100,000 years remain to be divided between the two intervals of nondeposition. There can be little doubt that the development of the underclay required a considerably longer time than the interval represented by the unconformity because weathering profiles have not been recognized at any of the unconformities. If the ratio of these two intervals were as 3 is to 1, an average of 75,000 years would be allowed for the development of the underclay, which might be sufficient under favorable conditions.

However, it is not at all unlikely that a considerably longer time was actually available. The faunas of the Upper Mississippian and Lower Pennsylvanian are so strikingly similar in many ways that the two periods may not have been separated by so long an interval as

[1] J. Barrell, "Rhythms and the Measurements of Geologic Time," *Bulletin Geol. Soc. Amer.*, Vol. XXVIII (1917), p. 885.

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20,000,000 years. The accumulation of sediments may have required much less than 75 per cent of Pennsylvanian time. It is also highly probable that the development of an underclay actually required more than three times that represented by the unconformity. In view of these considerations, the time available for the development of an underclay might be reasonably increased to 250,000 years. Whatever assumptions may be selected, it is evident that Pennsylvanian time was amply sufficient to accommodate all of the sedimentary cycles that have been recognized, numerous though they may be.

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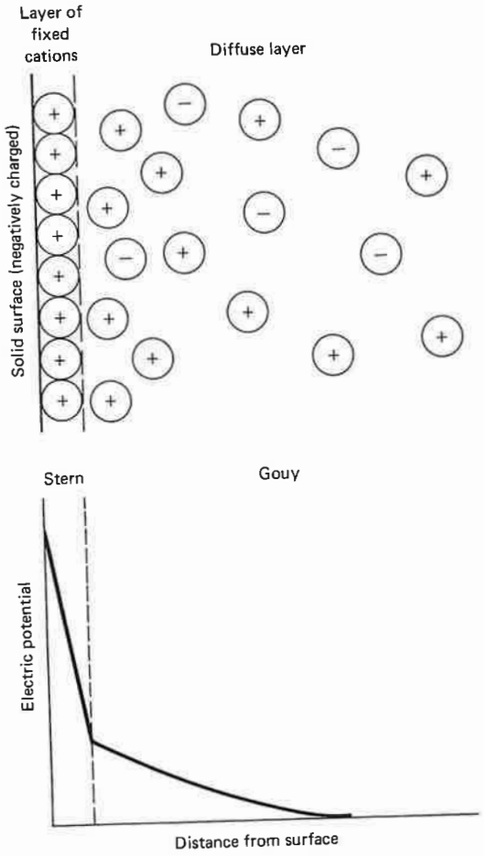


Figure 5-11 Schematic picture of the fixed (Stern) and diffuse (Gouy) layers.

by purely electrostatic forces or by formation of complexes with groups on the surface of the solid (see Chapter 15).

The stability of a colloidal suspension depends on the thickness of the Gouy layer, which depends on the potential at the outside of the fixed layer and, approximately, on the ionic strength of the solution. When two particles approach each other, the Gouy layer on one particle is repelled electrostatically by the Gouy layer on the other. This keeps the particles apart, and a stable suspension results. As ionic strength increases, the Gouy layer becomes compressed close to the particle. When this happens, the electrostatic repulsion that tends to keep the particles apart is not sufficient to counteract the van der Waals force, which attracts the particles toward each other, and the suspension is no longer stable. This is why clay minerals commonly form stable suspensions in fresh water, but flocculate in more saline solutions such as seawater. Although the stability of colloidal suspensions is approximately related to ionic strength, polyvalent cations have a disproportionately greater effect in causing flocculation than monovalent cations. For this reason polyvalent cations are often used in water treatment to cause flocculation.

Membrane Filtration

When the solid particles in a clay–water system are compacted, the Gouy layers on adjacent particles overlap. The solution in pores between adjacent grains will be made up of the Gouy layers only, and consequently anions will be almost excluded from the pores (Fig. 5-12), an effect called *anion exclusion*. When a pressure gradient is imposed on the solution in a clay–water system, water molecules can move through the pores but, as a consequence of anion exclusion, ions cannot (the theory is discussed by Hanshaw and Coplen, 1973). The clay thus behaves as a semipermeable membrane, allowing the passage of water but not ions. Clays do not act as perfect semipermeable membranes; they retain different ions with different degrees of effectiveness, causing a chemical fractionation as water passes through (Kharaka and Berry, 1973). Membrane filtration has been suggested to be a major process affecting the composition of water trapped in deeply buried sedimentary rocks (e.g., Graf, 1982). It would be effective only when the original sediments have undergone compaction, so it is not an important process in near-surface (depth less than 1 km or so) environments. It could be effective at shallower depths where the solution is very dilute (lake sediments) and hence the Gouy layers extend far from the particle, but this has not been documented in nature. There is considerable disagreement in the literature as to the overall importance of membrane filtration in influencing the chemistry of underground waters.

Ion Exchange

Clay minerals all exhibit ion exchange behavior to some degree, as do zeolites, colloidal oxyhydroxides, and natural organic compounds. In soil science and geology, cation-exchange capacity (CEC) is often measured by (and hence defined by) uptake and release of ammonium ions from 1M ammonium acetate solution at pH 7.0, al-

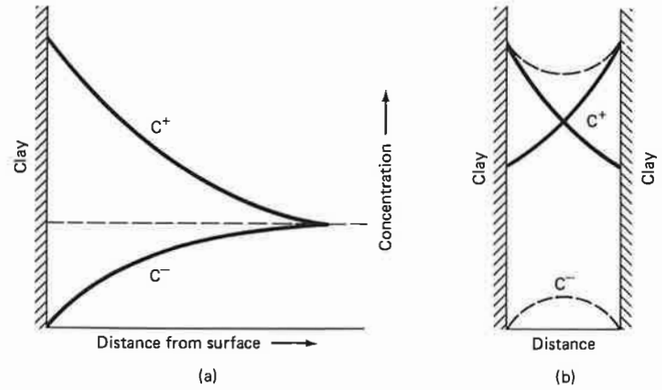
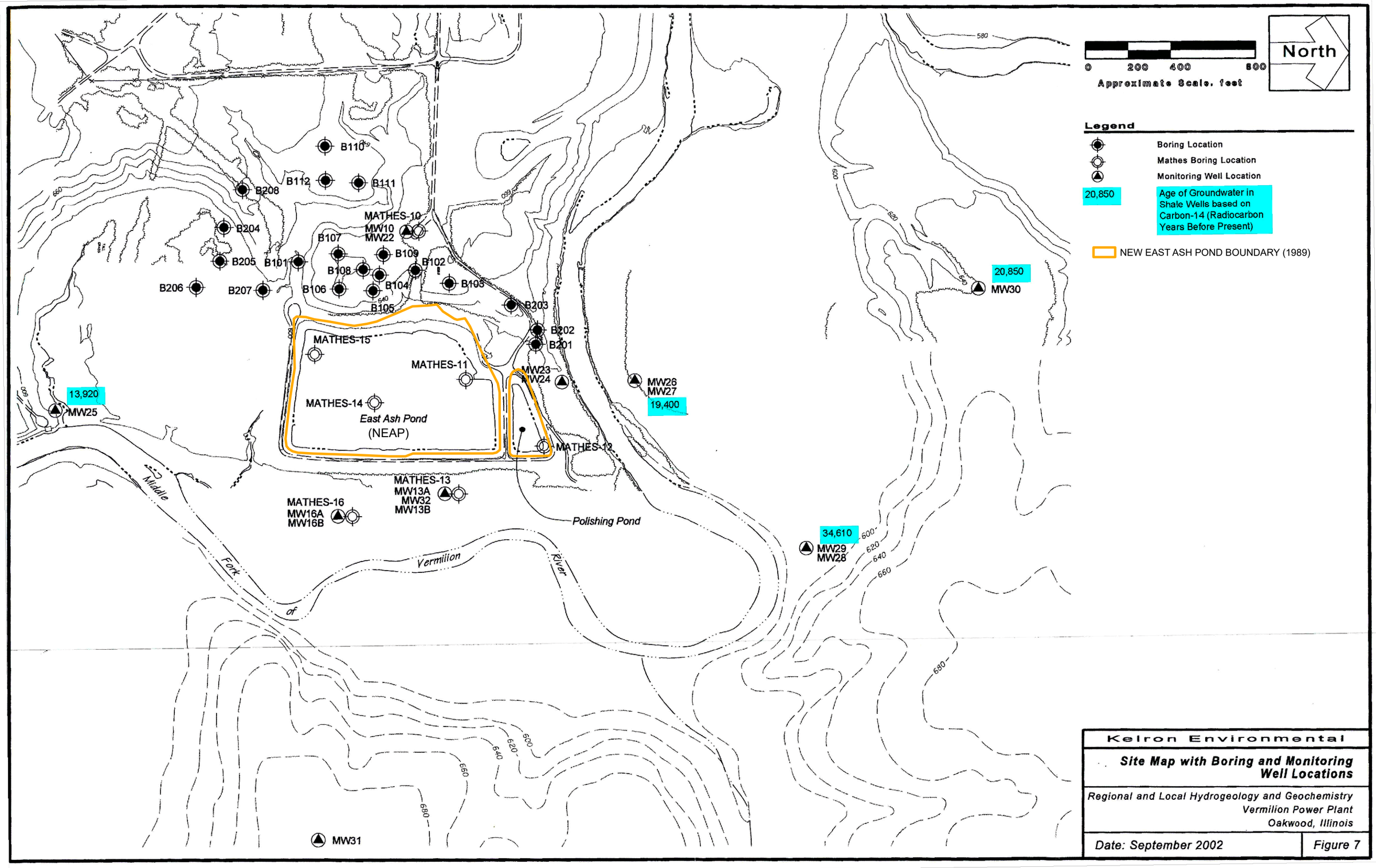


Figure 5-12 Concentrations of cations (C^+) and anions (C^-) (a) in the diffuse double layer of a single particle, and (b) in a pore between two closely approaching clay particles. Note how anions are excluded from the narrow pore.

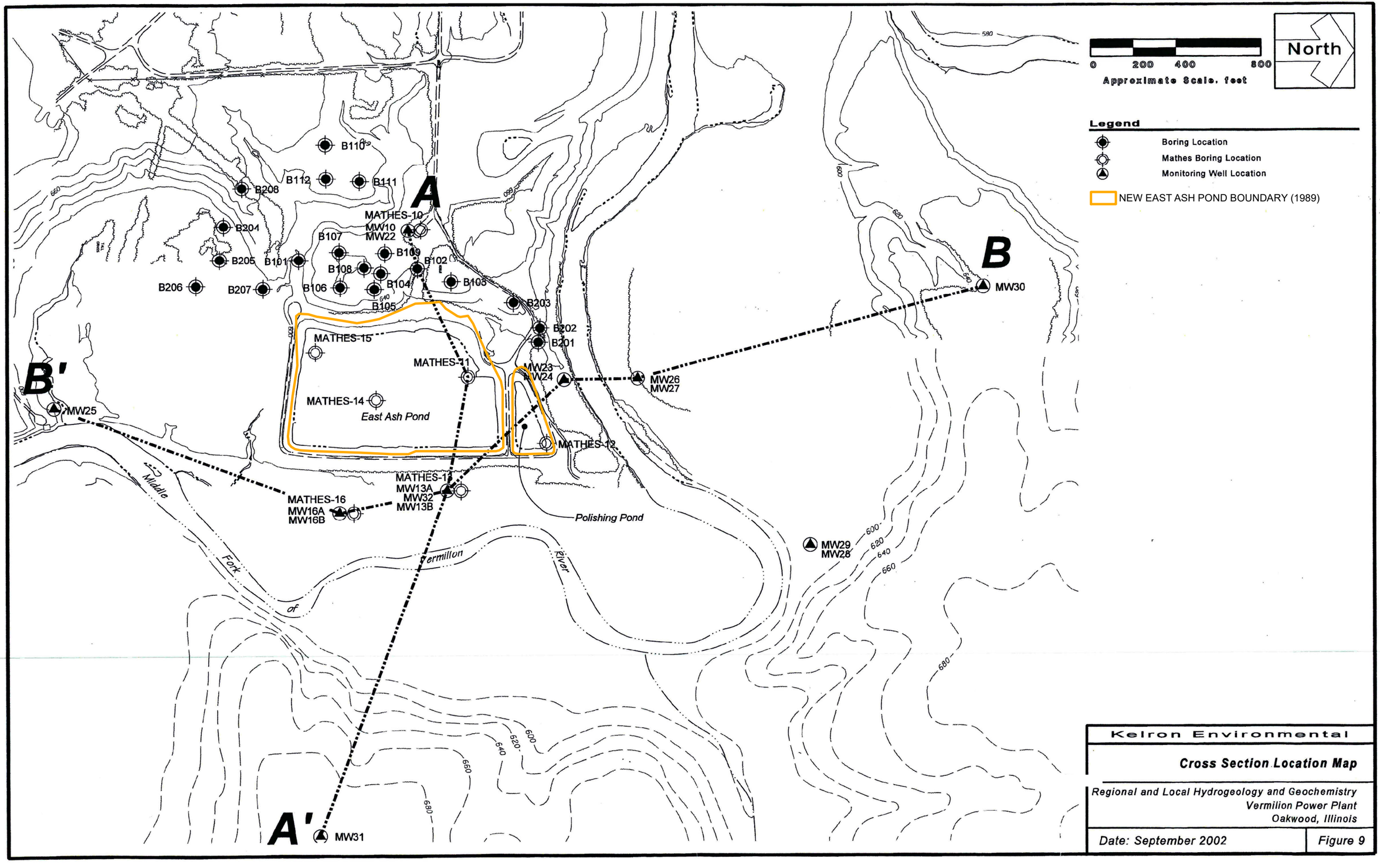
APPENDIX E
Excerpted figures from Kelron, 2003

Y:\Mapping\Projects\222285\MXD\Alt_Source_Dem\Vermillion\NEAP_912IE006\ASD_E006.aprx\Appendix F. Figure 7. Monitoring Wells



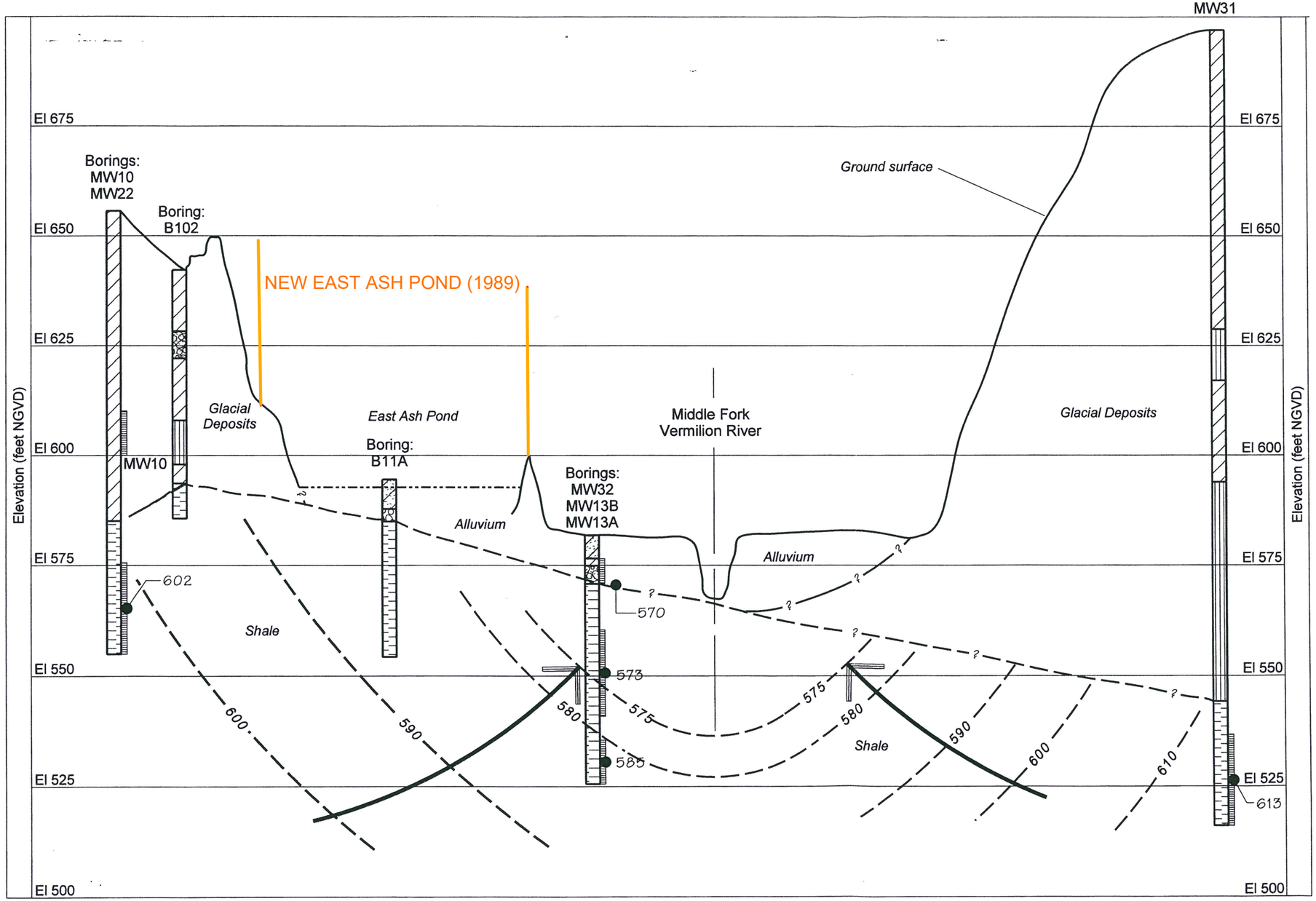
PROJECT: 169000XXXX | DATED: 12/10/2024 | DESIGNER: GALARNMC

Y:\Mapping\Projects\22\2285\MXD\Alt_Source_Dem\Vermillion\NEAP_912\E003\appendix\AppD. Figure 9. Cross Section Location Mapmxd.mxd



PROJECT: 169000XXXX | DATED: 5/2/2024 | DESIGNER: galarmmc
Service Layer Credits:

A West — A' East



0 150 300 600

Approximate Horizontal Scale: 1 in = 300 ft.
Approximate Vertical Scale: 1 in = 25 ft.
Vertical Exaggeration: 12x

Legend

Geology

- CL — Clay, silty clay, sandy clay, gravelly clay
- ML — Silts, clayey silts
- SC-SM — Clayey to silty sand
- SP-SW — Sand, gravelly sand
- GC-GM — Gravel. with silt and/or clay
- GP-GW — Gravel; gravel-sand mix
- SH — Shale

Monitoring Well Screen Interval

580 — Estimated Equipotential Lines (Lines of Equivalent Head)

Kelron Environmental

Equipotential Lines and Flowlines for Groundwater in the Shale Based on Observed Hydraulic Head in January 2002

Regional and Local Hydrogeology and Geochemistry
Vermilion Power Plant
Oakwood, Illinois

Date: September 2002 | *Figure 28*