Luminant

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

January 16, 2025

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 supplement to the Alternative Source Demonstration (ASD) submitted to IEPA December 20, 2024, 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.

In support of the previously submitted ASD referenced above, materials referenced within the document were included as attachments to the ASD or could be accessed at publicly accessible internet addresses provided in the References section. Reproduction licenses for the attached articles have since been granted by the journals.

Sincerely,

Dianna Tickner

Dianna Tickner
Sr. Director – Decommission and Demolition

Enclosures

Cartwright, K., 1970. Groundwater discharge in the Illinois Basin as suggested by temperature anomalies. Water Resources Research 6, No. 3: 912-918. https://doi.org/10.1029/WR006i003p00912. © John Wiley & Sons, Inc.

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Groundwater Discharge in the Illinois Basin as Suggested by Temperature Anomalies

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Abstract. Areas where ground water in the Illinois basin is moving vertically should be reflected by temperature anomalies. To test this hypothesis, an isothermal map for a depth of 500 feet was constructed, based on bottom hole temperatures of deep wells. This map was compared with a theoretical isothermal map for a depth of 500 feet that was made by projecting temperature gradients (calculated from the thermal conductivities of the rock) downward from the surface where mean annual air temperatures were known. The residual temperature map that was made on the basis of this comparison (calculated minus observed temperature) shows several warm and cool anomalies that are postulated to be discharge and recharge areas, respectively. Analysis of the curvature of the earth's thermal profile calculated for the basin suggests that approximately 59,000 acre-feet of ground water per year are discharged upward from the deep rocks in the Illinois basin. This figure is of the same magnitude as an estimated excessive groundwater discharge into the region's streams of 43,000 acre-feet, based on comparison of unit-area discharge of streams in the basin with streams in similar areas outside the basin. From a simplified model of the basin, a groundwater inflow of about 36,500 acre-feet from the surrounding highlands is estimated. A significant portion of this discharge must be through fracture zones associated with faults and anticlines in the basin, inasmuch as this amount of flow would require that the shales have a vertical permeability from one to three orders of magnitude higher than is generally observed. One such discharge area in southwestern Illinois is suggested by field data.

INTRODUCTION

Movement of ground water within the lithosphere has long been known to affect the flux of heat within the earth. *Van Orstrand* [1934] suggested that the movement of ground water caused variations in the geothermal gradient in the Salt Creek oil field, Wyoming. The effect of groundwater movement is significant because the natural heat flux density from the earth is small.

Stallman [1960] presented the basic equation for the simultaneous transfer of heat and water within the earth and suggested they might be used to measure the rates of groundwater movement. *Bredehoeft and Papadopulos* [1965] and *Stallman* [1965] presented solutions of the basic equations applied to the vertical movement of water for certain boundary conditions. The Bredehoeft and Papadopulos solution is used in this paper to estimate the quantity of ground water discharge from the Illinois basin.

The general differential equation for simultaneous nonsteady flow of heat and fluid through fully saturated, isotropic, homogeneous, porous medium was developed [*Stallman,* 1960] from consideration of a unit volume of the medium. The equation is

$$\frac{\delta^2 T}{\delta x^2} + \frac{\delta^2 T}{\delta y^2} + \frac{\delta^2 T}{\delta z^2} - \frac{c_w \rho_w}{k} \left[\frac{\delta(v_x T)}{\delta x} + \frac{\delta(v_y T)}{\delta y} + \frac{\delta(v_z T)}{\delta z} \right] = \frac{c\rho}{k} \frac{\delta T}{\delta t} \quad (1)$$

where

- v, velocity of fluid flow; direction of flow specified by subscripts x, y, z;
- T, temperature at any point at time t;
- t, time since flow started;
- c, specific heat of rock fluid complex;
- c_w, specific heat of fluid;
- ρ, density of rock fluid complex;
- ρ_w, density of fluid;
- k, thermal conductivity of rock fluid complex;
- x,y,z, Cartesian coordinates.

For steady one-dimensional (vertical) flow of heat and fluid, equation 1 according to *Bredehoeft and Papadopulos* [1965] becomes

$$k\frac{\delta^2 T}{\delta z^2} - v_z c_w \rho_w \frac{\delta T}{\delta z} = 0 \qquad (2)$$

which when solved subject to the boundary conditions

$$T_z = T_0 \text{ at } z = 0 \qquad (3)$$

$$T_z = T_L \text{ at } z = L \qquad (4)$$

where T_z is the temperature measurement at any depth z, T_0 is the uppermost temperature measurement, T_L is the lowermost temperature measurement, and L is the length of vertical section over which temperature is measured, yields

$$\frac{(T_z - T_0)}{(TL - T_0)} = f(\beta, z/L) \qquad (5)$$

where

$$f(\beta, z/_L) = \frac{[\exp(\beta z/L) - 1]}{[\exp(\beta) - 1]} \qquad (6)$$

and

$$\beta = \frac{c_w \rho_w v_z L}{k} \qquad (7)$$

β is a dimensionless parameter that is positive or negative depending on whether v_z is downward or upward. *Bredehoeft and Papadopulos* [1965] presented a table and type curves for the solution of equation 6.

ILLINOIS BASIN

The Illinois basin is an oval-shaped structural and topographic depression with over 9000 feet of maximum relief in the granite basement [*Bell et al.*, 1964] and 1000 feet maximum topographic relief. Definition of the exact limits of the basin vary. However, at its broadest defined limits the basin extends from the Ozark uplift on the southwest to the Cincinnati and Kankakee arches on the east and northeast.

Very little is known of the distribution of hydrostatic head within the rocks of the basin. The difference in head between the rocks on the periphery of the basin and the water table at the center is 100 to at least 500 feet [*Bredehoeft et al.*, 1963]. Theoretical analyses by *Toth* [1963] and *Freeze and Witherspoon* [1966; 1967; 1968], and work by *Hitchon* [1969] in the Western Canadian sedimentary basin suggest that basins of this general shape should be discharging water upward from the deep, basin-wide flow system.

A mechanism for the concentration of the highly saline brine found in the basin was suggested by *Bredehoeft et al.* [1963]. The character and origin of these brines were further discussed in a series of papers by *Clayton et al.* [1966] and *Graf et al.* [1965; 1966]. The consensus of these studies is that the water in the deep formations of the basin is in motion and that some upward discharge of ground water is taking place through the clay shales that act as an osmotic membrane.

This study estimates the quantity of water being discharged, and where and how the major portion of discharge may be taking place. Most, if not all, of the fluid being discharged is in areas of high vertical permeability associated with the structural features of the basin.

TEMPERATURE ANOMALY

To test the hypothesis of upward flow of water and its effect on the geothermal gradients, an isothermal map for a depth of 500 feet was constructed from recorded bottom hole temperatures of deep wells. The wells are not evenly distributed throughout the mapped area (Figure 1). The first six wells (maximum of two per section where many datum points are available) for each Congressional township were selected from the mineral resource records of the Illinois State Geological Survey. Only wells over 1000-feet deep were chosen and records of obviously poor quality were eliminated from the sample. About 2000 well records were used. The temperature at 500 feet was calculated for each well by assuming that a linear gradient existed between the bottom hole temperature and the mean annual air temperature [*Jones*, 1966]. The mean of the temperature at 500 feet for all the selected wells was calculated for each township and plotted as a single point in the township. The inaccuracies of this type of temperature data are well known, but the fairly high degree of internal consistency in the data suggests the approach is valid.

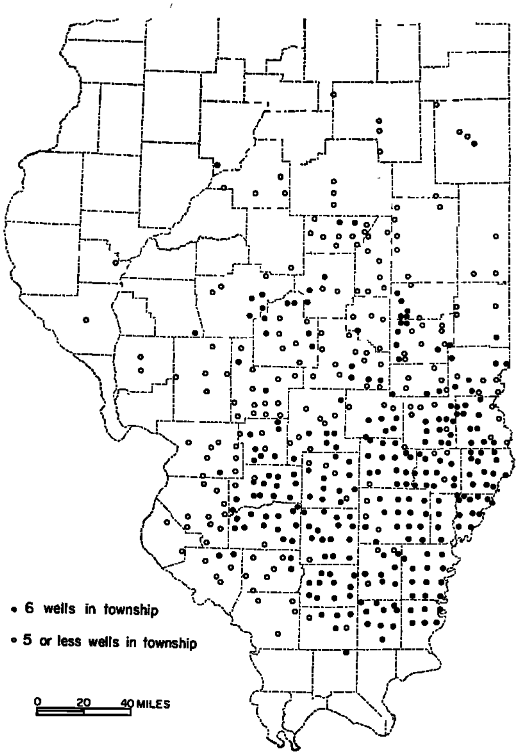

Fig. 1. Distribution of deep wells used in compiling isothermal map for 500-foot depth.

The resulting isothermal map (Figure 2) is a reasonable representation of the distribution of temperatures at the 500-foot depth. Two striking features appear on the map: (1) a general decrease in temperature from south to north reflects the trend of the mean annual air temperatures, and (2) the warm areas generally coincide with anticlinal areas and fault zones in the Illinois basin, which are also the principal oil producing areas in the state.

A theoretical isothermal map for the 500-foot depth was prepared (Figure 3) for comparison with the map based on well temperatures. For the theoretical map, temperatures at the 500-foot depth were calculated by estimating temperature gradients (based on assumed thermal conductivities of the rocks and geothermal gradient given below), and projecting the gradients downward from the surface where mean annual air temperatures were known. The air temperature data were from weather stations in the state [*Jones*, 1966]. The following thermal conductivities and geothermal gradients were used [*Cartwright*, 1968]:

Glacial sediments	0.0025 cgs units (cal/cm sec °C)
Pennsylvanian rocks	0.005 cgs units
Deep carbonate rocks	0.007 cgs units (and 1°F per 100 ft temperature gradient)

The thickness of the glacial drift in wide areas around the various weather stations was averaged.

A residual map (Figure 4) was then made to show the difference between the two isothermal maps by subtracting the observed temperature data from the calculated temperature data. The warm (negative) areas were assumed to be zones of upward movement (discharge) of water from deep aquifers in the basin, and the cool (positive) areas are zones of downward movement (recharge). Temperature anomalies in the northern third of the map probably are of little significance inasmuch as the data are sparse, and the thickness

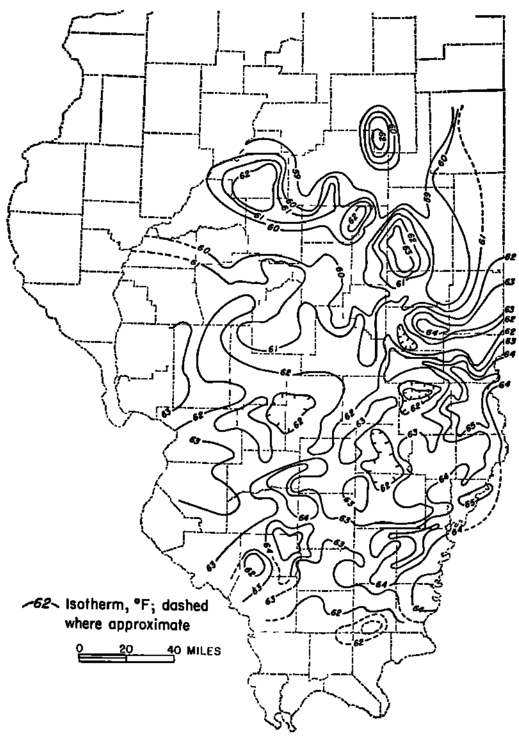

Fig. 2. Isothermal map for the 500-foot depth, based on temperature data from deep wells.

of glacial drift, which has the greatest effect on the calculated temperature values, varies greatly. The Mahomet buried bedrock valley [*Horberg,* 1950], for instance, which contains 300 to 400 feet of fill, is reflected on the map as a cool area. This could be the result of the permeable drift's acting as a recharge zone, but it is probably due to not taking the effect of the thick drift when the temperature was calculated completely into account.

The residual map (Figure 4) also reflects some of the structural features of the area. The Wabash valley fault zone and the DuQuoin-Louden anticlinal belt are anomalously warm and probably are the principal discharge areas. In the latter area, saline waters too brackish for human consumption immediately underlie the water table. The area along the Shawnee hills to the south and the Mississippi river area to the west are both cool areas, and data suggest that recharge is probably occurring.

VOLUME OF DISCHARGE

The mean velocity of upward movement of water in the Illinois basin was calculated from

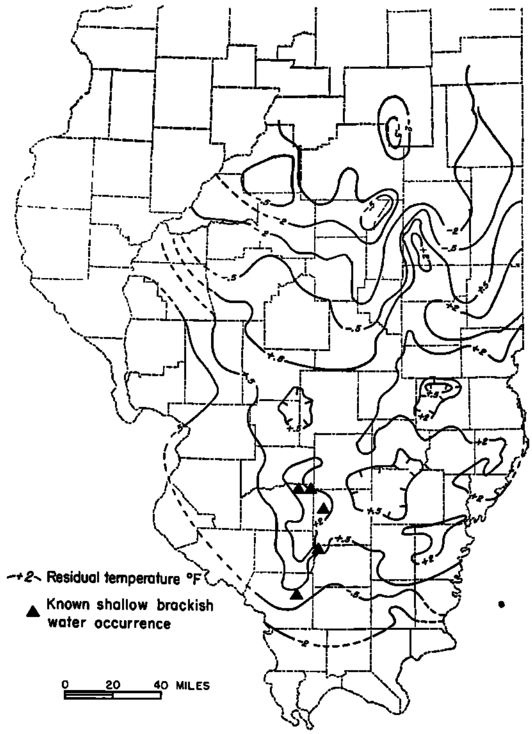

Fig. 4. Residual temperature map (calculated temperature minus observed temperature), showing anomalously warm (positive) and cool (negative) areas.

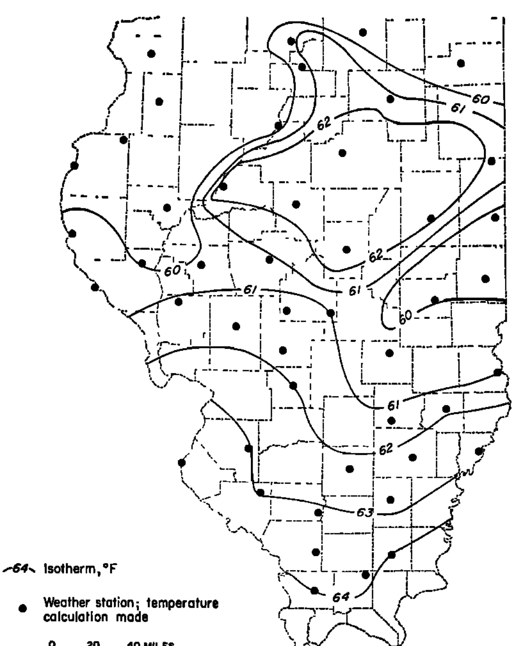

Fig. 3. Isothermal map calculated for 500-foot depth on basis of mean annual surface temperatures and thermal conductivity of the rocks.

the temperature data with equation 5. The average temperature in the warm discharge areas was determined at intervals of 300 feet for depths between 500 and 3500 feet, the range of depth that includes most oil wells in Illinois. At each 300-foot interval all points that fell within 50 feet of that depth were averaged to obtain a single value. The temperatures for 500 and 800 feet were determined by an upward extrapolation of the temperature data. The plotted temperature curve (Figure 5) compared with the type curves of *Bredehoeft and Papadopulos* [1965] yielded a velocity of 0.16×10^{-8} feet per second. The very small velocity can be detected because of the relatively large vertical distance over which the temperature is observed.

Most of the discharge probably takes place in the anomalously warm areas within a radius of 100 miles from the center of the basin. This is approximately 1800 square miles. The quantity of water discharged was calculated by using

$$Q = V_z A \quad (8)$$

where Q is the quantity of fluid discharge per unit of time, V_z is the velocity of fluid flow (upward), and A is the area over which discharge takes place. The discharge amounts to 59,000 acre-feet per year.

The quantity of water flowing into the Illinois basin was estimated by using the simplest model of *Bredehoeft et al.* [1963], which assumes the change of head over distance is linear (2.8×10^{-4} feet per feet). According to the model, all the water would pass through the sandstone aquifers (principally the Mt. Simon, St. Peter, Chesterian, and basal Pennsylvanian), which were assumed to average 3000 feet thick and have the permeability of the Mt. Simon sandstone of northern Illinois (1.34 feet per day according to *Walton and Csallany* [1962]). The discharge would be equal to the water that passes into the basin through the circumference of a circle with a radius of 100 miles, the center of which is the center of the basin. From this model it was calculated that 36,500 acre-feet of water per year moves into the basin.

Streams and rivers presently draining the central part of the Illinois basin have a normal annual groundwater runoff of about 2,670,000 acre-feet per year [*Walton,* 1965] exclusive of flow in the Wabash River which crosses the eastern part of the basin. The 59,000 acre-feet of discharge from the deeper rocks of the basin is only 2.2% of the total groundwater runoff, and only 0.7% of the total average stream discharge of 8.26 million acre-feet per year [*Mitchell,* 1957].

To determine whether streams of the Illinois basin have different discharge characteristics,

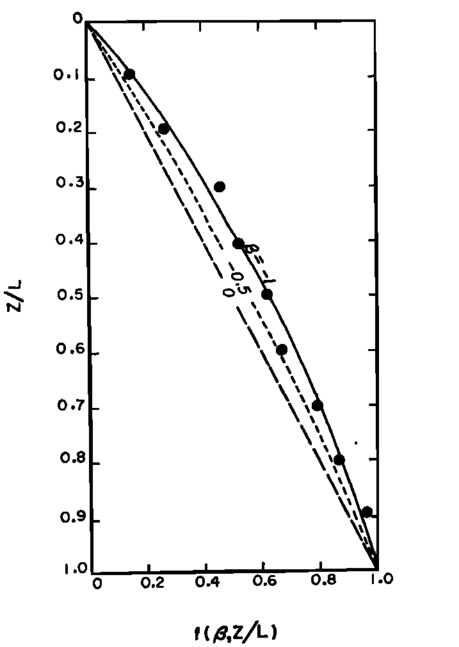

Fig. 5. Temperature profile (dots) in the Illinois basin compared with type curves of *Bredehoeft and Papadopulos* [1965]. The depth and temperatures of the profile are plotted as the ratios

$$\frac{Z - Z_0}{L} \quad \text{and} \quad \frac{T_z - T_0}{T_L - T_0} \qquad \text{(equation 5)}$$

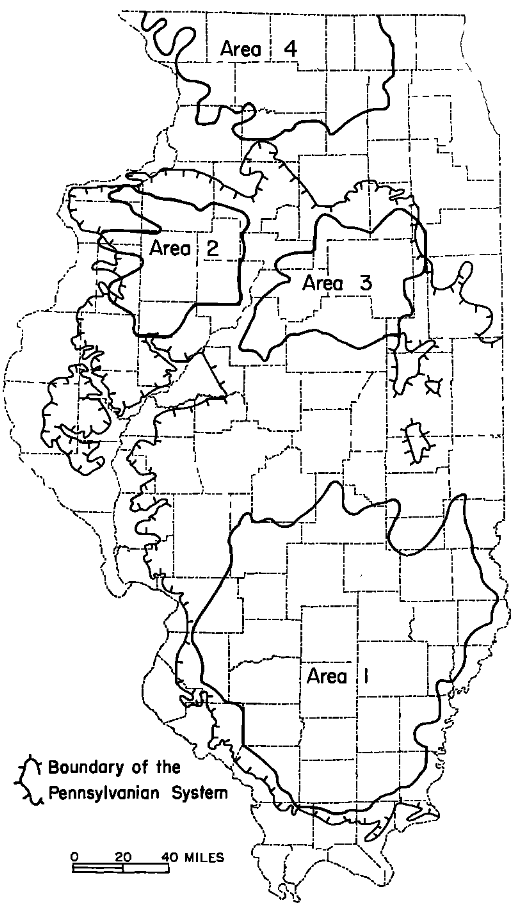

Fig. 6. Drainage areas studied for comparison of the groundwater discharge characteristics between years of normal and below normal precipitation.

TABLE 1. Average Annual Groundwater Runoff

Region	Precipitation, inches	Runoff in Year of Normal Precipitation, cfs/mi²	Runoff in Year of Below Normal Precipitation, cfs/mi²	Percent of Below Normal Year's to Normal Year's Runoff	Area of Drainage Basin, mi²
1	35 to 45	0.19	0.11	57.9	10,161
		0.23*	0.14	60.9	6,609
2	34 to 37	0.19	0.09	44.3	4,731
3	33 to 37	0.16	0.06	37.5	2,984
4	33 to 34	0.31	0.21	67.7	9,663

* Stream with high drought period flow only.

a comparison was made of the annual groundwater runoff or base flow of streams, for four regions of the state [*Walton,* 1965]. The regions are shown in Figure 6. Region 1 is the area where discharge from the Illinois basin occurs. Regions 1, 2, and 3 are geologically similar and contain generally thin glacial tills [*Piskin and Bergstrom,* 1967] overlying rocks of the Pennsylvanian system, principally shale. Region 4 is different and has generally thin glacial tills overlying permeable Ordovician and Silurian carbonates. The evapotranspiration in the four regions varies in a pattern similar to the variation in precipitation [*Jones,* 1966] (Table 1). The variability in precipitation is slightly greater in region 1 than in the other three areas [*Huff and Changnon,* 1963].

The figures in the table suggest that the groundwater runoff characteristics of region 1 resemble those of region 4 rather than those of regions 2 and 3, even though region 1 is more similar geologically to the latter two.

Region 1 had a higher groundwater runoff in drought years in comparison to the other three regions and at least part of it must be discharge of deep basin waters. All areas except region 1 have 0.10 cfs/mi² differences between below-normal and normal years; area 1 has only a 0.08 cfs difference or a 0.09 cfs difference if we consider only streams with more than 55% of below-normal to normal discharge. This may be merely fortuitous; nevertheless, I assumed that the 0.01 cfs extra groundwater runoff of the streams with high flow during drought years is the result of discharge of water from the deep basin groundwater flow system. This amounts to 43,000 acre-feet of water per year.

If the shale of the Illinois basin has the same permeability of 0.13×10^{-4} feet per day found in the Ordovician shales of northern Illinois [*Walton,* 1960] and 100 feet of hydraulic head, the possible leakage upward would be only 2000 acre-feet per year. Thus, possibly as much as 95% of the discharge must be moving upward through vertical fractures. Concentration of fractures are present within the main structural features of the basin and therefore saline water discharges in the area of these features.

Regions where naturally brackish water is encountered immediately below the water table are shown on Figure 4. Brackish water also is found elsewhere, but from data presently available, it cannot be determined with certainty whether those occurrences are natural or related to the activities of man. The brackish water occurs within the areas of anomalously warm temperatures (Figure 4) near the main structural features of the basin. Furthermore, the anomalously cool area along the southern edge of the map coincides with the region of recharge to the thick basal Pennsylvanian sandstones that dip steeply toward the center of the basin.

DISCUSSION

Hydrogeologists working in the Illinois basin area have long believed that ground water is circulating in the basin. Lack of data on the fluid potentials in the water transmitting zone has necessitated reliance on chemical data and the theoretical explanation of these data. Theoretical calculations supported by chemical data suggest hydrodynamic rather than hydrostatic conditions. This paper further corroborates this hypothesis, and suggests that the quantity of groundwater discharge is about 40,000 to 60,000 acre-feet per year.

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Groundwater

Recharge and Groundwater Flow Within an Intracratonic Basin, Midwestern United States

by Samuel V. Panno[1], Zohreh Askari[2], Walton R. Kelly[3], Thomas M. Parris[4], and Keith C. Hackley[5]

Abstract

The conservative nature of chloride (Cl^-) in groundwater and the abundance of geochemical data from various sources (both published and unpublished) provided a means of developing, for the first time, a representation of the hydrogeology of the Illinois Basin on a basin-wide scale. The creation of Cl^- isocons superimposed on plan view maps of selected formations and on cross sections across the Illinois Basin yielded a conceptual model on a basin-wide scale of recharge into, groundwater flow within and through the Illinois Basin. The maps and cross sections reveal the infiltration and movement of freshwater into the basin and dilution of brines within various geologic strata occurring at basin margins and along geologic structures. Cross-formational movement of brines is also seen in the northern part of the basin. The maps and cross sections also show barriers to groundwater movement created by aquitards resulting in areas of apparent isolation/stagnation of concentrated brines within the basin. The distribution of Cl^- within the Illinois Basin suggests that the current chemical composition of groundwater and distribution of brines within the basin is dependent on five parameters: (1) presence of bedrock exposures along basin margins; (2) permeability of geologic strata and their distribution relative to one another; (3) presence or absence of major geologic structures; (4) intersection of major waterways with geologic structures, basin margins, and permeable bedrock exposures; and (5) isolation of brines within the basin due to aquitards, inhomogeneous permeability, and, in the case of the deepest part of the basin, brine density effects.

Introduction

The geochemical origin and the movement of brines within intracratonic sedimentary basins have been the subject of numerous studies for much of the latter half of the 20th century (e.g., Bethke et al. 1988; Hanor 1994). An understanding of these influences on the groundwater chemistry within the basin is important for water resource evaluation and natural resource exploitation. Moreover, reservoirs in intracratonic basins have been used for storage of natural gas, and the disposal of a variety of industrial, oil field, and other types of wastes (e.g., Bergstrom 1968). The magnitude of this disposal has increased considerably with injection of flow-back waters from unconventional oil and gas reservoirs and could increase with geologic carbon sequestration (Locke et al. 2013).

The Illinois Basin in the U.S. Midwest (Figure 1) is an anomaly among intracratonic basins because it contains no known halite-bearing evaporite sequences that could contribute to brine formation. The chemical composition and origin of brines in the Illinois Basin have been shown to be unique for Cambrian, Ordovician, Silurian–Devonian, and Mississippian–Pennsylvanian strata (Stueber et al. 1987; Walter et al. 1990; Stueber and Walter 1991, 1994; Panno et al. 2013). Groundwater movement within the Illinois Basin was studied by Cartwright (1970) using thermal anomalies in the southern half of Illinois and by Siegel (1989) using stable isotopes in northern Illinois. Both concluded that groundwater flows toward the center of the basin becoming more sluggish with depth, and discharges upward across confining units. Cartwright (1970) further suggested that upward movement of groundwater should occur along fractures associated with geologic structures.

Total dissolved solids (TDS) and chloride (Cl^-) concentrations of brines within intracratonic basins typically increase with depth (Domenico 1972). Within the Illinois Basin, Cl^- concentrations range from about 1 mg/L in shallow aquifers to over 200,000 mg/L for the deepest Paleozoic strata (Panno et al. 2013). Variable permeability and hydraulic gradients within Paleozoic

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Article impact statement: Development of a conceptual model of recharge to and groundwater flow within and through the Illinois Basin using chloride concentrations on plan-view maps and cross section.

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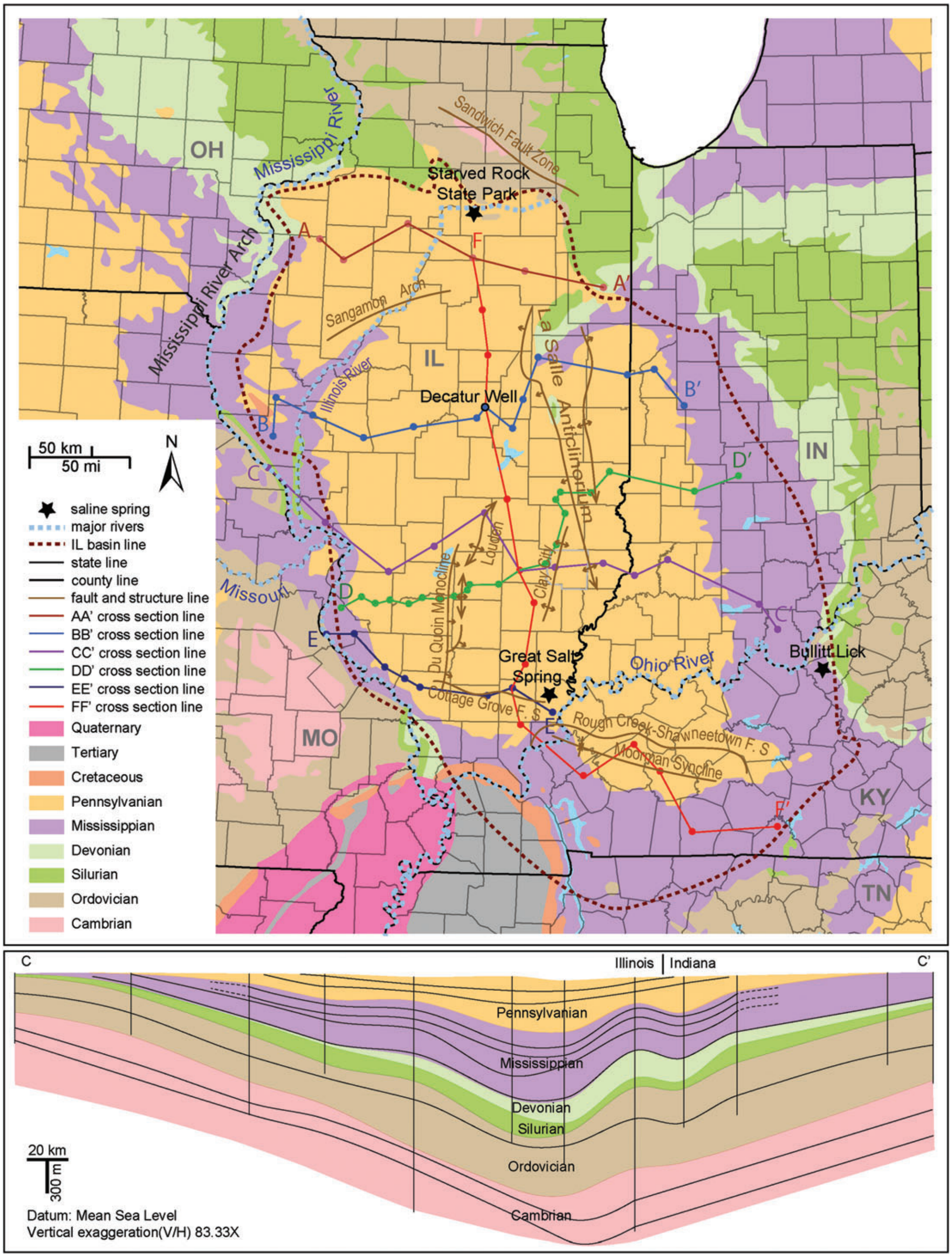

Figure 1. Cross section location map showing bedrock geology and structural features within the Illinois Basin. The bedrock geology was modified from Young (1992). East-west cross section C–C′ (at the bottom of the figure) shows the major strata, by age, of the basin.

strata, freshwater recharge at the margins of the basin and along zones of high permeability, and migration of brines through fractures associated with structural features all can cause departures from a monotonic increase in TDS and Cl^- concentrations with depth. Given the absence of halite-containing evaporites within the Illinois Basin, the conservative nature of Cl^- should allow it to act as a natural tracer revealing zones of recharge and preferential groundwater flow paths into, through, and out of the Illinois Basin (Figure 1). Chloride distribution should also indicate zones of low and high permeability, as well as zones of low flow, stagnation, or both. Mapping the distribution of Cl^- concentration in cross sections provides an efficient means of identifying dilution of basin brines within Paleozoic strata, mixing between aquifers, the isolating effects of aquitards, and potential flow paths along geologic structures (e.g., Panno et al. 1994).

Whereas, there has been a great deal of research on the Illinois Basin, previous studies have focused on selected formations and only portions of the basin. No basin-wide scale study has been done that would provide a comprehensive understanding of the hydrogeology of the Illinois Basin. Consequently, there is limited information regarding groundwater movement within and only speculation regarding discharge from the basin. The purpose of this investigation was to develop a conceptual model of recharge to, groundwater movement within, and discharge from the Illinois Basin on a basin-wide scale. To do this, we created plan-view maps of selected formations and detailed cross sections extending across the Illinois Basin and added Cl^- concentration data from oil and gas wells, municipal and private water wells, gas-injection wells, and published data. The Cl^- concentrations are represented with symbols and isocons on maps and cross sections that yield information regarding the current hydrogeologic state of the basin. This is important because recharge, groundwater movement within, and discharge from the basin can have a direct bearing on the transport of hydrocarbons, the feasibility of the sequestration of CO_2, and maintaining groundwater quality in those areas affected by basin brines and could provide insight into the source or flow paths of brines for the formation of Mississippi Valley-type ore deposits.

Geology and Hydrogeology of the Illinois Basin

The geology of the Illinois Basin is summarized from Collinson et al. (1988) and Kolata and Nelson (2010). Briefly, the Illinois Basin developed on Precambrian crystalline basement and now underlies most of the state of Illinois, western and southwestern Indiana, western Kentucky, and a portion of northwestern Tennessee (Figure 1). The basin is filled with Paleozoic marine sedimentary rocks ranging from Cambrian through Pennsylvanian that gently dip toward the center of the basin and extend to a depth of up to 9144 m along the Rough Creek Graben in western Kentucky (Goetz et al. 1992; Figure 1). The geometry, distribution, and interrelationships of the carbonate rocks, sandstones, and shales of the basin play a key role in recharge to and groundwater flow within the basin. Paleozoic sandstones and carbonate rocks whose groundwater is brackish to saline elsewhere in the basin, constitute productive aquifers in the northern-most part and along the eastern and western margins of the Illinois Basin, and shales constitute effective aquitards within the basin.

Cambrian and Ordovician aquifers are used extensively as a source of potable water in the northern third of Illinois (Larson and Herzog 2004). The Cambrian Mount Simon Sandstone is rarely used because it is only potable in the northern one-fifth of the state and has a moderately low permeability due to its well-cemented nature. Shale, siltstone, and dolomite of the overlying Eau Claire Formation act as a confining unit. The overlying Ironton-Galesville Sandstone is made up of a well-sorted and fine-grained sandstone, confined by overlying dolomites, shales and some sandstones, and provides a reliable potable water source. The Ordovician Glenwood-St. Peter Sandstone and overlying fractured and creviced Galena-Platteville Dolomite constitute major aquifers for northern Illinois. Because of their close proximity, these aquifers and are often combined into a single hydrogeologic unit referred to as the Cambrian-Ordovician aquifer. The St. Peter Sandstone is a relatively thick, well-sorted, fine-to medium-grained and loosely cemented sandstone of marine origin and belongs to the Ancell Group, which includes the overlying Glenwood Formation made up of sandstone, dolomite, and shale (Willman et al. 1975). In addition to being a prolific aquifer, the St. Peter Sandstone has long been known as a source of high-quality pure quartz sand in northern Illinois where it is exposed at the surface near, within, and north of Starved Rock State Park (Lamar 1928). The St. Peter Sandstone ranges from 1 to up to 275 m thick, averages between 30 and 100 m thick throughout the Illinois Basin (Willman et al. 1975), and is either exposed or shallowly buried in northern Illinois and at the northern margin of the basin. In this article, we focused on the water quality data from the St. Peter Sandstone. The Upper Ordovician Maquoketa Shale constitutes a confining unit between the underlying Cambrian-Ordovician aquifer and overlying Silurian strata.

Silurian strata consist of mostly fractured and creviced dolomite in the northern part of the basin and limestone in the southern part of the basin. Because of its karst nature, water yields range from small to very large. Devonian strata are predominantly limestone with some dolomite and shale; these strata are not present in the northern part of the basin because of erosion. These strata yield only small to moderate volumes of groundwater and are confined from the overlying Mississippian strata by the New Albany Shale (Larson and Herzog 2004).

Similarly, Mississippian strata are missing from the northern part of the basin because of erosion and are made up of limestone, with lesser amounts of dolomite, shale, siltstone, and sandstone. These strata are exposed on the margins of the Illinois Basin in western and southwestern Illinois and on the eastern margin in central Indiana, and are well known for their karst nature. Overlying Pennsylvanian strata are made up of predominantly shale with beds of sandstone, siltstone and limestone, and coal measures. These strata are thin to missing in the extreme northern part of the Illinois Basin due to erosion. Pennsylvanian strata typically constitute an aquitard, although some of its sandstone and limestone layers can yield small amounts of potable groundwater in the vicinity of outcrop areas. In much of Illinois and Indiana, Paleozoic rocks are capped by a thick layer of Pleistocene glacial drift that includes thick sand and gravel layers that are typically sandwiched between clay-rich tills. The sand and gravel deposits are used extensively in these states as freshwater aquifers; the Mahomet aquifer is a classic example of a glacial drift aquifer (e.g., Kempton et al. 1991).

Groundwater of the Illinois Basin ranges from extremely fresh Ca-HCO_3^- type water at the near surface to concentrated mixed-cation-Cl^- brines at the deepest part of the basin where Cl^- concentrations can be hundreds of grams per liter (Clayton et al. 1966). The salinity of the groundwater within the basin is typically stratified (Panno and Hackley 2010) with most shallow groundwater containing Na and Cl^- concentrations in sand and gravel aquifers between 1 and 15 mg/L for each ion (Panno et al. 2006). The sources of the Na-Ca-Cl-type brines of the Illinois Basin were studied by Stueber et al. (1987), Walter et al. (1990), Stueber and Walter (1991, 1994), Panno et al. (2013), and Labotka et al. (2015, 2016). These studies suggested, based on halide–halide and halide–cation ratios, and stable isotopes ($^{87}Sr/^{86}Sr$, δD and $\delta^{18}O$), that brines of the Illinois Basin originated as evaporated seawater and are composed of four geochemically distinct fluid regimes (Cambrian, Ordovician, Silurian–Devonian, and Mississippian–Pennsylvanian). Petroleum is found in Ordovician through Pennsylvanian rocks in the central and southern parts of the basin, and groundwater within these strata is highly saline. Because of the high salinity, few systematic hydrogeological studies have been conducted in these regions.

Methodology

Five east-west and one north-south cross section were constructed to illustrate the subsurface distribution of Cl^- in the Illinois Basin (Figure 1). The geologic data for the cross sections were compiled from geophysical logs from the Illinois State Geological Survey (ISGS) database and imported to GeoGraphix Discovery v5000 software (LMK Resources Inc., Houston, Texas) to create the cross sections and index maps. Boreholes that provided geologic data are represented as vertical lines in the cross sections; geologic structures were compiled from Nelson (1995).

The cross sections were populated with more than 600 Cl^- concentrations for groundwater samples from Cambrian through Pennsylvanian strata. Chloride concentration data are from Bartow et al. (1909), Meents (1952), Keller (1983), McIntosh et al. (2002), Panno et al. (2013), the Illinois State Water Survey (ISWS) Groundwater Quality Database (data available from ISWS on request), and the Kentucky Geological Survey (unpublished data). Well depths and screened intervals (or formation[s] from which groundwater was accessed) are available from these sources. Where brine data were acquired from oil fields, we used only samples collected before the onset of waterflood operations in oil fields to avoid possible contamination by mixing of brines or fresher waters from different stratigraphic units or dilution/contamination from drilling fluids. The Cl^- concentrations are represented with symbols, and by hand-contoured isocons, which represent locations of equal Cl^- concentrations. Adobe Illustrator CC 2015 (Adobe Systems, Incorporated, San Jose, California) was used for final editing and adding Cl^- concentration data for cross sections.

Chloride and TDS concentrations are highly correlated for these samples. The following equations developed by the authors of this article from data collected from fresh water aquifers, NaCl-enriched groundwater, and oil field brines in Illinois, were used to convert TDS concentrations to Cl^- concentrations (both in mg/L). Equations 1 and 2 were used for samples with TDS concentrations less than and greater than or equal to 5000 mg/L, respectively:

$$< 5000\,\mathrm{mg/L} : \mathrm{Cl}^- = 0.0022 \times \mathrm{TDS}^{1.5328} \quad \left(R^2 = 0.895\right) \tag{1}$$

$$\geq 5000\,\mathrm{mg/L} : \mathrm{Cl}^- = 0.637 \times \mathrm{TDS} \quad \left(R^2 = 0.989\right) \tag{2}$$

The relationship between TDS and Cl^- is supported by others working with a spectrum of water ranging from fresh to concentrated brines (Frape et al. 1984). For this article, the conversion was used for a direct comparison of Cl^- concentrations in cross sections and plan-view maps.

In addition to the cross sections, Cl^- isocon maps using simple interpolation were prepared for the Cambrian Mount Simon Sandstone (Figure 2) and the Ordovician St. Peter Sandstone (Figure 3). It is not clear, based on the sources of our data, whether the wells intersected both the Glenwood and St. Peter Sandstones or just the St. Peter Sandstone. Given their close proximity, and for our purposes we refer to the aquifer as the St. Peter Sandstone. The shaded counties contain one or more data points used in creating and contouring the St. Peter Sandstone map. A similar map, prepared for the Mount Simon Sandstone based on TDS data reported by Mehnert and Weberling, (2014; Figure 2), allowed comparison of Cl^- isocons with those of the St. Peter Sandstone (Figure 3). Not all cross sections and plan-view maps have the same density of data; consequently, some uncertainty/bias may be present in the interpretations. However, given the drilling activity in searching for fresh groundwater in the Illinois Basin, it is unlikely that formations containing potable groundwater would have gone undiscovered for more than a century.

Results and Discussion

Here we present, for the first time, plan view maps of selected formations and cross sections of the Illinois Basin containing Cl^- concentrations and isocons whose variability and patterns reflect the effects of freshwater recharge into and within a brine-dominated flow system. These patterns may be used as indicators of recharge, freshwater-brine mixing, cross-formational and flow-through movement of groundwater, and areas of brine stagnation within the basin.

Cambrian–Ordovician Aquifers

The aquifers of the Cambrian Mount Simon Sandstone, and the Ordovician Ironton-Galesville Sandstone, Glenwood-St. Peter Sandstone and Galena-Platteville Dolomite were referred to as the Cambrian-Ordovician Aquifer by Siegel and Mandel (1984) and Siegel (1989). However, they did not include the lowermost Mount

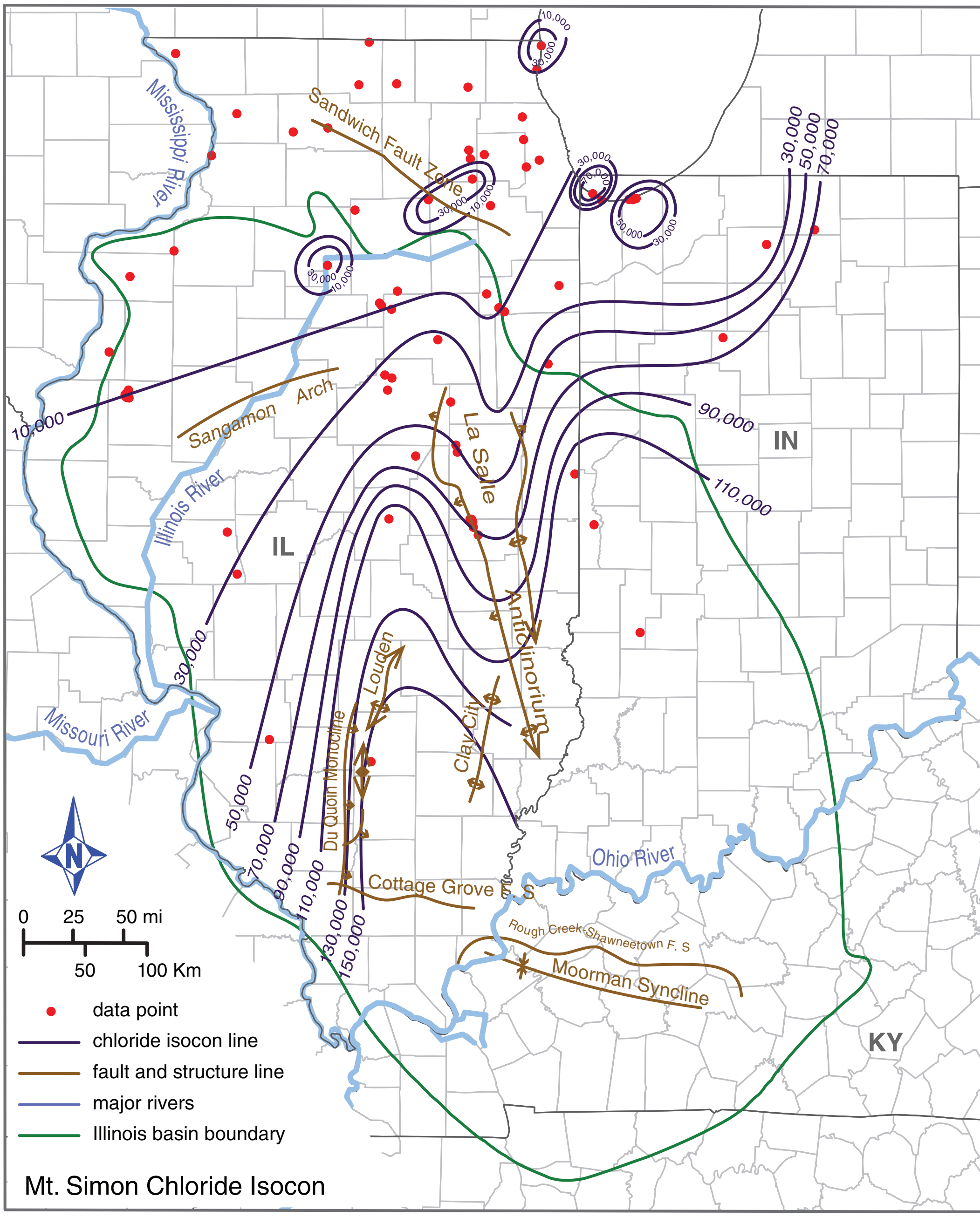

Figure 2. Chloride isocons in groundwater for the Mount Simon Sandstone. Water quality data (as TDS) are from Mehnert and Weberling (2014) and were converted to Cl^- concentrations using Equations 1 and 2.

Simon Formation because of the relatively high salinity of groundwater within this sandstone. These formations are used extensively in the northern third of Illinois for potable groundwater by municipalities and industries with wells that are often open to multiple aquifers (Larson and Herzog 2004).

Mount Simon Sandstone

The Mount Simon Sandstone represents the base of the Paleozoic sedimentary rock sequence that makes up the Illinois Basin. Unlike the St. Peter Sandstone, the Mount Simon Sandstone is rarely used as a freshwater resource because of its elevated TDS throughout the Illinois Basin. Mehnert and Weberling (2014) prepared a map of the distribution of TDS of brines within the Mount Simon Sandstone for much of the Illinois Basin. The data for this formation are from wells that are screened only within the Mount Simon Sandstone. We converted the TDS into Cl^- concentrations (for consistency within this investigation), contoured the data by hand, and added the Illinois River and pertinent geologic structures for interpretation purposes (Figure 2).

The Mount Simon isocon map shows preferential recharge from the northern, northwestern, and western boundaries of the Illinois Basin, and from north to south along the LaSalle Anticlinorium. The map also shows

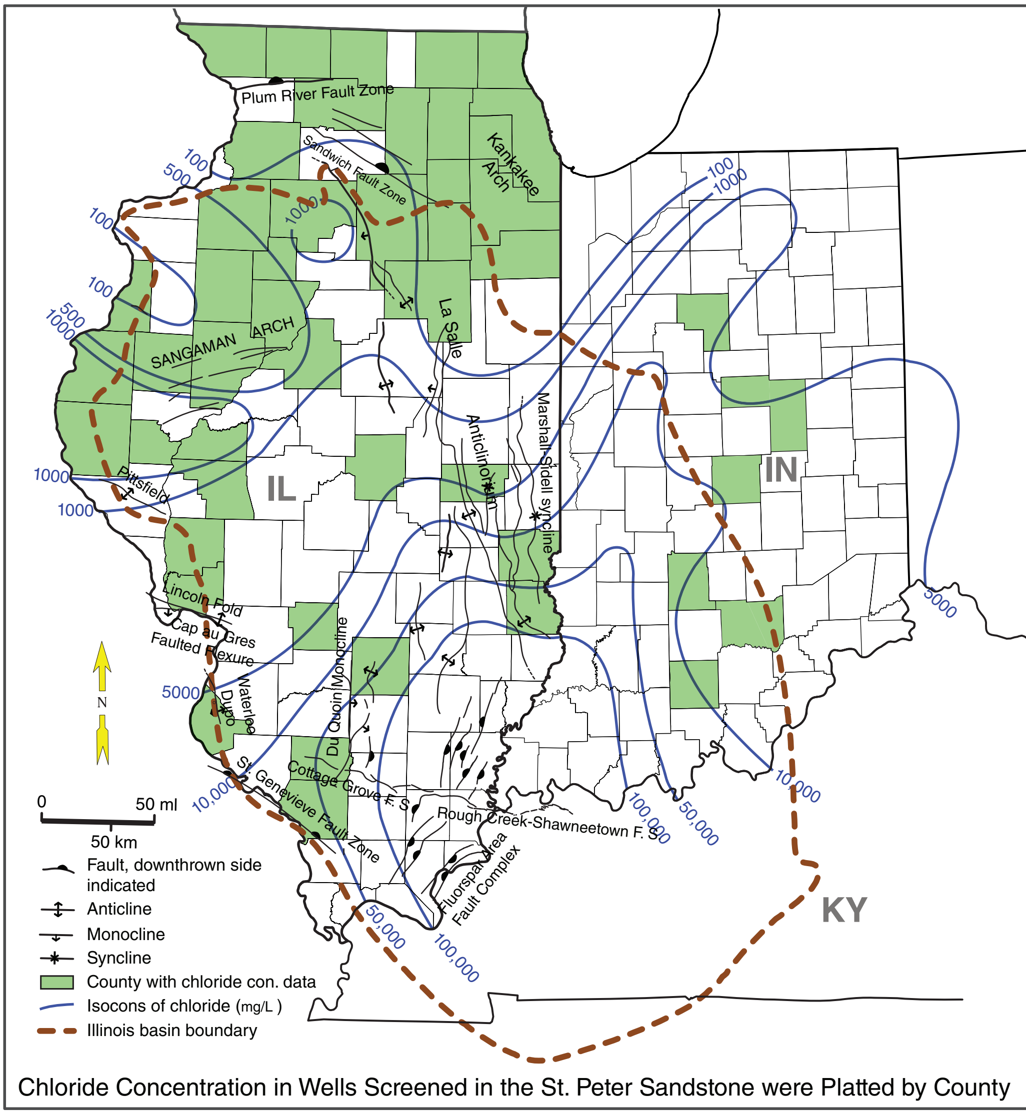

Figure 3. Chloride isocons in groundwater for the St. Peter Sandstone. Water quality data are from groundwater samples from wells screened in the St. Peter Sandstone. All concentrations are from published data and were plotted by county.

the presence of concentrated brines in the center of the basin in southern Illinois. Preferential recharge along the LaSalle Anticlinorium is of particular interest. The LaSalle Anticlinorium is a large geologic feature made up of numerous subparallel structures that collectively extend from southeastern Illinois to north-central Illinois and include anticlines, domes, monoclines, and synclines (Nelson 1995). Uplift of the LaSalle Anticlinorium occurred primarily during the late Paleozoic Era (Late Mississippian) but before the Pennsylvanian, and resumed after the Pennsylvanian. The anticlinorium was interpreted by Nelson (1995) to be the result of fault movement and displacement within the crystalline basement during the Late Paleozoic Era. Nelson (1995) suggests that the faults die out as they cut upward into the sedimentary rocks, and the structures of the LaSalle Anticlinorium become essentially drape folds. Recent seismic-reflection profiles by Kamp et al. (2016) suggest that the anticlinorium may be a fault system with strike-slip displacement.

The Mount Simon Cl^- isocon map (Figure 2) shows that salinity anomalies in the northern part of the basin and around the edge of Lake Michigan coincide with the Illinois River and the Sandwich Fault Zone. The saline anomaly farthest west and along the Illinois River (within and near Starved Rock State Park) contains nearly 40,000 mg/L of Cl^-. Just north and south of the anomaly, Cl^- concentrations are only 319 mg/L or less, and 7000 mg/L or less, respectively. This saline anomaly is coincident with the Illinois River and is probably associated with saline springs (Willman and Payne 1942) and relatively shallow saline wells (Panno, ISGS, unpublished data) of the Starved Rock State Park and surrounding area. The very low Cl/Br mass ratio of this groundwater (149 to 216; Panno, ISGS, unpublished data) suggests that the salinity originates from a mixture of brines from the underlying Cambrian and Ordovician strata, and perhaps crystalline basement brines (Table S1, Supporting Information). The upwelling of crystalline basement brines at least into lower Cambrian strata is likely, based on work by Panno et al. (2013) and Labotka et al. (2015, 2016).

St. Peter Sandstone

The distribution of Cl^- on the isocon map for the St. Peter Sandstone suggests that recharge takes place along the northwestern (from Iowa) and central and northeastern parts (from northern Illinois) of the margins of the Illinois Basin (Figure 3). Recharge in these areas and groundwater flow into the Illinois Basin within this formation is consistent with groundwater flow directions for the northern and northeastern portion of the Illinois Basin identified by Siegel (1989) and Young (1992) based on predevelopment potentiometric surface data. Stable isotope data were determined from saline water samples from the St. Peter Sandstone collected from a well near Decatur, IL located about 160 km south of Starved Rock State Park (Figure 1), about 50 km south of Siegel's (1989) study area. The Decatur, Illinois, sample showed isotopically light (δD and δ^{18}O of −61.7 and −9.13, respectively) indicating a component of Pleistocene glacial meltwater (Panno and Fanta, unpublished report, Electronic Supplement). These data are consistent with those of samples collected from wells within the St. Peter Sandstone located in the vicinity of the Decatur well (Kelly, ISWS, and Panno, ISGS, unpublished data; Figure 1).

The Cl^- isocons also show that enhanced recharge is occurring horizontally along the LaSalle Anticlinorium (Figure 3) similar to that of the Mount Simon Sandstone (Figure 2). Dilation of fractures along faults and folds associated with the anticlinorium could provide preferential groundwater flow paths for groundwater (e.g., Bethke 1986). The Cl^- isocons of the St. Peter Sandstone (Figure 3) reveal that enhanced recharge is occurring horizontally along the LaSalle Anticlinorium (Figure 3) very similar to that of the Mount Simon Sandstone (Figure 2). We suggest, based on these isocon maps, that the LaSalle Anticlinorium provides structural controls on recharge and groundwater movement within the Illinois Basin and serves as a preferential flow path from north to south probably along fractures and faults associated with the anticlinorium. Stueber and Walter (1994) noted that the δ^{18}O of brines from the Ordovician Galena Formation had a meteoric-water signature for only those samples collected along the LaSalle Anticlinorium. These data support the concept of its role as a zone of enhanced anisotropic permeability with greater and/or more rapid recharge and groundwater movement along this structure within at least Cambrian and Ordovician strata. This structure also has been identified as the location of thermal anomalies and saline springs (Cartwright 1970; Panno et al. 1994; Panno, ISGS, unpublished data) suggesting the anticlinorium is a zone of enhanced permeability throughout the entire Paleozoic sequence. In addition, the LaSalle Anticlinorium has been described by Bethke (1986) as a structure that may have "funneled" ore-forming solutions from the southern part of the Illinois Basin to the host rocks of the Upper Mississippi Valley ore district to the north (Figure 1) in post-Pennsylvanian time. Finally, whereas Devonian rocks are exposed in isolated locations along the LaSalle Anticlinorium, it is unlikely that recharge via these "windows" through the Pennsylvanian strata is responsible for the preferential flow patterns in the St. Peter Sandstone or the Mount Simon Sandstone.

Cross Sections of the Illinois Basin

Chloride isocons on the cross sections (Figures 4–8 and S1) reveal patterns of recharge, stratification, paths of preferential groundwater flow, zones of near stagnation, and flow directions within and through the basin. The isocons often reveal strong contrasts in groundwater Cl^- concentrations in adjacent stratigraphic units, which suggests areas with limited to negligible vertical mixing and near stagnant brines. Some of the cross sections also show the effects of the LaSalle Anticlinorium on enhanced recharge into the basin. In addition, the isocons show that the shales of the Pennsylvanian strata, where present, provide a low flow boundary for recharge into the underlying strata. The cross sections are discussed in detail further.

The northernmost part of the Illinois Basin is characterized by exposures of Cambrian and Ordovician strata. Consequently, these strata are more easily recharged and groundwater in this area contains the lowest concentrations of Cl^- in the Illinois Basin (Figure 4). As a result, some of the lowest Cl^- values (e.g., all values are below that of average seawater of 19,800 mg/L; Table S1) are found in this part of the basin. Here, the shallowest bedrock (Pennsylvanian strata) contains Cl^- concentrations that are typically less than 100 mg/L, and concentrations barely exceed 20,000 mg/L in the deeper, typically briny, Mount Simon Sandstone. The isocons of A–A′ (Figure 4) indicate recharge of low Cl^- water to all Paleozoic formations along the northernmost margins of the Illinois Basin where the Ordovician St. Peter Sandstone is exposed at and near Starved Rock State Park. The low Cl^- concentrations in this area are consistent with findings by Siegel (1989, 1991) and Panno et al. (2013), who showed, using groundwater chemistry and stable isotopes, that Pleistocene recharge extended into the Illinois Basin from the north and west. McIntosh et al. (2002) showed a similar recharge into Devonian and Mississippian strata from the east. As cross section A–A′ (Figure 4) shows evidence of several isolated/narrow plumes of groundwater with elevated Cl^- concentrations, it is likely that there is an upward hydraulic gradient where deeper, saline groundwater is welling up to the surface. The widespread saline anomaly within and in the vicinity of Starved Rock State Park (Willman and Payne 1942; Panno, ISGS, unpublished data) is coincident with these plumes. The sporadic occurrence of saline wells, springs, and plumes of saline groundwater in this area suggest the upward movement of saline groundwater along faults and fractures.

Farther south, freshwater recharge is evident along the western margin of the basin and along the LaSalle Anticlinorium where Pennsylvanian shale is thin to absent (Figure 5). The greatest recharge appears to have been to

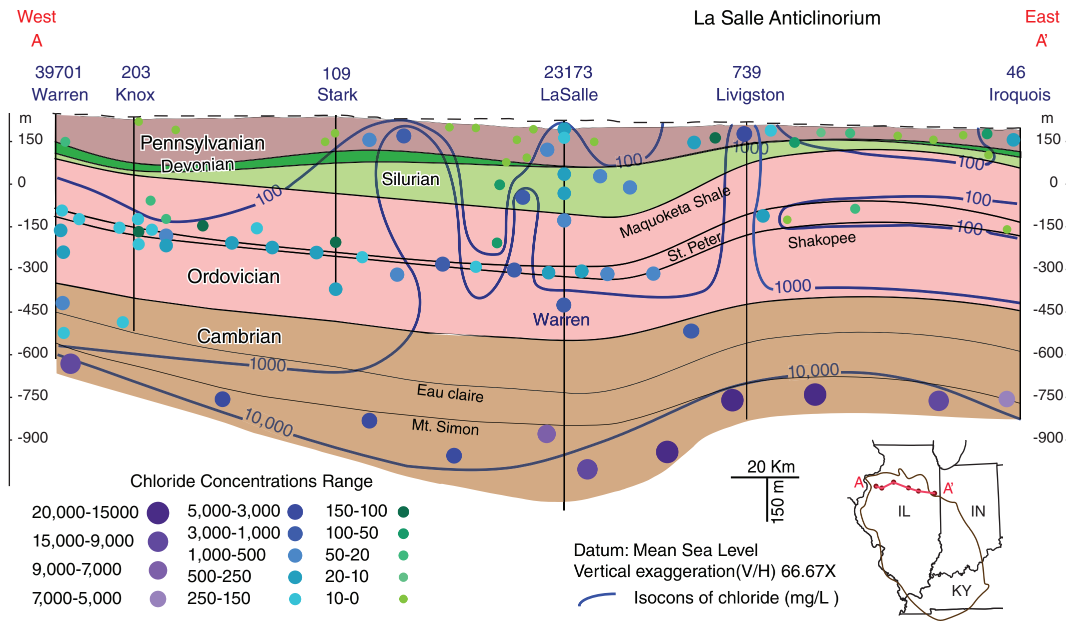

Figure 4. Cross section A–A′ extending east-west across northern Illinois. The most dilute groundwater in the Illinois Basin is found in the northern part of the basin because of the shallowness or exposure of the formations in this area, or both. Recharge is apparent from dilution effects from the west and east, and an upward movement of brines near the center of the cross section in the vicinity of the Illinois River.

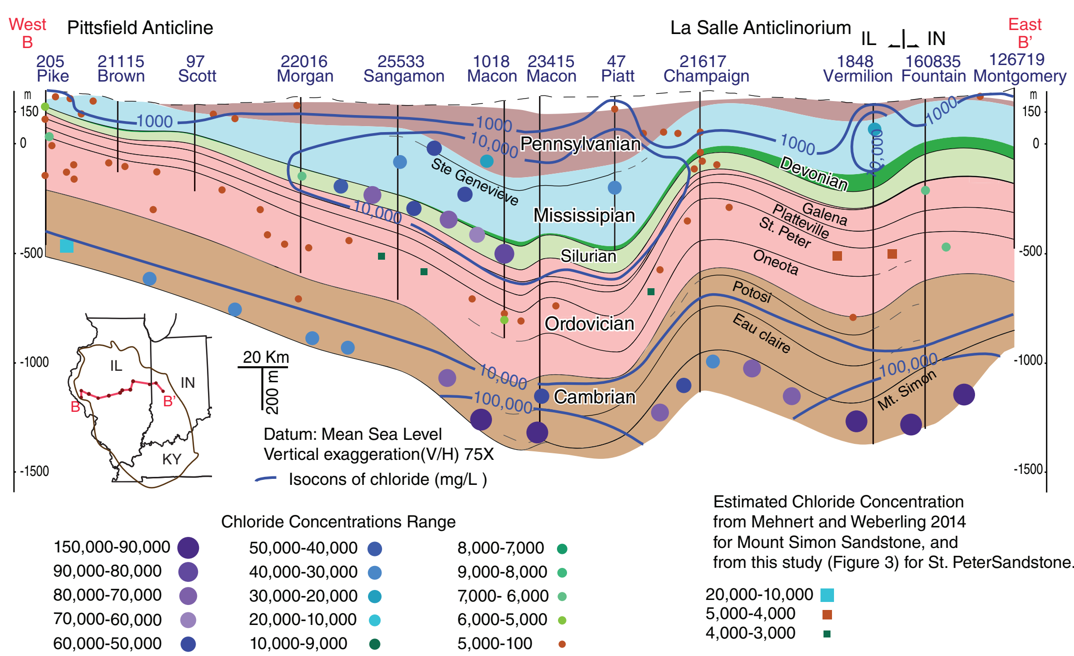

Figure 5. Cross section B–B′ extending east-west across central Illinois and central Indiana. The effects of freshwater recharge are apparent where Pennsylvanian strata are thin or absent and along the western and eastern margins of the basin and along the LaSalle Anticlinorium. Residual brines are present near the center of the cross section in Silurian–Devonian and Mississippian strata. The most concentrated brines are present near the center and far western part of the Cambrian strata.

Ordovician strata, primarily into the St. Peter Sandstone. Some of the lowest Cl^- concentrations are located along the LaSalle Anticlinorium. In the central region of cross section B–B′ (Figure 5), pools of dilute groundwater within the St. Peter Sandstone extend below pools of basin brines where Pennsylvanian strata are thickest. Greater concentrations of Cl^- lie within the Silurian, Mississippian, and Pennsylvanian strata above (many greater than 50,000 mg/L) and the Cambrian strata below (some greater than 100,000 mg/L). The greatest Cl^- concentrations are found within Cambrian strata on either side of the LaSalle Anticlinorium probably related to the effects of north to south fresh-water recharge within the Cambrian along the anticlinorium (Figure 2).

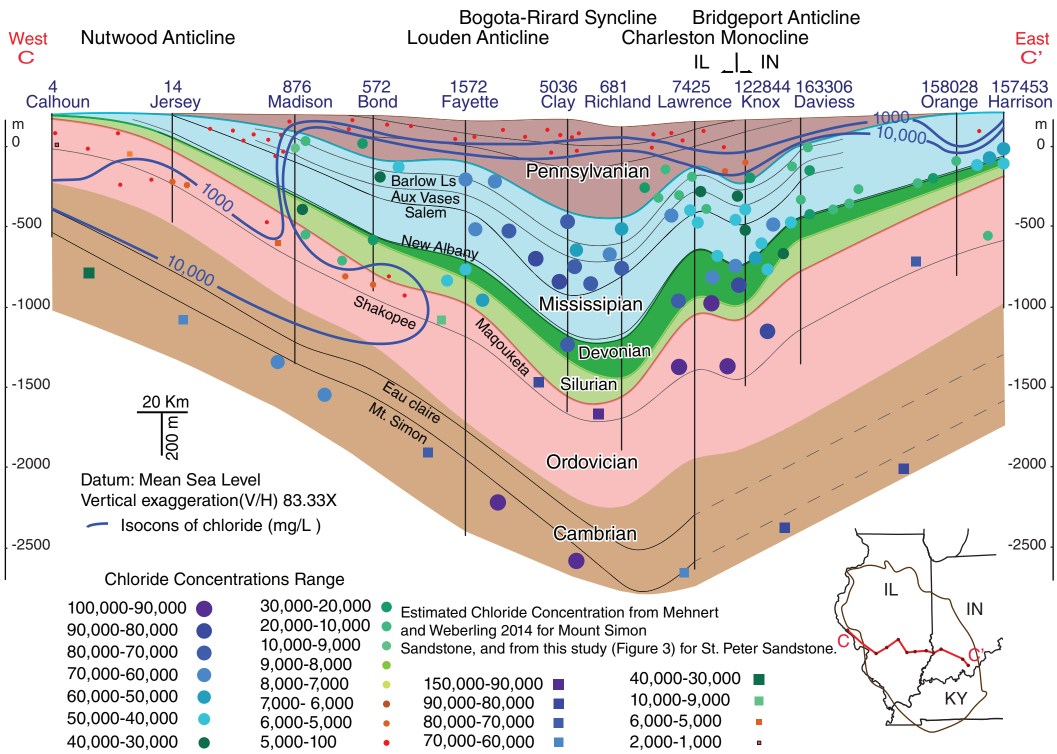

Figure 6. Cross section C–C′ extending east-west across southern Illinois and southern Indiana. The effects of freshwater recharge are most prominent at the western edge of the basin and in upper 200 m of Pennsylvanian strata. The most concentrated brines are present in the Cambrian Mount Simon Formation near the center of the basin.

Across the central portion of the Illinois Basin, cross section C–C′ reveals dilution of brines along zones of recharge at the western and, to a lesser extent, at the eastern edges of the basin where Pennsylvanian strata have been eroded (Figure 6). A relatively large plume of freshwater from the west has penetrated deep into the basin along Ordovician strata. The exposure of Ordovician, Silurian–Devonian, and Mississippian strata along the Mississippi River is a likely location for focused recharge, probably from glacial meltwaters during the Pleistocene Epoch. As the plume approaches the deepest part of the basin, it is bounded above by the Maquoketa Shale, below by the Eau Claire Formation, as well as above and below by brines with greater Cl^- concentrations. Dilution of brine within the Mount Simon Sandstone is also present from both the west and east, but to a lesser extent.

Freshwater recharge is indicated for much of the Pennsylvanian strata where Cl^- concentrations are less than 100 mg/L for the upper 50 to 100 m. Conversely, Cl^- concentrations in Mississippian through Silurian strata near the center of the basin exceed 50,000 mg/L where they are bounded above by thick Pennsylvanian strata and below by the New Albany Shale. Brines within these dominantly carbonate rock strata are diluted by freshwater recharge from both the west and east (Figure 6).

Just south of cross section C–C′, cross section D–D′ reveals similar conditions, but extends no deeper than Ordovician strata due to the paucity of geologic and geochemical data in this area (Figure 7). As with cross section C–C′, Cl^- concentrations suggest active recharge from the west and east where Pennsylvanian strata are thin or absent. Recharge from the east and west extends into Paleozoic strata from both sides of the basin. The eastern portion of the cross section within Indiana reveals greater recharge from the east within Silurian through Mississippian strata. This is supported by McIntosh et al. (2002) who found that the Silurian–Devonian strata provided a hydrologic pathway for recharging Pleistocene meltwater to depths up to 1 km across the eastern margin of the basin, and recharge from Mississippian strata, through underlying fractured New Albany Shale, and into Silurian–Devonian strata in the southeastern part of the Illinois Basin. Cross section D–D′ suggests recharge from the west is entering exposed Ordovician and Mississippian strata along the Mississippi River Arch (Figure 7).

Freshwater recharge is limited within the center of the basin where Pennsylvanian strata are thick (more than 600 m). Dilution of Cl^- concentrations of 1000 mg/L or less is consistent across Pennsylvanian strata to a depth of 60 to 120 m; however, limited data suggests that Cl^- concentrations rapidly increase, with depth, to greater than 10,000 mg/L within Pennsylvanian strata. Chloride concentrations within the center of cross section D–D′ (along the deepest part of the basin) reveal the presence of concentrated brines within all strata. Freshwater recharge from the north is apparent within the LaSalle Anticlinorium in the eastern half of the cross section and occurs within Upper Ordovician through Mississippian strata.

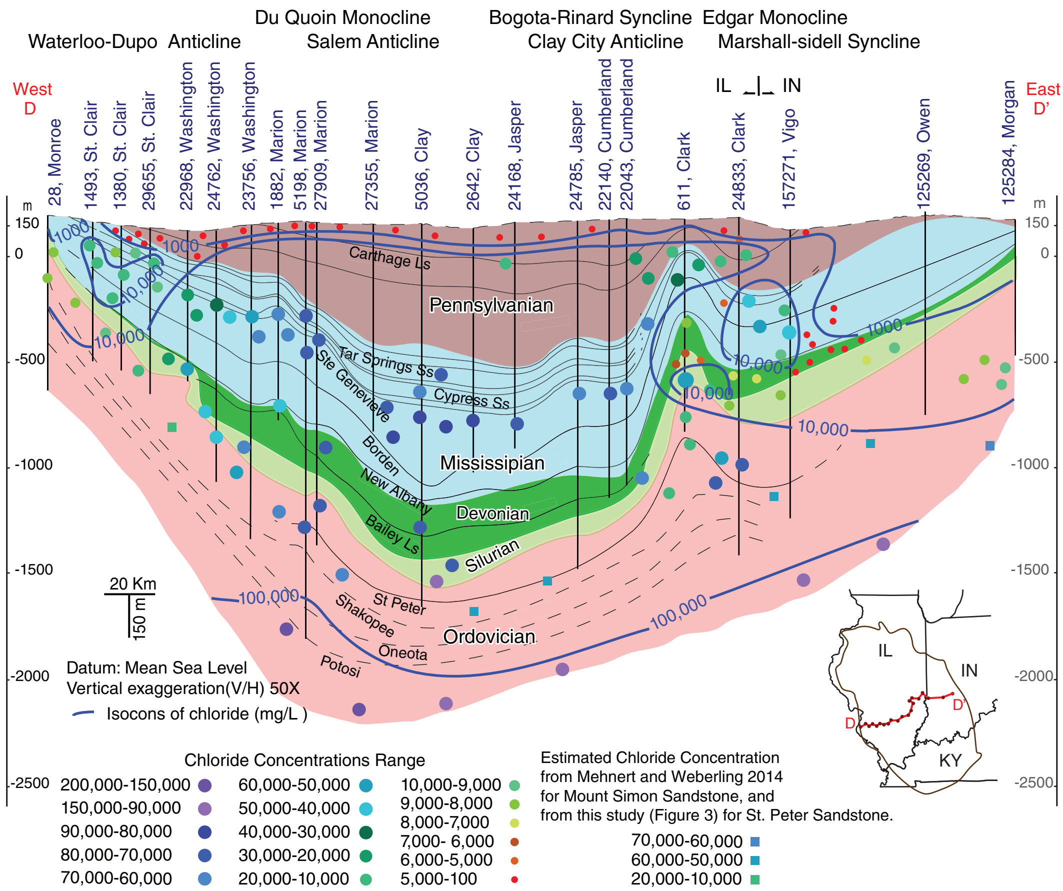

Figure 7. Cross section D–D′ extending east-west across southern Illinois and southern Indiana. Freshwater recharge affects the western and eastern margins of the basin, but not to the extent seen in cross sections farther north. Brines are also diluted along the LaSalle Anticlinorium (groundwater movement toward the reader). Again, the most concentrated brines are present in the Cambrian strata.

Farther south, cross section E–E′ does not extend beyond the Illinois-Indiana border and does not extend below Ordovician strata because of the paucity of geologic data (Figure S1). As with the cross sections C–C′ and D–D′, to the north, Cl^- concentrations show a plume of dilute water extending into the basin from the west. The absence of Pennsylvanian shale in the west has facilitated groundwater recharge where Ordovician through Mississippian strata are exposed along the Mississippi River Arch and in southwestern Illinois.

Constructed along the long axis of the Illinois Basin, cross section F–F′ reveals the effects of recharge, groundwater flow, and zones of stagnation within nearly the entire basin. It was used, in conjunction with the plan-view maps and east-west cross sections, as a conceptual model of recharge into, distribution of brines and brine-freshwater mixing within, and groundwater flow within and through the Illinois Basin. Based on the Cl^- concentrations and associated isocons, freshwater recharge is entering all Paleozoic formations including Cambrian strata in northern Illinois as seen in cross section A–A′ and B–B′ (Figures 4 and 5), and from the east and west (Figures 6, 7, and S1). Along the northern basin margin, Cl^- concentrations reveal a pool of dilute groundwater extending from Pennsylvanian strata at the surface downward into the Cambrian Mt. Simon Sandstone (Figure 8). The effects of freshwater recharge along the LaSalle Anticlinorium are seen in a short segment of the Mount Simon Formation about 200 km from the northern edge of the cross section. Here, Cl^- concentrations of Mount Simon brines are diluted below 100,000 mg/L. The overall distribution of isocons and Cl^- concentrations indicates groundwater flow from north to south through Ordovician strata with preferential recharge to and groundwater movement through the St. Peter Sandstone. The isocons also reveal a pattern of increasing Cl^- concentrations with distance from northern and western recharge areas about two thirds of the way to the southern end of the basin. Beyond the recharge zone to the north, thick Pennsylvanian strata protect brines within Silurian–Devonian and Mississippian strata from dilution by recharge; this is in contrast to the dilution of brines seen in these formations in the southern part of the basin where Pennsylvanian strata are thin to absent.

The separation of the 100,000 mg/L isocon within Cambrian strata in the northern third of cross section F–F′ is associated with dilution of brines along the LaSalle Anticlinorium. The deepest part of the basin contains the greatest concentration of Cl^- (and TDS) that extends from

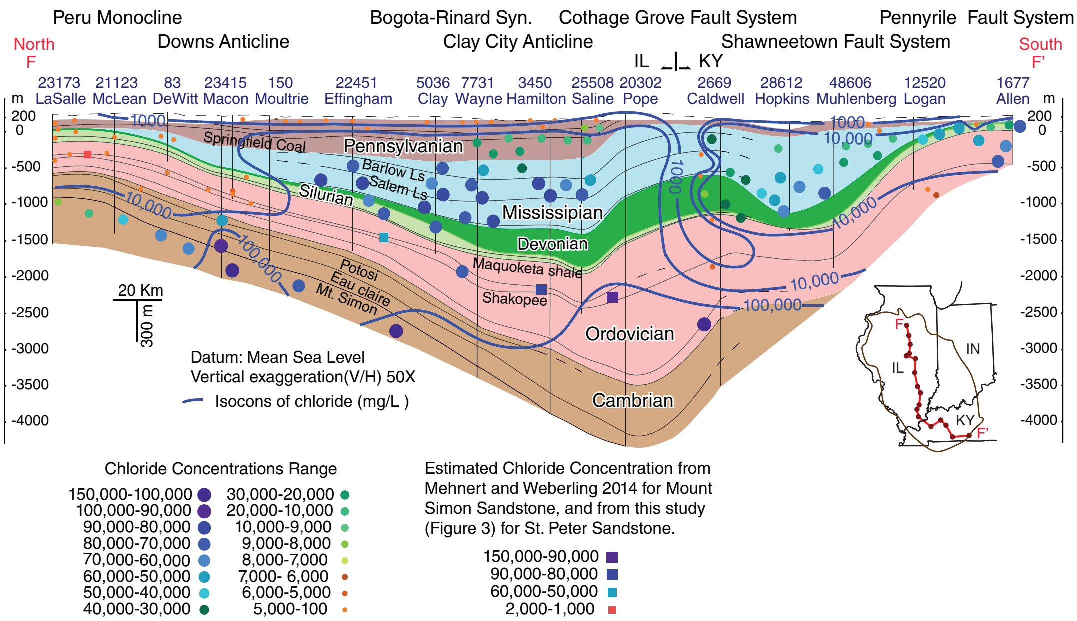

Figure 8. Cross section F–F′ extending north-south from northern Illinois to southwestern Kentucky. This cross section reveals the effects of freshwater recharge in the northern part of the basin, where much of the Paleozoic strata are exposed or near surface. The greatest dilution is apparent in the St. Peter Sandstone aquifer, and the most concentrated brines are present in Cambrian strata and up into Ordovician strata at the center of the basin. Focused recharge deep into Ordovician strata is apparent in the vicinity of the Ohio River near the Rough Creek-Shawneetown Fault System, where Pennsylvania strata is thin to absent.

Cambrian strata up into Ordovician strata. Cartwright (1970) and Siegel (1989) suggested that discharge of concentrated brines in southern Illinois may be by upward migration across leaky confining units. The area in this cross section where the greatest Cl^- concentrations extend into Ordovician strata is immediately beneath the Great Salt Spring located near Equality, Illinois with saline springs on either side of the Saline River indicating points of discharge. However, the saline water of the Great Salt Spring appears to be characteristic of Pennsylvanian strata based on Cl/Br mass ratios and not derived from Cambrian and Ordovician strata (Panno, ISGS, unpublished data). The saline springs in this area may suggest an upward hydraulic gradient, perhaps with mixing of the brines prior to reaching the surface. In addition, it is possible that concentrated crystalline basement brines are upwelling into the original brines of the Cambrian Mount Simon Formation near the center of the basin as was observed in the Decatur well to the north by Panno et al. (2013) and Labotka et al. (2015, 2016).

The inferred pattern of north-to-south brine migration is interrupted in the southern part of the basin at or near the Ohio River (Figure 1). Here, recharge occurs where the Ohio River intersects the Rough Creek-Shawneetown Fault System. In this area, Pennsylvanian strata are thin or missing and Cl^- contours indicate the presence of a fresh-water plume, presumably from the Ohio River (perhaps including Pleistocene glacial meltwaters) recharging carbonate bedrock aquifers. Surface waters are probably recharging underlying aquifers as they flow through Mississippian and Silurian–Devonian strata, and into Ordovician strata. The Cl^- isocons further suggest that the freshwater recharge within Ordovician strata flows to the south-southeast into Kentucky toward the southern end of the Illinois Basin. The freshwater recharge is probably mixing with basin brines as it flows through Ordovician strata. We speculate that the resulting saline groundwater from the southeastern margin of the Illinois Basin may be discharging to the numerous salt licks found in northern and central Kentucky (e.g., Bullitt's Lick; Figure 1). These salt licks were used by Native Americans and frontiersmen as a source of salt and as hunting spots where herds of bison, deer, and elk would frequent the area and where bison "licked out deep trenches in the salt-impregnated clay" (McDowell 1956). Based on the Cl/Br mass ratio of Bullitt's Lick (189), one of many salt licks located just southeast of Louisville, Kentucky, the saline water is Cambrian-Ordovician in origin (Panno, ISGS, unpublished data), which is consistent with the inferred flow patterns and groundwater mixing within the Illinois Basin.

Conclusions

We develop, for the first time, a conceptual model of the hydrogeology of the Illinois Basin on a basin-wide scale. This model, based on Cl^- isocons on plan-view maps of selected formations and cross sections across the basin, reveal the infiltration and movement of freshwater recharge into the basin and dilution of brines within all of the Paleozoic strata, inter-formational interactions, and groundwater flow within and through the Illinois Basin. Pathways of greater permeability (e.g., highly conductive lithologies and fractures associated with geologic structures) resulted in zones of dilute groundwater migrating through areas bounded on all sides by brines. Restrictions or barriers created by aquitards have created areas of near isolation/stagnation of concentrated brines within the basin. The Cl^- isocons suggest that the current chemical composition of groundwater and distribution of brines within the Illinois Basin is dependent on five parameters: (1) the presence of bedrock exposures along basin margins; (2) the permeability of geologic strata and their distribution relative to one another; (3) the presence or absence of major geologic structures; (4) the intersection of major rivers with geologic structures, basin margins, and permeable bedrock exposures; and (5) the isolation of brines within the basin resulting from aquitards, inhomogeneous permeability, and, in the case of the deepest part of the basin, brine density effects.

Cambrian Mount Simon Sandstone is bounded below by crystalline basement and above by the Eau Claire Formation and contains original brines (as determined by Labotka et al. 2016). Groundwater within the deepest part of the basin located in far southern Illinois may be under near stagnant conditions, or at least that part of the basin constitutes a zone of low flow within Cambrian and lower Ordovician strata. Based on previous work by McIntosh et al. (2002); Siegel (1989, 1991), and this study, groundwater flow through the basin appears to be from the northern, eastern, and western margins of the basin and dominantly through the Ordovician St. Peter Sandstone, and carbonate rocks of the Silurian–Devonian and Mississippian strata. Silurian–Devonian strata, consisting of mostly carbonate rocks, are bounded by the underlying Ordovician Maquoketa Shale and the overlying Devonian New Albany Shale. Similarly, the carbonate rocks of the Mississippian strata are bounded below and above by the New Albany Shale and the shale-dominated Pennsylvanian strata, respectively, where remnant brines remain. Our findings are consistent with Stueber and Walter (1994) who suggested that the remnant brines within the Silurian–Devonian and Mississippian strata are due to the bounding shale layers. We suggest that the inhomogeneous hydraulic characteristics of the Silurian–Devonian and Mississippian strata (i.e., dual porosity) probably help maintain brine compositions within these strata.

Pennsylvanian strata, where present, act as a confining unit to protect brines of the underlying Mississippian strata from freshwater recharge. Where Pennsylvanian strata are thin or absent, brines of the Mississippian strata have been diluted to various degrees, and, in some cases, to potable groundwater. Exposures of formations near basin margins allow recharge from meteoric water and, in the past, glacial meltwaters. Where the Mississippi River intersects bedrock exposures along the Mississippi River Arch (western margin of the Illinois Basin), enhanced recharge is likely responsible for freshwater plumes that extend deep into the basin from the west. The intersection of major rivers with major geologic structures is responsible for relatively rapid fresh-water recharge and movement of groundwater through the Illinois Basin. Evidence of Pleistocene meltwater recharge is observed along the LaSalle Anticlinorium where associated faults and fractures have created a zone of enhanced anisotropic permeability. Glacial meltwaters appear to have flushed out much of the brines within the St. Peter Sandstone within the northern part of the Illinois Basin during the Pleistocene based on data by Siegel (1989, 1991) and this study. Subsequently, deep-seated brines welled up along fault and fracture planes and created saline springs and the sporadic occurrence of saline wells near the Illinois River.

Chloride isocons within the Cambrian Mount Simon Sandstone and the St. Peter Sandstone reveal a marked dilution along the LaSalle Anticlinorium that extends into southern Illinois. This pattern of dilution also was observed in younger formations along the anticlinorium in the cross sections. In far southern Illinois, the intersection of the Rough Creek–Shawneetown Fault System (a major fault zone across the southern part of the basin) and the Ohio River has resulted in enhanced recharge deep into the Illinois Basin extending from surficial Mississippian strata, through Devonian and Silurian strata, and continuing to near the base of Ordovician strata. Within Ordovician strata, we speculate that the freshwater plume joins groundwater flowing through Ordovician strata via the St. Peter Sandstone and continues south into Kentucky where it discharges to numerous salt licks and saline springs near and south of Louisville and perhaps into northern Tennessee. These observations are consistent with an overall north to south flow of groundwater within the Illinois Basin and discharge along its southern boundaries.

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Supporting Information

Additional Supporting Information may be found in the online version of this article. Supporting Information is generally *not* peer reviewed.

Appendix S1. Chloride Content and Cl/Br Ratios of Brines of the Illinois Basin and References.

Table S1. Maximum Cl^- concentrations and median Cl/Br ratios (the $\pm$ refers to range) reported for geologic strata within the Illinois Basin. The Cl^- concentrations of seawater and Precambrian Shield brines are added for comparison.

Figure S1. Cross section E–E′ extending east-west across far southern Illinois. Because this cross section is truncated at the Illinois–Indiana state boundary, the effects of freshwater recharge are only seen along the western margin of the basin.

Appendix S2. Illinois State Geological Survey Unpublished Report.

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