# Water Quality in the Mahomet Aquifer: Chemical Indicators of Brine Migration and Mixing

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Special Report 7 2020

# ILLINOIS STATE GEOLOGICAL SURVEY

Prairie Research Institute University of Illinois at Urbana-Champaign **ILLINOIS** Illinois State Geological Survey PRAIRIE RESEARCH INSTITUTE *Front cover:* Dr. Keith Hackley sampling groundwater from a farm well screened within the Mahomet aquifer. Photograph by S.V. Panno. Used with permission.

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Suggested citation: Panno, S.V., and W.R. Kelly, 2020, Water quality in the Mahomet aquifer: Chemical indicators of brine migration and mixing: Illinois State Geological Survey, Special Report 7, 7 p.

# Contents

| Abstract   | 1 |
|--|---|
| Introduction   | 1 |
| Chemical Composition of Groundwater from the Mahomet Aquifer | 1 |
| Chloride/Bromide Mass Ratios                                 | 3 |
| Manlove Field  | 4 |
| Conclusions  | 6 |
| Acknowledgments  | 6 |
| References   | 6 |
|  |   |

### Table

| 1    | Maximum chloride concentrations and median chloride/bromide (Cl/Br) mass ratios reported for geologic strata within the Illinois Basin | 5 |
|------|--|---|
| Figu | ires   |   |
| 1    | Map of buried sand and gravel deposits that form the Mahomet aquifer   | 1 |
| 2    | Longitudinal section of the Mahomet aquifer showing bedrock formations and   |   |
|      | glacial deposits   | 2 |
| 3    | Distribution of chloride in the Mahomet aquifer showing the effects of discharge of  |   |
|      | more saline groundwater from bedrock into the Mahomet aquifer  | 3 |
| 4    | Detail of the chloride distribution from Figure 3 showing the distribution of chloride   |   |
|      | concentrations in the area of Mahomet, Illinois  | 4 |
| 5    | Area near the central portion of the Mahomet aquifer with the greatest chloride  |   |
|      | concentrations   | 5 |
|      |  |   |

### ABSTRACT

Illinois Basin brines have unique chemical signatures (e.g., chloride/bromide [Cl/Br] mass ratios) that are useful in identifying the geologic formations from which they originated. Here we present a methodology for identifying the source of brines that have mixed with freshwater aquifers, and in this specific case, the Mahomet aquifer, a major source of water for more than 500,000 people in 15 counties throughout eastcentral Illinois. The use of Cl/Br mass ratios is generally applicable to water chemistry results from wells throughout the Mahomet aquifer and can be used in conjunction with other water chemistry analyses to evaluate water quality. In addition, this technique potentially could be used to evaluate water quality results from domestic water wells in the vicinity of Mahomet, Illinois, where a subsurface natural gas leak occurred in 2016 from a well in a gas storage field.

#### **INTRODUCTION**

The Mahomet aquifer in east-central Illinois is a classic example of a buried bedrock valley aquifer from the glaciated Upper Midwest of the United States (Kempton et al. 1991). The sand and gravel aquifer lies within an eastwest-trending buried bedrock valley in east-central Illinois that extends into western Indiana. The aquifer material is composed of sand and gravel (up to ~197 ft [60 m] thick and averaging 98 ft [30 m]) that was deposited during a time of continental glaciation and later buried beneath up to 328 ft (100 m) or more of glacial till (Kempton et al. 1991).

The aquifer is an extensive and prolific source of high-quality, fresh groundwater in central Illinois (Figure 1) and provides an estimated 220 million gallons of water per day to communities, agriculture, industry, and rural wells (Mahomet Aquifer Protection Task Force 2018). The aquifer is replenished by natural processes. In northeast Champaign County near the Sangamon River, the replenishment potential of the aquifer, known as recharge, is great because of the abundance and connection of permeable, water-bearing geologic deposits (Panno et al. 1994; Roadcap et al. 2011).

# CHEMICAL COMPOSITION OF GROUNDWATER FROM THE MAHOMET AQUIFER

An initial investigation of the groundwater chemistry of the Mahomet aquifer (Panno et al. 1994) revealed the presence of geochemical regions within the aquifer caused by the natural movement of groundwater from deeper bedrock formations up into the sand and gravel of the Mahomet aquifer. Panno et al. (1994) initially observed the intrusion of saline groundwater into the Mahomet aquifer from the bedrock below (Figure 2). The term "saline" is used here to refer to water with total dissolved solids (TDS)



**Figure 1** Map of the buried sand and gravel deposits that form the Mahomet aquifer. AMSL, above mean sea level. Modified from Roadcap et al. (2011). Used courtesy of the Illinois State Water Survey.



Figure 2 Longitudinal section of the Mahomet aquifer showing bedrock formations and glacial deposits. From Panno and Korab (2000). Copyright © 2000 University of Illinois Board of Trustees. Used with permission.

concentrations of >1,000 milligrams per liter (mg/L; https://water.usgs.gov/ edu/saline.html). Bedrock consists of layers of shale and carbonate rock (limestone and dolomite) that make up the Illinois Basin. The Illinois Basin is a spoon-shaped structure that lies mostly within the borders of the state of Illinois and consists of layers of sedimentary rock that were deposited hundreds of millions of years ago when oceans periodically covered much or all of Illinois. The infiltration and migration of recent freshwater recharge and ancient basin brines into transmissive aquifers and along geologic structures has diluted brine concentrations throughout much of the Illinois Basin (e.g., McIntosh et al. 2002; Panno et al. 2018).

Chloride concentrations in groundwater in the eastern part of the Mahomet aquifer are very low, generally measuring <10 mg/L and often as low as  $\leq$ 1 mg/L (Figure 3). Panno et al. (2006) used cumulative probability curves to identify the natural background for chloride concentrations in waters of Illinois (both surface water and groundwater) at 1 to 15 mg/L. The background for chloride in the eastern Mahomet aquifer is lower, at 1 to 3.5 mg/L. Chloride concentrations this low are unusual for such a deep



**Figure 3** Distribution of chloride in the Mahomet aquifer showing the effects of discharge of more saline groundwater from bedrock into the Mahomet aquifer. From Kelly et al. (2012). Used courtesy of the Illinois State Water Survey.

aquifer and indicate an area of recharge in central Champaign County in the vicinity of the Sangamon River (Panno et al. 1994; Figures 1 and 3). Hackley et al. (2010) suggested that the infiltration and movement of dilute glacial meltwaters within the aquifer during the Pleistocene Epoch, which ended approximately 12,000 years ago, may be responsible for such low chloride concentrations in the aquifer. Stable isotope data from Hackley et al. (2010) indicated that groundwater from the Mahomet aquifer is too young to be glacial meltwater but that recharging glacial meltwaters probably leached chloride (and other constituents) from the glacial deposits of the recharge areas and the aquifer materials, resulting in very low chloride concentrations.

In the central part of the aquifer, near the Piatt County-Champaign County border, chloride concentrations increase abruptly (Figure 4). This is where the north-northwest- to south-southeasttrending geologic structure known as the Osman Monocline (part of the La Salle Anticlinorium) intersects the aquifer. The La Salle Anticlinorium is a series of deep-seated north-northwestto south-southeast-trending folds and faults that extend from far southeastern Illinois to far northern Illinois. These structures and associated fractures are capable of providing pathways for groundwater flow, both laterally and vertically. Saline springs and saline seeps are not uncommon in the Illinois Basin (Panno et al. 2017) because of such geologic structures. Near Bement, Illinois, in south-central Piatt County, water quality sampling suggests that naturally occurring saline water is discharging from the bedrock into the base of the Mahomet aquifer. Here, private wells have elevated chloride concentrations as high as 500 mg/L. Chloride concentrations decrease with distance to the northwest, away from the saline seepage, as the saline groundwater mixes with more dilute groundwater. The average chloride concentration in the western part of the aquifer is approximately 70 mg/L (Figures 3 and 4).

The highest chloride concentrations in eastern Piatt County are near a thermal anomaly identified by Cartwright (1970; Figure 5). In a 1970 paper, Cartwright identified anomalously warmer groundwater at a depth of about 427 ft (130 m), which he determined was coincident with known saline springs found near geologic structures within the Illinois Basin. Cartwright reasoned that warmer groundwater must be flowing upward through faults and fracture zones associated with structures within the basin.

#### CHLORIDE/BROMIDE MASS RATIOS

Chloride and bromide have minimal interaction with aquifer materials and the associated geochemical processes. Consequently, they are often referred to as conservative chemical elements, and the chloride/bromide (Cl/Br) mass ratio has been used to distinguish different sources of water and associated contaminants (e.g., Panno et al. 2006). This is an important tool for use in the Illinois Basin, where brines (water with TDS concentrations >35,000 mg/L) from different geologic units can seep into the overlying groundwater and surface waters. Chloride concentrations in some Illinois Basin brines can exceed 120,000 mg/L (Table 1). The Cl/Br mass ratios of water from the Mahomet aquifer are typically low (often <100) compared with the underlying bedrock formations of the Illinois Basin. Chloride/bromide mass ratios of brines within the Pennsylvanian strata, the youngest bedrock underlying the Mahomet aquifer region, exceed 400. Brines within the older Silurian-Devonian strata have Cl/Br mass ratios close to 300 (Walter et al. 1990), and brines within Cambrian strata typically have Cl/Br mass ratios of <200 (Table 1).



**Figure 4** Detail of the chloride distribution from Figure 3 showing the distribution of chloride concentrations in the area of Mahomet, Illinois (blue star).

Panno et al. (1994) showed, by using Cl/Br mass ratios, that saline groundwater from deeper Pennsylvanian strata is entering the Mahomet aquifer and mixing with the shallower fresh groundwater with very low TDS. Near the Piatt County–Champaign County border, wells in the Mahomet aquifer have Cl/Br mass ratios of >400. Chloride concentrations in the Pennsylvanian strata in this area range from 100 to 5,000 mg/L (Panno et al. 2018); as a result, infiltration of even a relatively small volume of brine into the Mahomet aquifer may be detectable. In addition, the resulting Cl/Br mass ratio would reflect a chemical signature more like that of the brines shown in Table 1 because of the great difference in their chloride and bromide concentrations.

#### MANLOVE FIELD

The Manlove gas storage field is located about 1.9 miles (3 km) north of Mahomet, Illinois. This is an area where natural gas (predominantly methane) is injected into the brines of a permeable formation at a depth of about 4,495 ft (1,370 m) below land surface. Chloride concentrations at depths near the bottom of these wells are about 50,000 mg/L



**Figure 5** Area near the central portion (narrowest part) of the Mahomet aquifer with the greatest chloride concentrations (see Figure 4). Concentration contour lines (isocons) illustrate where areas of higher concentration occur. Panno et al. (1994) and Hackley et al. (2010) described this as an area of discharge (or seepage) of basin brines into the Mahomet aquifer. The seepage is near anticlines and a monocline associated with the La Salle Anticlinorium and a thermal anomaly. The tongue-shaped feature associated with the anticline in the lower right of the figure represents the location of a thermal anomaly identified by Cartwright (1970). The blue star indicates the location of Mahomet, Illinois.

| Age of formation   | Chloride, mg/L | Cl/Br mass ratio | Source                 |
|--------------------|----------------|------------------|------------------------|
| Pennsylvanian      | 55,560         | 429 ± 129        | Walter et al. (1990)   |
| Mississippian      | 95,670         | 417 ± 59         | Walter et al. (1990)   |
| Silurian–Devonian  | 136,900        | 294 ± 18         | Walter et al. (1990)   |
| Ordovician         | 84,340         | 257 ± 109        | Walter et al. (1990)   |
| Cambrian           | 120,000        | 189 ± 27         | Panno et al. (2013)    |
| Precambrian Shield | 207,000        | 106 ± 36         | Fritz and Frape (1982) |
| Seawater           | 19,800         | 281              | Mason (1966)           |

 Table 1
 Maximum chloride concentrations and median chloride/bromide (Cl/Br) mass ratios reported for geologic strata within the Illinois Basin<sup>1</sup>

<sup>1</sup>The plus-minus sign (±) refers to the range. The chloride concentrations of seawater and Precambrian Shield brines have been added for comparison. From Panno et al. (2018, Supporting Information). Reprinted from *Groundwater* with permission of the National Ground Water Association, copyright 2018.

(Panno et al. 2013) with a Cl/Br mass ratio of  $189 \pm 27$  (Table 1). The shallowest bedrock beneath the Mahomet aquifer in the area is Devonian limestone, and it occurs at a depth of about 328 ft (100 m). Chloride concentrations in Silurian-Devonian bedrock range from 5,000 to 137,000 mg/L and have a Cl/Br mass ratio of 294 ± 18, depending on their depth and location within the bedrock (Walter et al. 1990). Chloride concentrations in the Mahomet aquifer in the area are typically 1 mg/L (Panno et al. 1994). The use of Cl/Br ratios (in association with other parameters) could potentially be used to evaluate water quality results from water wells in the area to identify mixing of brine and freshwater. One concern that has been expressed is that increased pressures in the bedrock resulting from the 2016 natural gas leak that occurred at the McCord #2 well could be a mechanism capable of moving brine or saline water from bedrock into the Mahomet aquifer.

# CONCLUSIONS

Because chloride concentrations in the Mahomet aquifer east of the Champaign County-Piatt County line are relatively low (typically 1 mg/L), groundwater quality data can be used to determine if and where brine or saline groundwater has been discharged into the aquifer. Panno et al. (1994) found groundwater from one well with a chloride concentration of 17 mg/L near the aquifer margin located about 13 miles (21 km) north of Mahomet, Illinois. According to previous studies and available data, groundwater with chloride concentrations >10 mg/L warrant further investigation to evaluate the potential cause or causes. For example, water quality analyses from wells screened in the Mahomet aquifer within several kilometers of an area of suspected discharge of brine or saline water from bedrock would help define water quality conditions and spatial variability. If chloride concentrations from multiple wells exceeded 10 mg/L (similar to the increased concentrations shown in Figures 3 and 4), then potential mechanisms for migration of the brine or saline water would need to be evaluated. One or more mechanisms could be responsible. For example, relatively high

chloride concentrations are found in groundwater from wells near the lateral margins of the Mahomet aquifer, where groundwater from bedrock can seep into the aquifer naturally or as a result of well pumping (Kelly et al. 2012; Figure 4). Groundwater from the bedrock could also potentially migrate upward into the Mahomet aquifer if pressures in the bedrock were increased as the result of the release of pressurized fluid from a gasstorage well (e.g., a gas-injection/extraction well). Chemical analysis of groundwater samples for a range of constituents (including chloride and bromide) would be helpful in determining whether brine or saline water movement has affected groundwater quality in the Mahomet aquifer. Further, Cl/Br mass ratios may indicate the formation(s) from which they originated. It is important to note that the use of chloride distributions and Cl/Br mass ratios may not provide definitive evidence of brine or saline water seepage or migration. If anomalies are identified, they would need to be assessed in the context of other water quality, geochemical, hydrogeological, and geological data to determine the extent of and mechanisms for groundwater movement, mixing, and associated geochemical changes.

# ACKNOWLEDGMENTS

This effort was made possible with the support of the Illinois State Geological and Water Surveys within the Prairie Research Institute, University of Illinois at Urbana-Champaign. The authors thank Randall Locke and Steve Whittaker for reviewing the manuscript, Susan Krusemark for editing the manuscript, and Michael Knapp for assistance with the figures and preparing the manuscript for publication.

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