Chemical and isotopic indicators of groundwater evolution in the basal sands of a buried bedrock valley in the midwestern United States: Implications for recharge, rock-water interactions, and mixing

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ABSTRACT

Buried bedrock valley aquifers can be found throughout Canada and the northern United States where glacial deposits have filled in previously exposed bedrock valleys. The Mahomet bedrock valley is an east-west–trending buried valley in central Illinois containing basal Pleistocene sands and gravels making up the Mahomet aquifer and the contemporaneous Sankoty Mahomet aquifer, which are the major sources of freshwater for east-central Illinois. The hydrochemical characteristics of the Mahomet and Sankoty Mahomet aquifers change significantly across the buried bedrock valley. To determine the geochemical processes controlling the chemistry of the water, possible groundwater mixing, and the regions of major recharge, over 80 samples from the Mahomet aquifer, the Sankoty Mahomet aquifer, and shallower aquifers were analyzed for their chemical and isotopic composition, including $\delta^{18}O$, δD, $\delta^{13}C$, $\delta^{34}S$, ^{14}C, and ^{3}H.

Four geochemical regions were observed across the aquifers. The central and eastern region of the Mahomet aquifer had dilute chemistry and medium ^{14}C activities, suggesting relatively recent recharge from the surface. The northeastern Mahomet aquifer region had variable sulfate and $\delta^{34}S$ values, medium chloride concentrations, and low ^{14}C activity, suggesting mixing with bedrock groundwater along with sulfate reduction. The western Mahomet aquifer region had the highest chloride, dissolved organic carbon, and methane concentrations and showed a continuous decrease in ^{14}C activity, suggesting seepage from bedrock units, strong reducing conditions, and isolation from surficial recharge. Characteristics of the Sankoty Mahomet aquifer indicated rapid freshwater recharge and mixing with western Mahomet aquifer water.

The δD and $\delta^{18}O$ values indicated little to no Pleistocene water in the Mahomet bedrock valley aquifer system, suggesting an age limit of ca. 11,000 yr B.P. for most of the groundwater. The tritium data indicated modern recharge in some shallower aquifers, but little to none in the Mahomet aquifer and Sankoty Mahomet aquifer, except near a river where stacked sands may have created a hydrologic window to the Mahomet aquifer. It appears that most of the Mahomet aquifer is well protected from surficial contamination. The approach used in this study enabled us to better understand and identify the processes that control the groundwater chemistry within the buried Pliestocene aquifer in central Illinois; processes that may be prevalent in other buried bedrock valley aquifers distributed throughout much of North America.

INTRODUCTION

Groundwater is an important source of freshwater for much of the population in the United States, making up 22% of all freshwater withdrawals (Solley et al., 1998). As population and industry continue to expand across the country, the availability of groundwater resources becomes a more critical issue. In some parts of the country, such as the high plains, groundwater is the major source of freshwater, and usage is outpacing recharge (Alley et al., 1999). Maintenance of water quality in potable aquifers is another concern. For example, in the midwestern United States, the quality of water in some of the shallower aquifers has been degraded due to infiltration of agricultural chemicals (USGS, 1999a). In addition, road deicers in the north-central and northeastern United States are contaminating shallow aquifers (Pilon and Howard, 1987; Kelly and Wilson, 2003).

Approximately 21% of the people in Illinois rely on groundwater as their primary source of drinking water (USGS, 1999b). Like most of the midwestern states, Illinois has abundant groundwater resources located within both bedrock units and shallower unlithified glacial deposits. A few of the glacial aquifers are major freshwater resources for numerous municipalities. This investigation focused on the Mahomet aquifer (MA) and the Sankoty-Mahomet aquifer, which are contemporaneous Pleistocene-age unlithified sands and gravels filling ancient bedrock valleys in east-central Illinois. The Mahomet aquifer is an east-west–trending aquifer deposited in the Mahomet bedrock valley. The Mahomet aquifer extends from western Indiana to central Illinois, where it intersects the north-south–trending Sankoty Mahomet aquifer in the Mackinaw bedrock valley (Fig. 1). The Mahomet aquifer and the Sankoty Mahomet aquifer have been supplying high-quality freshwater to municipalities, industries, homeowners, and farmers for more than four decades. Over the last two decades, the use of, and interest in, the Mahomet and Sankoty Mahomet aquifers has increased due to expanding population and industry in east-central Illinois, as well as depletion of surrounding communities' surface-water reservoirs during periods of drought (Illinois State Water Plan Task Force, 1997). The increase in withdrawal and potential future use of these aquifers have raised questions concerning the quality and quantity of water in the aquifers and their future integrity.

Although the geology and hydrogeology of the buried Mahomet bedrock valley have been the subject of several previous studies over the

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Figure 1. Isopach map of the Mahomet sand in the Mahomet bedrock valley (MBV) as defined by the 500 ft elevation contour (modified from Kempton et al., 1991). MSL—mean sea level.
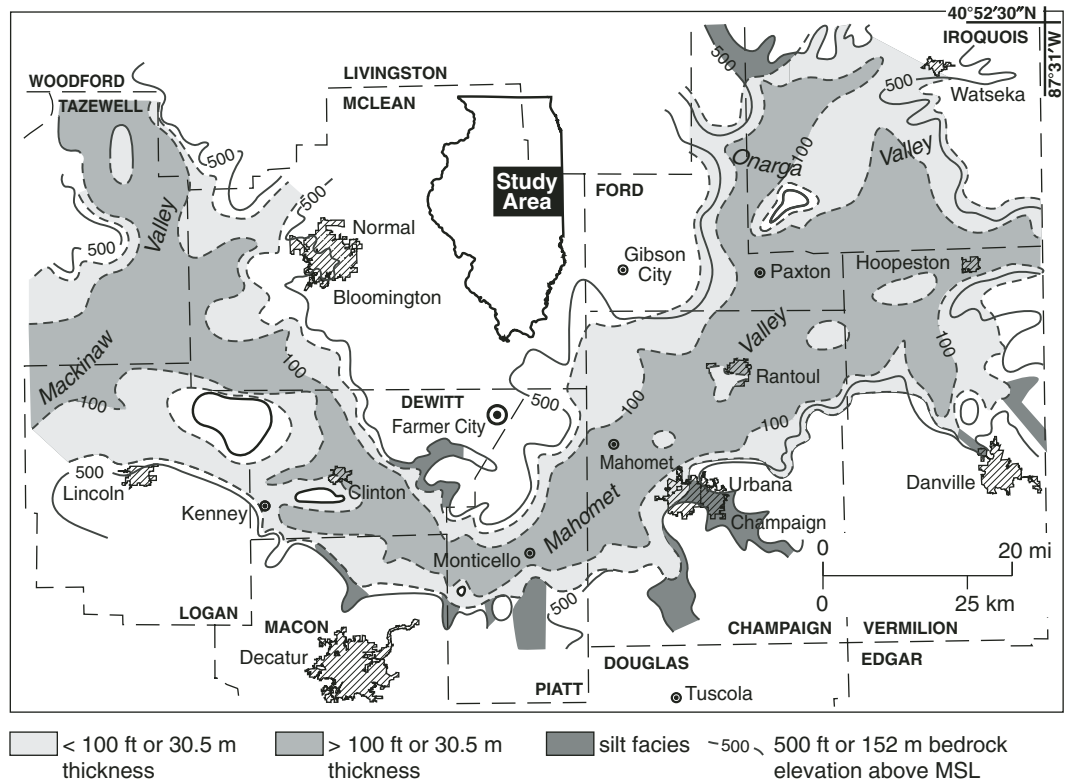
past 60 yr (Horberg, 1945; Stephenson, 1967; Visocky and Schicht, 1969; Kempton et al., 1982, 1991; Wilson et al., 1998), the geochemical reactions that control the chemistry of the groundwater, the major areas of recharge, and the age of the groundwater have only begun to be studied (Panno et al., 1994; Hackley, 2002). Arsenic is also a concern for some parts of the Mahomet aquifer and shallower units (Warner, 2001; Warner et al., 2003; Kirk et al., 2004; Kelly, 2005).

To help improve our understanding of the geochemical characteristics of the groundwater in central Illinois, we conducted a geochemical study of the Mahomet aquifer and Sankoty Mahomet aquifer systems using both chemical and isotopic analyses of the water and many of its dissolved constituents. The major objectives of this investigation were to: (1) determine the geochemical reactions controlling the chemical and isotopic composition of groundwater within the aquifers, and (2) identify the major areas of recharge.

Chemical and isotopic variations observed in the groundwater within the Mahomet and Sankoty Mahomet aquifers and their bounding aquifers have been used to help define the geochemical evolution, including microbial processes and possible mixing of different groundwater sources. Indicators of biogeochemical reactions within the buried aquifers change

along the groundwater flow path from areas where there is little obvious microbial influence to areas where there is significant microbial influence, including sulfate reduction and methanogenesis. The redox conditions that are associated with changes in sulfate and methane concentrations are reflected in other parameters as well, such as the bicarbonate concentration and the stable carbon isotope values of dissolved inorganic carbon. For example, sulfate reduction in groundwater is usually coupled with oxidation of organic matter, which typically leads to more negative carbon-13 isotopic compositions and positive sulfur-34 isotopic compositions. On the other hand, groundwater with substantial microbial methane generation typically contains very little to no sulfate and exhibits more positive carbon-13 isotopic compositions. Changes in carbon-13, carbon-14, and chloride concentrations across the Mahomet and Sankoty Mahomet aquifers reflect different degrees of water-rock interaction, biogeochemical reactions, as well as influxes of younger and fresher water from above or older, more saline groundwater from underlying bedrock. A combination of the chemical and isotopic data for both the inorganic and organic components of the groundwater allows us to create a more complete understanding of the reactions that control the bulk chemistry and helps to delineate locations where the groundwater is receiving significant recharge.

Geological Setting and Background

The Mahomet aquifer is a major aquifer made up of sands and gravels originating from glacial outwash deposited by Pleistocene continental glaciers in an extensive bedrock valley in east-central Illinois. The Mahomet aquifer was once considered part of the larger "Mahomet-Teays" buried drainage system, which was believed to extend eastward into Virginia. However, as discussed by Melhorn and Kempton (1991), studies have indicated that the Teays drainage system was not a single cohesive drainage system. The Mahomet aquifer is just one of many buried bedrock valley aquifers that exist across much of the Midwest, not to mention the northern United States and parts of Canada (NRCAN, 2008; Warner and Arnold, 2005; Shaver and Pusc, 2005; Bleuer et al., 1991).

A number of studies have examined the physical nature of the Mahomet aquifer, delineating the basic shape, size, and stratigraphy of the deposits within the bedrock valley, as well as the geology and hydrogeology of the aquifer (Horberg, 1945, 1953; Stephenson, 1967; Visocky and Schicht, 1969; Kempton et al., 1982, 1991). When using the 153 m (500 ft) bedrock elevation contour to define its boundaries, the Mahomet bedrock valley in Illinois is over 200 km (124 mi) long and ranges from ~13 km (8 mi) wide at the Illinois-Indiana border to ~32 km (20 mi) at its widest

points. The Mahomet aquifer begins in western Indiana and extends to central Illinois, where it intersects, in a large confluence area, with the north-south–trending Sankoty Mahomet aquifer in the Mackinaw bedrock valley. The Mackinaw bedrock valley is filled with sands and gravels of the Sankoty Sand Member of the Banner Formation, which make up the Sankoty Mahomet aquifer and are contemporaneous with the sands and gravels of the Mahomet aquifer (Kempton et al., 1991).

The sand and gravel that constitute the Mahomet aquifer and occupy the basal parts of the buried Mahomet bedrock valley are known as the Mahomet Sand Member of the Banner Formation and are generally greater than 30 m thick (Fig. 1). The Banner Formation is estimated to have formed more than 400,000 yr ago (Grimley, 1996) and is regarded as pre-Illinoisan in age (Willman et al., 1975; Hansel and Johnson, 1996). The Mahomet Sand Member is overlain by tills of the Banner, Glasford, and Wedron Formations (Fig. 2). The three major formations are typically separated by weathered zones, in some cases, with substantial soil development, periodically enriched with organic matter, and, in some places, peat deposits. Most of the Glasford Formation is of Illinoian age (more than 150,000 yr old) (Grimley, 1996) and contains locally important sand and gravel layers and lenses intercalated with the till. These sands and gravels are referred to as the Glasford Sand, and they form a significant aquifer in some parts of the Mahomet bedrock valley. The Glasford Formation is overlain by Wisconsinan Stage deposits, including the Robein Silt, Henry Formation, and the Wedron Formation (Fig. 2). Both the Wedron and Henry Formations contain relatively small sand and gravel outwash deposits that are thinner and much more limited in scope than either the Mahomet aquifer or Glasford Sand. The Robein Silt contains a large amount of organic matter, including wood fragments, peat deposits, and an organic-rich paleosol known as the Farmdale Geosol (Curry and Follmer, 1992).

The bedrock exposed in the floor and walls of the Mahomet bedrock valley includes rocks of the Silurian, Devonian, Mississippian, and Pennsylvanian systems (Fig. 3) (Kempton et al., 1991). Very few wells in the Mahomet bedrock valley area are screened in the bedrock units because of their low yields and increasing salinity with increasing depth (Visocky and Schicht, 1969). The western portions of the Mahomet and the Mackinaw bedrock valleys are cut predominantly through Pennsylvanian rocks consisting mostly of shale interbedded with thin limestones, sandstones, and coal seams. The Pennsylvanian rocks generally have low permeability
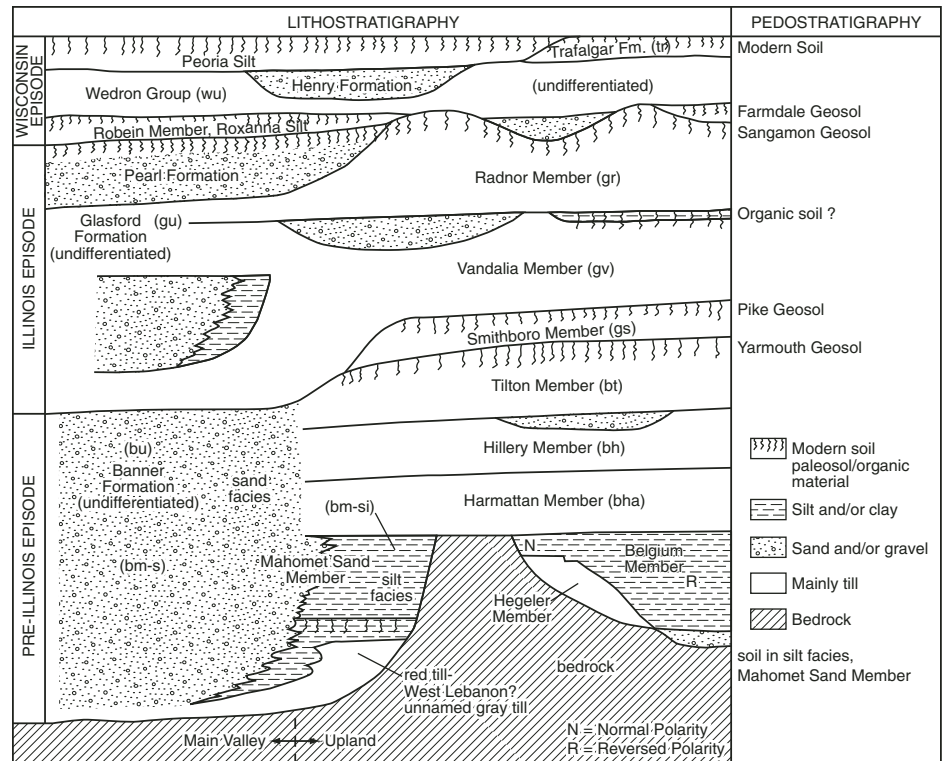

Figure 2. Schematic diagram showing relative stratigraphic relationships between Pleistocene and bedrock formations (modified from Kempton et al., 1991).

and are not an important aquifer in this area (Visocky and Schicht, 1969). However, beyond the bedrock valley, in the bedrock upland areas where the glacial deposits generally are thin and lack significant sands and gravels, the Pennsylvanian rocks are used to supply water for farms and small municipalities (Csallany, 1966). Wells developed in the Pennsylvanian units seldom penetrate more than 200 or 300 ft (61 or 91 m) and usually are screened in the thin limestones and sandstones (Csallany, 1966). The central and eastern portions of the valley expose rocks of the Mississippian, Devonian, and Silurian systems and some of the Pennsylvanian system. The Mississippian, Middle Devonian, and Silurian rocks are predominantly limestone and dolomite, but very few wells in east-central Illinois are developed in these carbonate units (Csallany and Walton, 1963). The Mississippian limestones generally have low permeability and only yield small supplies of water where the rock is fractured and creviced (Csallany and Walton, 1963). The Upper Devonian strata are primarily shale. The Middle Devonian limestone is rarely used as a source of water due to the paucity of secondary permeability and associated solution openings. The water-yielding properties of the Silurian carbonates are highly variable. The greatest yields are obtained in areas where

the Silurian carbonate rock is near the bedrock surface and the top of the limestone or dolomite is weathered and contains crevices and dissolution features (Csallany and Walton, 1963). In east-central Illinois, wells producing groundwater from the Silurian carbonate bedrock are primarily in northern Ford county and Iroquois Counties (Woller, 1975; Hamdan, 1970).

Hydrologic characteristics of the Mahomet aquifer and the Glasford aquifer were originally described in Visocky and Schicht (1969), Gibb (1970), Sanderson (1971), and Kempton et al. (1982), and summarized in Kempton et al. (1991). The hydrologic characteristics of the Sankoty Mahomet aquifer sands were described in Wilson et al. (1998). According to Kempton et al. (1991), the hydraulic conductivities for the Mahomet aquifer and the Glasford Sand average ~1.3 × 10^{-3} m/s and 4 × 10^{-4} m/s, respectively. The hydraulic conductivities measured for the Sankoty Mahomet aquifer and Glasford Sand in the Mackinaw bedrock valley average 9.7 × 10^{-4} m/s and 2.6 × 10^{-4} m/s, respectively. The confining glacial-till layers have average vertical conductivities ranging from ~8.8 × 10^{-10} m/s to 2 × 10^{-7} m/s (Wilson et al., 1998; Kempton et al., 1991). The hydraulic gradient for most of the Mahomet aquifer is ~0.19 m/km, except near the cone of depression that has recently developed

Figure 3. Bedrock geology for the area of east-central Illinois containing the Mahomet aquifer. The Mahomet bedrock valley is outlined relative to the 500 ft elevation contour (modified from Kempton et al., 1991; Kolata et al., 2005). Ls—limestone.
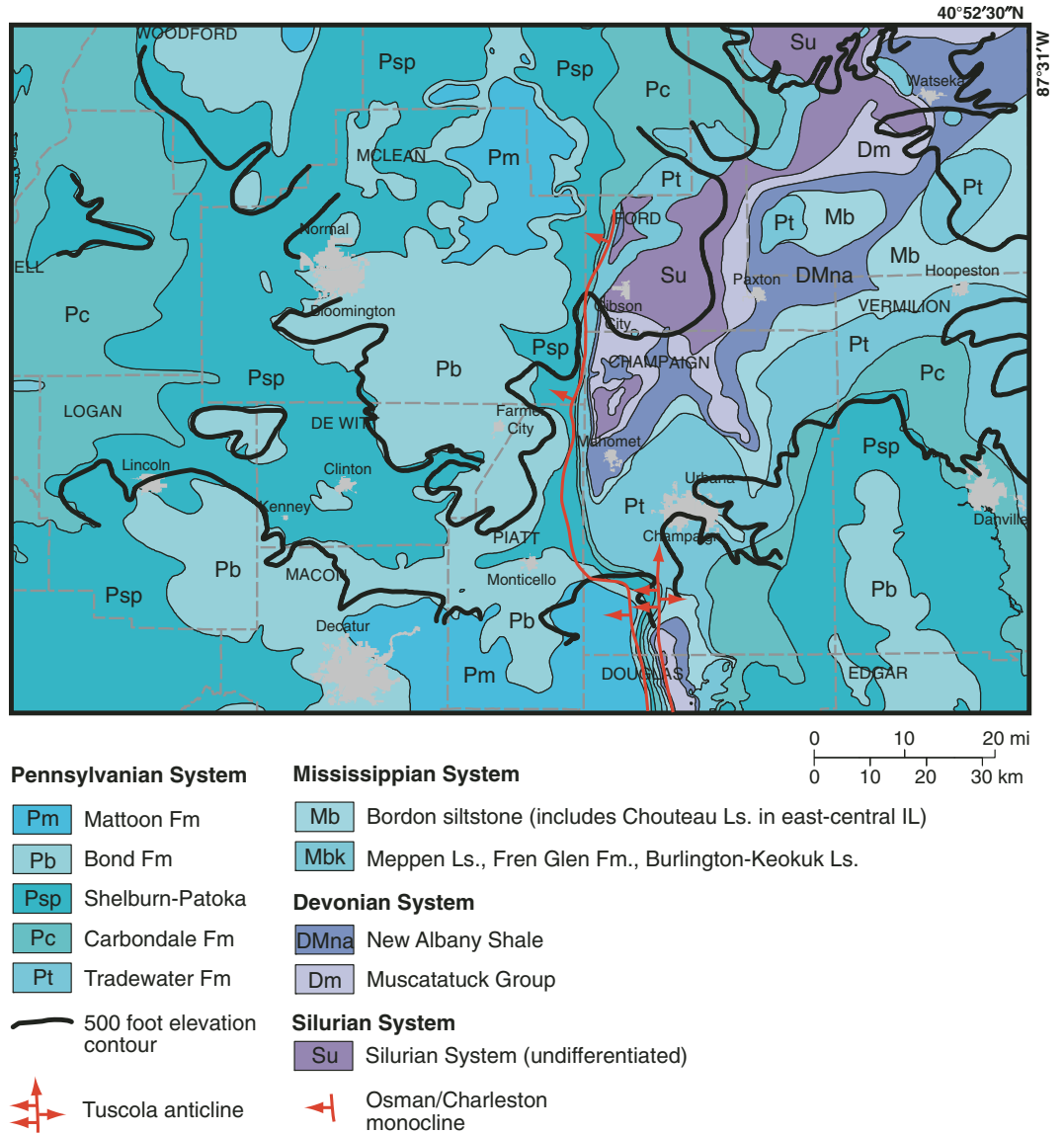
near the cities of Champaign-Urbana (Fig. 4). There is a substantial gradient change in the confluence area where the gradient increases from ~0.22 m/km in the western Mahomet aquifer to 0.78 m/km in the middle of Tazewell County (Wilson et al., 1998). The potentiometric heads in the confluence area indicate there is a groundwater divide that gradually deflects the flow of groundwater from the Mahomet aquifer to the north and to the south as it enters the confluence region (Fig. 4). The potentiometric head of the Glasford Sand aquifer is ~1.5–9 m above that of the Mahomet aquifer, but the Glasford Sand is typically separated from the Mahomet aquifer by ~15–30 m of confining glacial till. Historical records indicate the highest hydraulic heads for the Mahomet aquifer were located in northern Champaign, southern Ford, and northwestern

Vermilion Counties (Kempton et al., 1991). In the northeastern portion of the Mahomet aquifer, known as the Onarga Valley, hydraulic head data indicate that groundwater gradients are reversed (Hamdan, 1970). Groundwater may originate from surrounding uplands, percolate down into the bedrock valley, and recharge the Mahomet aquifer and up into the Glasford Aquifer in the central portion of the Onarga Valley (Hamdan, 1970).

Hydrochemically, three water types have been identified in the Mahomet aquifer (Panno et al., 1994). Groundwater in the central portion of the aquifer is a dilute-type water characterized by Ca^{2+}, Mg^{2+}, and HCO_3^-. Onarga Valley groundwater has more total dissolved solids (TDS) and is characterized by Ca^{2+}, Mg^{2+}, HCO_3^-, and SO_4^{2-}. Groundwater in the western

portion of the Mahomet aquifer is characterized by Ca^{2+}, Mg^{2+}, and HCO_3^-, with relatively large concentrations of Na^+ and Cl^-. The greater Cl^- and Na^+ concentrations were interpreted to be the result of groundwater upwelling from bedrock near the edge of the Charleston Monocline (part of the La Salle anticlinorium), which runs approximately perpendicular to the trend of the buried bedrock valley near the border of Piatt and Champaign Counties (Fig. 3).

SAMPLING AND ANALYTICAL METHODS

This paper includes the analytical results from 86 groundwater samples collected from throughout the Mahomet bedrock valley and much of the Mackinaw bedrock valley (Fig. 4).
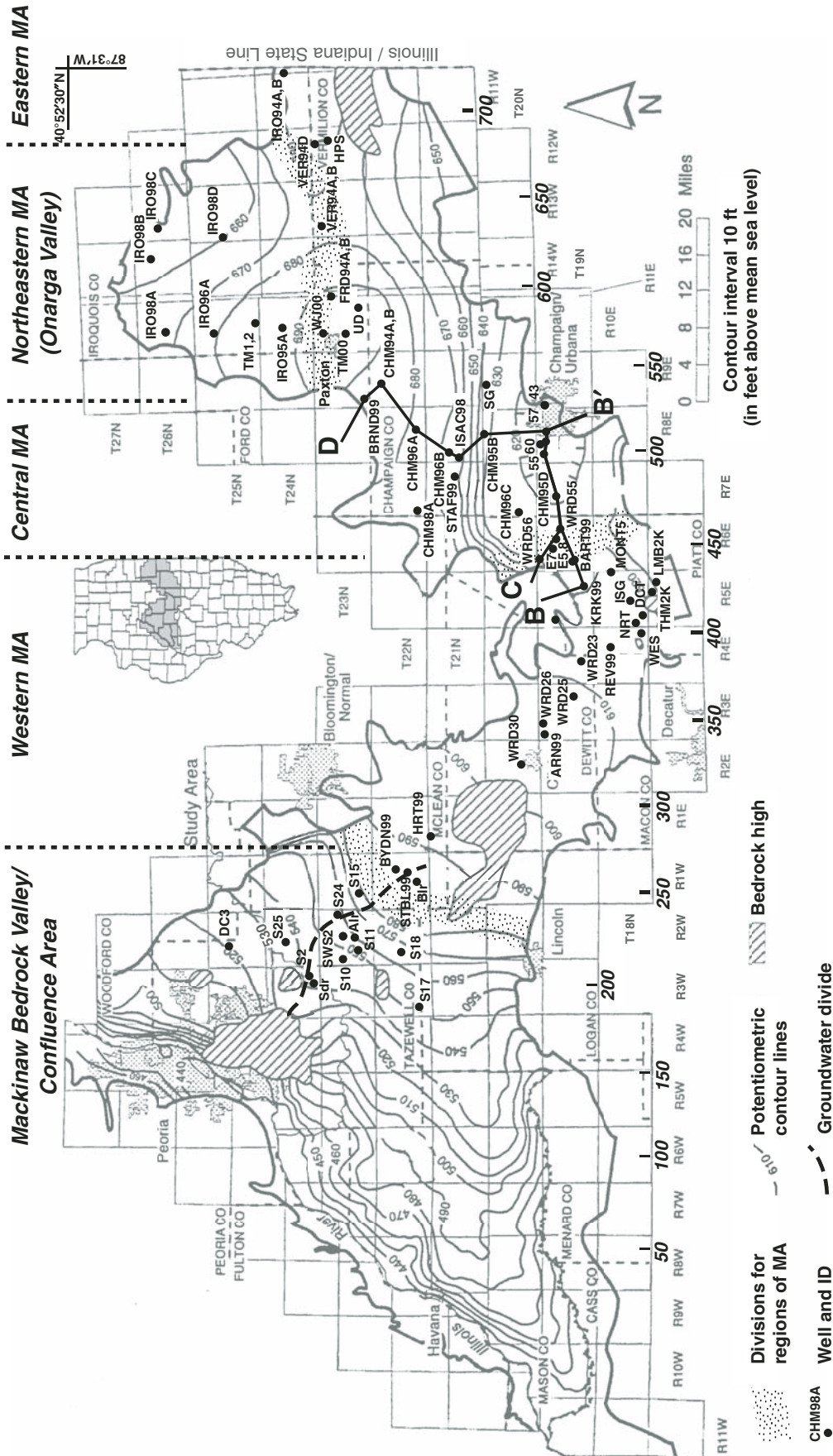
Figure 4. Map showing the location of the wells sampled from the Mahomet bedrock valley aquifer system. The contours are the potentiometric surface for the basal Mahomet aquifer (MA) (Wilson et al., 1998). The Illinois plane coordinate system (divided by 1000) is shown at southernmost township lines. Major regions are separated by shaded line and labeled across the top of the diagram. Cross-section lines B-B′, C-B′, and D-B′ are also included.

Sampling sites extend from the Indiana-Illinois border westward to the central part of Illinois (Tazewell County). Most of the groundwater samples were obtained from the basal Mahomet and Sankoty Sand Members of the Banner Formation, some from the overlying, more localized, sands within the Glasford Formation, and a few from relatively shallow sands in the Wedron Formation above the Glasford Formation. Water samples were collected from residential wells, monitoring wells drilled by the Illinois State Water Survey and the Illinois State Geological Survey, a few municipal water supply wells near Champaign-Urbana (Champaign County) and Monticello (Piatt County), Illinois, and one spring in the western part of the Mahomet bedrock valley.

Sample Collection

Water samples from residential wells were collected from outside spigots that were not connected to water softeners (commonly used in rural areas). Samples from municipal wells were collected from spigots located on the discharge pipe at the wellheads. At each site a "Y" connection was fastened to the spigot, to which a long hose and a short Viton tube were attached. The water was allowed to run for ~20–30 min through the hose and tubing while field parameters were monitored. Once field parameters stabilized, a high-capacity 0.45 μm filter was attached to the short tubing and flushed with ~500 mL of water prior to collecting samples for most chemical and isotope analyses.

Field parameters, including pH, Eh, specific conductance, and temperature, were measured for each sampling site. The pH and specific conductance meters were automatically compensated for temperature. All the electrodes were calibrated in the field with appropriate standards prior to sampling. The techniques used to collect the groundwater samples for chemical analyses are described by Wood (1981). Samples for cations and anion analyses were filtered in the field through the high-capacity in-line filters and collected in 30 and 60 mL high density polyethylene (HDPE) bottles, respectively. The cation samples were acidified in the field with concentrated nitric acid to a pH <2. Samples for dissolved organic carbon (DOC) analyses were collected in precleaned 250 mL amber glass bottles and preserved with 0.25% sulfuric acid. These water samples were placed in a cooler packed with ice for transportation to the laboratory, where they were stored at 4 °C until analyzed. DOC is reported as nonvolatile organic carbon (NVOC).

Groundwater samples taken for methane gas determination were collected in 1 gallon (4 L) collapsible containers having caps that were fitted with plastic spigots. The containers were evacuated in the field using a portable direct-drive pump. Thirty mls of 0.13% Zephrin chloride solution, a preservative, was added to the containers prior to evacuation. The collapsible containers were then immediately connected to the Viton tubing via the spigot in the cap. Unfiltered water was allowed to flush the connecting tubes and spigot for several seconds to rid the system of air bubbles, and then the valve was opened to collect the water sample. The sample container was filled with slightly less than one gallon of water and brought back to the laboratory for processing that same afternoon. These large samples were not kept chilled.

Water samples collected for isotopic analyses were filtered in the field. Samples for δD and $\delta^{18}O$ were collected in 30 mL glass amber bottles using a cap fitted with a cone-shaped plastic insert to ensure a tight seal. The $\delta^{13}C$ samples were collected in 125 mL HDPE bottles, and the $\delta^{34}S$ and ^3H samples were collected in 1 L HDPE bottles. The samples were transported to the laboratory in an ice-filled cooler and stored at 4 °C until analyzed. Samples taken for carbon-14 (^{14}C) analysis of dissolved inorganic carbon (DIC) were collected in collapsible five-gallon (20 L) containers. A stir bar was placed in the container, which was evacuated in the field prior to being filled with water. Filtered water samples were directly passed into the evacuated container using a thick-walled Tygon tubing connected to the container's spigot valve. The Tygon tubing and spigot valve were purged with the formation water through a small opening in the valve prior to filling the container. The direct connection to the sample container minimized degassing and contact with atmospheric carbon dioxide. These samples were too large for refrigeration in the laboratory and were processed as quickly as possible for ^{14}C analysis (within 48 h).

Those samples containing significant methane (CH_4) gas were analyzed for $\delta^{13}C$ and δD. Samples taken for stable isotope analyses on CH_4 were collected in quart-size (1 L) glass jars using the water-displacement technique as described by Meents (1960).

Analyses

The groundwater samples were analyzed chemically for major and minor cations, anions, DOC, and CH_4 concentration. Concentrations of cations were determined by the Illinois State Water Survey (ISWS) using a Model 1100 Thermo-Jarrell Ash inductively coupled argon–plasma spectrometer (ICAP). Anion concentrations were determined at the ISGS using a Dionex 211i ion chromatograph (IC), following U.S. EPA Method 300 (O'Dell et al., 1984). The DOC concentration was determined at the ISWS using a Dohrmann total organic carbon analyzer and following methods similar to those described in ASTM D-4839–88 (1994).

The concentration of dissolved CH_4 in the water was determined by analyzing the composition of the gas bubble from the 4 L collapsible container and using a best-fit polynomial for CH_4 solubility data between 0 and 30 °C (Dean, 1992) to calculate the concentration of CH_4. The sample containers were brought back to the laboratory and weighed immediately. The quantity of water was determined from the difference between the full and empty weights of the collapsible sample containers. By the time the sample was returned to the laboratory, the dissolved gases had equilibrated to atmospheric pressure and come out of solution, making a bubble inside the container. The gas was extracted from the containers that same afternoon using an appropriate-size graduated syringe and needle. Prior to extracting the gas, saturated sodium sulfate solution was used to fill the needle and dead space at the end of the syringe in order to minimize air contamination of the samples and prevent dissolution of the gas sample into the solution while in the syringe. The gas was extracted by pushing the needle directly through the plastic collapsible container and drawing the gas bubble into the syringe. The quantity of gas extracted was measured using the graduated marks on the syringe and was injected into a previously evacuated glass vial (Vacutainer®) fitted with a septum. The gas samples were then analyzed on a gas chromatograph (GC).

Stable isotopic analyses included $\delta^{18}O$ and δD of the water, $\delta^{13}C$ of the DIC, $\delta^{34}S$ of the dissolved SO_4^{2-} sulfur, and $\delta^{13}C$ and δD of the CH_4. The $\delta^{18}O$ value of the water samples was determined using a modified CO_2-H_2O equilibration method as originally described in Epstein and Mayeda (1953), with modifications described in Hackley et al. (1999). The δD of water was determined using the Zn-reduction method described in Coleman et al. (1982) and Vennemann and O'Neil (1993), with modifications described in Hackley et al. (1999). The $\delta^{13}C$ of DIC was determined using a gas-evolution technique. Approximately 10 mL of water were injected into an evacuated vial containing 100% phosphoric acid and a stir bar. The CO_2 evolved from the water sample was cryogenically purified on a vacuum system and sealed into a Pyrex break tube for isotopic analysis. The $\delta^{34}S$ of the SO_4^{2-} was determined by precipitating the SO_4^{2-} as $BaSO_4$ and converting the sulfur to SO_2 by combustion with a V_2O_5-SiO_2 mixture, similar to that described by Yanagisawa and Sakai

(1983) and Ueda and Krouse (1986). The $\delta^{13}C$ and δD values of the CH_4 samples were determined by combusting the CH_4 and collecting the products CO_2 and H_2O as described by Hackley et al. (1999).

The δD, $\delta^{13}C$, $\delta^{18}O$, and $\delta^{34}S$ values were determined on a dual inlet ratio–mass spectrometer. Each sample was directly compared to an internal standard calibrated versus an international reference standard. The final results are reported versus the international reference standards. The δD and $\delta^{18}O$ results are reported versus the international Vienna Standard Mean Ocean Water (V-SMOW) standard. The $\delta^{13}C$ results are reported versus the Peedee belemnite (PDB) reference standard. The $\delta^{34}S$ results are reported versus the Canyon Diablo Troilite (CDT) standard. Analytical reproducibility for δD, $\delta^{18}O$, $\delta^{13}C$, and $\delta^{34}S$ is equal to or less than $\pm 1.0\permil$, $\pm 0.1\permil$, $\pm 0.15\permil$, and $\pm 0.3\permil$, respectively.

Radioisotope analyses included ^{3}H on the water and ^{14}C on the DIC. The ^{3}H analyses were done by the electrolytic enrichment process (Ostlund and Dorsey, 1977) and the liquid scintillation counting method. The electrolytic enrichment process consists of distillation, electrolysis, and purification of the ^{3}H enriched samples. The precision for the tritium analyses reported in this study is $\le \pm 0.25$ TU.

The ^{14}C activity of the DIC was analyzed using conventional techniques, and results were corrected for $\delta^{13}C$ compositions. The DIC was extracted from the water samples by acidification; the released CO_2 was quantitatively collected on a vacuum line. The CO_2 from acidification was cryogenically purified and converted to benzene as outlined in Coleman (1976). The ^{14}C activity was measured using the liquid scintillation spectrometry technique developed by Noakes et al. (1965, 1967). The ^{14}C results are reported as percent modern carbon (pMC) relative to the NBS reference material (oxalic acid #1). Modern carbon (100 pMC), by convention, is defined as 95% of the activity of the oxalic acid reference standard (Clark and Fritz, 1997).

RESULTS AND DISCUSSION

The chemical and isotopic results (GSA Data Repository, Tables DR1, DR2, and DR3[1]) show important patterns across the basal sands of the Mahomet aquifer and Sankoty Mahomet aquifer. Four hydrochemical facies were observed in

the basal sands of the Banner Formation, each of which had different ^{14}C and/or $\delta^{13}C$ characteristics. Groundwater in the central and eastern regions of the Mahomet aquifer (Champaign County, southern Ford County, and parts of Vermillion County) is primarily Ca-Mg-HCO_3 water with very low Cl^- concentration and ^{14}C values around 30 pMC. Groundwater in the western region (Piatt County, DeWitt County, and McLean County) is a Ca-Mg-HCO_3 water with a notable influence from Na-Cl–type waters. Groundwater in this western region also shows decreasing ^{14}C values toward the west and the greatest $\delta^{13}C$ values observed for DIC compared to the rest of the Mahomet aquifer. Groundwater in the northeastern region of the Mahomet aquifer (the Onarga Valley), in Iroquois County and parts of northern Vermillion County, is primarily Ca-Mg-HCO_3 with some Ca-Mg-SO_4 waters and exhibits smaller ^{14}C concentrations and more negative $\delta^{13}C$ values than the central and eastern regions of the aquifer. The groundwater in the Sankoty Mahomet aquifer is primarily Ca-Mg-HCO_3 water with variable Na^+ and Cl^- concentrations and a large range of ^{14}C and $\delta^{13}C$ values. The dominance of major cations

and anions for the different facies is shown in a trilinear diagram (Fig. 5). These results suggest trends from Ca-Mg-HCO_3 waters to Ca-Mg-SO_4– and Na-Cl–type waters in the aquifers of the Mahomet bedrock valley system, based on the generalized evolution of groundwater due to water-rock interactions (Chebotarev, 1955; Schoeller, 1959). However, as indicated in the following discussions for each region of the buried bedrock aquifers, many of the chemical variations observed are actually due to mixing of younger, more dilute groundwater with older, more mineralized groundwater seeping from bedrock units in the various regions of the bedrock valley or mixing of relatively fresh recharge water with groundwater emerging from a part of the Pleistocene aquifer that is more confined. The isotopic composition ($\delta^{18}O$ and δD) of most of the water sampled from the Mahomet and Sankoty Mahomet aquifers is similar to present-day precipitation, suggesting the age of the water is no older than the start of the Holocene. There are a couple of samples that have slightly more negative isotopic compositions, and these are in regions of the aquifer that have evidence of inputs from bedrock units.
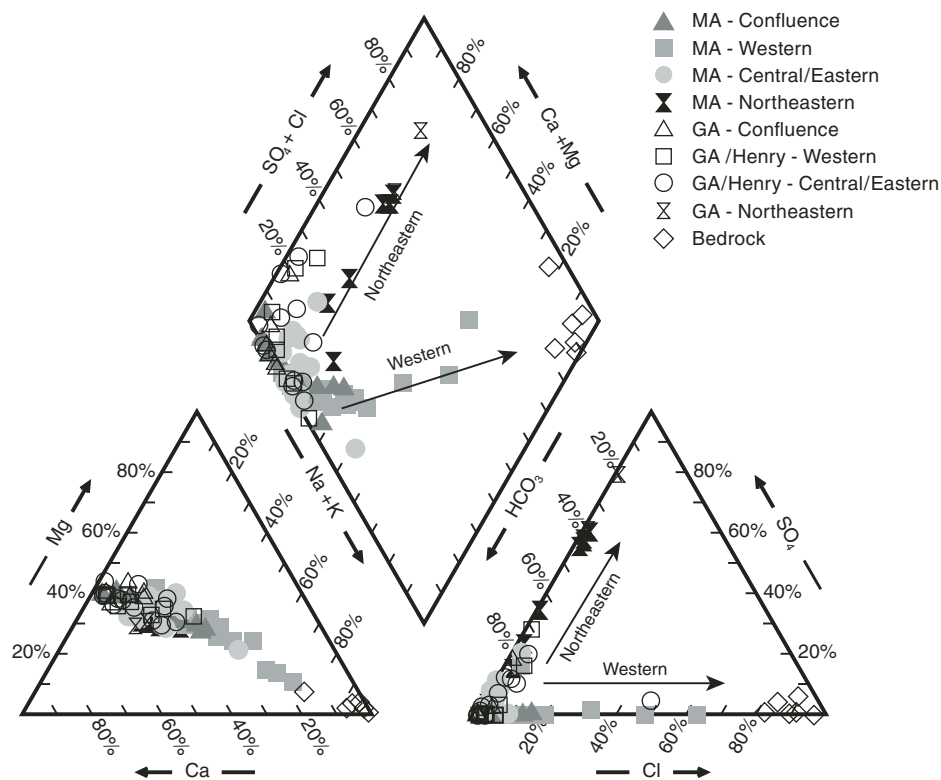

Figure 5. Trilinear and piper diagrams of groundwater samples from the Mahomet bedrock valley hydrologic system. Different symbols represent samples from the Mahomet and shallower aquifers in the different regions across the Mahomet Valley. Bedrock data are from Panno et al. (1994). Arrows depict geochemical evolutionary trends observed in the western and northeastern regions.

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[1]GSA Data Repository item 2009286, data tables and additional text and figures referred to in the main document, is available at http://www.geosociety.org/pubs/ft2009.htm or by request to editing@geosociety.org.

Central-Eastern Mahomet Aquifer Region

Groundwater in the central and eastern regions of the Mahomet aquifer has the smallest total dissolved solids content, as exemplified by the small chloride concentrations (Fig. 6) and the relatively low specific conductance values (Fig. DR1 [see footnote 1]). The low specific conductance and chloride concentrations suggest significantly less water-rock interaction compared to the rest of the Mahomet aquifer. The relatively dilute nature of this groundwater led Panno et al. (1994) to suggest that there is more rapid recharge from the surface in the central region than the western and northeastern regions of the Mahomet aquifer. The greater ^{14}C activity in central-eastern area of the Mahomet aquifer, near 35 pMC (Fig. 7), supports this hypothesis. There is an unusually thick sequence of stacked sand deposits (Panno et al., 1994; Hackley, 2002) in the central region of the Mahomet bedrock valley that corresponds to the potentiometric high (Fig. 4), providing additional geologic and hydrologic evidence that the area is an important recharge zone for the Mahomet aquifer.

Typically, assuming the lithology and geochemistry of the local geology and aquifers are similar, one would expect the $^{14}C_{DIC}$ activity in the groundwater near a recharge zone to be relatively large compared to groundwater at a similar stratigraphic level further away from the recharge zone. Most wells screened in the Glasford Formation in Champaign and Ford Counties, had relatively large $^{14}C_{DIC}$ activities (58–65 pMC), as would be expected for a relatively shallow aquifer near a recharge zone. However, the $^{14}C_{DIC}$ results from a few wells in the same area suggest the situation is complicated. For example, one of the Glasford wells, BRND-99, on the border of southern Ford County and northern Champaign County, had a relatively low $^{14}C_{DIC}$ activity (28.1 pMC) compared to most other wells drilled to a similar stratigraphic level in the bedrock valley (Table DR3B [see footnote 1]). Relatively low ^{14}C values were also observed in other wells in the Glasford aquifer (CHM-94B and TM-00), as well as in the Mahomet aquifer (CHM-94A and WJ-00), which are located in or near the same area of stacked sands and topographical high in northern Champaign and southern Ford Counties. Biogeochemical reactions such as sulfate reduction and methanogenesis may help to explain the lower ^{14}C values in these wells. The $\delta^{13}C$ values for some of the wells are more negative ($<-14\permil$) than most of the other wells in the central and eastern regions, suggesting the input of isotopically lighter carbon, probably due to oxidation of organic matter related to the sulfate
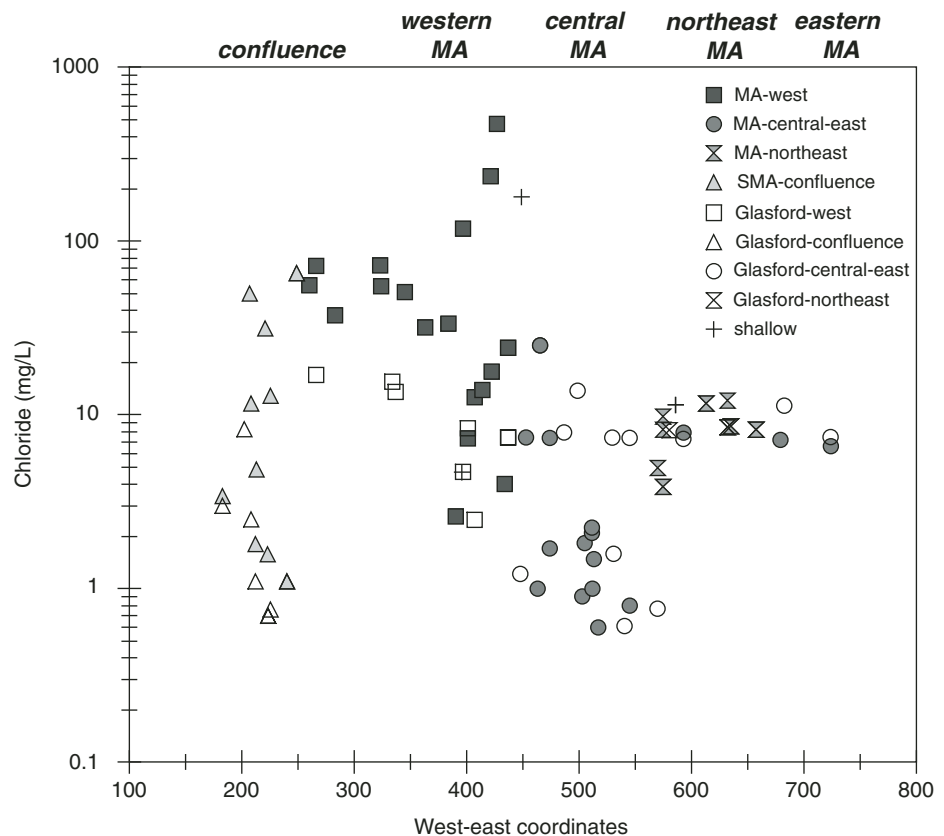

Figure 6. Distribution of Cl⁻ concentrations for groundwater samples plotted geographically across the Mahomet bedrock valley system. Different symbols are used for different regions of the Mahomet Valley. Closed symbols are samples from the Mahomet aquifer, while open symbols are from the shallower Glasford and Wedron aquifers (Coordinates used for *x*-axis are Illinois plane coordinates divided by 1000; see location map Fig. 3.).

reduction. Most of these wells with low $\delta^{13}C$ values also had positive $\delta^{34}S$ values, with concentrations ranging from below detection limits to 51 mg/L (Tables DR2 and DR3 [see footnote 1]). The well with no detectable sulfate, BRND-99, had detectable CH_4, suggesting that after sulfate concentrations were depleted, fermentation reactions associated with methanogenesis took over, which could have contributed additional ^{14}C-depleted bicarbonate to lower $^{14}C_{DIC}$ values. The fermentation reactions that occur along with methanogenesis break down complex organic compounds into simpler molecules such as fatty acids, carbon dioxide, protons, and hydrogen (Klass, 1984).

Northeastern Mahomet Aquifer (Onarga Valley) Region

Groundwater in the Onarga Valley, the segment of the Mahomet bedrock valley that trends north-northeast, contains low $^{14}C_{DIC}$ activities (Fig. 7) and high SO_4^{2-} concentrations (Table

DR2 [see footnote 1]). The bedrock consists of Silurian and Devonian marine limestones and dolostones and Pennsylvanian shales, sandstones, and coals. Panno et al. (1994) suggested that the source of the high SO_4^{2-} concentrations is the dissolution of sulfate minerals associated with the weathered bedrock units. Because of the minimal amounts of dissolved oxygen available in groundwater, the SO_4^{2-} concentrations observed in the Onarga Valley are not possible by pyrite oxidation alone but are plausible by dissolution of sulfate minerals as determined by geochemical modeling (Panno et al., 1994). The additional low (negative) $\delta^{34}S$ results for samples with large SO_4^{2-} concentrations reported in this study support the suggestion that the sulfate minerals being dissolved were originally derived from the oxidation of pyrite in the Pennsylvanian coal and shales as well as Devonian shales. The $\delta^{34}S$ associated with sulfur from reduced sulfides such as pyrite are typically negative (Hackley and Anderson, 1986; Kaplan, 1983; Goldhaber and Kaplan,
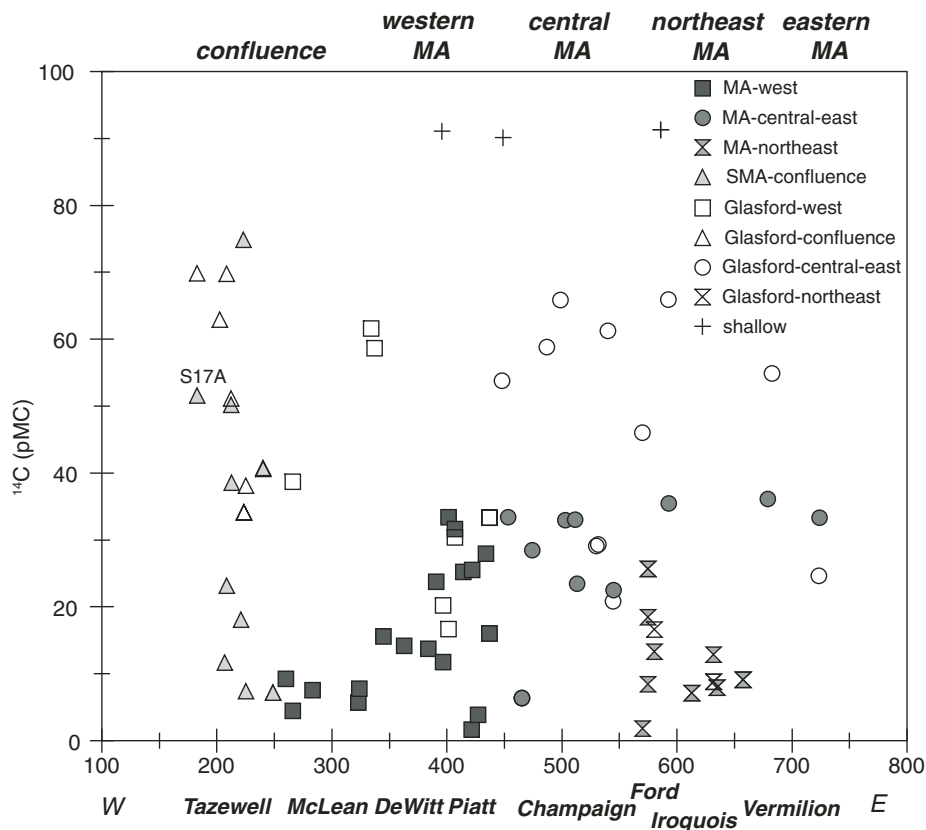
Figure 7. ¹⁴C activity of dissolved inorganic carbon (DIC) for samples taken from the Mahomet bedrock valley system plotted geographically from west to east across the bedrock valley. Different symbols are used for different regions of the Mahomet Valley. Closed symbols are all from the Mahomet aquifer, while open symbols are from the shallower Glasford and Wedron aquifers.

1980, 1974). Prior to deposition of the Pleistocene sediments, bedrock units exposed in the valley would have undergone weathering for a prolonged period. For example, secondary gypsum and iron-sulfate formation from pyrite oxidation has been observed in recent soils and lignite overburden piles (Wagner et al., 1982; Nettleton et al., 1982; Dixon et al., 1982). Thus, gypsum and iron sulfates may be present in the weathered bedrock surface of the Mahomet bedrock valley in this region.

If gypsum is present at the base of the Mahomet bedrock valley, along with dolomite and calcite, then there is the possibility that de-dolomitization may be occurring in the Onarga Valley region. De-dolomitization has been reported in other aquifers containing gypsum in the presence of limestones and dolomite (Back and Hanshaw, 1970; Wigley et al., 1978; Back et al., 1983; Plummer et al., 1990). Although no physical evidence of gypsum was reported in the geological logs from the drilling records in the northeastern Mahomet aquifer, the trends observed between concentrations of

Ca, Mg, and HCO_3 versus SO_4 suggest that de-dolomitization has probably occurred (see GSA Data Repository [see footnote 1]).

The relatively low $^{14}C_{DIC}$ activities in both the Mahomet aquifer and shallower Glasford aquifer in the Onarga Valley region (Fig. 7) are consistent with upward movement of groundwater passing through bedrock units up into the Pleistocene deposits in the central part of Onarga Valley (Hamdan, 1970). Dissolution of the Paleozoic bedrock carbonates would add ^{14}C-free carbonate ions to the DIC pool, diluting the ^{14}C activity. In addition, $\delta^{13}C_{DIC}$ values in this region are unusually negative (–14‰ to –21‰) (Fig. 8; Table DR3 [see footnote 1]), suggesting that oxidation of organic matter has also contributed to the DIC. Organic carbon, dissolved or sedimentary, would be isotopically depleted compared to the DIC of groundwater. For example, the $\delta^{13}C$ values of sedimentary organic matter collected from glacial deposits throughout Illinois range between –24‰ to –30‰ (Liu and Coleman, 1981; Liu et al., 1986). Thus, input of dissolved CO_2 from the oxidation of

organic compounds would shift the carbon isotopic composition of the DIC to more negative values. The high SO_4^{2-} concentration observed in the groundwater of this northeastern region is a likely source of electron acceptors for anaerobic oxidation of organic matter within the aquifer. Dissolved CO_2 from the oxidation of DOC or sedimentary organic matter originating from the Illinoian or pre-Illinoian Pleistocene sediments or the Paleozoic bedrock strata would also dilute the ^{14}C content. Thus, the low $^{14}C_{DIC}$ concentrations in the northeastern region of the Mahomet aquifer can be attributed to a combination of older groundwater passing through previously exposed bedrock valley units, resulting in the dissolution of sedimentary carbonates, plus the oxidation of buried sedimentary organic matter through sulfate reduction.

The relationship between $\delta^{34}S$ and $[SO_4^{2-}]$ in the northeastern region and surrounding areas of the Mahomet bedrock valley can be used to estimate the relative importance of SO_4^{2-} reduction and groundwater mixing as the controlling factors for the variable SO_4^{2-} concentration observed in the Mahomet aquifer (Fig. 9). Because much of the Onarga Valley is topographically lower than surrounding areas, groundwater could be percolating down in the perimeter regions of the Onarga Valley and flowing through and mixing with groundwater from bedrock units. Thus, the isotopic composition and concentration of SO_4^{2-} observed in the shallow sands of the Wedron and Glasford Formations, as well as the Mahomet aquifer beyond the immediate vicinity of the Onarga Valley, would be important to consider for evaluating mixing and sulfate reduction influences. The mixing curve in Figure 9 was calculated using the groundwater samples from the vicinity of the northeastern Mahomet bedrock valley with the highest and lowest SO_4^{2-} concentration and their respective $\delta^{34}S$ values as end members. The Rayleigh fractionation curves in Figure 9 were calculated using a fractionation factor of $\alpha = 1.015$, which is reasonable for fresh groundwater systems (Busby et al., 1991; Eberts and George, 2000). The different calculated Rayleigh curves show the trends that would be expected if the sulfate reduction process were initiated at different SO_4^{2-} concentrations. The trend of $\delta^{34}S$ values and SO_4^{2-} concentration for most of the samples falls closer to the mixing relationship rather than the Rayleigh fractionation curves, especially the overall fractionation curve initiated from the highest SO_4^{2-} concentration.

Although SO_4^{2-} reduction is probably not the dominant process responsible for the decrease in SO_4^{2-} concentration in the Mahomet aquifer in the northeastern region and surrounding areas, the $\delta^{34}S$ and $[SO_4^{2-}]$ data do show that
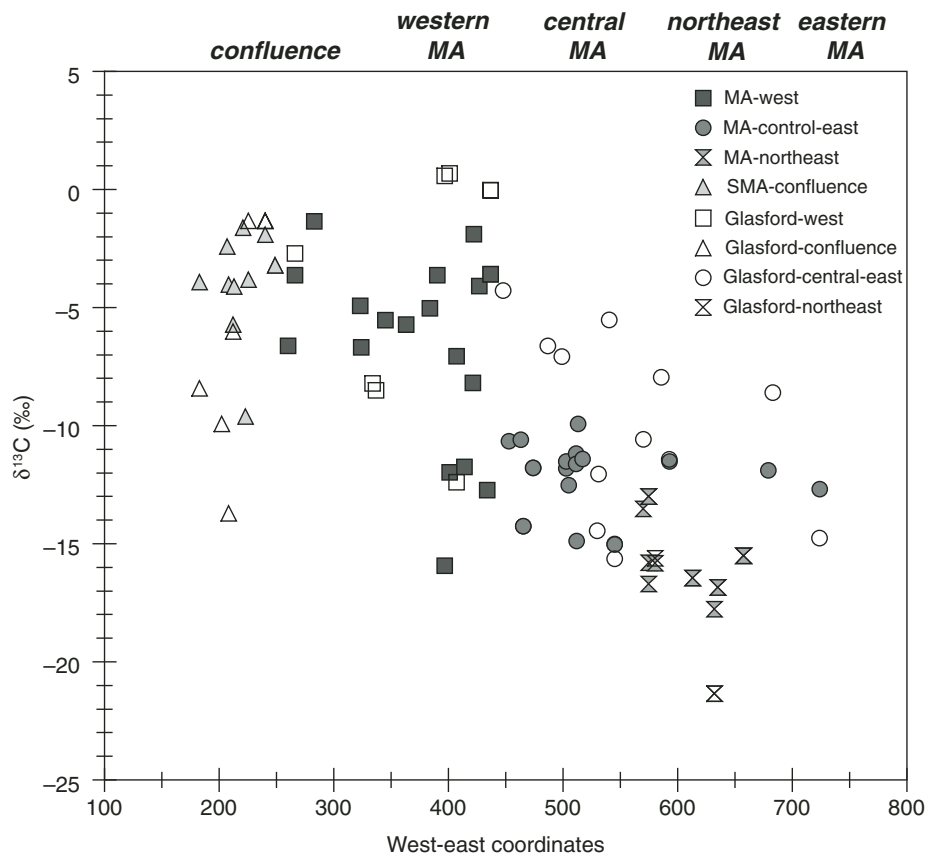
Figure 8. Distribution of $\delta^{13}C_{DIC}$ values for groundwater samples plotted geographically across the Mahomet bedrock valley system. Different symbols are used for different regions of the Mahomet Valley.

SO_4^{2-} reduction is definitely occurring, and in some cases may be dominant. The very positive $\delta^{34}S$ values in groundwater from shallower sands (+15‰ to +30‰) overlying the Mahomet aquifer in the Mahomet bedrock valley (central-eastern and the western regions) are most likely due to SO_4^{2-} reduction. The primary source of dissolved SO_4^{2-} in the shallow tills would be the oxidation of pyrite, which typically has negative $\delta^{34}S$ values (−10‰ to −16‰, according to Van Stempvoort et al., 1994). The low SO_4^{2-} concentrations and very positive $\delta^{34}S$ values measured in samples from these shallower aquifers are probably characteristic of the SO_4^{2-} in groundwater that eventually infiltrates the deeper Mahomet aquifer in areas of downward gradients. In addition to these shallower groundwater samples, one of the deeper samples (I98C) in the Mahomet aquifer in the northeastern region also had a very positive $\delta^{34}S$ value (+57‰), strong evidence of SO_4^{2-} reduction being a dominant process for this site. The $\delta^{34}S$ values of other samples from the northeastern region suggested that SO_4^{2-} reduction has overprinted the general mixing trend exhibited for most of

the Mahomet aquifer samples in the region. For example, assuming the chosen end members are correct, groundwater at sites I98B, I95A, and especially I98D have significantly more positive $\delta^{34}S$ values than would be expected from mixing alone. The more positive $\delta^{34}S$ values at these sites are likely due to microbial SO_4^{2-} reduction occurring in conjunction with mixing. Groundwater at sites I96A, V94A, and T2 also appears to have been slightly influenced by SO_4^{2-} reduction processes (Fig. 9). Sulfate reduction in the Mahomet aquifer samples is supported by their more negative $\delta^{13}C_{DIC}$ values relative to most of the other samples in the central and eastern portion of the Mahomet aquifer (Table DR3a [see footnote 1]; Fig. 8). The more negative $\delta^{13}C$ values suggest an input of isotopically light carbon by the oxidation of organic matter, which would occur during the SO_4^{2-} reduction process.

Thus, the chemical and isotopic data suggest that the wide range in SO_4^{2-} concentrations in the eastern half of the Mahomet aquifer is caused by a combination of groundwater mixing and SO_4^{2-} reduction. Mixing occurs between upwelling high-SO_4^{2-} groundwater from the

Onarga Valley in northeastern region and lower-SO_4^{2-} groundwater in the basal Mahomet sand from the central region. The large SO_4^{2-} concentration in the Glasford Sand and Mahomet aquifer in northern Vermilion (V94B&A) suggests that the upwelling groundwater from the Onarga Valley has also mixed with groundwater in parts of Vermilion County. In the rest of the Mahomet aquifer, it would appear that groundwater from the shallower aquifers has percolated down to the Mahomet aquifer, with SO_4^{2-} subjected to various degrees of sulfate reduction. The microbial SO_4^{2-} reduction contributes to the decrease in SO_4^{2-} concentration as well as an increase in the $\delta^{34}S$ of the remaining SO_4^{2-}. This reduction process also results in more negative $\delta^{13}C_{DIC}$ values and adds to the dilution of ^{14}C activity of the DIC, which is already low in the northeastern region of the Mahomet aquifer as a result of the upwelling older groundwater from the bedrock in this area.

Besides the elevated SO_4^{2-} concentrations, groundwater samples in the vicinity of the northwestern region are anomalously high in other constituents including B and Sr, which appear to be related to the local lithology (Hackley, 2002; Table DR2; Figs. DR3 and DR4 [see footnote 1]). Boron is typically associated with minerals such as tourmaline, biotite, and amphiboles (Hem, 1992) or perhaps with shales and coals (Krauskopf, 1967). The Upper Devonian New Albany, the Mississippian Bordin Siltstone, and the Pennsylvanian Tradewater Formations exposed in the bedrock in the northeastern and central parts of the Mahomet bedrock valley (Kolata et al., 2005) contain shales, coals, siltstones, and argillaceous sandstones, some with noticeable mica flakes (Willman et al., 1975), and they are probably the primary source of the elevated boron in this part of the Mahomet aquifer. The source of Sr is probably the Mississippian, Silurian, and Devonian carbonates (Fig. 3) or clastics from these formations, which make up most of the exposed bedrock for this region of the valley.

Western Mahomet Bedrock Valley Region

Within the transition zone between the central and western regions of the Mahomet aquifer, there appears to be a fraction of rather young groundwater percolating down through sand units beneath the Sangamon River, as indicated by the tritium results. Two groundwater samples from the basal sands in this region contained a small amount of detectable tritium (Table DR3A [see footnote 1]). The tritium data support recent seismic and water-well pumping studies that indicate there is a hydraulic connection between the Sangamon River and the Mahomet aquifer in
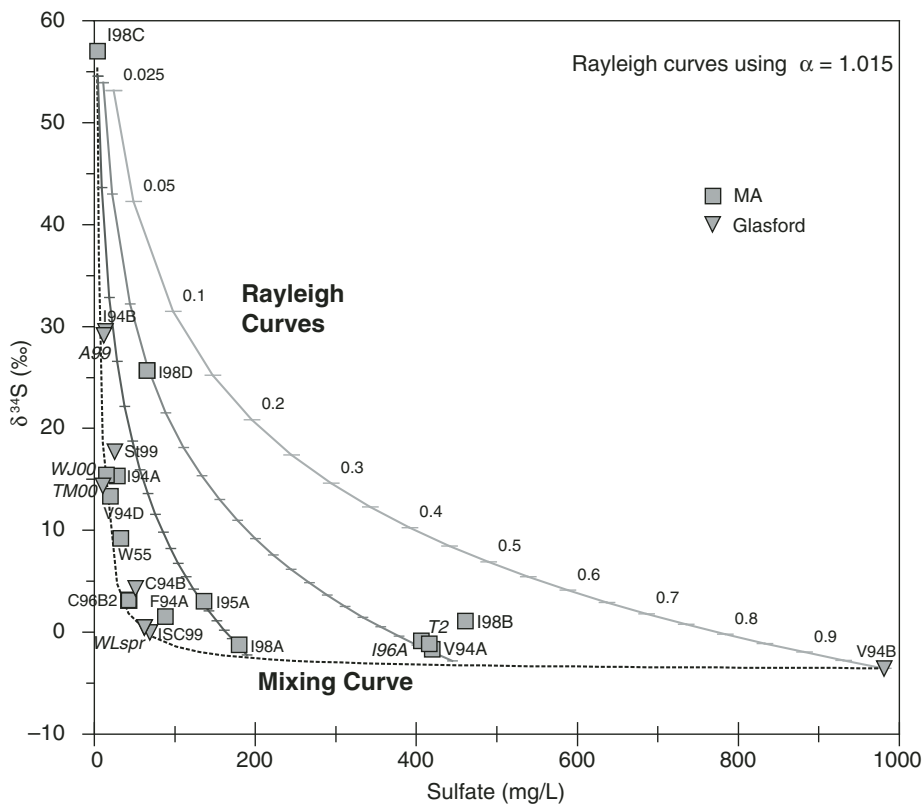
Figure 9. δ^{34}S versus [SO$_4^{2-}$] for groundwater samples collected from the Mahomet aquifer and shallower sands. Diagram includes a calculated mixing curve and Rayleigh fractionation curves to help determine whether physical mixing or redox processes are affecting the variability of [SO$_4^{2-}$]. The multiple Rayleigh curves show how sulfate reduction reactions could overprint the overall mixing process. (Tick marks on Rayleigh curves indicate fraction of original [SO$_4^{2-}$] remaining.)

this area (Carstens, 2004; Roadcap and Wilson, 2001). The ^{14}C activity of these two samples did not show an increase; in fact, the ^{14}C of one was similar to other samples in the central region (30 pMC), while the other sample was quite low (11 pMC), suggesting that there has been significant amounts of groundwater with less than 30 pMC mixing with the younger water percolating down from near the surface. There was also CH$_4$ detected in the Mahomet aquifer and Glasford aquifer in the same area, indicating degradation of buried organic debris (including fermentation reactions), which would tend to dilute the ^{14}C activity of the DIC as well as influence the δ^{13}C and concentration of DIC.

Just west of the boundary between the central and western parts of the Mahomet aquifer, (in Piatt County), SO$_4^{2-}$ concentrations drop to very small values, often below detection limits, and CH$_4$ concentrations increase abruptly (Fig. 10). In the sequence of microbial reduction processes, SO$_4^{2-}$ is consumed prior to microbial production of CH$_4$ (Oremland and Taylor, 1978). This is because SO$_4^{2-}$-reducing

bacteria are more efficient in utilizing the available energy sources, such as hydrogen and acetate, and out-compete methanogens (Martens and Berner, 1974; Abram and Nedwell, 1978; Kristjansson et al., 1982). Thus, in groundwater where methanogenesis occurs, SO$_4^{2-}$ concentrations are usually quite small or not detectable. The δ^{13}C and δD values of CH$_4$ from the Mahomet aquifer indicate that the CH$_4$ is of microbial origin, formed by the CO$_2$ reduction pathway (Fig. 11). This is in agreement with the results of Coleman et al. (1988), who studied the origin of CH$_4$ in several glacial drift and shallow Paleozoic deposits throughout Illinois.

The western Mahomet aquifer also shows an east-west trend of progressively higher specific conductance (Fig. DR1 [see footnote 1]) and Cl$^-$ concentrations (Fig. 6) compared to the rest of the aquifer. Sodium concentrations also increase in this part of the Mahomet aquifer. The increases in Na$^+$ and Cl$^-$ concentrations suggest contribution of more saline groundwater from bedrock units. The main influx of saline groundwater probably occurs near the west flank of the

La Salle anticlinorium (Panno et al., 1994). The largest concentrations of Cl$^-$ and the lowest ^{14}C concentrations observed in this study were from samples located in Piatt County, just west of the Osman-Charleston monocline (Fig. 3), which is associated with the La Salle anticlinorium in central Illinois.

Both the change in bedrock lithology (Fig. 2) associated with the Osman-Charleston monocline and the seepage of groundwater from bedrock units in the western region of the Mahomet aquifer may contribute to the strongly reducing conditions, as indicated by the disappearance of SO$_4^{2-}$ and elevated levels of CH$_4$ concentration as one moves further west along the Mahomet aquifer from the central region. The units exposed along the bottom of the bedrock valley in the western region are the Pennsylvanian Modesto and Bond Formations (Kempton et al., 1991; Willman et al., 1975). These Pennsylvanian shales, coals, and argillaceous limestones, or perhaps clastics from these units, in the western part of the Mahomet bedrock valley probably contain relatively large amounts of sedimentary organic matter, which would result in more reducing conditions compared to the Mahomet aquifer overlying primarily carbonate bedrock units in the central and eastern regions. Organic carbon is a strong reductant and an important substrate for many microbial oxidation-reduction reactions (Stumm and Morgan, 1981). Influx of groundwater from the organic-bearing bedrock units may contain high levels of DOC, or DOC may be leaching out of clastics from the bedrock units, which would enhance reducing conditions in this part of the Mahomet aquifer. The data show a dramatic increase in DOC in the western part of the Mahomet aquifer that starts rather abruptly near the Piatt-Champaign County line (Fig. 12). However, the constituents that indicate strongly reducing conditions (CH$_4$ and NVOC) do not correlate well with the increased Cl$^-$ concentrations, which are believed to be associated with upwelling groundwater from the bedrock units in this region. For example, the correlation coefficient (r^2) between Cl$^-$ and CH$_4$ is 0.25, and r^2 between Cl$^-$ and NVOC is 0.04 for the western Mahomet aquifer. Furthermore, some of the samples from the shallower Glasford aquifer, especially in the western region, also have quite elevated NVOC values (as high as 8.3 mg/L with a mean of 4.1; Table DR2B [see footnote 1]). Thus, a substantial amount of the DOC in the western Mahomet aquifer may be associated with the paleosols and peat deposits often found within the glacial tills themselves, typically located between the Pleistocene formations (Fig. 2) (Kempton et al., 1991). The organic matter associated with the Pleistocene deposits is much younger and
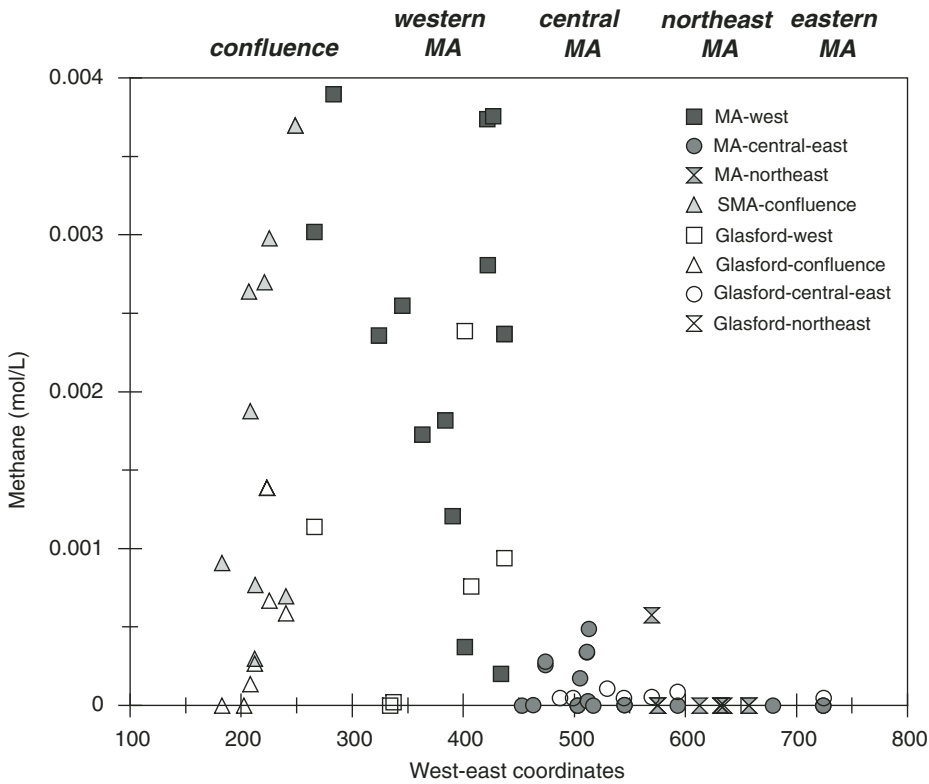
Figure 10. Methane concentration for groundwater samples versus geographic location from west to east in the aquifers of the Mahomet bedrock valley system.
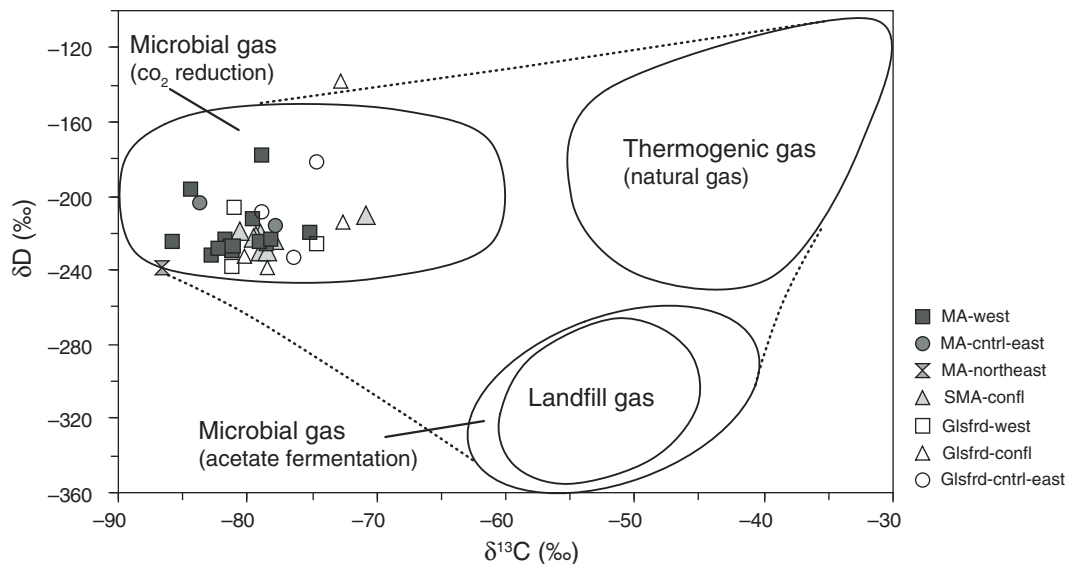
should be more labile compared to the Paleozoic bedrocks; however, the substantial increase in NVOC geographically correlates with the change in bedrock lithology from carbonates to Pennsylvanian shale and coal. As indicated by McMahon and Chapelle (1991), DOC can dif-

fuse into aquifers from surrounding aquitards; thus, the elevated levels of NVOC in the western portion of the Mahomet aquifer are probably due to a combination of influx from the surrounding tills and the organic-rich Pennsylvanian bedrock units. Another consequence of the strongly re-

ducing conditions and minimal SO_4^{2-} concentrations in the western part of the Mahomet aquifer is the elevated concentrations of arsenic (As) observed in this area, which are believed to be due to its mobilization from the reduction of iron oxyhydroxides within the aquifer sands and gravel (Kelly, 2005; Kirk et al., 2004; Warner, 2001; Panno et al., 1994).

The ^{14}C activity and the $\delta^{13}C$ of the DIC in the western region of the Mahomet aquifer are quite different compared to the central region. There is a progressive decrease in ^{14}C westward in the thalweg of the Mahomet bedrock valley toward the confluence area (Fig. 7), and the $\delta^{13}C$ values are more positive (Fig. 8). There are several possible reasons for the lower ^{14}C activity of the DIC in the western portion of the Mahomet aquifer, including: influx of older groundwater from bedrock, CH_4 production, and isolation from surficial recharge. The simplest explanation is that groundwater in this portion of the Mahomet aquifer is more isolated from surficial recharge and simply ages as it slowly moves westward. However, the strong reducing conditions associated with larger DOC concentrations and CH_4 production also help to explain the lower ^{14}C activity. The elevated concentrations of CH_4 suggest there has been excess CO_2 added to the water by fermentation reactions associated with methanogenesis. In the Mahomet aquifer, the microbial reactions associated with methanogenesis would generally add ^{14}C-depleted carbon to the groundwater, increasing the DIC concentration, diluting the ^{14}C content, and altering the $\delta^{13}C$ of the DIC. As observed in other aquifers where methanogenesis occurs (Barker and Fritz, 1981; Grossman et al., 1989; Hackley et al., 1992; Arevena et al., 1995),

Figure 11. δD and δ^{13}C of CH$_4$ from groundwater of the Mahomet bedrock valley system. Enclosed areas represent isotopic compositions typically observed for different sources of methane (Whiticar et al., 1986; Coleman et al., 1993; Hackley et al., 1996).
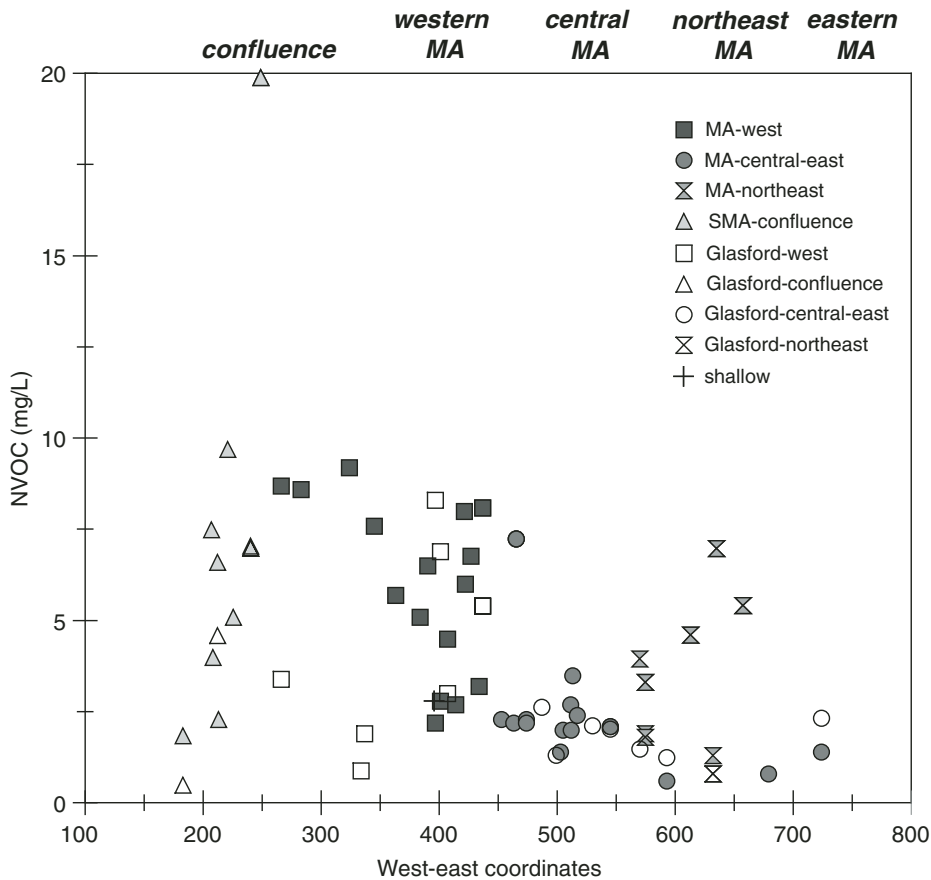
Figure 12. Distribution of dissolved organic carbon (as nonvolatile organic carbon [NVOC]) in Mahomet bedrock valley system.

Confluence and Sankoty-Mahomet Region

Within the Sankoty Mahomet aquifer, the chemistry becomes more dilute, specific conductivity decreases (Fig. DR1 [see footnote 1]), Cl^- concentration decreases (Fig. 6), CH_4 concentration decreases (Fig. 10), and the ^{14}C values increase sharply (Fig. 7) compared to the up-gradient western part of the Mahomet aquifer. These trends suggest that there is significant flux of younger freshwater into the Sankoty Mahomet aquifer in the confluence area. This fits well with the decreased amount of glacial till covering the sands in this region (Herzog et al., 1995). The samples containing the highest Cl^- and CH_4 concentrations and lowest ^{14}C activities in the confluence area tend to follow a groundwater divide that has an east-west trend within this area (Fig. 4). The groundwater chemistry becomes more dilute and has greater ^{14}C activity as the water flows to the south and north away from the groundwater divide and around a bedrock high toward the Illinois River. The rather rapid change in geochemistry is strong evidence that there is substantial recharge from the surficial units to the Sankoty Mahomet aquifer in the confluence area compared to the rest of the Mahomet aquifer. For example, the correlation coefficient between Cl^- and two other constituents in the Sankoty Mahomet aquifer that had relatively high concentrations in the western Mahomet aquifer, CH_4 and Na^+, was 0.70 and 0.68 respectively. However, the correlation coefficient between Cl^- and $^{14}C_{DIC}$ was only 0.52, suggesting other mechanisms besides dilution have affected the variability of constituents, especially $^{14}C_{DIC}$, in the confluence area.

In addition to mixing, the microbial processes involved with methanogenesis appear to have significantly influenced the groundwater geochemistry of the Sankoty Mahomet aquifer. The $\delta^{13}C$ value of the DIC in the confluence area was rather enriched in the heavier isotope and ranged from $-5.7‰$ to $-1.6‰$, with the exception of one sample that was $-9.6‰$. The more positive $\delta^{13}C$ compositions reflect the influence of microbial CH_4 production. The isotopic composition of the CH_4 is similar to the other samples in the Mahomet aquifer and representative of microbial drift gas (Fig. 11). The concentration of CH_4 in the Sankoty Mahomet aquifer ranged from ~0.9 to 3.7 mmol/L, which is greater than that observed in the shallower Glasford Sand (0.1–0.7 mmol/L). As discussed earlier, fermentation reactions associated with methanogenesis add ^{14}C-depleted CO_2 to the groundwater. The correlation coefficient between the CH_4 concentration and ^{14}C activity of the DIC is 0.90 (Fig. 14). Thus, it appears that there is an additional input of microbial methane

significantly more positive $\delta^{13}C$ values occur in the western region of the Mahomet aquifer compared to the eastern half of the aquifer (Fig. 8). The increased $\delta^{13}C$ values primarily result from the fractionation effect associated with methanogenesis in which the isotopically light carbon (^{12}C) is preferentially used in the microbial process to produce CH_4, leaving the remaining CO_2 enriched in ^{13}C. Additionally, inputs of CO_2 due to fermentation reactions could also result in dissolution of carbonates, which are relatively enriched in ^{13}C ($\delta^{13}C$ ~ 0‰; Anderson and Arthur, 1983). Thus, the carbon isotopic fractionation associated with methanogenesis and the dissolution of carbonates would overwhelm any isotopically light carbon input from the fermentation reactions of organic matter (^{13}C-depleted carbon). It is also possible that the CH_4, or at least some of the CH_4, may be associated with the upwelling saline water from the bedrock units, which would add ^{14}C-depleted and possibly ^{13}C-enriched DIC to the western portion of the Mahomet aquifer, diluting the ^{14}C concentration and increasing the $\delta^{13}C$ values. Unfortunately, we do not have any groundwater
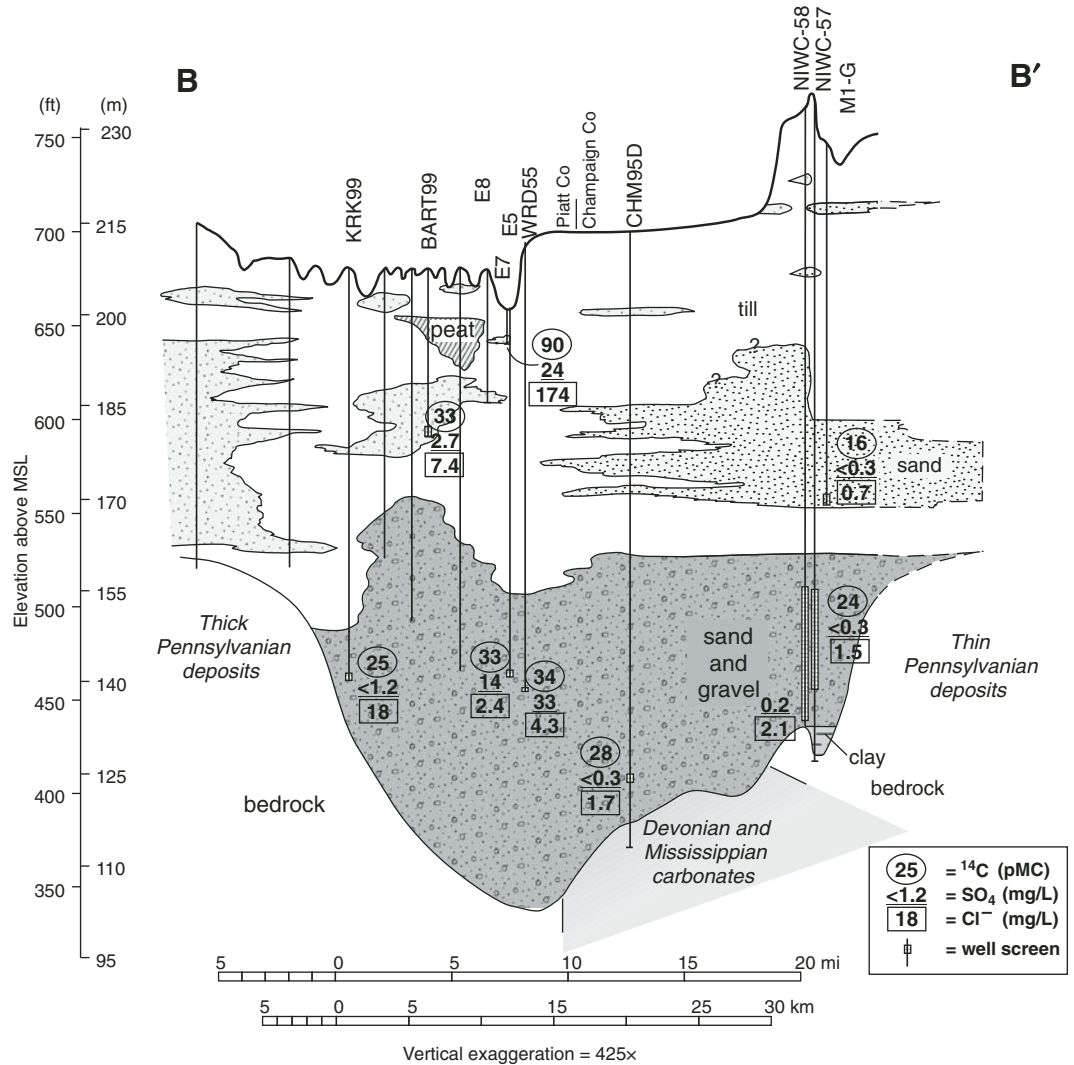
samples from bedrock beneath the Mahomet bedrock valley, but a sample collected where the Pennsylvanian bedrock is closer to the surface (112 m), ~40 km to the southeast, contained significant amounts of methane and had a $\delta^{13}C_{DIC}$ value of +25‰.

Although methanogenesis and the influx of older bedrock water are important, these do not appear to be the only causes for the progressive decrease in ^{14}C observed in the western Mahomet aquifer system. Sample KRK-99 has a high concentration of CH_4 but a $^{14}C_{DIC}$ value that is only a few pMC less than those samples up-gradient just to the east (WRD-55 and CHM-95D). As previously discussed, there is also evidence that the area near KRK-99 may be close to stacked sands, as indicated by the cross section in Figure 13, and/or a groundwater window where recharge from the surface is more open compared to wells sampled toward the east and western parts of the Mahomet aquifer. Thus, isolation from surficial recharge and natural radioactive decay must also contribute to the progressive decrease in $^{14}C_{DIC}$ activity in the western part of the Mahomet aquifer.

Figure 13. Cross section (B-B′) of the Mahomet bedrock valley including ¹⁴C, [SO₄²⁻], and [Cl⁻] data for several wells (modified from Hackley, 2002). Note the lower ¹⁴C activities and higher Cl⁻ concentrations near the sides of the valley, especially on the west side where the bedrock is all Pennsylvanian deposits. MSL—mean sea level.

to the Sankoty Mahomet aquifer in the confluence area. As in the western Mahomet aquifer, strong reducing conditions associated with methanogenesis also affect the arsenic concentrations, which are relatively high in the confluence region (Kelly, 2005; Warner, 2001; Holm, 1995). Thus, although a good deal of the variability in the geochemical composition of the groundwater in the Sankoty Mahomet aquifer is probably due to mixing between groundwater from the western Mahomet aquifer and fresher, young recharging groundwater from the shallower zones, there is also significant influence on the geochemistry due to the methanogenesis processes taking place in this region.

Conceptual Model

Based on the trends in chemistry and isotopic composition throughout the basal aquifers of the Banner Formation and the shallower Glasford Sands, we developed a fundamental conceptual model of groundwater evolution for the Mahomet aquifer and the Sankoty Mahomet aquifer. A plot of the Cl⁻ concentration and ¹⁴C$_{DIC}$ activity across the Sankoty Mahomet aquifer and Mahomet aquifer shows the large variations in the data from the confluence area to the easternmost Mahomet aquifer in Illinois (Fig. 15). The arrows and text on the diagrams in Figures 15A and 15B summarize the major influxes of groundwater to the Mahomet aquifer, depicting the overall conceptual model. The chloride concentration is very low in the central part of the Mahomet aquifer, while the ¹⁴C activity of the DIC has some of the largest values (excluding the Sankoty Mahomet aquifer in the confluence region). These observations support Panno et al.'s (1994) suggestion that the central area of the Mahomet aquifer is the primary recharge area. This is consistent with historical head data published by Kempton et al. (1991), which showed a potentiometric high in the northern Champaign and southern Ford Counties area. Recent head measurements for the aquifer also indicate potentiometric highs in the area of southern Ford County and near the Illinois-Indiana border, with flow primarily to the south and west (Wilson et al., 1998; Roadcap and Wilson, 2001). The geochemical data are also consistent with the geology, which indicates that the central region has several stacked sand deposits, many of which appear to be connected. The stacked sand deposits may help explain the very low Cl⁻ concentrations (0.6–2.3 mg/L) observed for much of the central Mahomet aquifer region. Such low Cl⁻ concentrations suggest that this area was flushed with high volumes of freshwater, perhaps from glacial meltwaters, which leached much of the more soluble minerals from the stacked sand deposits.

The large range of SO₄²⁻ and δ³⁴S values plus the more negative δ¹³C values and low ¹⁴C
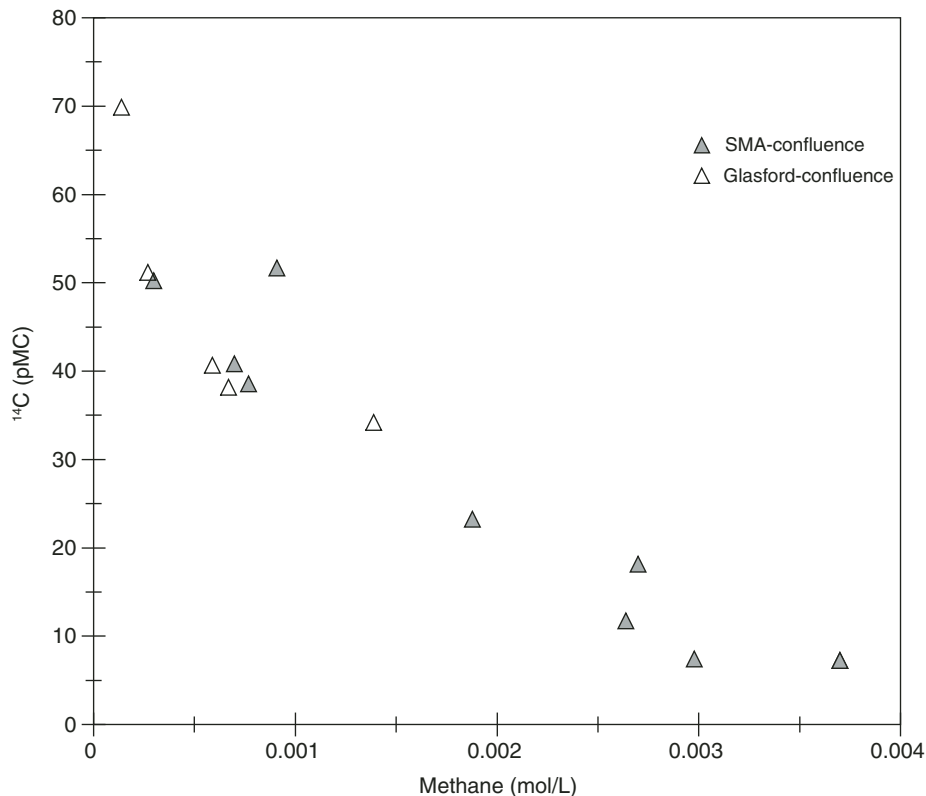
Figure 14. Comparison of ^{14}C and CH$_4$ concentration in the confluence region; r^2 for the Sankoty Mahomet aquifer data is 0.9.

activities observed in groundwater from samples of the Mahomet aquifer and the Glasford Sand in the northeastern part of the Mahomet bedrock valley indicate a mixture of deeper upwelling groundwater and shallow infiltrating groundwater plus sulfate reduction occurring in parts of the northeastern region of the Mahomet bedrock valley. The mixture of groundwater from bedrock units in the northeastern region appears to extend into northern Vermillion County. The increased Cl$^-$ concentrations and continuous drop in ^{14}C activities observed for the western part of the Mahomet aquifer (Fig. 15) suggest there has been greater isolation from surficial recharge and seepage from bedrock units mixing with the Mahomet aquifer groundwater flowing from the central region westward. The cross sections that cut the Mahomet bedrock valley diagonally (Figs. 13 and 16–17) show the relationships among the shallower aquifers, the deep basal sand aquifer, and the sides of the bedrock valley from where the lithology of the bedrock changes abruptly near the Piatt-Champaign County line to where the bedrock is primarily carbonate in Champaign County. Chloride concentrations and ^{14}C activities are included on the cross sections. The results show an increase in Cl$^-$ and decrease in ^{14}C activity near the sides of the val-

ley, especially close to the Pennsylvanian-age bedrock on the western side of the aquifer (see Fig. 3 for bedrock lithology). This emphasizes the relationship of the Pennsylvanian-age bedrock to the seepage of older more saline groundwater into the western Mahomet aquifer compared to the carbonate bedrock in the central portion of the Mahomet aquifer.

As the groundwater from the Mahomet aquifer flows into the Sankoty Mahomet aquifer, the chemical composition and ^{14}C activity change dramatically. In this confluence area, the geochemical makeup of the groundwater of the basal Pleistocene sands and gravels is strongly influenced by a combination of relatively rapid recharge of younger, more dilute water infiltrating from the surface and the microbial processes associated with methanogenesis.

SUMMARY AND CONCLUSIONS

The chemical and isotopic characteristics of the groundwater in the aquifers of the Mahomet bedrock valley and adjacent confluence area have revealed many important aspects of the groundwater evolution in aquifers that have been created from glacial deposits filling in the topographic undulations of the previous bed-

rock land surface. The δD and δ^{18}O values for most of the groundwater in the Mahomet aquifer and the shallower Glasford sands are quite similar to present-day precipitation. These data indicate that there is little to no Pleistocene water remaining in the aquifer system, putting an upper age limit for most of the groundwater at the start of the Holocene, ca. 11,000 yr B.P. The tritium results indicate that there is modern recharge into the Wedron sands and some of the Glasford sands, but very little modern water occurs in the basal sand of the Mahomet bedrock valley. Of the sites sampled, only one area in the Mahomet aquifer near where the Sangamon River crosses the bedrock valley had detectible tritium. These tritium data are consistent with recent seismic and monitoring well drawdown studies by the ISGS and ISWS that have suggested a hydraulic window where groundwater discharges to the Sangamon River when the river is low and groundwater recharges during periods of high stage or excessive groundwater pumping (Roadcap and Wilson, 2001).

The central-eastern region of the Mahomet aquifer contained the highest ^{14}C activity and most dilute groundwater compared to the rest of the Mahomet aquifer, indicating that the groundwater in this region has gone through the least water-rock interaction. These isotopic and geochemical characteristics imply that this region is the area of most rapid recharge for most of the Mahomet aquifer, as proposed by Panno et al. (1994). The very low Cl$^-$ concentrations in the central Mahomet aquifer region suggest that high volumes of freshwater (glacial meltwaters) probably flushed the stacked sand deposits and leached the more soluble minerals so that the present-day groundwater has relatively low dissolved solids concentration.

The chemical and isotopic results for the Mahomet aquifer in the western and northeastern (Onarga Valley) regions indicate that these areas of the aquifer are relatively isolated from surficial recharge and have been significantly influenced by the infiltration of older (low ^{14}C$_{DIC}$ activity) groundwater from bedrock units with greater dissolved ion concentrations. The enrichment of SO$_4^{2-}$, Ca^{2+}, Mg^{2+}, Na$^+$, and B, and Sr^{2+} in the Onarga Valley is probably the result of water-rock interactions with bedrock lithology, including Silurian, Devonian, and Mississippian carbonates and Pennsylvanian cyclothem type deposits (shales, coals, and argillaceous limestones and sandstones). The δ^{34}S and δ^{13}C values as well as the SO$_4^{2-}$ and DIC concentrations in and around the Onarga Valley region suggest that groundwater upwelling through bedrock units is dissolving secondary gypsum, precipitating calcite, and mixing with fresher groundwater in the Mahomet and Glasford
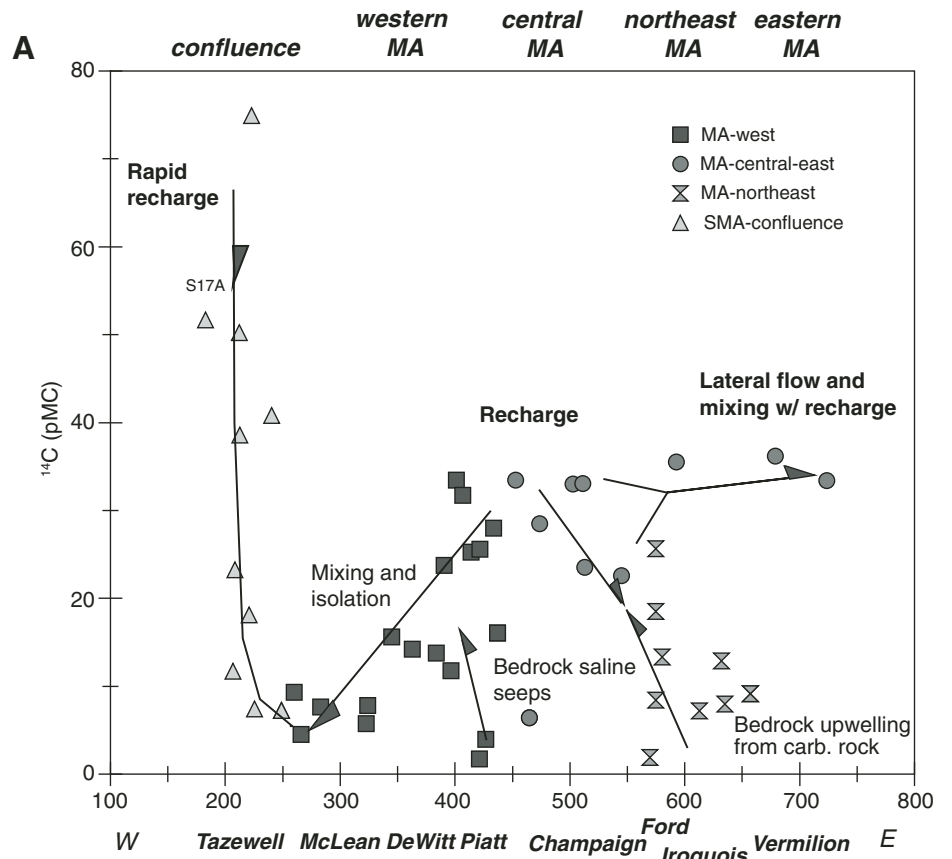
Figure 15. ¹⁴C activity of dissolved inorganic carbon (DIC) (A) and chloride concentration (B) for Mahomet bedrock valley ground-water system and interpretation of data.
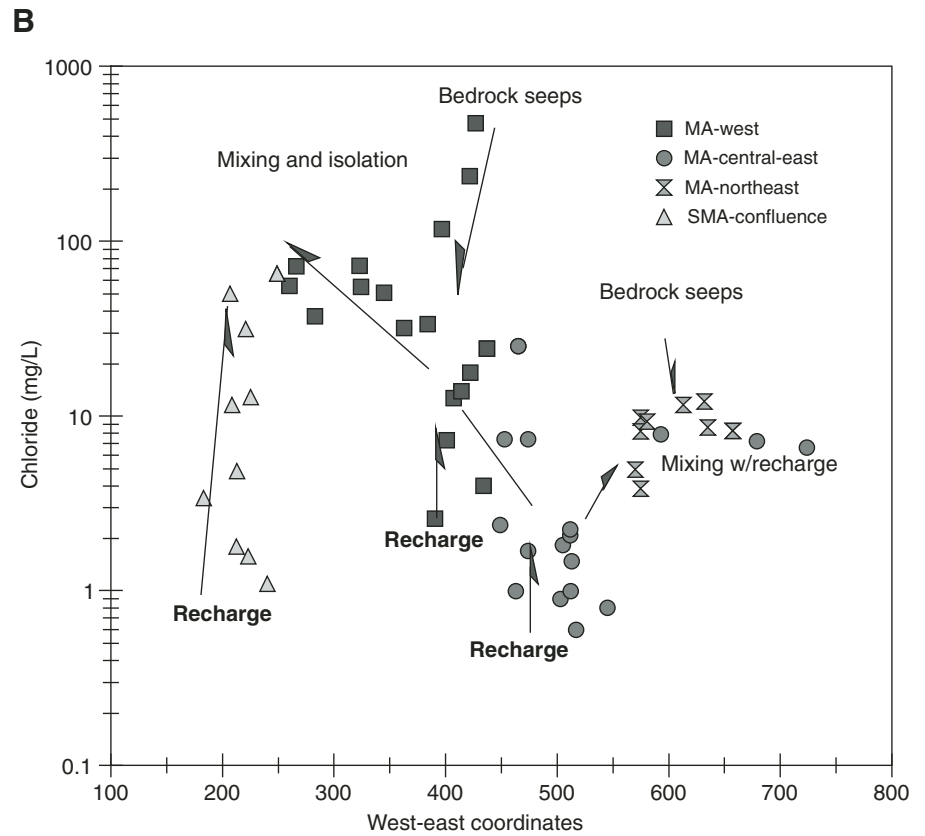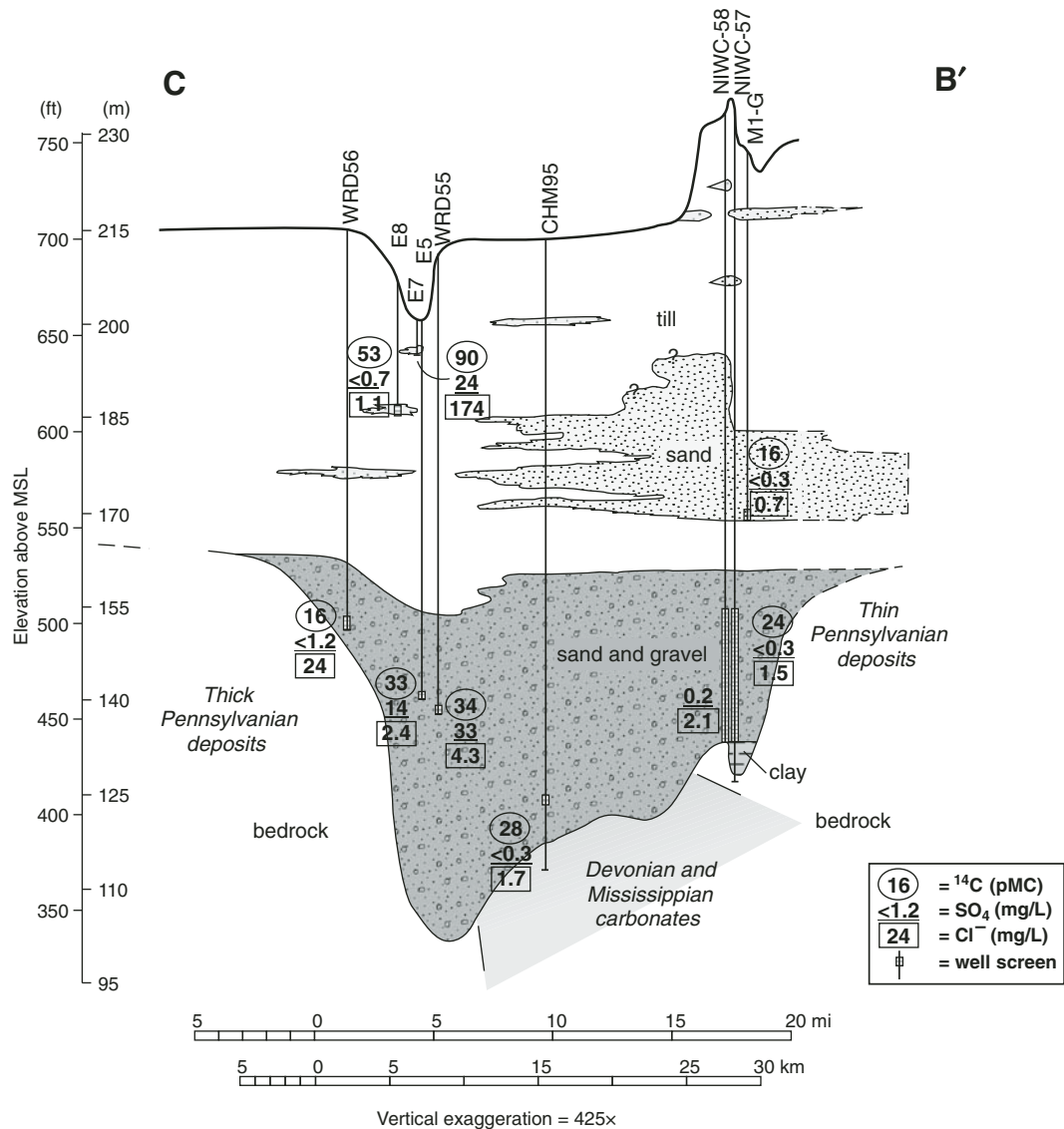
Figure 16. Cross section (C-B′) of the Mahomet bedrock valley including ^{14}C, $[SO_4^{2-}]$, and $[Cl^-]$ data for several wells (modified from Hackley, 2002). Note the lower ^{14}C activities and higher Cl^- concentrations near the western side of the valley, where the bedrock is composed of Pennsylvanian deposits. MSL—mean sea level.

sands. The isotopic data also indicate that SO_4^{2-} reduction and oxidation of organic carbon occur as the groundwater moves up into the Mahomet aquifer and shallower sands. Evidence of mixing between infiltrating groundwater from bedrock in the Onarga Valley and groundwater from the Mahomet and Glasford sands extends into northern Vermillion County. The low ^{14}C activities observed in this area are due to the influx of older groundwater from bedrock units, dissolution of carbonates, and oxidation of organic matter due to SO_4^{2-} reduction.

The western region of the Mahomet aquifer is characterized by higher concentrations of CH_4, DOC, Cl^-, Na^+, and HCO_3^-, greater $\delta^{13}C$ values, and a progressive decrease in $^{14}C_{DIC}$ activities to the west. The isotopic data support the hypothesis that the higher concentrations of chemical constituents (especially Cl^- and

Na^+) are primarily explained by the influx of saline groundwater from the Pennsylvanian-age bedrock (Panno et al., 1994). Methane production is undoubtedly a consequence of strong reducing conditions in this part of the aquifer. The relatively high DOC concentrations in the western Mahomet aquifer could also be associated with the influx of deeper groundwater from the Pennsylvanian-age bedrock units or perhaps leaching of organic matter in clastics from these bedrock units and/or diffusion from organic rich Plieistocene deposits. The progressive decrease in $^{14}C_{DIC}$ activity is probably a consequence of several processes: infiltration of older groundwater from bedrock units, methanogenesis, and the dissolution of carbonates in the aquifer, as well as radioactive decay as the water slowly migrates westward. The progressive decrease in ^{14}C and the lack of significant shallow sand de-

posits above the Mahomet aquifer in the western region imply that this area is fairly isolated from surficial recharge.

The confluence area where the Mahomet aquifer and Sankoty Mahomet aquifer meet shows large variations in ^{14}C activity and chemical constituents, including Cl^- concentrations. This area is significantly influenced by a combination of groundwater mixing between relatively dilute infiltrating surficial water that has high ^{14}C activities and low Cl^- concentrations with older groundwater emerging from the basal sands of the Mahomet aquifer containing a greater amount of dissolved constituents and the microbial processes associated with methanogenesis.

The isotopic and chemical characteristics of groundwater in the basal sands of the Mahomet and Mackinaw bedrock valleys indicate that
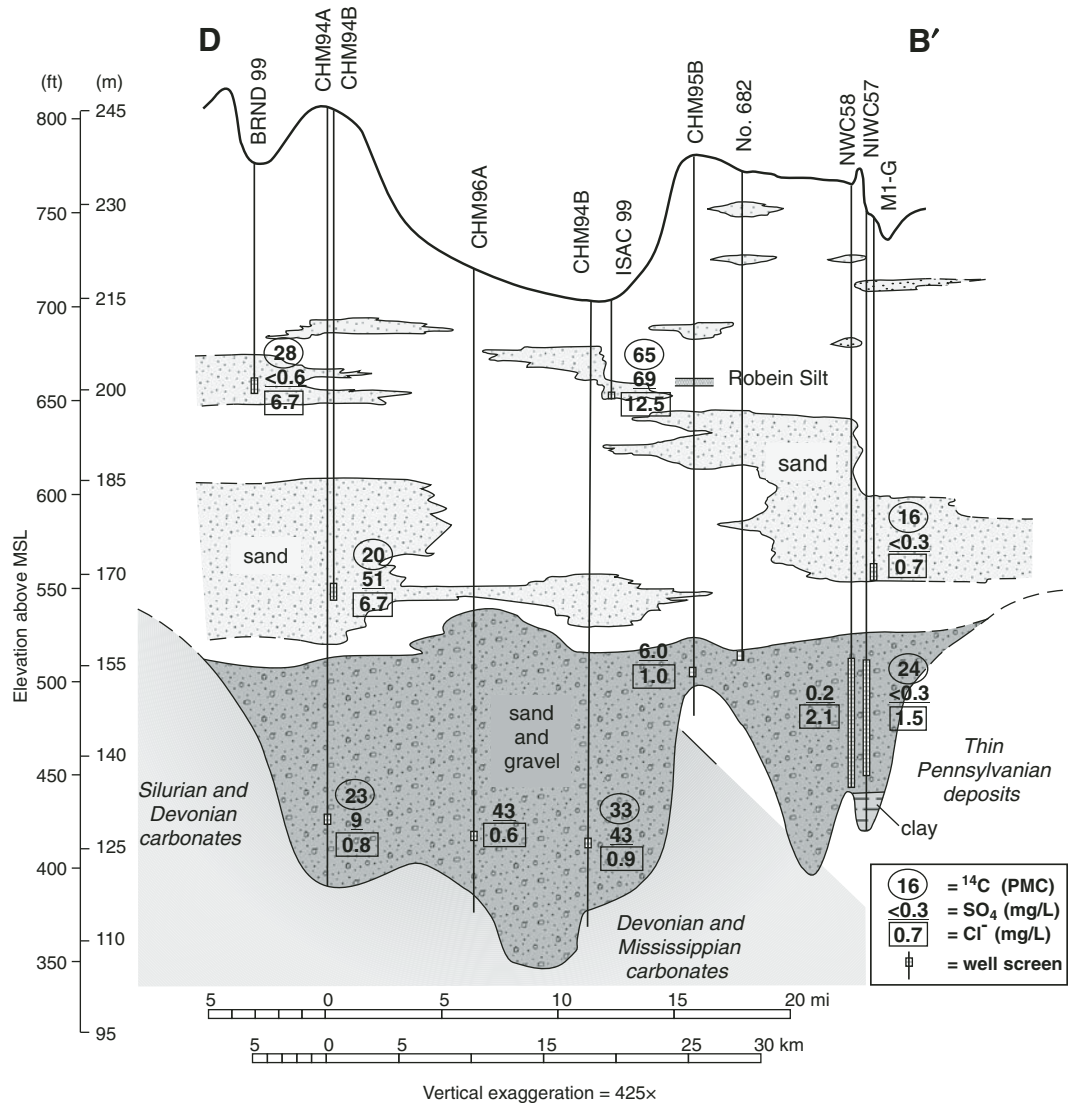
Figure 17. Cross section (D-B′) of the Mahomet bedrock valley including ^{14}C, [SO$_4^{2-}$], and [Cl$^-$] data for several wells (modified from Hackley, 2002). Bedrock lithology is primarily carbonates across this part of the valley. Note low Cl$^-$ concentration across Mahomet aquifer. MSL—mean sea level.

this is a complicated geochemical groundwater system. The hydrochemical characteristics appear to be controlled by a combination of bedrock lithology and structure as well as the variability of stacked sands in the Pleistocene deposits above the basal sands in the bedrock valley. Additional information from more detailed studies of the aquifers using geochemical as well as geophysical tools will help to pinpoint hydrologic windows in the aquifer system and quantify the influence of upwelling water from bedrock units. Such data will assist hydrologic modeling for predicting drawdown and future groundwater usage.

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