Hydrochemistry of the Mahomet Bedrock Valley Aquifer, East-Central Illinois: Indicators of Recharge and Ground-Water Flow

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Abstract

A conceptual model of the ground-water flow and recharge to the Mahomet Bedrock Valley Aquifer (MVA), east-central Illinois, was developed using major ion chemistry and isotope geochemistry. The MVA is a "basal" fill in the east-west trending buried bedrock valley composed of clean, permeable sand and gravel to thicknesses of up to 61 m. It is covered by a thick sequence of glacial till containing thinner bodies of interbedded sand and gravel. Ground water from the MVA was found to be characterized by clearly defined geochemical regions with three distinct ground-water types. A fourth ground-water type was found at the confluence of the MVA and the Mackinaw Bedrock Valley Aquifer (MAK) to the west.

Ground water in the Onarga Valley, a northeastern tributary of the MVA, is of two types, a mixed cation-SO_4^{2-} type and a mixed cation-HCO_3^- type. The ground water is enriched in Na^+, Ca^{2+}, Mg^{2+}, and SO_4^{2-} which appears to be the result of an upward hydraulic gradient and interaction of deeper ground water with oxidized pyritic coals and shale. We suggest that recharge to the Onarga Valley and overlying aquifers is 100% from bedrock (leakage) and lateral flow from the MVA to the south.

The central MVA (south of the Onarga Valley) is composed of relatively dilute ground water of a mixed cation-HCO_3^- type, with low total dissolved solids, and very low concentrations of Cl^- and SO_4^{2-}. Stratigraphic relationships of overlying aquifers and ground-water chemistry of these and the MVA suggest recharge to this region of the MVA (predominantly in Champaign County) is relatively rapid and primarily from the surface.

Midway along the westerly flow path of the MVA (western MVA), ground water is a mixed cation-HCO_3^- type with relatively high Cl^-, where Cl^- increases abruptly by one to $\geq$ two orders of magnitude. Data suggest that the increase in Cl^- is the result of leakage of saline ground water from bedrock into the MVA. Mass-balance calculations indicate that approximately 9.5% of recharge in this area is from bedrock. Concentrations of Na^+, HCO_3^-, As, and TDS also increase in the western MVA.

Ground water in the MAK is of a Ca^{2+}-HCO_3^- type. Mass-balance calculations, using Cl^- as a natural, conservative tracer, indicate that approximately 17% of the ground water flowing from the confluence area is derived from the MVA.

Introduction

Ground-water use in the midwestern states of the United States has increased significantly in recent years resulting in an increased reliance on local and regional aquifers. Bedrock valley aquifers have been found to be extensive and a prolific source of fresh water for many midwestern and eastern states. The Teays-Mahomet System is a well-known example of a bedrock valley aquifer system that was once thought to be a single bedrock valley extending from southeastern West Virginia to western Illinois (Kempton et al., 1991).

The Mahomet Bedrock Valley (MVA) is the western part of the Teays-Mahomet System and is a major source of fresh water in east-central Illinois. A great deal of geological, hydrogeological, and hydrochemical data are available in the literature and from the State Geological (ISGS) and Water Surveys of Illinois on this aquifer system. The geology and hydrogeology of the study area have been addressed by Horberg (1945), Stephenson (1967), Kempton et al. (1982), Melhorn and Kempton (1991), and others. The hydrogeology of the aquifer system was addressed by Visocky and Schicht (1969) and Kempton et al. (1991). However, in spite of the availability of hydrochemistry data, the ground-water chemistry of the MVA has never been examined for anything other than local water quality.

An initial examination of the ground-water chemistry in the MVA (Panno et al., 1992) showed the occurrence of distinct geochemical ground-water regions in very close proximity to one another along the reaches of the aquifer. The relationships observed suggested that leakage from bedrock sources may be occurring in parts of the MVA, and that recharge is not totally from surface sources as was generally assumed by earlier workers (e.g., Visocky and Schicht, 1969; Kempton et al., 1982). A detailed examination of the geology and associated ground-water chemistry of the MVA and associated aquifers was conducted to investigate this possibility. Because little information on ground-

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water flow and recharge to the MVA is available (Kempton et al., 1991), proper management of the ground-water resources of this area cannot come about without a clear understanding of these parameters. Consequently, the final goal of this effort was to develop a conceptual model of recharge, ground-water flow, and rock-water interaction for the MVA and associated aquifers of the study area.

Geological and Hydrogeological Setting

The MVA is both a lithostratigraphic unit (the Mahomet Sand Member of the Banner Formation) and a hydrostratigraphic unit. The roughly east-west trending buried Mahomet Bedrock Valley in east central Illinois and western Indiana was once thought to be part of the larger "Teays" drainage system that extended from Illinois eastward to West Virginia. However, recent studies have indicated that the Teays was not a single, coherent system (e.g., Melhorn and Kempton, 1991). The Mahomet Sand Member is composed of glacial outwash sand and gravel laid down within the confines of the Mahomet Valley Lowland. The outwash was subsequently buried by tills deposited during Pleistocene continental glaciation (Figure 1). A recent publication edited by Melhorn and Kempton (1991) details the geology and hydrogeology of the Teays-Mahomet Bedrock Valley System in a series of papers from a symposium on the subject. The following is a summary from a paper in that publication outlining the geology and hydrogeology of the MVA system in east-central Illinois (Kempton et al., 1991).

The Mahomet Bedrock Valley is incised in bedrock and buried beneath 100 or more meters of Pleistocene glacial drift. Using the 152-meter elevation contour to define the upper limit of the valley, the valley ranges in width from 13 km to 18 km (Kempton et al., 1991). The valley intersects the Mackinaw Bedrock Valley that contains the Mackinaw Bedrock Valley Aquifer (MAK) in southwestern Tazewell County. This aquifer was deposited by the Ancient Mississippi River and lies beneath the present course of the Illinois River (Kempton et al., 1991). The Sankoty Sand Member of the Mackinaw Bedrock Valley is contiguous with the Mahomet Sand Member of the Mahomet Bedrock Valley; the intersection of the two sand members constitute a confluence area for ground waters from each aquifer (Kempton and Visocky, 1992).

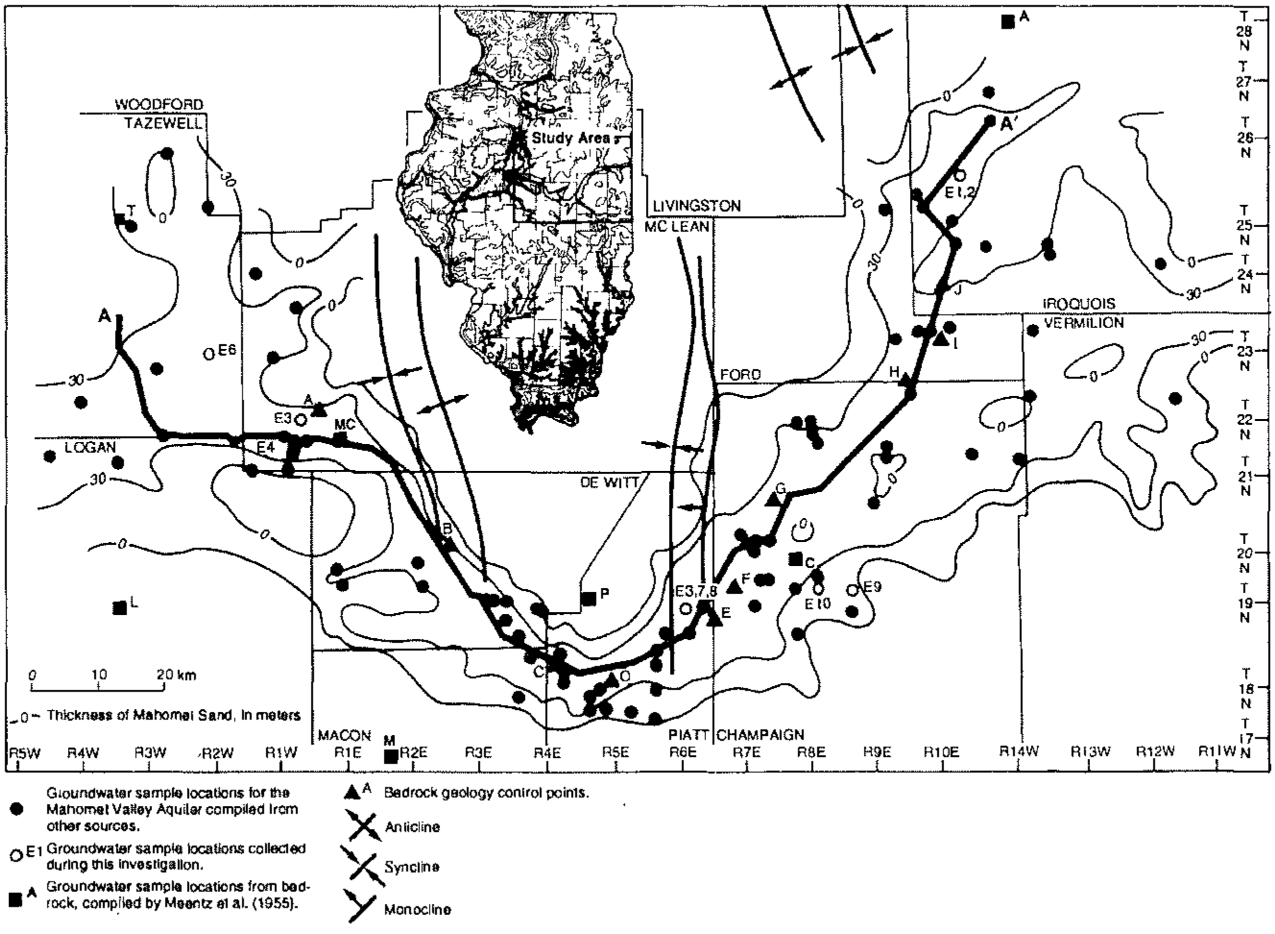

Fig. 1. The Mahomet Valley Aquifer showing thickness of Mahomet Sand (modified from Kempton et al., 1991), sample location and trace of longitudinal cross section A-A′. The inset map was modified from a bedrock topography map by Willman and Frye (1970). Shading indicates elevation above mean sea level and delineates the trace of the Mahomet Bedrock Valley. The MVA is generally contained within the deepest part of the valley (darkest shading = lowest elevation within the study area).

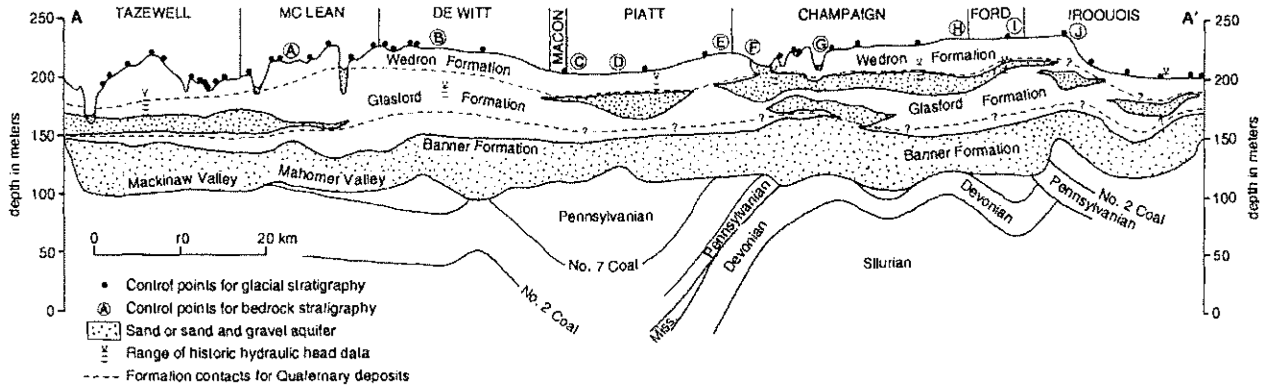

Fig. 2. Longitudinal cross section A-A' showing the stratigraphy of the study area along the thalweg of the MVA and across the MAK.

The main channel of the Mahomet Bedrock Valley and its tributary channels are filled with clean sand and gravel (as much as 60 m thick and averages 30 m) that provide east-central Illinois with abundant ground water (Figure 1). The MVA is generally coincident with the Mahomet Sand Member of the Banner Formation, and is overlain by the Glasford and the Wedron Formations (Figure 2). Sand and gravel outwash deposits within the overlying Glasford Formation are usually most extensive where they are associated with the Vandalia Till Member and constitute a second productive aquifer that is locally important.

Horberg (1953) reported that the sands of the MVA were composed of ". . . sand and gravel in roughly equal proportions and is composed of a wide variety of rocks and minerals, dominantly of sedimentary origin. Silty beds occur throughout. Many horizons are strongly oxidized." The sand of the Mahomet Sand Member is made up of predominantly quartz, lesser amounts of K-feldspar and Ca-Na feldspar (Willman and Frye, 1970), and minor amounts of translucent heavy minerals that include (in descending order of abundance) hornblende, garnet, epidote, and hyperenstatite (Manos, 1961). Carbonate minerals are present in both aquifers, but differ in that dolomite dominates the Glasford sands and calcite dominates the Mahomet sands (H. Glass, ISGS, personal communications, 1992).

The bedrock geology of the study area consists of Pennsylvanian, Mississippian, Devonian, and Silurian rocks. The western half of the valley is dominated by Pennsylvanian rocks (typically shale with thin limestone, sandstone, and coal). The eastern part of the valley is underlain by rocks of the Pennsylvanian, Mississippian, and Devonian. The northwest-southeast trending La Salle Anticlinal Belt intersects the eastern part of the MVA and is responsible for the subcrop of the younger bedrock in this area. Associated with this structural belt are a series of north-south trending anticlines, synclines, and monoclines that intersect the MVA (Figure 1). The Onarga Valley, a northeastern tributary of the MVA, is dominated by bedrock of Middle Devonian and Silurian age strata that consists of dolomite and the Pennsylvanian Caseyville, Abbott, and Spoon Formations that contain thin coals, black shale, and thin limestone (Willman et al., 1967).

The hydraulic characteristics of the MVA have been determined from pumping tests conducted on high-capacity wells. Transmissivities for the Mahomet Sand Member range from 7×10^{-4} to 8×10^{-2} m^2/s, with median hydraulic conductivity of 1.4×10^{-3} m/s. The potentiometric surface of the MVA mimics the surface of the Mahomet Sand Member (Figure 2) with a hydraulic gradient of approximately 19 cm/km (as compiled from other references in Kempton et al., 1991).

Recharge to the MVA is believed to occur as a result of vertical leakage of precipitation and snowmelt through overlying glacial deposits. Visocky and Schicht (1969) estimated the average annual recharge rate for the Mahomet Sand Member in east-central Illinois at 250,000 $l/day/km^2$ (107,000 $gallons/day/km^2$) from water-balance calculations. This volume is consistent with more recent calculations based on vertical hydraulic conductivities for confining units that range from 1×10^{-9} to 2×10^{-7} m/s (Kempton et al., 1991). A potentiometric surface prepared from historical water-level data (Figure 2) shows the probable predevelopment ground-water flow directions. The highest hydraulic heads were found in the northeastern Champaign, northwestern Vermilion, and southern Iroquois Counties. Ground-water flow was originally to the north, east, and southwest from this area prior to the establishment of large pumping centers (Kempton et al., 1991).

Methods of Investigation

The ground-water chemistry of the MVA and associated aquifers was evaluated using 10 detailed analyses of ground-water samples collected from public and private wells (Table 1), water quality data selected from over 500 analyses of the Illinois State Water Survey's (ISWS) ground-water quality data base, and published analyses (Hanson, 1950, 1958, 1961; Hamdan, 1964; Woller, 1974, 1975, 1992a, 1992b, 1992c).

Ground-water samples collected from private wells were taken from outside faucets that bypassed home water-treatment units and holding tanks, and directly from well-heads. All samples were analyzed for major and minor cations and anions, ^{13}C, ^{14}C, D, ^{18}O, and selected samples for ^{34}S. Analytical techniques for isotopes will be reported in

Table 1. Chemical Analyses of Major and Minor Constituents from Wells Sampled for This Investigation

Map no.	County	Location	Well depth (m)	Surface elev. (m)	Temp. (°C)	pH	Eh(mV)	Na	K	Ca	Mg	SiO_2	HCO_3	NO_3	SO_4	Cl	As	B	Ba	Br	F	Fe	Mn	Sr	TDS	Aquifer
E1	Iroquois	26N10E34	25	203	11.8	7.1	-52	72	2.5	155	57	20.7	351	0.05	461	8.2	BDL	0.70	0.02	0.07	0.77	2.55	0.06	NA	940	G
E2	Iroquois	26N10E34	64	203	11.8	7.2	-67	74	3.2	155	58	20.0	365	0.06	416	9.3	BDL	0.71	0.03	0.06	0.76	2.45	0.07	NA	970	MVA
E3	McLean	22N01W23	32	194	13.1	6.8	NA	19	1.7	87	39	22.5	506	BDL	0.16	1.0	0.07	0.01	0.18	BDL	0.26	2.02	0.07	0.45	462	G
E4	McLean	22N01W27	82	195	13.4	7.2	115	94	2.3	77	31	17.7	548	BDL	0.2	56	0.07	0.25	0.64	0.16	0.64	2.42	0.06	0.59	546	MVA
E8	Piatt	19N06E15	4.3	198	13.0	7.3	428	36	2.0	112	48	17.6	308	3.56	24	179	BDL	BDL	0.07	0.08	0.35	0.05	0.03	0.13	960	W
E7	Piatt	19N06E15	21	207	13.5	7.0	113	12	2.4	80	32	24.6	464	BDL	0.07	1.1	0.10	BDL	0.13	BDL	0.24	2.31	0.06	0.38	405	G
E5	Piatt	19N06E15	61	198	13.0	7.2	113	25	1.8	81	30	22.7	442	0.06	14	2.4	0.07	0.20	0.12	BDL	0.31	1.27	0.03	0.41	392	MVA
E9	Champaign	19N09E07	66	222	13.0	7.5	33	40	2.0	64	34	20.4	427	BDL	4.22	1.44	BDL	0.07	0.13	BDL	0.21	1.74	0.02	0.45	340	MVA
E10	Champaign	19N08E03	104	239	13.0	7.5	33	37	3.0	51	35	16.3	421	BDL	0.04	2.25	BDL	0.48	0.34	BDL	0.19	1.30	0.04	0.57	328	MVA
E6	Tazewell	23N02W21	37	195	14.0	7.4	NA	26	3.3	71	36	18.9	451	BDL	0.4	0.7	0.05	0.06	0.13	BDL	0.15	1.25	0.028	0.391	400	MAK
Detection limits								1.340	0.629	0.004	0.003	0.024		0.005	0.010	0.010	0.030	0.005	0.001	0.005	0.025	0.009	0.009	0.003		

All ions expressed in mg/l.
W = Wedron Formation, outwash sand and gravel.
G = Glasford Formation, outwash sand and gravel.
MVA = Mahomet Bedrock Valley Aquifer, Mahomet Sand Member, Banner Formation.
MAK = Mackinaw Bedrock Valley Aquifer, Sankoty Sand Member Banner Formation.
NA = Not available.
BDL = Below detection limits.

Hackley et al. (in preparation). Field analyses included temperature, Eh, pH, and alkalinity; Eh, pH, and temperature were monitored in a closed-cell flow-through system and were used as indicators of stabilization of the water chemistry. Samples were collected after stabilization was reached. The Eh and pH were measured in the field using the appropriate electrodes. Alkalinity was determined in the field using standard titration methods (e.g., Wood, 1981).

Ground-water samples were collected and analyzed (in the field) in accordance with techniques described in Wood (1981). Samples were collected in LPE polyethylene bottles and placed in an ice-filled cooler for transport to the laboratory where they were refrigerated at 4°C until analysis (within two weeks of sampling). All ground-water samples were filtered in the field through an in-line 0.45 μm filter. Samples analyzed for cations were acidified in the field with reagent-grade nitric acid to a pH of 2.0 to minimize precipitation and adsorption.

Ground-water samples were analyzed for cations using a Model 1100 Thermo-Jarrell Ash Inductively Coupled Argon Plasma Spectrometer. Anions were analyzed using a Dionex 2110i Ion Chromatograph, following U.S. EPA Method 300 for anions (O'Dell et al., 1984).

Depth-vs-concentration plots were constructed from the largest data set ($>$ 500 analyses) and represent general trends of ground-water components for the entire section above bedrock. A total of 165 ground-water sample analyses were selected from these data and used for preparation of maps showing aerial, and to a lesser extent, vertical distribution of selected ions (Figure 1). Water chemistry data were selected from these sources on the basis of completeness (although not all were complete), geographic and stratigraphic locations, and ion balance. All analyses containing complete major cations and anions yielded ion balances of $\leq$ 5%, and were used for construction of the trilinear diagram (85 analyses). Selected analyses containing pH, Eh, alkalinity, and all major ions were used for geochemical modeling. Those data were analyzed using the geochemical code REACT (Bethke, 1992) for ground-water mixing, saturation indices, and rock-water interactions.

Descriptive statistics for each of the regions of the MVA were prepared from a subset (128) of those data used for aerial distribution maps (Table 2). This subset was chosen for stratigraphic and geographical location; not all of the analyses used were complete. Data from multiple samples from the same well or well field were averaged (geometric mean); one-half the detection limit was used in statistical calculations to avoid truncation of the distributions.

A longitudinal cross section (Figure 2) was constructed from existing cross sections (Horberg, 1953; and Kempton and Visocky, 1992) and from statigraphic descriptions from public well records (Hanson, 1950, 1958, 1961) and private well records (ISGS Records Library). The section was used to show the stratigraphic distribution of selected ions that represent the most characteristic changes observed in the MVA and superjacent aquifers. Chemistry data were acquired from isocons of the areal-view maps, individual wells within the aquifers above the MVA, and from concentration vs depth plots from previously described data bases.

Table 2. Descriptive Statistics of Ground-Water Chemistry Data from Each of the Designated Regions of the MVA

		Temp.	pH*	Eh	Na	K	Ca	Mg	SiO_4	HCO_3	NO_3	SO_4	Cl	As	B	Ba	F	Fe	Mn	Sr	TDS
Central MVA	Max	14.0	8.5	195	99	3	101	42	24	677	7	72	27	0.05	0.70	0.50	0.80	15	0.10	0.61	576
	Min	13.0	7.2	-4	10	0.8	51	27	10	381	0.03	0.04	0.2	0.001	0.07	0.10	0.08	0.30	0.01	0.22	326
	N	4	40	6	52	37	53	53	49	54	24	38	47	9	21	16	41	52	17	6	54
	Geom. mean	13.50	7.64	86	27.4	1.67	69.5	31.9	17.3	436.2	0.389	7.87	2.51	0.005	0.287	0.157	0.255	1.55	0.037	0.467	382.6
	Std.	ND	3.25	0.89	0.13	0.59	0.03	0.03	0.07	0.01	1.48	0.58	1.18	0.24	0.43	0.28	0.37	1.47	0.16	0.46	0.02
Onarga Valley	Max	12.4	7.9	-67	85	3.8	188	77	27	428	7.2	604	26	0.002	1.11	0.10	0.76	4.0	0.20	0.84	1171
	Min	11.8	7.1	-67	52	2.2	75	35	9.3	341	0.06	165	1.0	0.001	0.71	0.03	0.14	0.20	0.01	0.84	582
	N	5	15	1	19	8	19	19	14	23	8	23	23	3	4	3	13	17	7	1	21
	Geom. mean	12.02	7.48	ND	67.2	2.97	132.4	57.6	18.42	391.2	0.418	350.7	5.70	0.001	0.989	0.056	0.356	1.43	0.072	ND	845.1
	Std.	ND	2.88	ND	0.03	0.15	0.05	0.04	0.08	0.009	1.66	0.06	0.59	ND	ND	ND	0.41	1.92	0.33	ND	0.03
Western MVA	Max	14.2	8.3	160	184	7.5	100	55	24	839	7.9	45	315	0.069	0.80	0.69	0.80	4.5	0.09	0.80	890
	Min	11.4	6.3	113	25	0.4	41	22	6	400	0.01	0.2	2.2	0.001	0.10	0.10	0.10	0.70	0.02	0.31	333
	N	5	26	3	45	25	42	43	39	52	25	20	52	24	19	16	36	48	14	7	52
	Geom. mean	13.18	7.54	130	73.1	2.10	69.1	31.7	15.4	525.0	0.471	4.62	20.2	0.018	0.364	0.281	0.388	2.42	0.040	0.453	501.8
	Std.	ND	4.89	ND	0.12	0.66	0.05	0.06	0.12	0.03	1.99	0.69	0.44	0.29	0.58	0.49	0.58	0.42	0.17	0.37	0.03

The data set was a compilation from the Illinois State Water Survey data base, Hanson (1950, 1958, 1961), Woller (1974, 1975, 1992a, 1992b, 1992c), and this investigation. All ions expressed in mg/l.

ND = Not determined.

Std. = Standard deviation of the log-transformed data. Standard deviation not determined for N ≤ 5.

*Mean and standard deviation is arithmetic for pH.

Results and Discussion

Ground-Water Chemistry

The ground-water chemistry of the study area reflects its geology, mineralogy, and hydrogeology. Figure 2 reveals the nature of the stratigraphy and hydrogeology that is responsible for the movement of ground water and water recharging the MVA and overlying aquifers. Historic water-level data indicate the lateral direction of ground-water flow within the MVA. Stratigraphic relationships within the glacial deposits, specifically the stacked aquifers of the central MVA, suggest areas that may be dominant sources of surface recharge to the MVA. Finally, the bedrock geology suggests the possiblility of structural controls on hydraulic connections between deep bedrock aquifers and the MVA. The variability of the ground-water chemistry of the MVA and associated aquifers was used to explore recharge to the MVA and rock-water interaction within the aquifer system.

There are clearly defined hydrochemical regions along the MVA. A plot of selected data on a trilinear diagram (Figure 3) indicates three distinct water types within the MVA: a very dilute water from the central MVA, and two waters which were modified through rock-water interactions and simple ground-water mixing. Ground water from the Glasford and Mahomet sands is supersaturated with respect to dolomite, and dolomite and calcite, respectively; an both ground waters are supersaturated with respect to quartz. This is consistent with mineralogical compositions of and differences between the two aquifers (presented earlier). Thus, Ca^{2+}, Mg^{2+}, and HCO_3^- are dominant ions within the MVA and Glasford Aquifers. Ground-water types and associated regions of the MVA include mixed cation-SO_4^{2-} type and mixed cation-HCO_3^- type waters in the Onarga Valley, a mixed cation-HCO_3^- type water in the central MVA, and a mixed cation-HCO_3^- type (with high Cl^-) water in the western MVA. Descriptive statistics of the ground-water chemistry of these regions are presented in Table 2 and

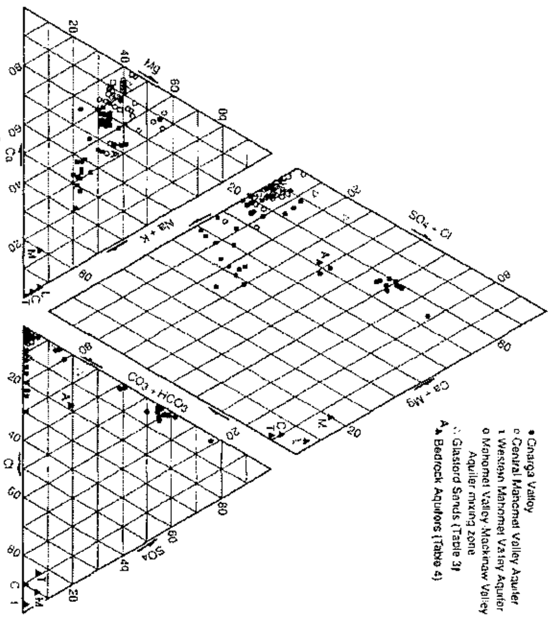

Fig. 3. Trilinear diagram of 85 selected ground-water samples from the MVA, the Glasford Sands, the MVA-MAK confluence area, and three bedrock aquifers.

yield an approximation of the typical chemistry of ground water in each region of the MVA.

The presence of distinct hydrochemical regions of the MVA is the result of several mechanisms: (a) relatively rapid recharge in areas of stacked aquifers (Figure 2), (b) rock-water interaction, (c) discharge of saline ground water into the MVA from bedrock, and (d) ground-water mixing at the confluence of the MVA and the MAK to the west. The effects of these mechanisms on ground-water chemistry are apparent on areal plots of selected ions in the MVA (Figures 4a through 4h). Each of the geochemical regions of the MVA are discussed in detail below.

The results of our isotopic investigation are presented by Hackley et al. (in preparation) and show that δD and $\delta^{18}O$ for all MVA waters fall on or near the global meteoric water line and have values similar to those of present-day precipitation. These data suggest that MVA waters were precipitated under climatic conditions similar to those of the present. Consequently, one might assume an upper age limit of 14,000 years BP for MVA waters because glacial-aged waters would be expected to be isotopically lighter than present-day waters. The $\delta^{13}C$ values and ^{14}C activities of dissolved inorganic carbon in MVA ground waters vary significantly along the reaches of the aquifer implying differences in geochemical evolution. The highest ^{14}C activities are found in the central MVA and at the confluence of the MVA and the MAK; ground water from both areas contains approximately 34 percent modern carbon (pMC), whereas ground water from other parts of the MVA contains from 9 to 13 pMC (Hackley et al., in preparation). The higher ^{14}C activity is consistent with more rapid recharge (as suggested by the stratigraphy and low TDS ground water) in the central MVA area and in the confluence area.

Descriptions of Chemical Patterns

Onarga Valley

Approximately contained within Iroquois County, the Onarga Valley arm of the MVA (Figure 1) and overlying aquifers contain ground water of a mixed cation-SO_4^{2-} type and a mixed cation-HCO_3^- type (Figure 3). Here, ground water is enriched in Na^+, Ca^{2+}, and Mg^{2+} (Figures 4a, b, c), with SO_4^{2-} concentrations greater than 500 mg/l (Figure 4f). Low HCO_3^- concentrations, and high concentrations of B and total dissolved solids (TDS), relative to the rest of the MVA, are also characteristic of ground water in the Onarga Valley (Figures 4e, h). Table 2 presents summary data on the ground-water chemistry that typifies this valley.

Water levels of wells screened in the basal sands of the MVA are well above land surface (Leverett, 1896; Hamdan, 1964) and indicate an upward hydraulic gradient. Water levels in this area for the Mahomet sands were 3.65 m above land surface at the time of measurement (fall, 1990) with an upward hydraulic gradient at one pair of wells of 0.002. Residents in the area have noted that when nearby irrigation operations (with wells in the MVA) commence in the spring, the head in Glasford wells drops below land surface (M. Tammen, personal communications, 1992). Such a drop indicates a hydrualic connection between the Mahomet Sand Member and the shallower Glasford sands.

Three possible sources for the high SO_4^{2-} in the ground water of the Onarga Valley were considered; (1) pyrite in overlying glacial tills, (2) pyrite or gypsum in underlying Silurian dolomite, and (3) underlying pyritic coals and shales of the Pennsylvanian strata. Each of these potential sources is discussed below.

Pyrite and marcasite are present in clayey tills over the Onarga Valley making up about 0.8 to 0.9% of the till (Moore, 1961). However, the possibility of glacial tills as a source of SO_4^{2-} in the Mahomet and Glasford sands is unlikely because of the shallow depth to which the tills of this area are weathered. Tills commonly weather to depths of 1.5 m and sometimes to a maximum depth of 4.6 m along discontinuities (L.R. Follmer, ISGS, personal communication, 1993) which is significantly shallower than these aquifers. Further, the upward hydraulic gradient in this area vitiates the likelihood that oxidized pyrite in till was a source for the deeper SO_4^{2-} enrichment of the ground water.

Ground water from most wells in the Silurian dolomite in Iroquois Co. contain relatively low concentrations of SO_4^{2-}. The geometric mean of nine ground-water samples from wells located in areas where the Pennsylvanian strata is absent (data from Hamdan, 1964) is 17.9 mg/l. This makes it unlikely that the Silurian dolomite is a primary source of the high-SO_4^{2-} waters.

A buried bedrock hill adjacent to the thalweg of the Onarga Valley in the southwestern corner of Iroquois Co. (Figure 2) consists of a subcrop of Pennsylvanian coals and associated black shale. Coals in this area are thin and typically contain several percent S in the form of pyritic S, organic S, and sulfate S (in order of relative abundance). Sulfate S increases with weathering of these strata (Gluskoter and Simon, 1969).

The Pennsylvanian Caseyville, Abbott, and Spoon Formations in Iroquois and Vermilion Counties correlate spatially with areas having both upward hydraulic gradients and relatively high SO_4^{2-} in overlying ground waters. The highest concentrations of SO_4^{2-} were observed in wells where Pennsylvanian strata overlies Silurian dolomite. The oxidation products of pyrite (as a result of exposure and weathering prior to burial) associated with thin coals and black shales of the Pennsylvanian bedrock are suspected of being responsible for the high sulfate waters in this valley. This interpretation is supported by the $\delta^{34}S$ values of SO_4^{2-} from the Onarga Valley and on equilibrium geochemical modeling results. The $\delta^{34}S$ data for SO_4^{2-} from wells in the Mahomet and Glasford sands were about -1‰, indicative of S originating from pyrite or the oxidation products of pyrite (Hackley et al., in preparation). The presence of limestone within the Pennsylvanian strata, the occurrence of calcite and dolomite within the Glasford and Mahomet sands, the relatively low HCO_3^- concentration, and the slightly alkaline pH observed in the Onarga Valley (Figure 4e) are inconsistent with the generation of H^+ resulting from pyrite oxidation and the resultant dissolution of carbonate minerals.

The vertical distribution of SO_4^{2-} (Figure 5) shows two distinct populations of SO_4^{2-} in the ground water of Iroquois County; the apparent random vertical distribution in the high-SO_4^{2-} population support an upward hydraulic

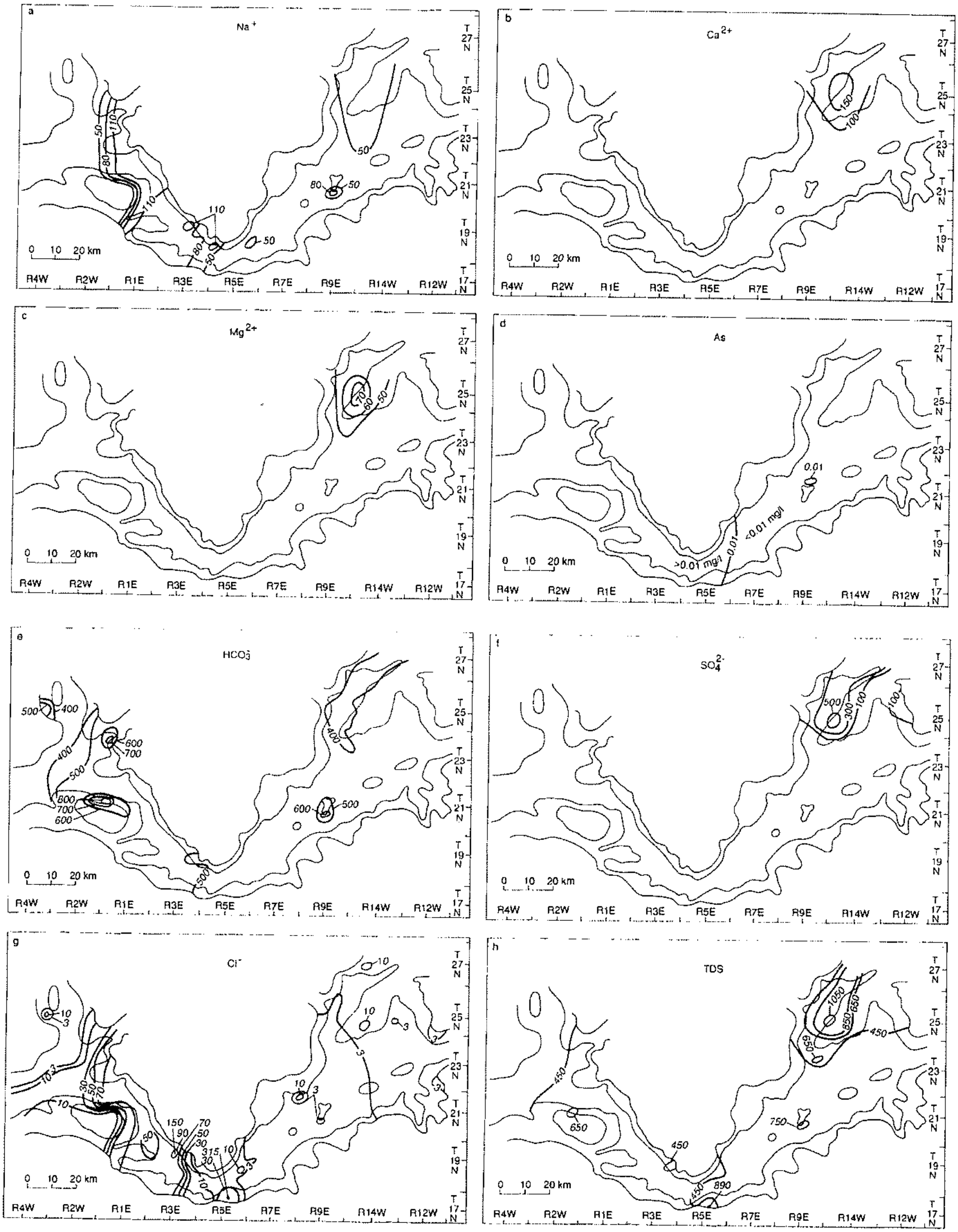

Fig. 4. Aerial distribution of selected ions in ground water of the MVA: a = aerial distribution of Na^+; b = aerial distribution of Ca^{2+}; c = aerial distribution of Mg^{2+}; d = aerial distribution of As; e = aerial distribution of HCO_3^-; f = aerial distribution of SO_4^{2-}; g = aerial distribution of Cl^-; h = aerial distribution of TDS. Isocons are in mg/l.

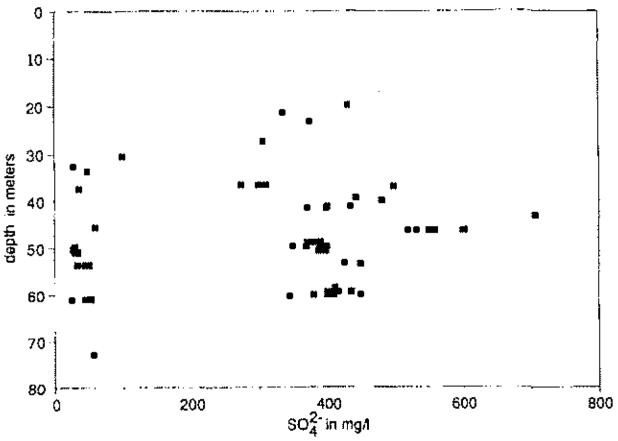

Fig. 5. SO_4^{2-} **as a function of depth in Onarga Valley (Iroquois County).**

gradient within the Onarga Valley. If the pattern of recharge is assumed to be delineated by the distribution of anomalously high concentrations of SO_4^{2-} and high ground-water levels, then upwelling of ground water from bedrock is probably occurring along the axis of the Onarga Valley segment of the MVA. The vertical distribution of SO_4^{2-} within three townships overlying the MVA (Figure 5) supports this hypothesis and indicates that there are two distinctly different ground waters present in Iroquois County. The second water type is on the periphery of the area of upwelling. The ground water in the Onarga Valley is also enriched in Ca^{2+} and Mg^{2+}; this is a twofold increase relative to concentrations from other regions of the MVA (Figures 4b, c). The Ca^{2+} enrichment is consistent with dissolution of the products of pyrite oxidation. Further, HCO_3^- is lowest within the area of suspected discharge (relative to the rest of the MVA) (Figure 4e) which is similar to the low HCO_3^- concentrations observed in the deeper ground waters of the Silurian dolomite (Table 2, A). The plot of bedrock ground water from the Onarga Valley and Silurian dolomite (A) on the trilinear diagram (Figure 3) is consistent with the above discussion. The plot shows a significant increase in SO_4^{2-} in Onarga Valley ground water relative to those of the Silurian dolomite.

Boron is enriched by a factor of approximately three in the ground waters of the Onarga Valley, relative to the other regions of the MVA (Table 2). The mean values for B in an "average shale" and for Illinois coal is 100 and 95 ppm (Mason, 1966, and Gluskoter et al., 1977, respectively). Because relatively high concentrations of B are associated with marine shales and Illinois coal, and because B is relatively soluble in fresh water, it is likely that the interaction of rising ground water with Pennsylvanian shale and coal underlying the Onarga Valley is responsible for its relative enrichment.

Geochemical modeling supports the hypothesis that the high-SO_4^{2-} waters of the Onarga Valley area are due to dissolution of SO_4^{2-} minerals such as gypsum and iron sulfate rather than pyrite. Model calculations involving the reaction of pyrite, in the presence of calcite and dolomite, with bedrock ground water from the Silurian dolomite (Iroquois Co.), resulted in very little increase in SO_4^{2-} in the resultant water. The Eh of the ground water from Silurian dolomite was calculated by REACT as approximately 340 mV based on the chemistry of the ground water which included the redox couple NO_3^--NH_4^+. When reacted with pyrite, only a very small portion of pyrite was predicted to dissolve. The Eh of the solution dropped to −155 mV while the SO_4^{2-} concentration rose to only 78 mg/l; this concentration is far below the 400 to 500 mg/l observed in the Onarga Valley ground waters. However, reaction of the bedrock ground water with gypsum, in the presence of calcite and dolomite, resulted in a large increase of SO_4^{2-} with little change in HCO_3^-. Dissolution of iron sulfate (exclusive of gypsum) resulted in a decrease in pH and an increase in Ca^{2+} due to calcite dissolution. The resultant pH and Ca^{2+} concentrations were significantly lower and higher, respectively, than those observed in the Onarga Valley for equivalent SO_4^{2-} concentrations. Thus, modeling results, which simulate equilibrium conditions, suggest that much of the SO_4^{2-} in the ground waters of the Onarga Valley probably resulted from the dissolution of gypsum and lesser amounts of iron sulfate derived from oxidized pyritic coal and shales in the bedrock high adjacent to the thalweg of the Onarga Valley.

The ground waters sampled from the Onarga Valley (from Mahomet and Glasford sands) are not only chemically, but isotopically identical. These ground waters have low ^{14}C activities relative to other parts of the MVA indicating that the ground water in this tributary is older than that of the rest of the MVA. A preliminary age estimate for this water is 10,000 radiocarbon years BP (Hackley et al., in preparation). On the basis of these results and the aforementioned data, recharge to the Onarga Valley may be as much as 100% from bedrock and lateral flow from the central MVA.

Central Mahomet Valley

South of the Onarga Valley and east of the Piatt County line is an area that contains the least mineralized ground water in the MVA. Here the ground water is a mixed cation-HCO_3^- type (Figure 3) with a relatively low TDS of typically 400 mg/l or less, and relatively low concentrations of Na^+, Cl^-, and SO_4^{2-}. Chloride and SO_4^{2-} are often ≤ 1 mg/l and below detection limits, respectively (Figures 4g, f). Chloride concentrations are lowest in Champaign County (Figure 4g); the vertical distribution of Cl^- in Champaign County (Figures 6 and 7a) reveals that ground water becomes fresher with depth. Table 2 presents a summary of the chemistry of this region of the MVA.

The relatively dilute, low-Cl^- ground water in the central MVA (Figure 4g and Table 2) suggests that rapid infiltration may be taking place (especially in the area of the Sangamon River Valley) relative to the whole MVA system. The thickness of the Glasford Aquifer in this area is between 15 and 45 m and intervening till is as thin as 1.5 m (J.P. Kempton et al., ISGS, unpublished manuscript). The chemistry of the ground waters from the sands of the Wedron, Glasford, and Banner Formations is very similar, suggesting that the aquifers of these formations are in hydraulic communication (Figure 2). Rapid recharge in this area is also

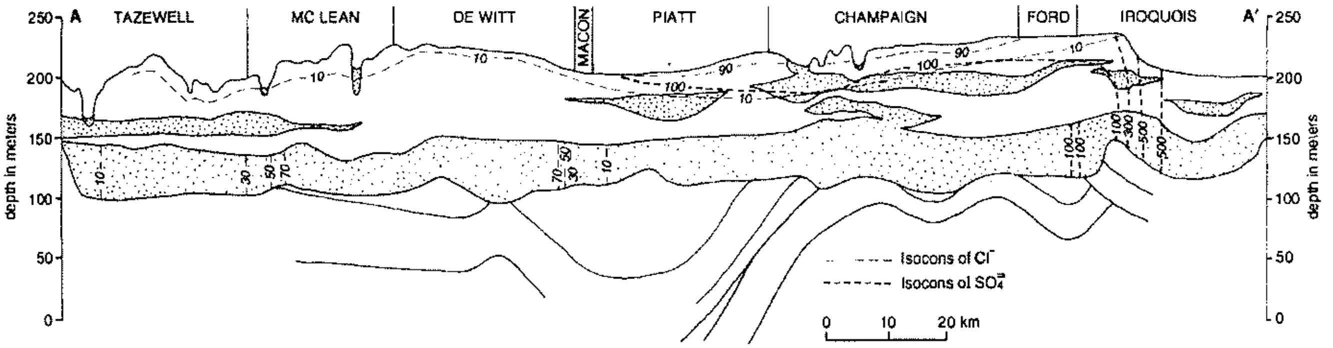

Fig. 6. Vertical distribution of Cl^- and SO_4^{2-} along longitudinal cross section A-A'.

supported by isotopic data which have a relatively high activity of ^{14}C. Preliminary age calculations suggest a range of 1700 to 5000 radiocarbon years BP for ground waters of the central MVA (Hackley et al., in preparation).

Sodium, Cl^-, Ca^{2+}, Mg^{2+}, NO_3^-, and SO_4^{2-} are relatively enriched in the upper ≈ 30 m of the till and shallow aquifers in Champaign and Piatt County (Figure 6 and Table 3). These ions are probably the result of surface contamination (e.g., road salt, agricultural activities) and oxidation of pyrite in overlying clayey till. Ion exchange, sulfate reduction, and other mechanisms probably have modified the vertical distribution of Na^+, Ca^{2+}, Mg^{2+}, NO_3^-, and SO_4^{2-}, but Cl^- should yield a conservative estimate of the depth to which surface contamination has migrated. The depth of infiltration in Champaign and Piatt Counties is greater than that observed in the counties farther west (Figure 6). This,

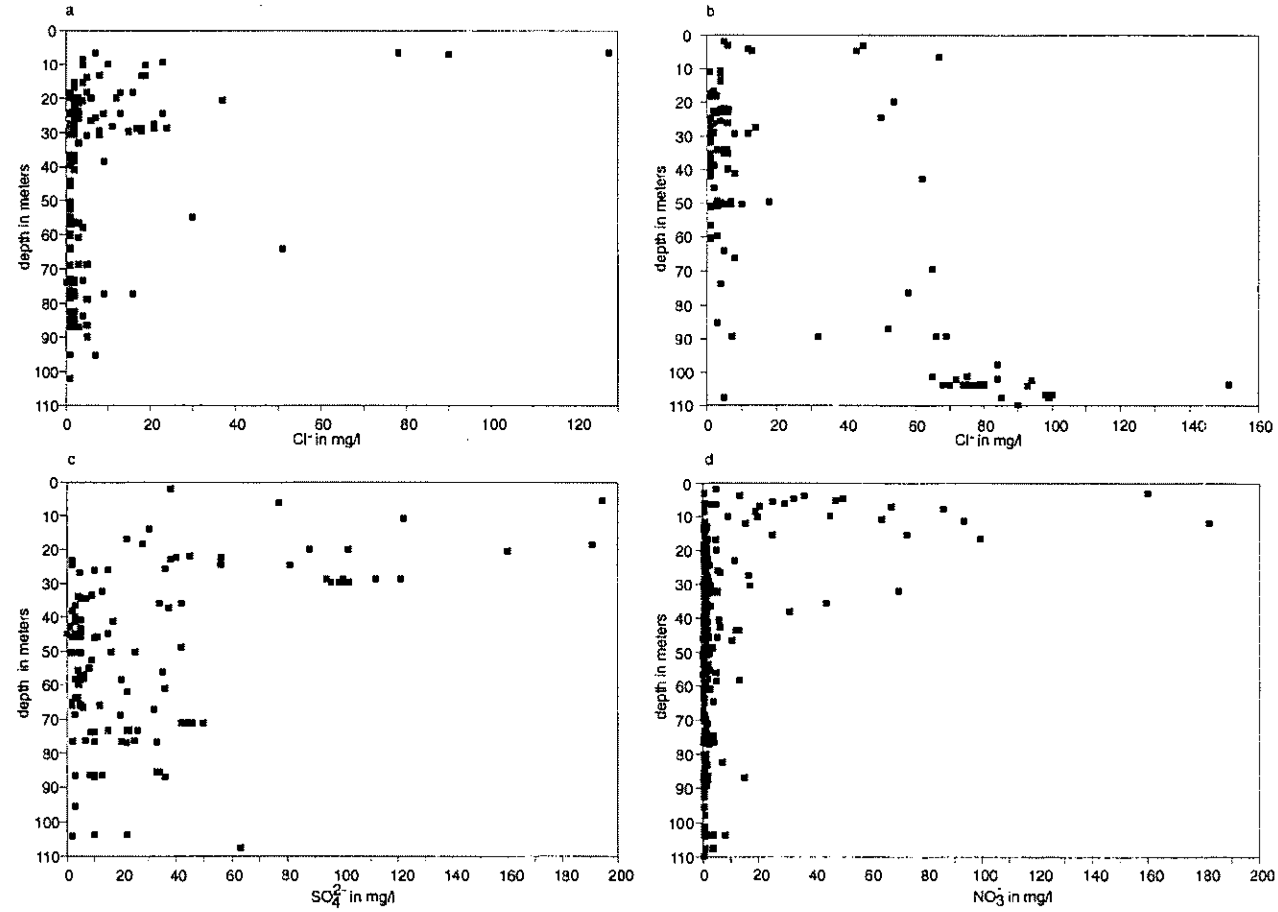

Fig. 7. Distribution of selected ions as a function of depth in various regions of the MVA: a = Cl^- in the central MVA (Champaign County); b = Cl^- in the western MVA (McLean and De Witt Counties); c = SO_4^{2-} in all regions of the MVA except the Onarga Valley; d = NO_3^- in all regions of the MVA.

Table 3. Ground-Water Chemistry of Ground-Water Samples from Aquifers of the Glasford and Wedron Formations

Map no.	County	Location	Well depth (m)	Surface elev. (m)	pH	Na	K	Ca	Mg	SiO_2	HCO_3	NO_3	SO_4	Cl	As	B	Ba	Br	F	Fe	Mn	Sr	TDS	Form.	Source
G1	Champaign	20N07E15	30	221	7.6	14	2.4	100	50	16	427	0.44	102	18		0.07		0.086	0.15	2.40	0.15	0.22	521	G	ISWS
G2	Logan	21N01W15	19	206	7.4			149	70		534		191	31						4.40			769	G	ISWS
G3	DeWitt	19N02E01	23	221	7.6	6.0	0.6	71	33	15	406	1.80	38	4.3	0.001	0.01	0.10		0.30	0.51	0.09		382	G	ISWS
G4	Piatt	18N06E02	6.1	213		17		100	44	10	383	29	77	25						0.20			507	W	ISWS

All ions expressed in mg/l.
W = Wedron Formation.
G = Glasford Formation.
ISWS = Illinois State Water Survey data base.

we believe, is due to the presence of a greater number of stacked aquifers in the central MVA. Because there are few shallow aquifers in the more western part of the MVA system, infiltration rates are probably lower as discussed below.

Western Mahomet Valley

The ground water of the western MVA is of the mixed cation-HCO_3^- type with relatively high-Cl^-, increasing in Na^+, As, HCO_3^-, Cl^-, and TDS just west of the Piatt-Champaign County line (Figures 4a, d, e, g, h). Chemical changes along the western MVA are abrupt, and the initial high variability of salinity within ground-water samples indicates the existence of several point sources near the county line. That is, the isolated occurrence of high-Cl^- ground water in this area indicates recharge from underlying bedrock aquifers and less permeable units containing ground waters of relatively high salinity (Table 4). Figure 3 shows the trace of evolution of western MVA ground water by the addition of Na^+ and Cl^- to central MVA-type water; ground-water evolution indicated on the trilinear diagram trends toward the saline ground water of the bedrock aquifers. The boundary between the two ground-water types is very close to the north-south trending Osman Monocline and the Colfax Syncline which are part of the larger La Salle Anticlinal system (Figure 1). Here, bedrock lithology changes abruptly as well. Additional structures along this portion of the MVA include the Downs Anticline and the Clinton Syncline (Figure 1). Recharge from bedrock through structural pathways is probably responsible for the distinctively higher Cl^- concentrations west of the monocline. More diffuse recharge of saline ground water from Pennsylvanian bedrock throughout the western MVA may also be a factor in this region.

Plots of Cl^- vs depth for wells in Champaign County (Figure 7a) and wells in De Witt and McLean Counties (Figure 7b) reveal the contrast between the vertical distribution of Cl^- in both ground waters. Data from Champaign County wells show Cl^- enrichment to be from surface contamination (e.g., road salt, agricultural activities, septic effluent). Data from De Witt and McLean County wells show Cl^- enrichment to be from both surface contamination and from a deep bedrock source. The upward migration of saline waters from bedrock is the most likely explanation for the relatively high Cl^- concentrations at the base of the MVA. Relatively high Cl^- concentratons (e.g., 151, 315 mg/l) occur in the MVA adjacent to the more typically low Cl^- concentrations (e.g., 2, 7 mg/l) prior to the overall increase in Cl^- and other ions in the western MVA (i.e., between Ranges 3 and 6E, Figure 4g). The nonuniform nature of the changes in ground-water chemistry here suggests the presence of localized discharge of saline ground water along structures associated with the La Salle Anticline.

Arsenic is present in very low concentrations (≤ 1 $\mu g/l$) east of the Piatt-Champaign County line, and at least an order of magnitude higher west of that line (Figure 4d). The reason for this distribution is not known; however, the county line is the approximate location of suspected upwelling of more saline ground waters from bedrock aquifers. It is

Table 4. Ground-Water Chemistry of Deep Ground-Water Samples from Bedrock Aquifers (from Meents et al., 1952, and Hanson, 1950)

Map no.	*County*	*Location*	*Well depth (m)*	*Surface elev. (m)*	*Temp. (°C)*	*pH*	*NH_4*	*Na*	*Ca*	*Mg*	*SiO_2*	*HCO_3*	*NO_3*	*SO_4*	*Cl*	*F*	*Fe*	*Mn*	*TDS*	*Aquifer*	*Source*
A	Iroquois	28N14W28	47	202	12	7.3	2.2	51	55	37	12.4	312	1.1	76	50	0.40	1.20	0.10	444	S	Hanson
C	Champaign	20N08E20	98	236			3.0	2235	21	28	8.0	621	5.7	12	3199		BDL	BDL	5792	D-S	Meents
P	Piatt	19N05E06	368	213											3500				6570	D-S	Meents
Mc	McLean	22N01E28	442	229											2075				4428	D-S	Meents
L	Logan	19N03W07	368	183		8.0	5.0	4757	56	117	6.0	439	9.0	BDL	7491		BDL	BDL	12918	D-S	Meents
M	Macon	17N02E30	895	213			2.0	2382	415	128	10	415	7.0	399	4245		0.8		8118	SP	Meents
T	Tazewell	25N03W18	366	229			0.2	1208	7	5	6.0	372	3.7	109	1591		BDL		3208	D-S	Meents

All ions expressed in mg/l.
Cl for Piatt Co. estimated from least-square fit of TDS and Cl from nearby deep wells in the same formation.
BDL = Below detection limits.
S = Silurian Dolomite.
D-S = Devonian-Silurian Dolomites.
SP = St. Peter Sandstone.
Hanson = Hanson (1950).
Meents = Meents et al. (1952).

possible that deeper ground waters are bringing As up into the MVA either from Pennsylvanian bedrock or deeper. Another possible explanation for the relatively high As concentrations is that redox conditions and bedrock mineralogy in the western MVA control As concentrations. Pyrite in coal and black shale of Pennsylvanian bedrock were exposed within the valley and were probably oxidized during that time. Subsequent burial by clay-rich glacial drift fostered reducing conditions at depth. Arsenate (As^{5+}) is adsorbed onto amorphous iron hydroxide [$Fe(OH)_3$], whereas arsenite (As^{3+}) is more mobile. Reduction of adsorbed arsenate to arsenite could result in the remobilization of adsorbed As. This mechanism would also help explain why Fe concentrations are approximately 40% higher in the western MVA than in the other regions of the MVA. That is, the dissolution of iron hydroxide and the concomitant desorption of As in response to a change to reducing conditions would account for the present chemistry of these constituents. Similar findings in confined bedrock aquifers in Missouri and Ohio were noted by Korte (1991) and Matisoff et al. (1982), respectively.

A mass-balance calculation for the area within the 40 mg/l isochlor (approximately 40 km^2) (Figure 4g) was conducted. The geometric mean of the Cl^- concentration from this area is 71 mg/l. We used the available hydraulic data determined by others and discussed above, and a N-S cross-sectional area for the MVA near the Piatt-Champaign County line (8.3×10^5 m^2). The calculations assume that ground water from bedrock is migrating upward into the MVA; the Cl^- concentration for upwelling ground water was assumed to be 2000 mg/l on the basis of bedrock ground-water chemistry (Table 4, Mc). Chloride concentrations in ground water from the east and from surface recharge were assumed to contain 1.5 mg/l Cl^-. Using available hydrologic data and recharge estimates from Visocky and Schicht (1969), recharge from the surface (Q_S) is 1.0×10^7 l/day (assuming an area of 40 km^2), ground water from lateral flow into the area (Q_L) is 1.9×10^7 l/day. We used the equation

$$(1.5 \text{ mg/l})(Q_L + Q_S) + (2000 \text{ mg/l})(Q_B) = (71 \text{ mg/l})(Q_B + Q_L + Q_S).$$

Solving for Q_B (leakage from bedrock), we found that approximately 1.045×10^6 l/day of saline ground water was leaking into the MVA in the designated area of the western MVA. Total recharge to this part of the MVA is approximately 1.1×10^7 l/day; thus, approximately 9.5% of total recharge to the MVA in this part of the aquifer is coming from bedrock leakage. Because the salinity of ground water in bedrock in this area increases with depth, this estimate is likely to be conservatively low. That is, the estimate for % leakage of saline water from bedrock will increase if the Cl^- concentration of deep ground water from bedrock is lower than assumed in the calculation. Preliminary age calculations of ground water in this region of the MVA is approximately 9400 radiocarbon years BP (Hackley et al., in preparation) which is consistent with the input of older ground water from bedrock.

Onarga.

Mackinaw Bedrock Valley Aquifer (MAK)

That portion of the MAK that receives ground water from the MVA was also examined. Some generalizations can be made about the character of the water in this aquifer. The ground water from the north and within the confluence area is a relatively dilute Ca^{2+}-HCO_3^- type water which differs from the mixed cation-HCO_3^- type waters of the MVA, but are similar to the shallower ground waters of the Glasford Formation. Chemically, the ground water of the MAK is closest to that of the central MVA; that is, both areas have relatively low concentrations of Na^+, Cl^-, SO_4^{2-}, HCO_3^-, and low TDS. A mixing zone was delineated at the confluence of this aquifer and the MVA on the basis of Cl^- concentrations (Figure 4g). Here, low Cl^- ground water flowing from the north (approximately 4 mg/l) mixes with relatively high Cl^- waters from the western MVA (approximately 70 mg/l). The resultant ground water has an intermediate Cl^- concentration of approximately 15 mg/l within and downgradient of the mixing zone. Although these concentrations constitute preliminary estimates, they do indicate that the volume of ground water moving through the MAK and entering (by recharge) the confluence area is almost five times that entering from the western MVA. That is, approximately 17% of the ground water in the MAK, just south of the confluence area, is coming from the MVA.

Isotopic data for one well from within the confluence area (based on ^{14}C) indicate that the ground water is younger than any of the samples collected from the three geochemical regions of the MVA (Hackley et al., in preparation).

Shallow Aquifers

The relatively shallow aquifers overlying the MVA contain waters that are typically Ca^{2+}-HCO_3^- type waters. The very shallow ground waters ($\leq$ 40 m deep) are enriched in Na^+, Cl^-, SO_4^{2-}, and NO_3^- (Table 3) (except in the Onarga Valley for reasons discussed earlier), probably as a result of application of road salt, agricultural activities, and oxidation of pyrite in glacial tills. However, poor well construction could contribute to ground-water quality degradation on a local basis.

Sulfate and NO_3^- concentrations are enriched near the surface for the entire study area (except the Onarga Valley) (Figures 6, 7c, 7d). Oxidation of pyrite within the glacial till and agricultural activities are believed to be responsible for the enrichment. The depth to which SO_4^{2-} and NO_3^- have migrated is probably dependent on stratigraphic considerations (as discussed earlier) and redox conditions (e.g., denitrification).

Enrichment of Na^+, Cl^-, SO_4^{2-}, and NO_3^- does not appear to extend more than 30 to 40 m below the ground surface (Figures 6, 7a-d), and is deepest in the central MVA region where overlapping aquifers probably provide less resistant pathways to the underlying MVA. The relatively wide range of concentrations of these ions in shallow aquifers is probably due to temporal and spatial variability that is typical of such enrichment (e.g., seasonal variations).

Conceptual Model

The ground-water chemistry in the MVA is consistent with lateral ground-water flow directions in the aquifer as described in Kempton et al. (1991). Historical head ranges provided by Kempton et al. (1991) reveal the approximate location of a ground-water divide located in northern Champaign County. The chemistry of ground water in aquifers that bound the MVA above and below indicate ground-water recharge to the MVA is not all from the surface. Specifically, the leakage of ground water from underlying bedrock aquifers is occurring in the Onarga Valley and the western MVA (Figures 8a, b). Recharge from the surface occurs most rapidly where overlapping or stacked aquifers are present (i.e., in the central MVA). Ground-water flow directions are to the north into the Onarga Valley, to the east toward Indiana, and to the southwest and west through Champaign County.

The Onarga Valley has an apparent upward hydraulic gradient, and ground water in the aquifers of this valley is enriched in Na^+, Ca^{2+}, Mg^{2+}, and SO_4^{2-}. Water chemistry data indicate that ground water from underlying Silurian dolomite is moving upward through oxidized pyritic Pennsylvanian coals and shales into the Mahomet and Glasford sands. Dissolution of gypsum and possibly iron sulfate from Pennsylvanian bedrock by ground water from underlying Silurian dolomite is believed to be the source of the solutes. Recharge to the aquifers of the Onarga Valley is probably 100% from bedrock leakage and lateral flow from the central MVA.

The central MVA contains relatively dilute ground water. However, ground water of the overlying Glasford and Wedron Formations contains higher concentrations of Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, and NO_3^-. These constituents have infiltrated to depths of approximately 30 m in this region, and anthropogenic contaminants and oxidation products from weathered till are probably the source for these constituents. Because of the thinness of the intervening clayey till between the shallow aquifers and the MVA, it is likely that recharge to the MVA is relatively rapid in Champaign County.

The western MVA begins just east of the Piatt-Champaign County line which is also the approximate location of the La Salle Anticline. Structural features (monoclines, synclines, and anticlines) appear to play a significant role in the chemistry of ground water in this stretch of the valley. West of the county line, Na^+, Cl^-, HCO_3^-, As, and TDS increase significantly and are believed to be due to the leakage of saline ground water from Pennsylvanian bedrock into the base of the MVA. Most notably, Cl^- and As increase in the western MVA by an order of magnitude (relative to the central MVA). Approximately 9.5% of recharge to this region of the MVA is from bedrock. The bedrock-derived constituents increase rapidly and stabilize until intersecting the Sankoty Sands of the MAK. Ground-water mixing and concomitant dilution occurs at the confluence of the MVA and the MAK in Tazewell Co. Here, the ground-water chemistry reveals the approximate location of mixing of the more saline MVA water with the fresher MAK water. On the basis of Cl^- concentrations and mass-balance calcula-

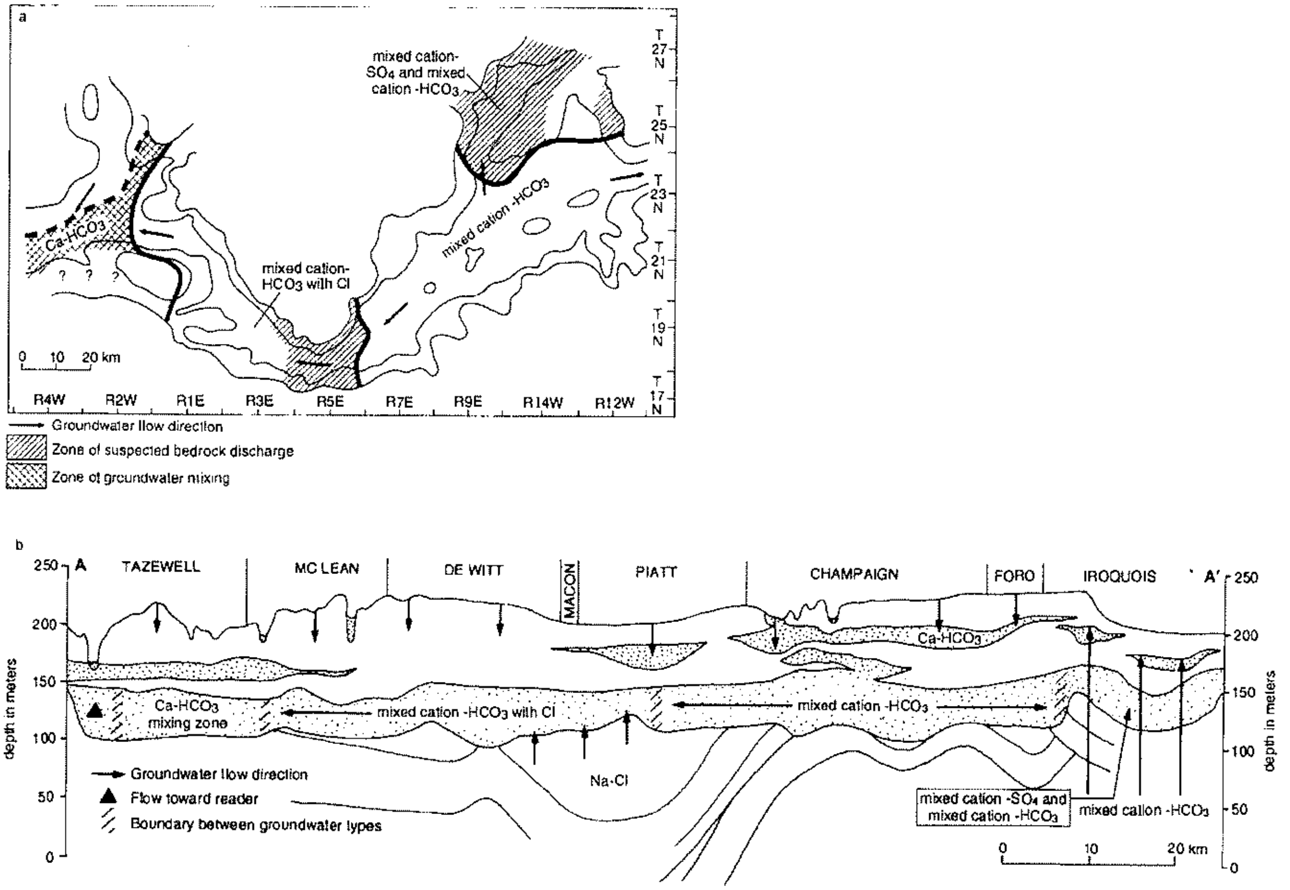

Fig. 8. Conceptual model of the MVA showing ground-water types, ground-water flow directions, areas of suspected leakage from bedrock, and the zone of ground-water mixing at the confluence of the MAK and MVA Aquifers: a = aerial view; b = longitudinal cross section A-A'.

tions, only about 17% of the ground water flowing from the confluence area is derived from the MVA.

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