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GEOLOGIC CONSTRAINTS ON ARSENIC IN GROUNDWATER WITH APPLICATIONS TO GROUNDWATER MODELING

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ABSTRACT

In the 1980s, high concentrations of arsenic were measured in the Fox River Valley, eastern Wisconsin. Research suggested mineralization occurring at the contact of the middle Ordovician St. Peter (Ancell Group) and Platteville formations (Sinnipee Group) as a source of the contamination. The stratigraphic units of the Ancell Group (St. Peter and Glenwood formations) and the Sinnipee Group (Platteville, Decorah, and Galena formations) were measured, described, and defined, and possible geologic sources of the arsenic contamination were investigated. Quarries and drill cores were examined to construct a stratigraphic framework of the region, define lithostratigraphic facies and hydrostratigraphic units, and locate mineral deposits that may be a source of arsenic contamination. Field and laboratory investigations of mineral deposits were performed to determine the presence of arsenic. Residential well data were used to determine if a statistical correlation exists between the suspected source of arsenic contamination and areas of known contamination. Stratigraphy of the Ancell and Sinnipee Groups is divided into three packages: the sandstones and minor shales of the St. Peter and Glenwood formations (Package A); the dominantly clay-free dolostones of the Platteville Formation (Package B); and the dolostones, argillaceous dolostones, and clays of the Galena Formation (Package C). Each of these packages is divided into lithostratigraphic units A1-A2, B1-B6, and C1-C5 based on argillaceousness, texture, and fossil content. Six hydrostratigraphic units are defined based on estimations of argillaceousness, porosity, and permeability. Mineralization was dominantly calcite and sulfides [pyrite (FeS) and less commonly sphalerite (ZnS) and marcasite (FeS_2)]. The mineralization was observed in three geologic settings across the study area: joint faces, porosity, and a cement horizon. The only volumetrically significant mineralization observed within the study area occurs as a sulfide-bearing secondary cement horizon immediately below the base of the Platteville Formation which we have termed the Sulfide Cement Horizon (SCH). Whole rock analyses of samples from several locations show concentrations of arsenic up to 212 ppm. SEM/Microprobe analysis found that the horizon is characterized by a complex digenetic succession of large and massive pyrite crystals. The SCH and water table generally intersect in a region approximately correlative with a region of high arsenic concentrations. Private well data show high arsenic concentrations where the water table lies at or immediately below the SCH. Fluctuating levels may have increased the leaching of arsenic from the SCH, possibly through exposure of the SCH to an oxygenated environment and consequent formation of sulfuric acid by oxidation of pyrite. More research is needed to understand the geochemical reactions between the mineralization and groundwater, and how private well use affects these reactions, before recommendations for remediating the contamination problem can be made.

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INTRODUCTION

In the late 1980's high concentrations of arsenic were measured in numerous wells in the Fox River Valley. Because the arsenic contamination occurs over a large region and approximately parallels the subcrop of the St. Peter Formation, it was postulated that the source of the arsenic in groundwater was from naturally occurring ores within the St. Peter Formation or neighboring formations.

Burkel (1993) and Burkel and Stoll (1995) suggested that sulfide mineralization occurring at the contact of the St. Peter and Galena formations was the predominant source of high arsenic concentrations in the groundwater. Because of this, the Wisconsin Department of Natural Resources (WDNR) established an advisory area extending 5 miles on either side of the St. Peter Formation subcrop in Outagamie and Winnebago Counties. Within the boundaries of this advisory area, well drillers are encouraged to case through the upper 80 feet of the St. Peter Formation so that well water will not be drawn from near the St. Peter/Galena contact. The WDNR continues to research the arsenic contamination problem, extending arsenic sampling to include Shawano, Oconto, and Marinette Counties, and by carrying out extensive monitoring and testing of groundwater at several locations of known high arsenic concentrations to determine various chemical characteristics of the contaminated groundwater. This includes continued monitoring of wells near Seymour, where a 1994 WDNR investigation identified a stratum of pyritized sandstone at the top of the St. Peter Formation. It was theorized that the pyritization caused the extremely low pH concentrations and high levels of arsenic and other metals in the wells.

The purpose of this study was to investigate, describe, and define the stratigraphic units of the Ancell Group (St. Peter and Glenwood formations) and Sinnipee Group (Platteville, Decorah, and Galena formations), to establish hydrostratigraphic units on which future groundwater flow or geochemical modeling could be based, and to determine any possible geologic controls (joints, particular bedding planes, etc.) on the occurrence of mineralization which could cause arsenic contamination of groundwater. The study area of this project covers Brown, Outagamie, and Winnebago Counties, where data from Burkel (1993) and WDNR studies are available.

More than 20 quarries and several drill cores in the region surrounding the study area were measured and stratigraphic sections described (Figure 1, Table 1). From this work a stratigraphic framework was developed, and lithographic facies and hydrostratigraphic units were described. Visual observations were made of all minerals that could have disseminated arsenic, and any geologic structures that might have controlled mineralization. Arsenic-bearing minerals were chemically analyzed by using a petrographic microscope and whole-rock and SEM/Microprobe analysis. Well data were used to determine if statistically significant correlation exists between the suspected arsenic-bearing mineralization and areas of known arsenic contamination.

The Ordovician stratigraphy in the study area has been generally divided into four packages: the dolomites, dolomitic sandstones, and shales of the Prairie du Chien Group; the sandstones and minor shales of the Ancell Group (St. Peter and Glenwood formations); the relatively clay-free dolostones of the Platteville Formation (Sinnipee Group); and the dolostones, argillaceous

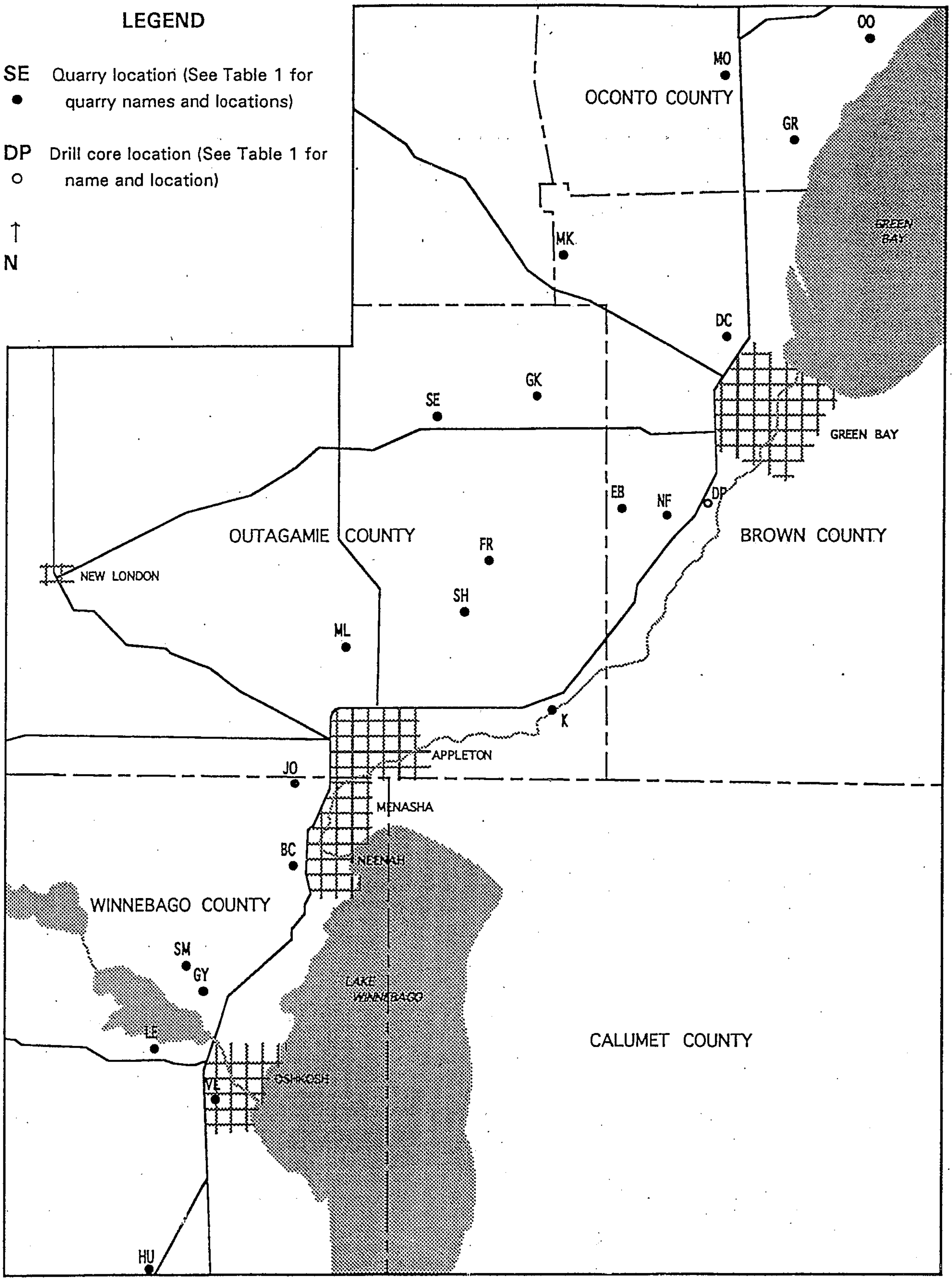


Figure 1. Location of quarries and drill core studied.

Table 1. Locations of quarries and drill core.

Symbol	Location
BC	Michels Ben Carrie Quarry: West side of Tular Rd. 1/8 mi. north of Hwy 114, Winnebago County; SW corner of section 29 T20N R17E
DC	Daanen and Janssens Duck Creek Quarry: North side of Glendale Rd. 1/8 mi. west of Hwy J, Howard, Brown County; SW corner of section 10 T24 N R20E
DP	De Pere drill core: Drilled by USGS, 1993, at West De Pere High School, De Pere, Brown County; NW corner of section 28 T23N R20 E
EB	Daanen and Janssens Ebben Quarry: South side of Hwy EE 4 mi. west of Hwy 41, Brown County; NE corner of section 27 T23N R19E
FR	Carews Freedom Quarry: South side of Center Valley Rd. 1 mi. west of Hwy 55, Outagamie County; NW corner of section 10 T22N R18E
GK	Ed Geysek Quarry: North side of Pearl rd. ½ mi. east of Hwy Y, Brown County; SE corner of section T24N R18E
GR	Foster and Sons Grosse Quarry: East end of Allen Rd., ½ mi. east of Hwy J, Oconto County; NE corner of section 30 T26N R21E
GY	Michels Grundy Quarry: South side of Hwy Y ¼ mi. west of Hwy T, Winnebago County; NE corner of section 33 T19N R16E
HU	Michels Hughes Quarry: North side of Hwy 26 4½ mi. sw of Hwy 41, Winnebago County; SE corner of section 31 T17N R15E
JO	Michels Jorgensen Quarry: South side of Hwy BB 1½ mi. west of Hwy 41, Winnebago County; NW corner of section 5 T20N R17E
K	Murphys Kaukauna Quarry: Immediately east of Grignon Park, Kaukauna, Outagamie County; SE corner of section 13 T21N R18E
LE	Michels Quarry, Leonary Road: West side of Leonard Road ½ mi. north of Hwy 21, Winnebago County; SE corner of section 7 T18N R16E
MK	McKeefry Quarry: North side of Quarry Rd. ½ mi. west of Hwy 32, Brown County; SE corner of section 18 T25N R19E
ML	Murphys Landwehr Quarry: West side of Quarry Rd. ½ mi. east of Hwy A, Outagamie County; NW corner of section 33 T17N R22E
MO	Foster and Sons Montevideo Quarry: West end of Montevideo Dr. ½ mi. west of Hwy 41, south of Abrams, Oconto County; SW corner of section 3 T26N R20E
NF	Northeast Asphalts Hwy F Quarry: North side of Hwy F 1 mi. west of Hwy 41, Brown County; SW corner of section 30 T23N R20E
OO	Foster and Sons Oak Orchard Quarry: East side of Hwy S 5 mi. northeast of Little Suamico, Oconto County; NE corner of section 32 T27N R21E
SE	Murphys Seymour Quarry: North side of Hwy 54 1 mi. west of Seymour, Outagamie County; SE corner of section 31 T24N R18E
SH	Murphys Skunk Hill Quarry: East side of Hwy C ½ mi. north of Hwy E, Outagamie County; NE corner of section 20 T22N R18E
SM	Michels Schmoker Quarry: North side of Brooks Rd. 1 mi. west of Hwy T, Winnebago County; SW corner of section 21 T19N R16E
VL	Vulcan Materials-Oshkosh Quarry: West side of Knapp St. 1/8 mi. north of Hwy 44, Oshkosh, Winnebago County; NE corner of section 27 T18N R16E

dolostones, and clays of the Galena Formation (Sinnipee Group). The argillaceous Decorah Formation (normally present between the Platteville and Galena formations) is believed to be absent in the study area (Templeton and Willman, 1963; LoDuca, 1986).

Each of the three packages of the Ancell and Sinnipee groups has been subdivided into 13 lithostratigraphic units by characteristics such as argillaceousness, texture, and fossil content, which are important to an understanding of the stratigraphic history, vertical and lateral distribution of the strata, and depositional environment of the units. Similarly, lithostratigraphic units define hydrostratigraphic units by their argillaceousness, porosity, permeability, and vertical variability. Six hydrostratigraphic units are defined, allowing more precise modeling of the Sinnipee Group (usually modeled as a homogenous unit of high porosity), by recognition of generally horizontal layers of varying porosity and permeability. In particular, the argillaceous, much less permeable strata of the lower Galena Formation contrasts sharply with the moderately porous and permeable strata of the underlying Platteville Formation. Additionally, it is recognized that the lower-porosity units in the Platteville Formation are partially replaced by more porous units to the north, while in the Galena Formation the higher-porosity units are replaced by less porous units to the north.

Amount and distribution of secondary mineralization (most likely to contain arsenic-bearing minerals) was observed in joints trending northwest-southeast at several locations, and occasionally in moldic porosity throughout the Platteville Formation. The total amount of mineralization contained in the joints and the moldic porosity, however, is believed to be insufficient to cause the arsenic concentrations observed in wells in the study area.

The predominant mineralization observed in the study area occurs as a sulfide-bearing secondary cement horizon which occurs immediately below the base of the Platteville Formation. This horizon occurs across the study area, is volumetrically important, and has a composition of up to 1.0 weight % of arsenic. The mineral cement is observed in several types: 1) a continuous bed up to 6 inches (15 cm) thick of well-cemented grains of St. Peter Formation; 2) a discontinuous layer, up to 2 feet (0.6 m) thick, composed of thin bands of sulfide mineralization within the upper foot (0.3 m) of the St. Peter Formation; 3) nodules of cemented grains of the St. Peter Formation occurring in the upper 4 feet (1.2 m) of the St. Peter Formation; and 4) as infilling of moldic porosity within the upper 4 feet (1.2 m) of the Prairie du Chien Group and, occasionally the lowest 3 feet (0.9 m) of the Platteville Formation, when the St. Peter Formation is not present. Because of the varying morphology of the cement, and because it cross-cuts strata, we have termed it the Sulfide Cement Horizon (SCH). The SCH generally dips 0.3° (30 feet/mile) to the southeast, and remains close enough to water table levels to interact and possibly contaminate groundwater in a region which is approximately correlative with the region in which the high arsenic concentrations were found. Well data from the region show high arsenic concentrations in wells drawing water from strata that underlie the SCH. These data also show a strong correlation between high arsenic concentrations and the location of the water table being at or immediately below the SCH.

GEOLOGY, STRATIGRAPHY, AND HYDROSTRATIGRAPHY

GEOLOGIC SETTING -- SYNDEPOSITIONAL

The Prairie du Chien, Ancell, and Sinnipee groups are Early to Middle Ordovician in age [505-460 million years ago (mya)] and form part of the Tippecanoe and Sauk second order sequences. Rocks deposited during this time represent a period of high global sea level that flooded the North American Craton, located during that time at approximately 13° south latitude. A major, craton-wide unconformity separated the Prairie du Chien Group from the Ancell and Sinnipee Groups. Figure 2 shows the stratigraphic units in Wisconsin, and the major unconformities. Deposition of strata in the study area was most directly influenced by the Wisconsin Arch to the west and the subsident Michigan Basin to the east.

The stratigraphy of the Prairie du Chien Group consists of dolomites with interbedded, thin sandstones and shales. The stratigraphy of the Ancell Group consists of the dominantly sandstone lithologies of the St. Peter and Glenwood formations, representing the progressive flooding of a regional, erosional unconformity (Figure 2). The Sinnipee Group (Platteville, Galena, and Maquoketa formations) consists of warm, open-marine deposits of dominantly dolostone and shale lithologies (Figure 2) that represent the maximum flooding of the craton. As is the case in several locations in south-central Wisconsin (on the Wisconsin Arch), the Decorah Formation is absent across the study area, due to non-deposition, facies change, or post-depositional erosion.

GEOLOGIC SETTING -- POST-DEPOSITIONAL

Post-depositional tectonic effects on the strata in the study area have been minimal, due to its location deep in the North American craton. Elsewhere in Wisconsin (southwest), the only known post-depositional tectonic effects on rocks of similar age are minor faults and joints, and subtle anticlines and synclines believed to be formed along basement faults reactivated by lateral compression, or by solution and thinning of strata controlled by joint trends (Heyl et al., 1970). Structural observations were divided into two different features: deformation in the Prairie du Chien Group; and anticlines, synclines, and joints affecting the Early and Middle Ordovician rocks. Deformation in the Prairie du Chien is significant because it causes substantial variation in the lithology and, therefore, in the hydrogeologic nature of the strata found immediately below the base of the Platteville Formation (where the SCH occurs). Jointing and anticlinal or synclinal features are significant by providing pathways for mineral-rich fluids and/or locations of deposition of minerals (anticlines appear to control the location of ore bodies in the lead-zinc district of southwest Wisconsin). Calcite and pyrite mineralization was observed on northwest-southeast trending joint faces in the study area. Anticlines and synclines, however, did not appear to localize mineral deposits in any observable manner.

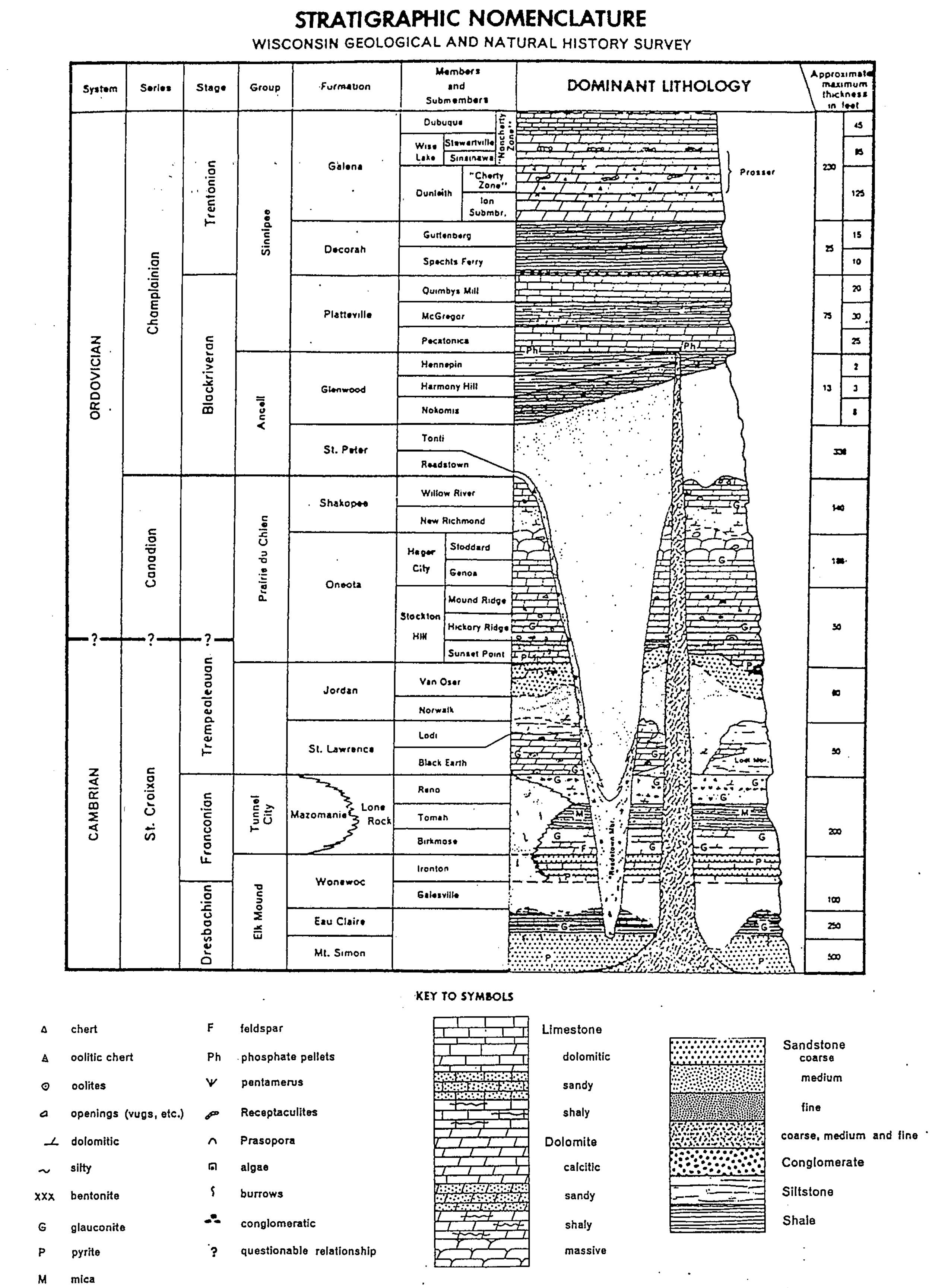


Figure 2. Generalized stratigraphic column for Wisconsin, with stratigraphic nomenclature used in this report (from Ostrom, 1967).

Prairie du Chien Group Deformation

In the study area the most notable structural feature is dips up to 15°, with highly variable strike, of strata of the Prairie du Chien Group in relation to the almost horizontal orientation of strata of the Ancell and Sinnipee groups. More striking, however, are localized dips of up to 50°. This localized deformation is observed in association with intraformational erosional surfaces and brecciation, suggesting that it is due to Ordovician-age karst and/or cave collapse that was initiated during the period of erosion prior to the deposition of Ancell and Sinnipee groups. Appendix A, Figure A-8 shows a typical example of this deformation. In some locations, sandstone bodies up to 7 feet (2.1 m) thick involved in the deformation cause lenses of highly permeable, highly porous strata surrounded above by the less permeable and less porous dolostones of the Platteville Formation and below by the Prairie du Chien Group.

Anticlines and Synclines

The dip of Ancell and Sinnipee strata within the study area is generally 0.3° (30 feet per mile) to the southeast. Anticline and syncline structures are observed within Sinnipee deposits. Dips of the flanks of these structures are generally <5°, and never >15°. Total width of these structures is on the order of hundreds of feet, and total height is on the order of tens of feet. No definite trends in the orientation of these structures are observed in the study area (Figure 3).

In several locations the anticlinal and synclinal features are observed where the Sinnipee Group directly overlies the Prairie du Chien. In one location (JO), a synclinal feature is observed directly over an area of the Prairie du Chien that appears to have undergone karsting. This evidence, along with the lack of any definitive trend in orientation of these features, suggests that these features result from settling of Sinnipee Group strata over areas of localized karsting in the Prairie du Chien Group, or result from dissolution of carbonate material in the Sinnipee Group strata itself, with the causal mechanisms similar to those postulated for the structures in southwest Wisconsin.

Joints

Joints are commonly observed in the study area. Figure 3 shows the orientations of the joints observed in Sinnipee Group strata. In general, joint trends of northwest-southeast and northeast-southwest were most common, with east-west trends observed less frequently. Cross-cutting relationships observed at location GR indicate that the northwest-southeast and northeast-southwest joint sets formed synchronously, while the east-west joint set formed later. The only joint showing evidence of vertical movement [2 inches (5 cm)] was at location FR.

Mineralization (calcite and iron sulfides) is observed frequently filling northwest-southeast joints, suggesting that some amount of lateral extension occurred approximately perpendicular to this joint trend later in the tectonic history of the region, allowing greater fluid flow and deposition of minerals in the joints.

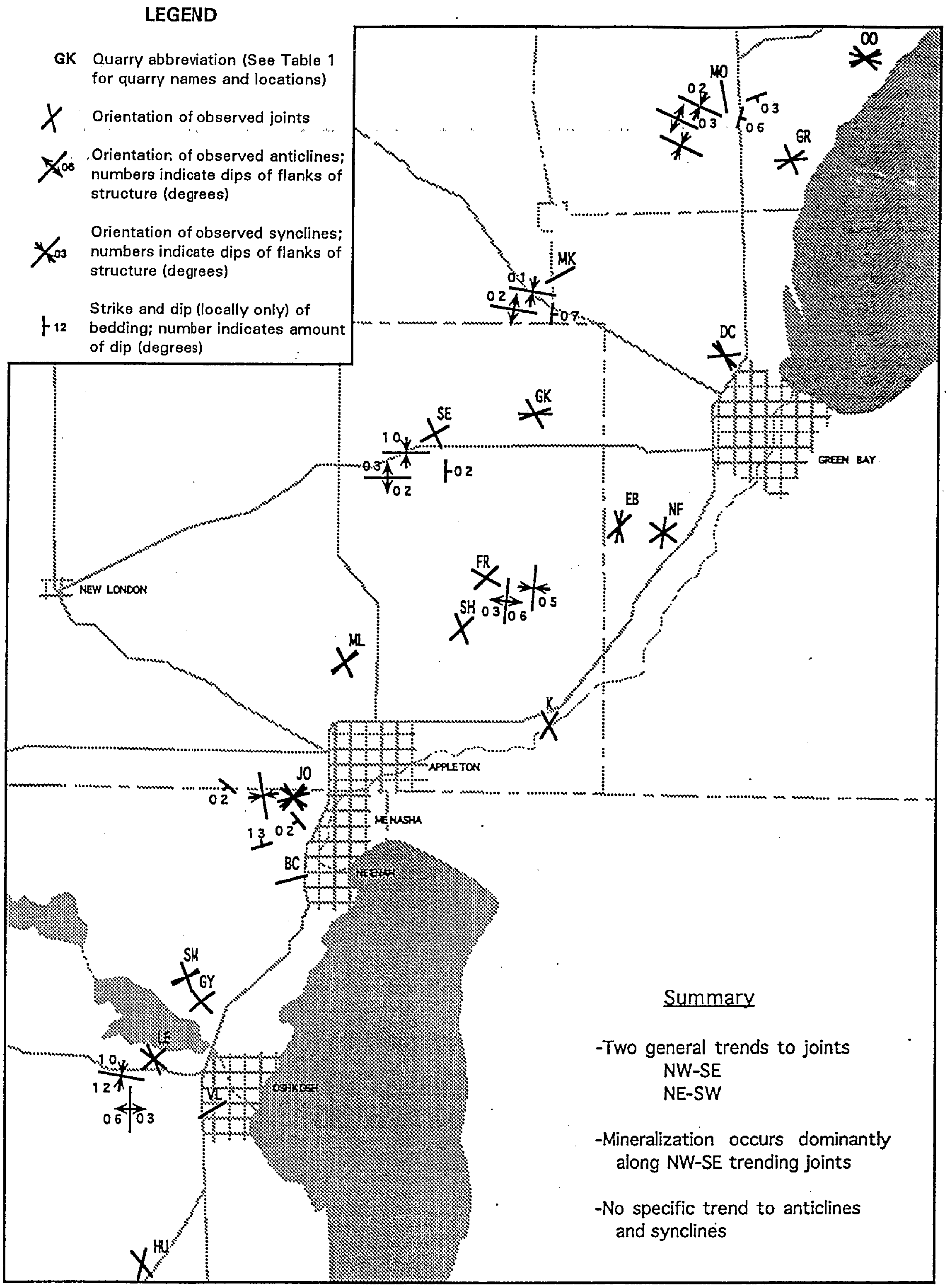


Figure 3. Location and orientation of post-depositional structural features within the study area.

STRATIGRAPHY

Previous stratigraphic work includes that of Thwaites (1923), Templeton and Willman (1963), and LoDuca (1986). Here it has been necessary to construct a more detailed stratigraphic framework of the study area region to improve understanding of groundwater behavior in the region and the location of mineralization related to arsenic contamination.

Early Ordovician

Though the goal of this research did not include the Prairie du Chien Group, it was discovered that the St. Peter Formation was absent over a large part of the study area, and the Prairie du Chien Group was present immediately below the Platteville Formation. Because the base of the Platteville Formation appears to be the stratigraphic location of arsenic-bearing mineralization, the strata of the Prairie du Chien Group may play an important role in groundwater behavior and interaction with this mineralization. Therefore, we have included the uppermost strata [approximately 20 feet (6.1 m)] of the Prairie du Chien Group in the study.

The lithology of the uppermost Prairie du Chien Group is highly variable, with alternating beds of sandy to pure dolostones up to 20 feet (6.1 m) thick, argillaceous to fairly non-argillaceous sandstone beds up to 7 feet (2.1 m) thick, and fissile clay beds up to 2 feet (0.6 m) thick. The interbedded nature of the lithologies causes a large vertical variability in porosity and permeability, and the slight angular unconformity between the Prairie du Chien Group and the Platteville Formation causes lateral variability in lithologies present immediately below the Platteville Formation. Smith (1991) studied the Prairie du Chien Group in Wisconsin and provides further details of the stratigraphy, intraformational unconformities, and karsting. Typical sandy to pure dolostone lithologies are shown in Appendix A (Figures A-1 and A-2).

Middle Ordovician

The stratigraphic succession of the Middle Ordovician rocks in eastern Wisconsin can be divided into three discrete packages of rocks (A, B, and C) based on their mineralogy, lithology, and texture. The lower package (A) consists of porous, siliciclastic sandstones, minor shales, and dolomitic sandstones of the St. Peter and Glenwood Formations. This package is highly variable in thickness [from 0 to >100 feet (30.5 m)], the result of deposition over an irregular erosional topography of the Lower Ordovician Prairie du Chien Group. The middle package (B) consists of several dolomites and argillaceous dolomites of the Platteville Formation. The package is fairly consistent in thickness, 35 to 45 feet (11 to 14 m) thick across the study area. The uppermost package (C) consists of dolostones and argillaceous beds of the Galena Formation. Thickness of the package is highly variable due to present day topography.

Each of these three packages has been subdivided into lithostratigraphic units, based on more subtle changes in lithology, texture, and faunal content within the packages. Table 2 through 4 summarize the characteristics, lateral changes, and interpreted environment of deposition of each lithostratigraphic unit.

Table 2. Lithostratigraphic unit characteristics for stratigraphic package A.[†]

	Package A	
Lithostratigraphic unit	A1	A2
Lithology, texture, color	Fine- to medium-grained, very well-sorted quartz s.s., white to light brown	Fine- to coarse-grained mod.-sorted argillaceous s.s.
Sedimentary structures, bedding	Finely laminated, large-scale cross-bedding	Massive
Faunal content	No fauna	Horizontal and occ. vertical burrows
Porosity, permeability	High intergranular porosity, high permeability	Mod. high intergranular porosity, mod. permeability
Occurrence, facies association	Infills paleovalleys in PdC Gp., absent on paleohighs	Caps package A, same lateral extent as A1
Depositional environment	Eolian sandstone	Shallow-marine platform
Geophysical characteristics	Low gamma (50-100 CPS) low resistivity	Ranges from low (50 CPS) to high gamma (150 CPS) depending on clay content; low resistivity (100-300 OHMS)

† Abbreviations used are: dom. = dominantly; FWB = fair weather wave based; SWB = storm wave base; mod. = moderately; and OCC. = occasionally.

Table 3. Lithostratigraphic unit characteristics for stratigraphic package B.†.

Lithostratigraphic	Package B					
unit	B1	B2	B3	B4	B5	B6
Lithology, texture, color	Light grey argillaceous dolostone, occly. contains quartz grains; dk grey horizontal burrow "spots" common	Grey argillaceous dolostone, with thin clay partings, wackestone to packstone beds common	Brown, fairly pure dolostone, dom. mudstone with occ. wackestone to packstone beds; occ. dk. grey horizontal burrow "spots;" occ. chert nodule layers	Grey argillaceous dolostone with thin clay partings, less argill. than B2, dom. wackestone with occ. packstone beds	Dark brown to orange-brown pure dolostone, with common vuggy porosity; dom. mudstone, occ. wackestone	Dark brown to orange-brown pure dolostone, with common vuggy porosity; dom. mudstone, occ. wackestone
Sedimentary structure, bedding	Massive	Thin, wavy bedding	Massive to thin-bedded	Thin-bedded	Massive	Massive
Faunal content	No fauna	Horizontal and occ. vertical burrows	Horizontal burrow, brachiopods, bryozoans, crinoids, cephalopods	Brachiopods, bryozoans, crinoids, trilobites	Brachiopods, horizontal burrows, bryozoans, crinoids, cephalopods	Slightly fossiliferous, dom. brachiopods
Porosity, permeability	Little or no porosity and permeability	Occ. shelter porosity, low permeability	Occ. moldic porosity or vuggy porosity where chert nodules have weathered out, low permeability	Rare shelter porosity, low permeability	Occ. moldic porosity or vuggy porosity where chert nodules have weathered out	Common vuggy porosity to 6 feet, low permeability
Occurrence facies association	Lowest unit of Package B, thin over PdC paleohighs	Occurs across the study area, thickness fairly consistent 8-12'	Occurs across the study area, thickness fairly consistent 5-12'	Across entire study area, but thickens to the south (to 20')	Occurs only in the northern part of the study area, thins from 9'	Caps package B, occurs across the study area, thickness never exceeds 5'
Depositional environment	Mod. shallow to mod. deep platform (below FWB, above SWB)	Moderately deep platform (below SWB)	Shallow to mod. shallow platform (above FWB)	Moderately deep platform (below SWB)	Shallow to mod. shallow platform (above FWB)	
Geophysical characteristics	Low gamma (10-30 CPS); low neutron (500-700 CPS); high resistivity (600-1200 OHMS)	Low gamma (20-40 CPS); low neutron (500-700 CPS); high resistivity (600-1200 OHMS)	Very low gamma (10-30 CPS); low-moderate neutron (600-800 CPS); very high resistivity (1100-1300 OHMS)	Low gamma (20-40 CPS); low neutron (500-700 CPS); high resistivity (1000-1500 OHMS)	Very low gamma (10-30 CPS); low-moderate neutron (600-800 CPS); very high resistivity (1100-1300 OHMS)	Very low gamma (10-30 CPS); low-moderate neutron (600-800 CPS); very high resistivity (1100-1300 OHMS)

† Abbreviations used are: dom. = dominantly; FWB = fair weather wave based; SWB = storm wave base; mod. = moderately; and OCC. = occasionally.

Table 4. Lithostratigraphic unit characteristics for stratigraphic package C.†

Lithostratigraphic	Package C				
Unit	C1	C2	C3	C4	C5
Lithology, texture color	Grey-green clay beds with thin argill. dolostone interbeds; generally recessive, dolostone beds more resistant than clay beds	Slightly argill. dolostone, light brown to grey, dom. mudstone to wackestone	Grey-green beds with thin argill. dolostone interbeds, generally recessive, dolostone beds more resistant than clay beds	Alternating resistant dolostone beds and argill. beds; dolostone beds dom. mudstone to wackestone, lt. grey; clay beds grey-green to green	Thin-bedded dolostone with thin clay partings; dolostone grey-brown to lt. grey, dom. wackestone to packstone; clay beds grey-green
Sedimentary structures, bedding	Beds to 8' thick, occ. lamination and cross-beds with intraclasts of black pebbles and receptaculites; scour surfaces	Massive, frequent hardgrounds	Beds to 8' thick, occ. lamination and cross-beds with intraclasts of black pebbles and receptaculites; scour surfaces	Beds to 18' thick; dolostone beds massive, clay beds fissile; occ. hardgrounds	Beds to 12' thick, clay interbeds to 2'
Faunal content	Dolostone layers quite fossiliferous with whole brachiopods, bryozoans, and mod.-sorted skel fragments; occ. whole rugose corals	Slightly fossiliferous, dom. brachiopods, bryozoans, crinoids	Dolostone layers quite fossiliferous with whole brachiopods, bryozoans, and mod.-sorted skel fragments; occ. whole rugose corals	Dolostone contain brachiopods, bryozoans, crinoids, trilobites, gastropods, and other skeletal fragments	Mod. fossiliferous, crinoids, brachiopods, trilobites, and other skeletal fragments; occ. large gastropods
Porosity, permeability	Rare shelter porosity, clays cause low permeability	Rare moldic porosity to ½" diameter, low permeability	Rare shelter porosity, clays cause low permeability	Occ. minor moldic porosity to 1" diameter, permeability low in dolostone beds but very low in clay beds	Moldic porosity to 1/8" diameter, increases in size closer to surface, low permeability

Table 4. Continued

Lithostratigraphic	Package C				
Unit	C1	C2	C3	C4	C5
Occurrence, facies association	Occurs across the study area, but clay content decreases to south so lithofacies thins to south	Occurs across the study area, conformable with C1 below	Present only in the northern part of the study area, clay content decreases rapidly to the south with facies grading to Ce	Clay content decrease to the south, so facies not distinguishable in southernmost part of the study area, lower beds may be distal equivalent of C3	Uppermost facies of package C, occurs everywhere but the western part of the study area where it has been eroded off, lower beds replace and may be equivalent to C4
Depositional environment	Deep platform (below SWB)	Shallow to mod. shallow platform (above FWB)	Deep platform (below SWB)	Intermediate between shallow and mod. deep platform	Moderately deep platform (below SWB)
Geophysical characteristics	High gamma (75-150 CPS); high neuron (800-1000 CPS); low resistivity (200-400 OHMS)	Moderate gamma (25-75 CPS); moderate neuron (600-800 CPS); moderate resistivity (400-600 OHMS)	High gamma (50-120 CPS); moderate-high neuron (700-1000 CPS); moderate resistivity (200-300 OHMS)	Gamma alternates from peaks (50-90 CPS) to lows (30-50 CPS); neutron alternates 700-900 CPS to 900-1100 CPS; low-moderate resistivity (200-600 OHMS)	Low-moderate gamma (40-100 CPS); low-moderate neuron (600-900 CPS); moderate resistivity (400-600 OHMS)

† Abbreviations used are: dom. = dominantly; FWB = fair weather wave based; SWB = storm wave base; mod. = moderately; and OCC. = occasionally.

Package A (St. Peter and Glenwood Formations). The lower contact of this package is not exposed in the study area, but is known to be a sharp contact with the underlying Prairie du Chien, with topographic relief of up to 300 feet (92 m) (Mai and Dott, 1985). The contact with the overlying dolostones and dolomitic sandstones of the Platteville Formation (package B) is sharp and only slightly undulatory.

The sediments of this package probably filled paleovalleys similar to those present in southwestern Wisconsin today, and thin out against Prairie du Chien highs (Appendix B). Because of the depositional topography, thickness variations in package A occur over short distances (tens of feet thickness change <1 mile). In many locations across the study area (BC, JO, LE, SH), package A is entirely absent and Prairie du Chien strata immediately underlie package B (Platteville Formation) (Figure 4).

This package records the transition from eolian to sub-marine conditions. The dominant lithostratigraphic unit (A1) is a well-sorted quartz arsenite that was probably deposited in an eolian environment. The package is capped by lithostratigraphic unit A2 which consists of dolomitic sandstone with minor amounts of clay interbeds. This lithostratigraphic unit is extensively bioturbated and probably represents initial flooding of the craton by rising sea level. Because of the large amount of intergranular porosity, lithostratigraphic unit A1 is the most porous and permeable unit observed. Unit A2 is slightly less permeable due to the greater clay content.

Unit A1 is recognizable in the subsurface by consistently low gamma ray (15 to 30 CPS) and resistivity (100 to 300 OHMS) values (Figure 5). Unit A2 contains one or more thin "peaks" of higher natural gamma ray (100 to 180 CPS) but similar resistivity (100 to 300 OHMS) values (Figure 6). These values change rapidly upward to the low natural gamma ray and high resistivity values of the overlying package B.

Package B (Platteville Formation). The lower contact is sharp with the bioturbated lithostratigraphic unit of package A below. The upper contact is sharp, but shows slight, broad relief interpreted as a sub-marine erosion surface.

The package occurs across the entire area, with thickness ranging from 35 to 45 feet. Package B consists of resistant dolostones and argillaceous dolostones deposited on a gently dipping sea floor environment. Lithostratigraphic units making up this package alternate between shallow-water dolostones and slightly deeper-water argillaceous dolostones, forming several shallowing-upward successions. Lithostratigraphic units B1, B2, and B4 are argillaceous dolostones that represent deeper water deposits with less bioturbation and greater preservation of bedding. Lithostratigraphic units B3, B5, and B6 are dolostones with greater bioturbation and, therefore, destruction of bedding. Lithostratigraphic unit B6, capping the entire package, is a massive dolostone variable in thickness [from 0 to 6 feet (0 to 1.8 m)] due to sub-marine erosion after deposition of B6 and prior to deposition of the overlying package C. In general, all the lithostratigraphic units remain consistent in thickness and character across the study area, however, the argillaceousness decreases to the north where shallow-water dolostones are more dominant. Typical lithostratigraphic units of package B are shown in Appendix A (Figures A-1, A-3, and A-5).

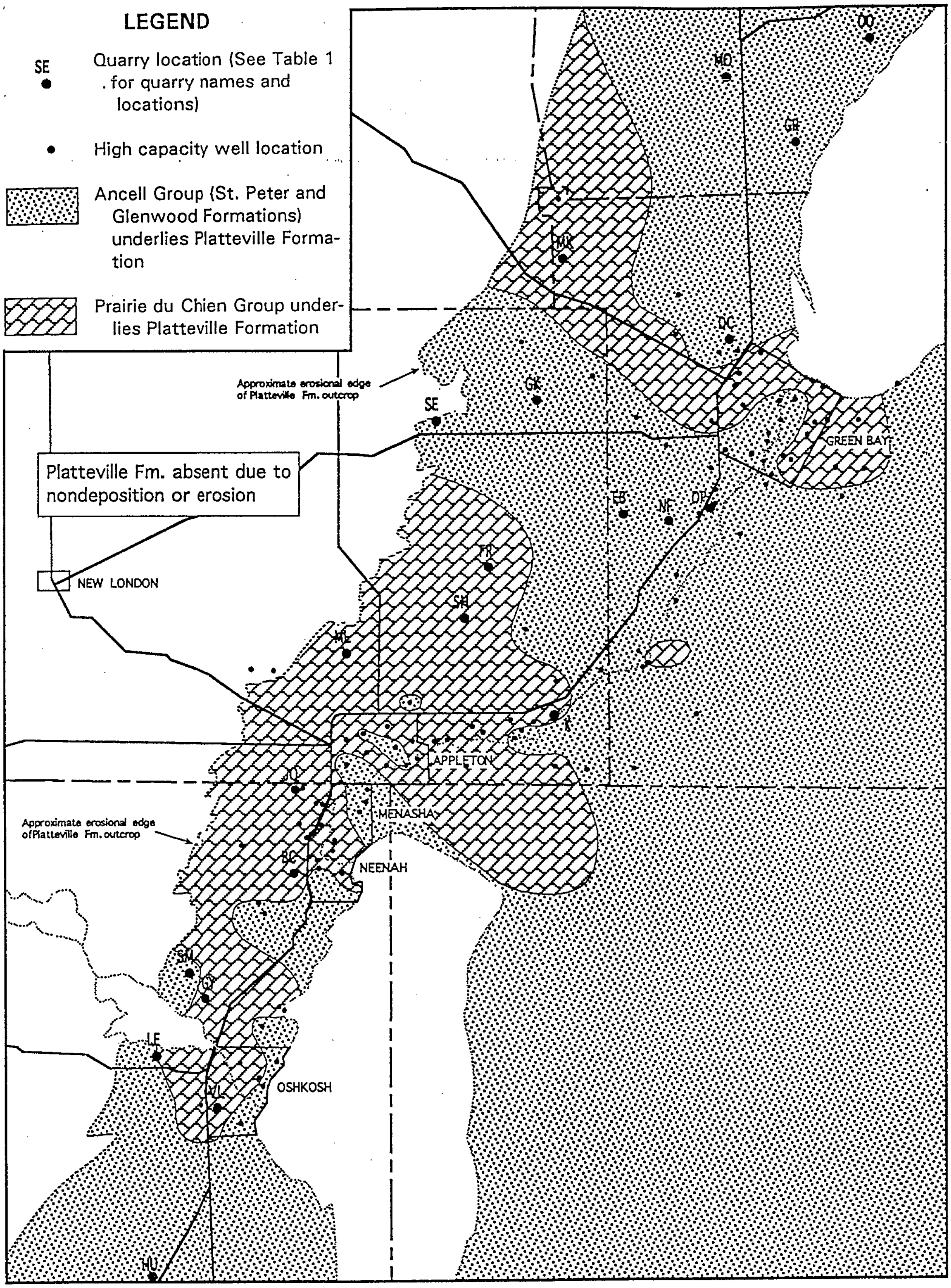


Figure 4. Sedimentary units found immediately below the Platteville Formation. Data from geologs of high-capacity wells, quarries, and drill core. Geolog data are not verified.

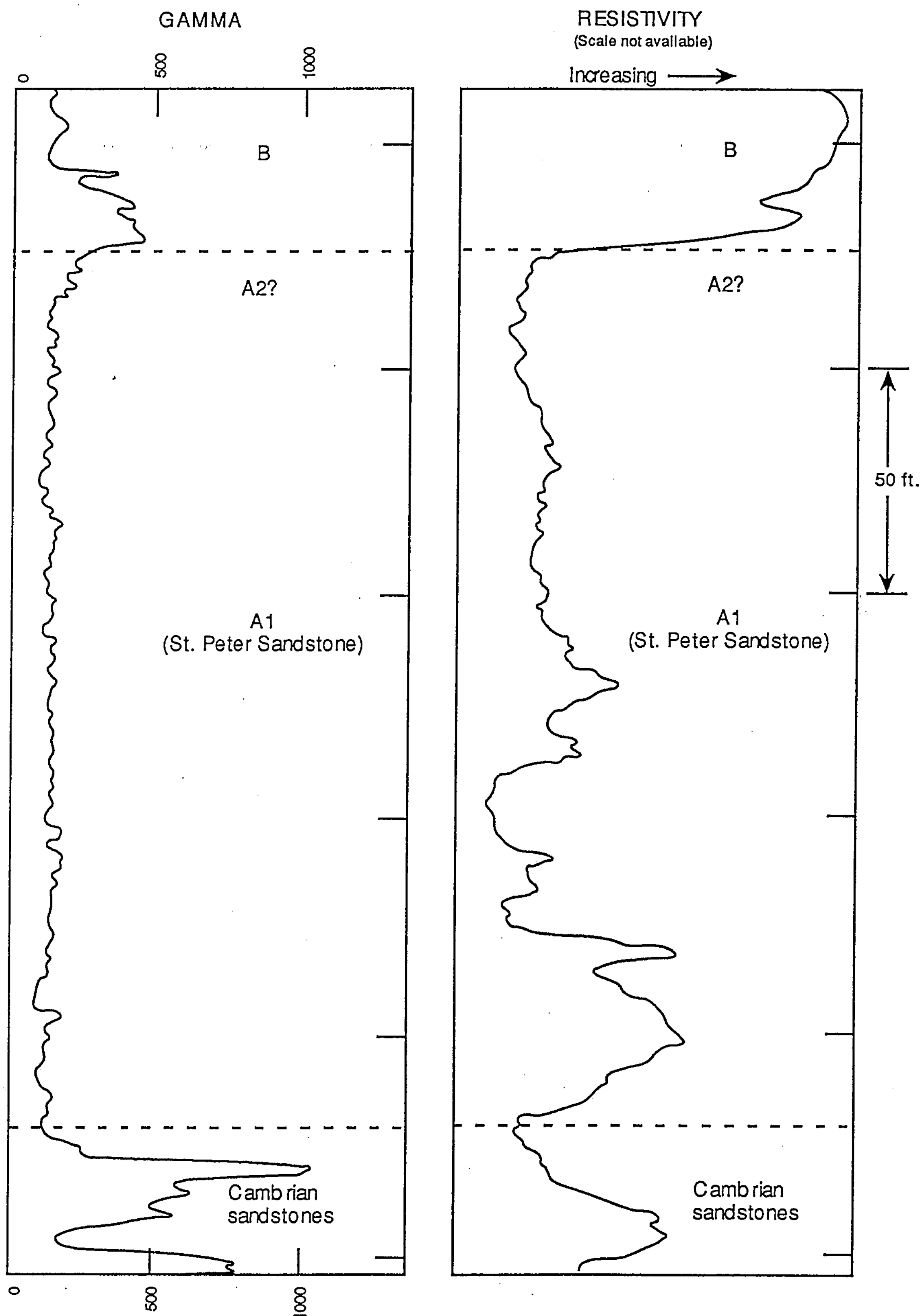


Figure 5. Typical gamma and resistivity log of lithostratigraphic unit A1. From Van Driest No. 1 well, Sheboygan County, Wisconsin (Moretti, 1971).

De Pere core (DP)

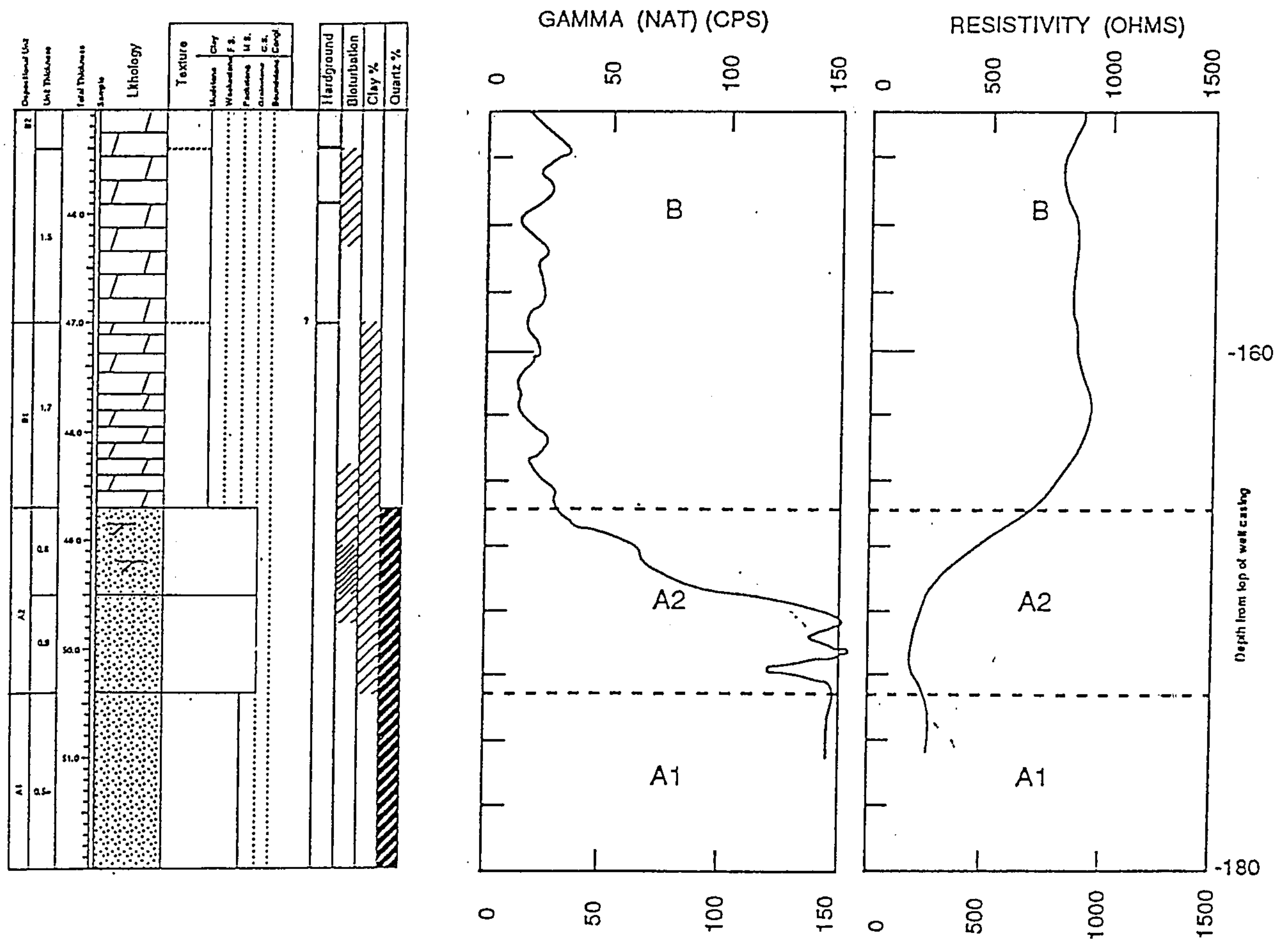


Figure 6. Lithologic section and gamma and resistivity logs of lithostratigraphic unit A2. No neutron log available. Numbers at right indicate depth below top of well casing. (See Appendix C for explanation of lithologic section.)

This series of sequences causes vertical alternations between moderately porous and permeable dolostones and less porous and permeable argillaceous dolostones over vertical distances of several feet (meters). The decrease in argillaceousness to the north also causes a slight overall increase in porosity and permeability in that direction.

Package B is recognizable in the subsurface by fairly constant, very low natural gamma ray levels (10 to 40 CPS) and low neutron values (500 to 800 CPS) and high resistivity values (600 to 1200 OHMS) (Figure 7). The highest gamma ray values are in the more argillaceous lithostratigraphic units (20 to 40 CPS), while the dolostone lithostratigraphic units have slightly lower values (10 to 30 CPS). Both the upper and lower contacts of this package are marked by large, rapid rises in gamma radiation and neutron values due to the clay content of the underlying (A2) and overlying (C1) lithostratigraphic units.

Package C (Galena Formation). The contact with the underlying package (B) is sharp and the upper contact corresponds to the present-day topography or is truncated by Pleistocene glacial deposits. East of the study area, the upper contact is an erosional unconformity overlain by the Ordovician Maquoketa shale (Templeton and Willman, 1963). Package C is present over all but the westernmost part of the area where it has been removed by Pleistocene erosion.

This package represents the deepest-water deposits of all the packages studied. Appendix B and Tables 2 through 4 show and describe the distribution of the lithotratigraphic units of package C. Lithostratigraphic unit C1 contains high amounts of clay, alternating with limestones with cross-stratification, and intraclasts of Receptaculites and black pebbles (probably derived from hardgrounds). Lithostratigraphic unit C2 consists of less argillaceous dolostones with frequent hardground development. Lithostratigraphic unit C3 records a return to a deeper water environment, with sediments and sedimentary structures similar to C1. This lithostratigraphic unit is distinguishable only in the northern part of the study area (Appendix B). Lithostratigraphic unit C4 records an alternation between argillaceous layers up to 2 feet (0.6 m) thick and argillaceous dolostones up to 6 feet (1.8 m) thick. The argillaceous content of the lithostratigraphic unit decreases dramatically to the south, thus this lithostratigraphic unit is not distinguishable in the southernmost locations (Appendix B). Lithostratigraphic unit C5 is a dolostone with thin shale partings between beds, and faunal content is indicative of a normal, open-marine environment. Typical lithostratigraphic units of package C are shown in Appendix A (Figures A-1 through A-6).

The high clay content of C1 and C3 causes low porosity and permeability, while the dolostones of C2, C4, and C5 have higher porosity and permeability. The thin clay interbeds which occur throughout C4, however, may act as aquicludes to vertical groundwater movement.

In the subsurface, high natural gamma radiation values (50 to 150 CPS) decreasing upward (to 25 to 75 CPS), high neutron values (700 to 1000 CPS), and low resistivity values (200 to 400 OHMS) characterize the highly argillaceous units such as C1 and C3 (Figure 8). Low gamma radiation (25 to 75 CPS) and neutron (600 to 700 CPS) values, and high resistivity values (400 to 600 OHMS) characterize the less argillaceous dolomitic units such as C2 and C5 (Figures 8, 9). The decrease in argillaceousness to the south makes units C3 and C4 indistinguishable by gamma, neutron, or resistivity measurement in the southern part of the study area (Figure 10). Unit C4 is

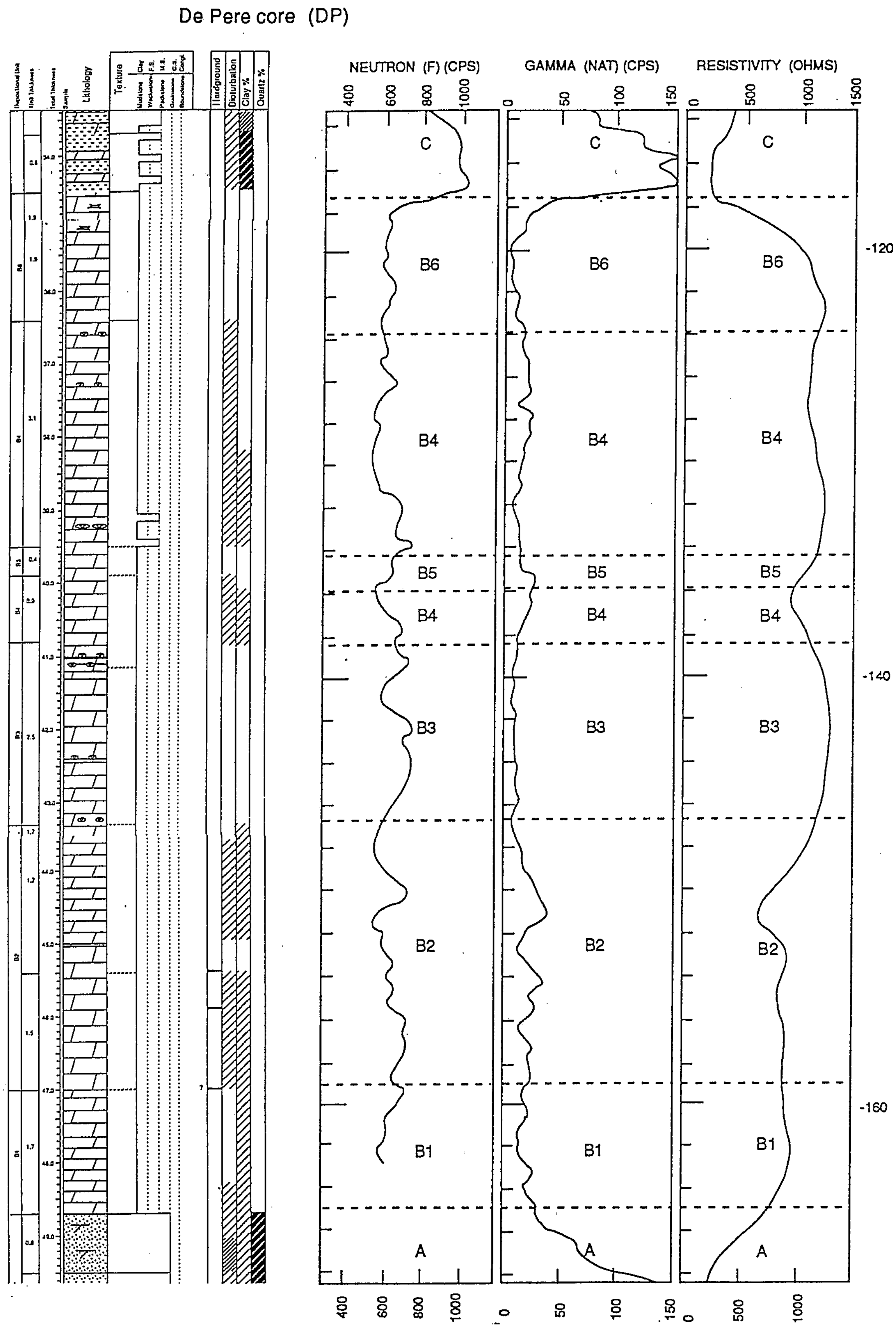


Figure 7. Lithologic section and gamma, resistivity, and neutron logs of stratigraphic package B. Numbers at right indicate depth below top of well casing. (See Appendix C for explanation of lithologic section.)

De Pere Core (DP)

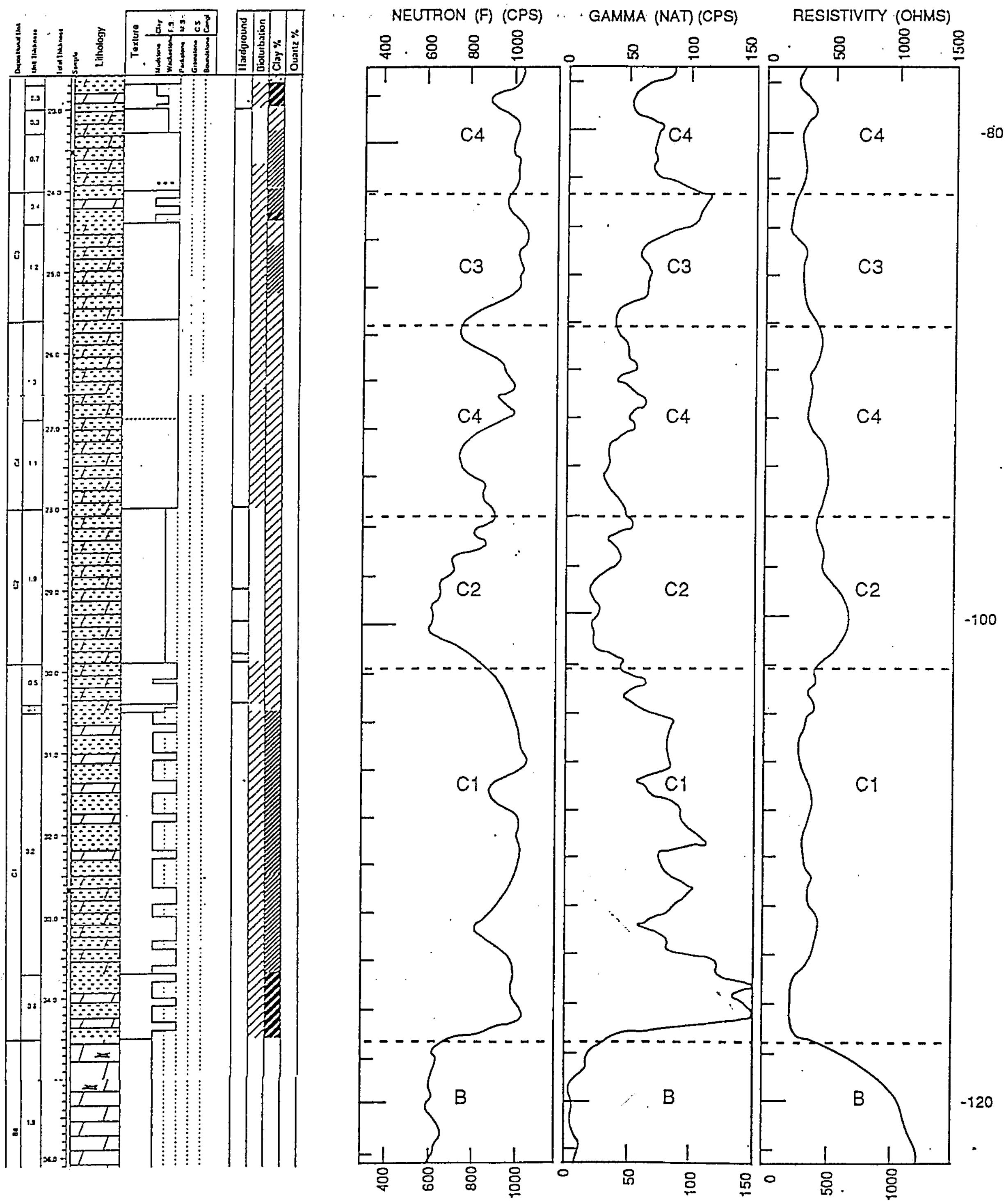


Figure 8. Lithologic section and gamma, resistivity, and neutron logs of the lower portion of stratigraphic package C. Numbers at right indicate depth below top of well casing. (See Appendix C for explanation of lithologic section.)

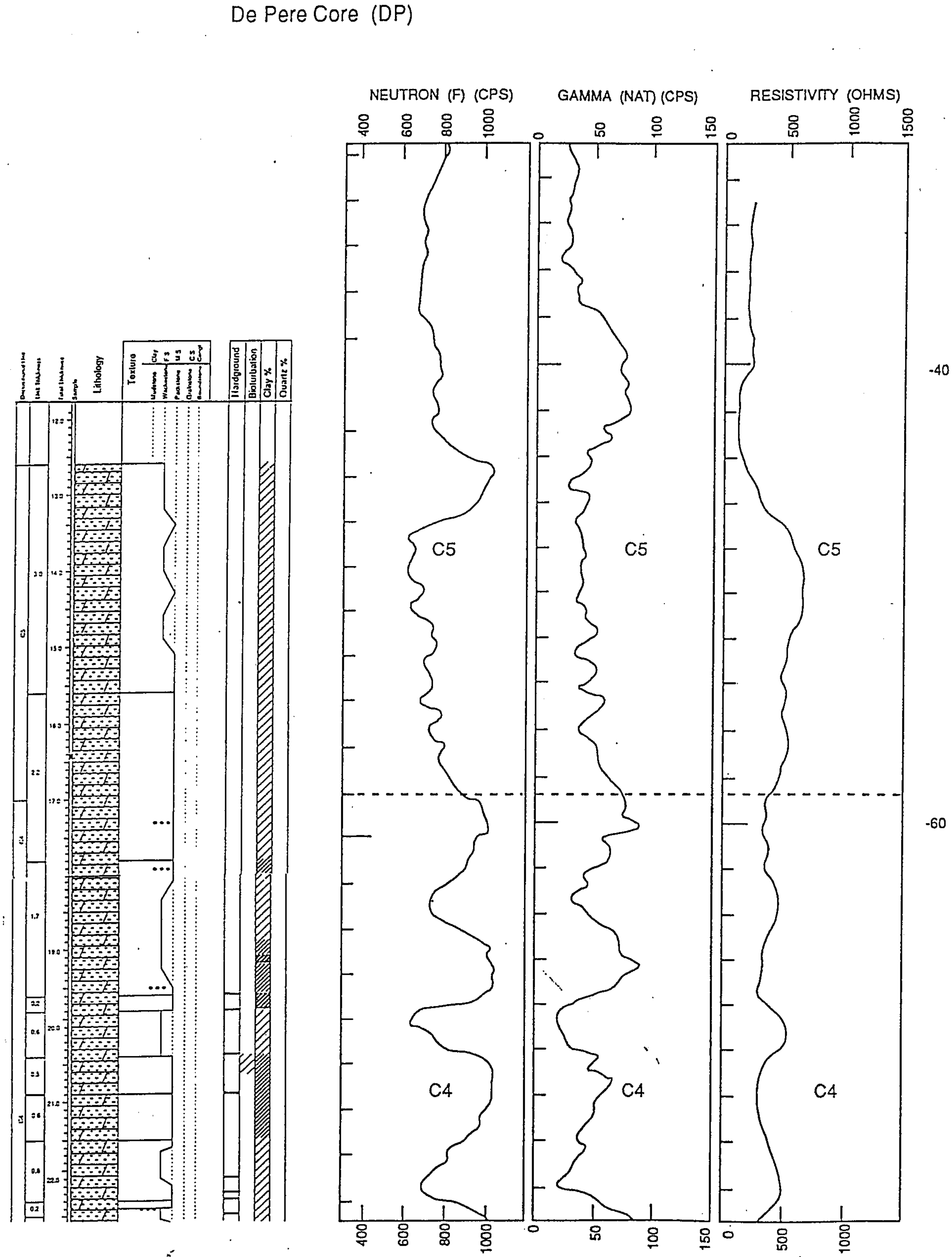


Figure 9. Lithologic section and gamma, resistivity, and neutron logs of the upper portion of stratigraphic package C. Numbers at right indicate depth below top of well casing. (See Appendix C for explanation of lithologic section.)

Vulcan Material's Oshkosh quarry (VL)

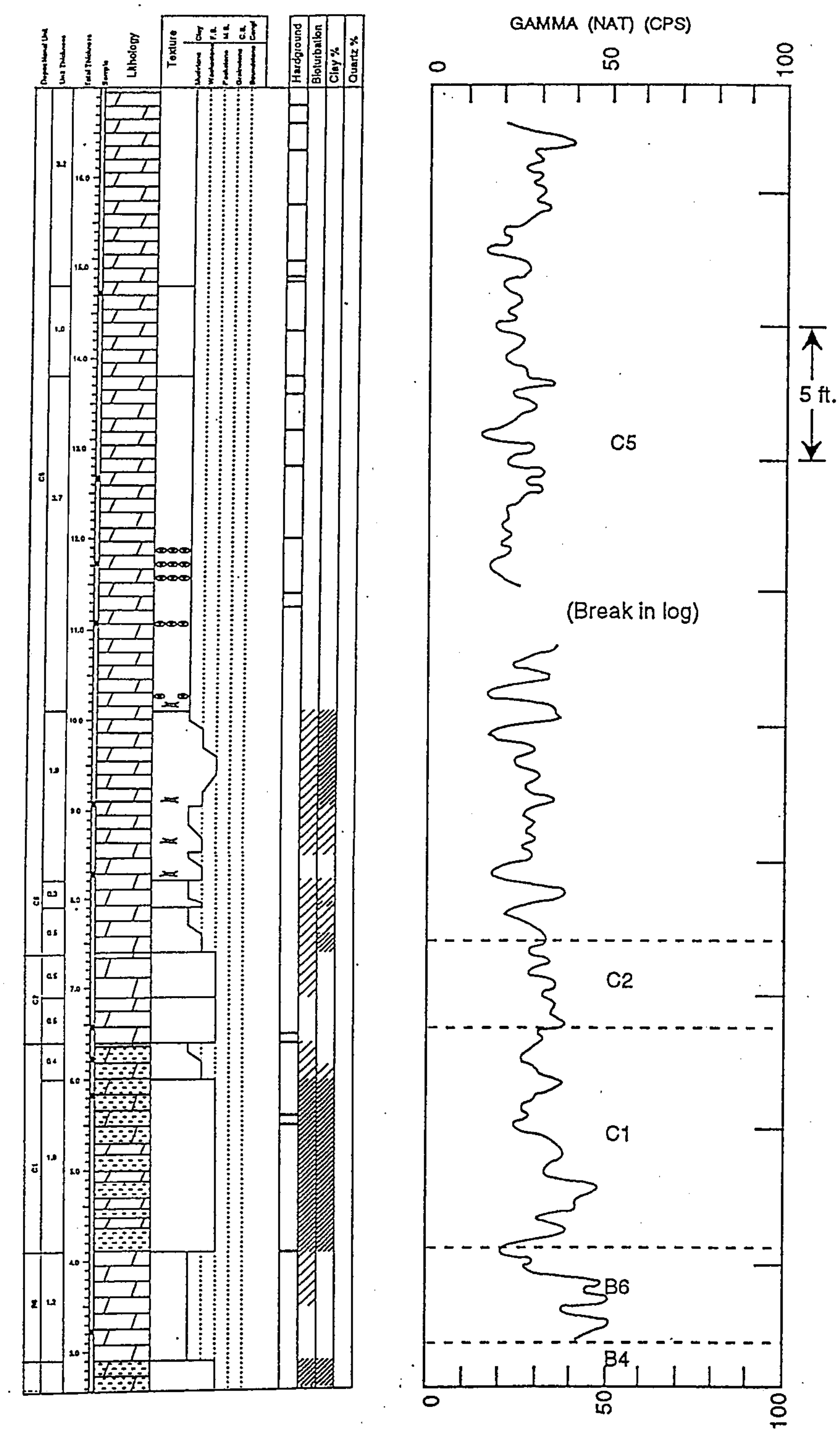


Figure 10. Lithologic section and gamma logs of stratigraphic package C in the southern part of the study area (location VL, Oshkosh) where lithostratigraphic units C3 and C4 are indistinguishable due to decreased argillaceousness. Because these measurements were taken on the quarry wall, gamma values appear lower than the DePere core; however, relative differences in gamma values between the lithostratigraphic units should be similar in data obtained from well logging. (See Appendix C for explanation of lithologic section.)

characterized by moderate gamma radiation values (30 to 100 CPS), high neutron values (600 to 1100 CPS), and moderate resistivity values (200 to 600 OHMS) (Figures 8, 9). Values of all of these characteristics in unit C4 are more variable than in the other units due to the alternation between argillaceous beds and dolostone beds that occur on a scale of ≥1 foot (≥0.3 m) or more throughout the unit. In general, the natural gamma ray values of this package are higher than package B, lower than package A, and more variable in range than both packages.

HYDROSTRATIGRAPHY

Previous researchers have modeled groundwater movement by characterizing the Sinnipee Group as a homogenous rock body. These studies, however, were conducted on a regional scale and did not require detailed vertical and horizontal quantification of the lithologic variations throughout the strata. Previous studies (Krohelski, 1986; Emmons, 1987; and Young, 1992) have included the Ancell Group as part of the St. Peter-Prairie du Chien-Jordan aquifer (or sandstone aquifer). For the aquifer as a whole, hydraulic conductivity, determined through packer tests and laboratory analyses, ranged from 0.16 to 26.9 feet/day (0.04 to 8.2 m/day) (Young, 1992), and vertical hydraulic conductivity, determined through modeling, ranged from $1x10^{-3}$ to $4x10^{-6}$ feet/day (0.3 to 1.2 m/day) (Emmons, 1987). Variability in hydraulic conductivity, due to lithologic variability in the Prairie du Chien Group or presence or absence of the St. Peter Formation, has not been quantified. The Sinnipee Group strata have been included in the Maquoketa Shale confining unit (Young, 1992). Measured hydraulic conductivity values range from $8.6x10^{-7}$ to $1.7x10^{-4}$ feet/day (2.6 to 0.5 m/day), and vertical hydraulic conductivity values, estimated from modeling, range from $7.0x10^{-5}$ to $3.0x10^{-3}$ feet/day (2 to 0.9 m/day) (Krohelski, 1986; and Emmons, 1987). These parameters, however, were determined through limited testing in areal and stratigraphic extent. A single value, or a limited range of values, has been used in these regional-scale models to characterize the entire Sinnipee (and Maquoketa Shale), with the only significant variation occurring between areas of the Sinnipee Group overlain by the Maquoketa Shale and areas where the Maquoketa Shale has been eroded away (and where dissolution of fractures has increased secondary porosity).

In this study the Sinnipee and Prairie du Chien groups were divided into seven hydrostratigraphic units based on characteristics important to groundwater modeling: porosity; permeability; and lateral and vertical variations. This allows more precise modeling of groundwater behavior on an intermediate scale which, in turn, allows a more precise understanding of the interaction between the arsenic source and groundwater and the storage and flow of arsenic-contaminated groundwater.

The lithostratigraphic units described in the previous section have been grouped into six hydrostratigraphic units based on field recognition of porosity and permeability characteristics and abundance of terrigenous clay. Table 5 summarizes the characteristics of each of these units. Quantification of porosity and permeability of these hydrostratigraphic units is preliminary at this time. Future research will more accurately quantify these characteristics.

The amount, depth, or cementation of joints was not quantified or characterized. The presence of joints may have a large effect on the vertical hydraulic conductivity in or across hydrostratigraphic units. Although vertical joints were observed throughout the area, whether their

Table 5. Hydrostratigraphic unit characteristics.†

Hydrostratigraphic Unit	Lithostratigraphic Units	Lithology	Porosity	Permeability	Occurrence
0	Upper strata of the Prairie du Chien Group	Alternation of dolostone, sandy dolostone, sandstone, and clay; massive to thin-bedded	Variable from moderate in clays and dolostones (moldic to 1'2" diameter) to high in sandstones (intergranular)	High vertical variability on scale of inches to several feet; from low (clays) to moderate (dolostones) to high (sandstones)	Varies across study area due to paleotopography of Prairie du Chien Group underlies Platteville Fm. from Neenah to north of Appleton
I	A1, A2	Well-sorted fine- to medium-grained quartz arenile, poorly cemented, minor clay and cement in uppermost beds	Intergranular porosity, total porosity high	Paucity of secondary cementation, high permeability	Occurrence varies across study area due to preexisting topography in Prairie du Chien Group below, thickness highly variable 0-150'+
II	B1, B3, C2, C5	Slightly argill. to pure dolostone	Occ. moldic and vuggy porosity commonly to 1" dia., vugs rarely to 5" total porosity moderate	Moderate due to dolomitiaztion and low clay content	Common throughout the study area, more common in south where it replaces units V and VI
III	B2, B4	Slightly argill. to very argill. dolostones, often thin-bedded	Occ. moldic and shelter porosity to 1" dia. total porosity low	Low vertical permeability due to clay beds, slightly higher horizontal permeability	Occurs across study are in Platteville strata, less common to north where it partially replaces unit II
IV	B6	Slightly argill. to pure dolostone, vuggy porosity common	Vuggy porosity to 3" common, occ. vugs to 5", total porosity high	Moderate due to dolomitiaztion and low clay content	Thin (1-6") unit capping Platteville strata
V	C1, C3	Thick clay beds (to 3") with thin argill. dolostone beds (to 1")	Occ. shelter porosity, total porosity low	Clay beds cause very low vertical permeability, may be slightly higher horizontal permeability	Occurs across study area, but thins significantly to the south (to 6")
VI	C4	Alternating beds of slightly argill. dolostone (to 10" thick) and clay beds (to 2" thick)	Occ. moldic porosity in dolostone beds, total porosity low to moderate	Vertical permeability low due to clay beds acting as acquicludes, horizontal permeability may be somewhat higher	Occurs across the study area, but thins to the south and is replaced by unit II, replaced by unit V to the north

† Abbreviations used are: argill. = argillaceous; dia. = diameter; dom. = dominantly; fwb. = fair weather wave base; mod. = moderately; and occ. = occasional.

presence was confined to several tens of feet of the surface or extended to greater depths was not determined.

Early Ordovician

The upper strata of the Prairie du Chien Group [within approximately 50 feet (15 m) of the base of the Platteville Formation) are defined as hydrostratigraphic unit 0 (Table 5, Figure 11). This unit is composed of thin to thick beds of varying hydrogeologic characteristics. The lithologies include: non-permeable clay beds up to 1 foot (0.3 m) thick; sandstones, dolomitic sandstones, and argillaceous sandstones up to 4 feet (1.2 m) thick with moderate to high permeability and porosity; and moderately permeable and porous dolostones, sandy dolostones, and argillaceous dolostones up to 20 feet (6 m) thick; all occurring as interbeds. Vertical changes in porosity and permeability occur over distances of inches to tens of feet. Because of this vertical variation and the lateral variation of the sub-Platteville Formation lithology caused by the angular unconformity between the Platteville Formation and the Prairie du Chien Group, characterization of this hydrostratigraphic unit for modeling purposes should be done on a very localized level. In general, the porosity and permeability of this unit appear to be moderate to low, with occasional beds of high porosity and permeability.

Middle Ordovician

Unit I is composed of lithostratigraphic units A1 and A2 (Table 5, Figure 11). It consists mainly of well-sorted, fine- to medium-grained quartz arenite of the St. Peter Formation. The sorting of the grains and the lack of much post-depositional cementation allows for high intergranular porosity and permeability; by far the highest of all the units studied. Minor amounts of clay and post-depositional cement of the Glenwood Formation are present in the upper 6 inches to 5 feet (15 cm to 1.5 m) of this unit. The total thickness is highly variable, from 0 to 150 feet (0 to >46 m), due to the infilling of paleovalleys by the St. Peter Formation.

Unit II is composed of lithostratigraphic units B1, B3, C2, and C5 (Table 5, Figure 11). This unit is the most common hydrostratigraphic unit across the study area, particularly in the upper beds of the Galena Formation where it is up to 50 feet (15 m) thick. The unit consists of dolostones to slightly argillaceous dolostones that have moderate porosity occurring as occasional moldic porosity or vuggy porosity. Though the vugs may occur to 5 inches (12.7 cm) in diameter, they are uncommon, and most porosity (moldic and vuggy) ranges up to 1 inch (2.5 cm) in diameter. Permeability throughout the unit is moderate due to dolomitization (which tends to increase intercrystalline porosity) and the lack of clay layers.

Unit III, composed of lithostratigraphic units B2 and B4 (Table 5, Figure 11), consists of thin-bedded, slightly argillaceous to very argillaceous dolostones. Occasional moldic and shelter porosity occurs up to 1 inch (2.5 cm) in diameter, but total porosity is low. The shelter porosity is usually associated with wackestone to packstone beds found within the unit. Vertical permeability is probably low due to clay beds, but horizontal permeability may be slightly higher.

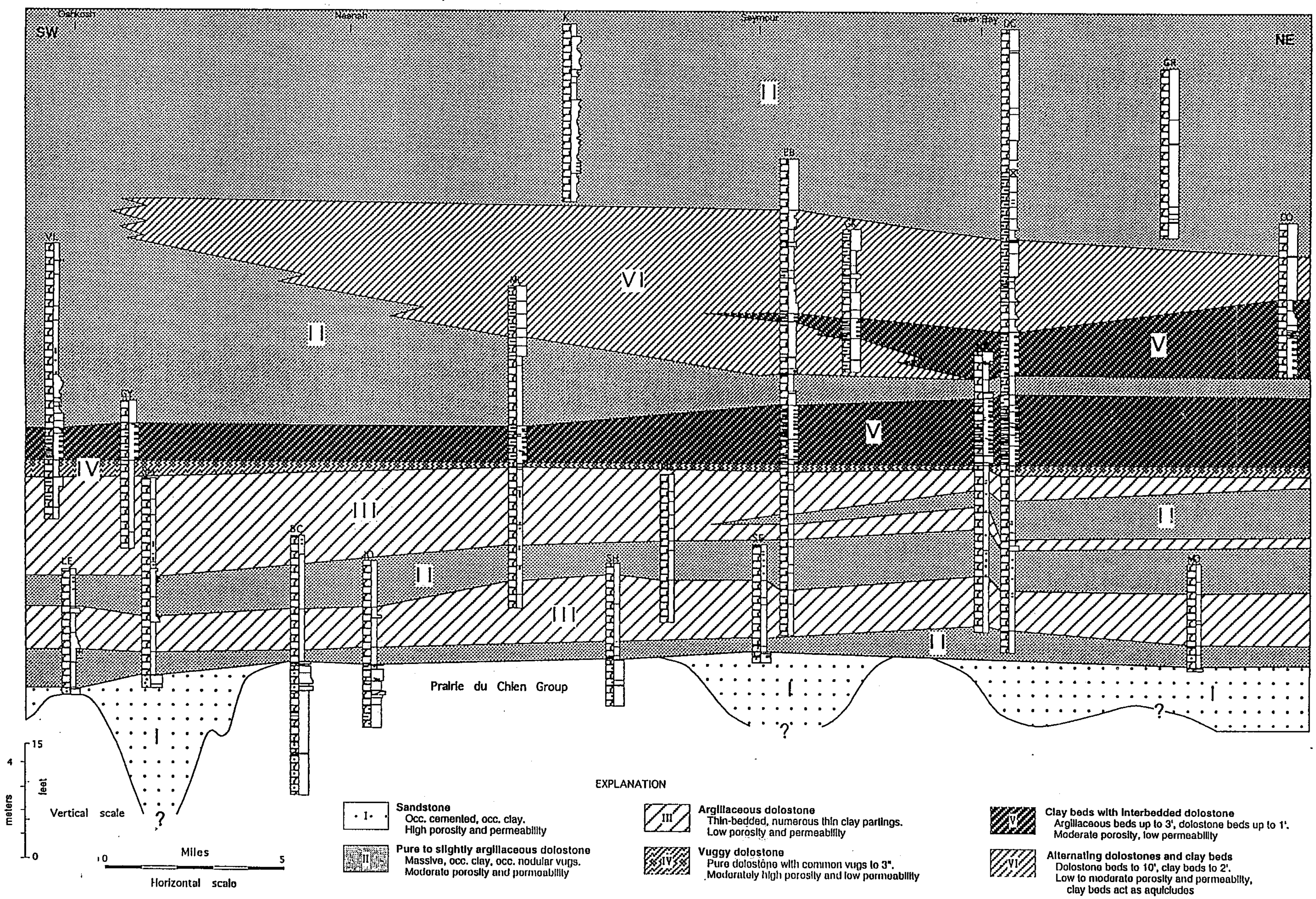


Figure 11. Correlation of hydrostratigraphic units across the study area.

Unit IV, consisting entirely of lithostratigraphic unit B6 (Table 5, Figure 11), is similar to unit II, but contains significantly more vuggy porosity. Vugs up to 3 inches (7.6 cm) in diameter are common, but vugs up to 5 inches (12.7 cm) were observed. Dolomitization and lack of clay allows for moderate permeability. This is a minor facies, capping the Platteville strata, usually 1 to 3 feet (0.3 to 1 m) thick but never exceeding 6 feet (1.8 m) thick.

Unit V is composed of lithostratigraphic units C1 and C3 (Table 5, Figure 11) and is the hydrostratigraphic unit with lowest porosity and permeability. It consists of thick [≤3 feet (≤1 m)] clay beds with thin [≤1 foot (≤0.3 m)] argillaceous dolostone interbeds. Porosity occurs only as occasional shelter porosity in packstone beds associated with the clay beds. The low porosity of the clays which dominate this unit may cause it to act as a significant aquiclude in the north, but the thinning of the unit (due to thinning of the clay beds and general reduction in argillaceousness) to the south may reduce its role as an aquiclude in that region.

Unit VI is composed entirely of lithostratigraphic unit C4 (Table 5, Figure 11), consisting of alternating beds of slightly argillaceous dolostones and clays. The dolostone beds vary from 0.5 to 10 feet (0.2 to 3 m) in thickness, and the clay beds range from 1 inch to 2 feet (2.5 cm to 0.6 m) in thickness. The only porosity occurs as occasional moldic porosity in the dolostone beds. Vertical permeability is probably low because the clay beds act as aquicludes, while horizontal permeability may be somewhat higher (moderate).

NATURAL OCCURRENCE OF ARSENIC

Arsenic is most commonly found in sedimentary rocks as secondary mineralization. The most common mineral containing arsenic is arsenopyrite (FeAsS). Less common minerals containing arsenic are known, most containing sulfur [e.g., enargite (Cu_3AsS_4) and cobaltite ((Co,Fe)AsS) found in the lead-zinc district of southwestern Wisconsin] (Heyl et al., 1970). Arsenic may also attach itself to minerals that do not contain arsenic in their crystal structure, causing arsenic-bearing variations of non-arsenic minerals.

In the study area, mineralization observed was dominantly calcite and sulfides [pyrite (FeS) and less commonly sphalerite (ZnS) and marcasite (FeS_2)]. The mineralization was observed in three geologic settings: joint faces; in pores; and in a cement horizon. A schematic summary of these settings, and the stratigraphic location in which mineralization occurs, is presented in Figure 12.

MINERALIZATION ALONG JOINT FACES

Calcite and iron sulfide (FeS) often lined joint faces, predominantly those trending northwest-southeast. Mineralization occurs as an almost continuous outer layer of FeS up to 0.25 inches (0.6 cm) thick, with coarse calcite crystals up to 0.5 inches (1.3 cm) thick infilling the remaining porosity.

Because of the lack of a significant amount of mineralization and the lack of correlation between joint trends and high arsenic occurrences, we believe that this mineralization is not a source of the arsenic contamination occurring in the region.

MINERALIZATION IN PORES

Iron sulfide crystals were observed filling moldic or vuggy porosity in some beds at some locations. Presence of FeS in particular beds was not consistent from location to location. In most cases, the FeS-filled moldic porosity did not exceed 1 inch (2.5 cm) in diameter. At one location, clusters of FeS crystals, formed by weathering from chert nodules and up to 4 inches (2.5 cm) in diameter, filled vugs. However, these FeS-filled vugs were rare even at that location.

Because of the rarity of this mineralization, we feel it is not a source of the arsenic contamination occurring in the region.

SULFIDE CEMENT HORIZON

A sulfide mineral cement occurred at the top of the St. Peter/Glenwood formations (package A). Because of the large amount of sulfide mineralization, the lateral extent and continuity of the mineralization, and the presence of the greatest amount of mineralization observed in areas where many wells have high arsenic concentrations (City of Seymour, Outagamie County; and Algoma Township, Winnebago County), we feel that this Sulfide Cement Horizon (SCH) is the most likely geologic source of arsenic contamination.

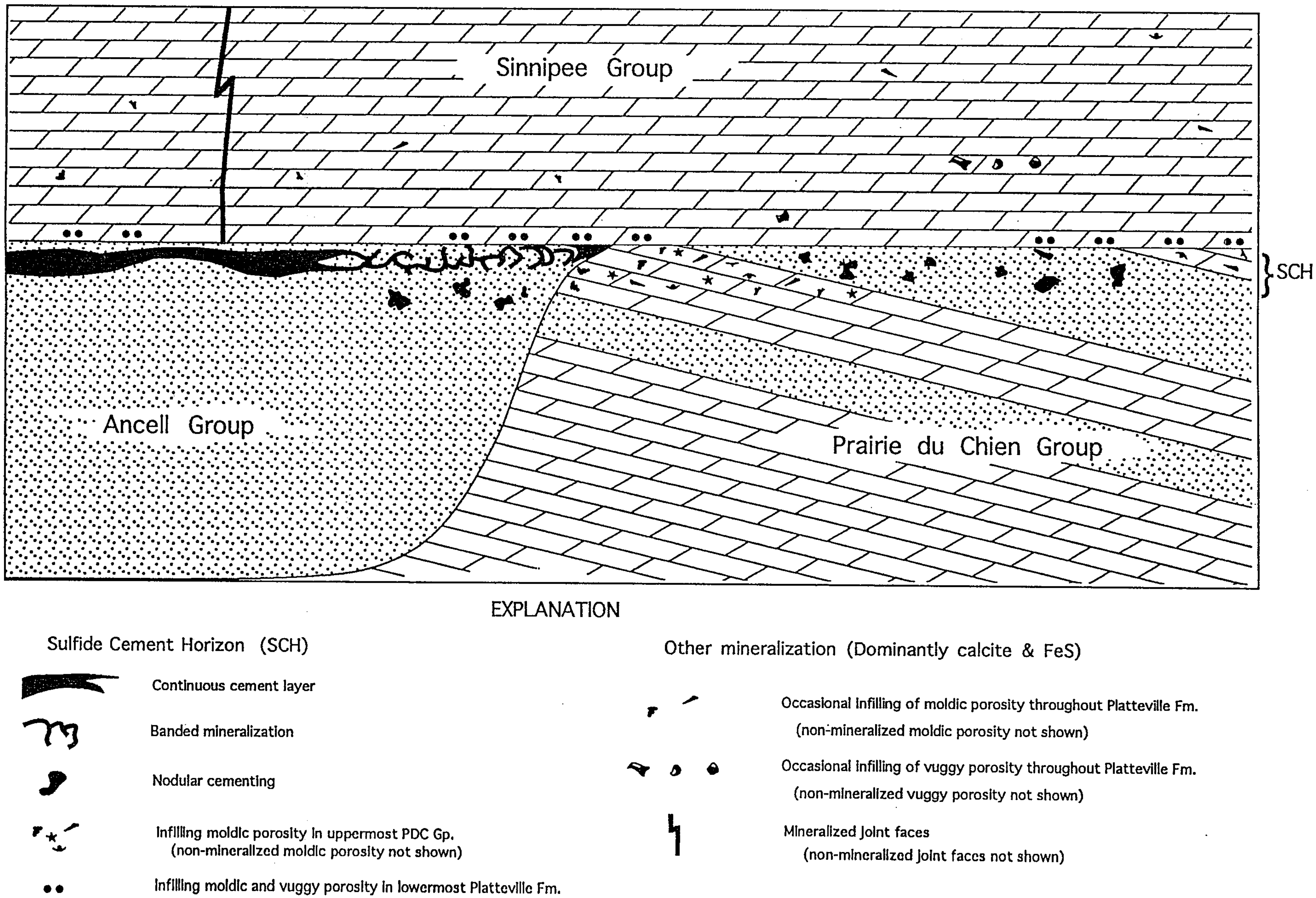


Figure 12. Schematic representation of stratigraphic locations of mineralization within the Ancell, Sinnipee, and Prairie du Chien Groups within the study area (not to scale).

Types of Mineralization in the Sulfide Cement Horizon

Mineralization in the SCH occurs in four forms: as a continuous and massive layer of cemented sandstone, as a zone of discontinuous and thin mineral "fronts" as a zone of nodules of cemented sand grains; and as infilling of moldic porosity. Figure 12 includes a schematic representation of the morphologies and stratigraphic position of the SCH.

The continuous cement layer is found in the Glenwood Formation (lithostratigraphic unit A2) as a resistant, dark-grey layer up to 6 inches (15 cm) thick. This layer is formed by the complete infilling of all intergranular porosity by a dark-grey weathering sulfide mineral cement. This cement layer was observed at locations LE, SE, SM, and in drill cores from Waukesha County.

The zone of mineral "fronts" is also formed by the grey sulfide mineral cement, but in this case the cement is visible as contorted grey bands, or mineralized fluid "fronts" up to 0.5 inch (1.3 cm) thick. Intergranular porosity is only partially filled, causing it to be generally more resistant than the underlying sandstone lithologies, but less resistant than the continuous cement layer described previously. These mineralization “fronts” observed at location LE, are laterally equivalent to the continuous cement layer in the Glenwood Formation (lithostratigraphic unit A2).

The nodular morphology occurs by discontinuous precipitation of sulfide cement nodules infilling intergranular porosity within the uppermost 4 feet (1.2 m) of the St. Peter and/or Glenwood formations. If these formations are absent, the nodular cement may occur within sandstones of the Prairie du Chien Group near the unconformity separating the Prairie du Chien and Sinnipee groups. The nodules are sub-rounded to highly irregular in shape, up to 1 foot (0.3 m) in diameter, have gradational rims, and are grey on weathered surfaces, yellow to grey on fresh surfaces. These nodules were observed at locations BC and LE.

This mineralization also occurs as infilling of moldic porosity in dolostones of the Prairie du Chien Group near the unconformity separating the Prairie du Chien and Sinnipee groups when the St. Peter and Glenwood formations are not present (Figure 12). At location JO, where beds of Prairie du Chien dolostone dip at approximately 10° in relation to the Platteville Formation, the SCH cross-cuts the bedding of the Prairie du Chien and it is only that portion of the individual beds within 4 feet (1.2 m) of the Platteville Formation that have this mineralization completely infilling moldic porosity. Elsewhere in these beds the porosity is still open.

At location SH, where the beds of dolostone and shale of the Prairie du Chien Group occur immediately below the Platteville Formation, an almost continuous layer of FeS crystals are found within the uppermost shale bed. At locations SH and JO, moldic porosity within the lowermost 4 feet (1.2 m) of the Platteville Formation was completely infilled with similar mineralization.

Stratigraphic Position and Distinction of the Sulfide Cement Horizon

The SCH is found in the uppermost Prairie du Chien Group and St. Peter, Glenwood, and Platteville formations. Because of its cross-cutting relationship, the stratigraphic location is best described as immediately below the base of the Platteville Formation. To understand the geographic distribution of the source of arsenic, it is necessary to map the base of the Platteville Formation (package B). The structure contour map of the base of the Platteville Formation provides a first approximation of the subsurface location of the SCH (Figure 13). The surface dips gently to the southeast, with a northeast-southwest strike. Areas with more data points show a slightly irregular topography due to structural features and/or subtle pre-depositional erosion of the underlying units. Thus, it must be assumed that the base of the Platteville and, therefore, the location of the SCH, is similarly irregular throughout the region and that the precise depth of the SCH could range up to several tens of feet above or below the mapped depth.

Mineral Composition of the Sulfide Cement Horizon

Whole rock analyses of five samples from several locations were performed at a commercial laboratory (Table 6). The highest concentration of arsenic was 212 ppm in sample SE-CR which is from location SE (Seymour).

Table 6. Whole rock analysis of samples containing sulfide cement horizon mineralization. See Table 1 for location descriptions (analysis by Bondar Clegg, Inc.).

Sample location	Sample number	Br	Cr	Zn	Mo	Ni	Co	Cd	As	Sb	Fe
		(ppm)									(%)
JO	BB-17	7.3	82	<100	<1	<10	<5	<5	30	0.3	1.8
JO	MJ-1	2.4	140	4,600	18	310	43	24	91	4.2	>10
SE	SE-CR	1.4	400	<100	8	52	6	<5	212	1.0	>10
SH	MSH-1	5.3	100	<100	16	130	48	<5	162	1.4	>10
PO†	FP-1	1.1	300	<100	17	77	8	<5	116	1.5	>10

†PO = Porterfield location, near Peshtigo in Marinette County. Samples FP-1, MJ-1 and MSH-1 were courtesy of Bruce Brown, Wisconsin Geological and Natural History Survey, Madison.

Following analysis of three SCH samples in the SEM/Microprobe it was found that the horizon is characterized by a complex diagenetic succession of large and massive pyrite crystals. Arsenopyrite (FeAsS) was not detected. However, a late alteration phase appears to have precipitated small crystals (1 to 10 μ) of arsenic-bearing pyrite throughout the pyrite cement. Preliminary Microprobe analysis of these crystals indicates arsenic concentrations of 1 to 2%. Although arsenic concentrations are not high, volumetrically the SCH is large, and is the most likely arsenic contamination source in groundwater.

SUMMARY AND INTERPRETATION

The most continuous and volumetrically most important mineralization is found in the SCH located at the base of the Platteville Formation. Apart from the SCH, no other significant mineralization was found in any form, across the study area. The strike and dip of the SCH are such that it intercepts the water table in the region of the study area (Figure 14). Data show high

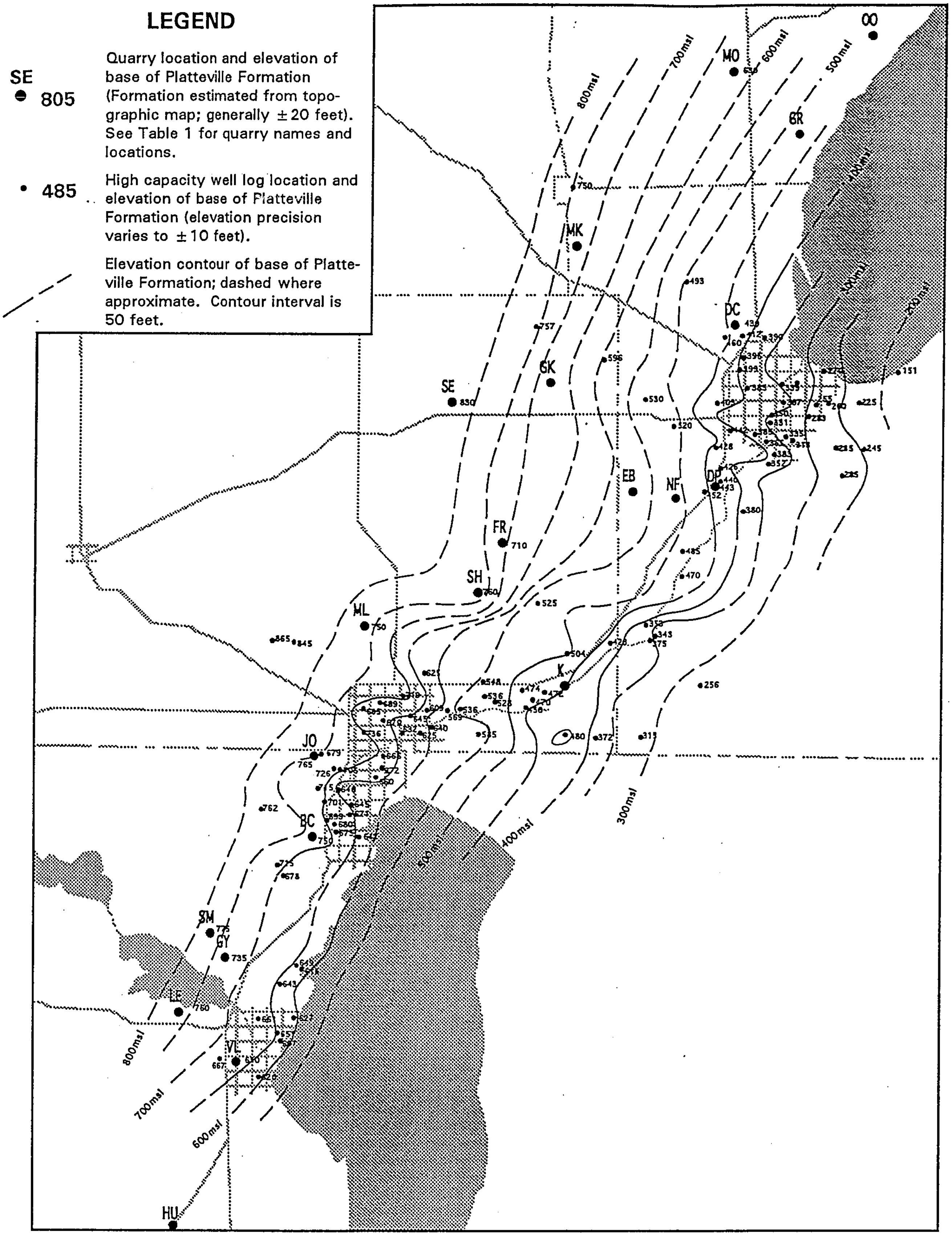


Figure 13. Structure contour map of the base of the Platteville Formation. Data from geologs of high capacity wells, quarries, and drill core. Geolog data not verified. Elevations above sea level.

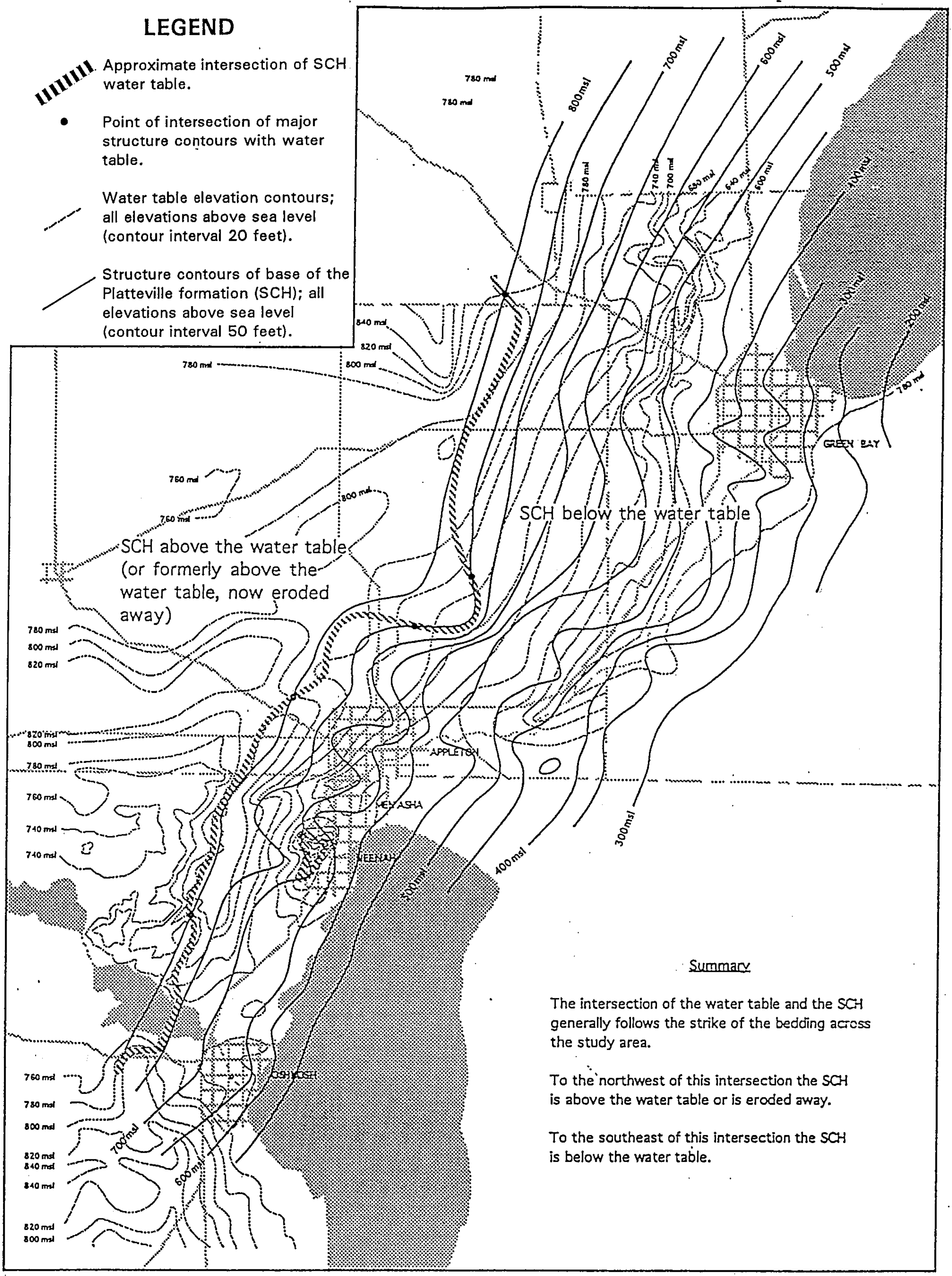


Figure 14. Relationship of the Sulfide Cement Horizon (SCH) (base of the Platteville Formation) and the water table. Water table data sources: Krohelski (1986) -- Brown County; LeRoux (1957) -- (Outagamie County); Olcott, (1966) -- Winnebago County.

concentrations of arsenic in groundwater occurring in areas down-gradient from the SCH where it is presently above the water table or where it was previously above the water table but is now eroded away (Figure 15). Fluctuating groundwater levels may have increased the leaching of arsenic from the SCH. Previous research by the WDNR (Burkel, 1993; Burkel and Stoll, 1995) suggested that the accelerated leaching was caused by exposure of the SCH to an oxygenated environment and the consequent formation of sulfuric acid by oxidation of pyrite; our research further supports that model.

The origin of the SCH may be hydrothermal brines which flowed from the Michigan Basin through the more permeable St. Peter Formation (and possibly Prairie du Chien Group). According to data collected by the National Uranium Resource Evaluation (NURE) program and summarized by Mudrey and Bradbury (1992), other metals associated with hydrothermal brines occur in groundwater in the same general region as the arsenic occurrences (Figure 16). However, the NURE data show only the areal distribution of these metals and it is not known whether they occur within, above, or below the strata studied.

The mineral-bearing fluids could have flowed upward, from east to west, through the rocks until the pinchout of the St. Peter Formation against the less permeable dolostones of the Prairie du Chien Group and Platteville Formation. The fluids would have spread out horizontally and may have cooled sufficiently at this point to cause deposition of the sulfide cement. Numerous iron-rich hardgrounds in the Glenwood Formation may have also acted as a surface on which the arsenic may have been more readily adsorbed.

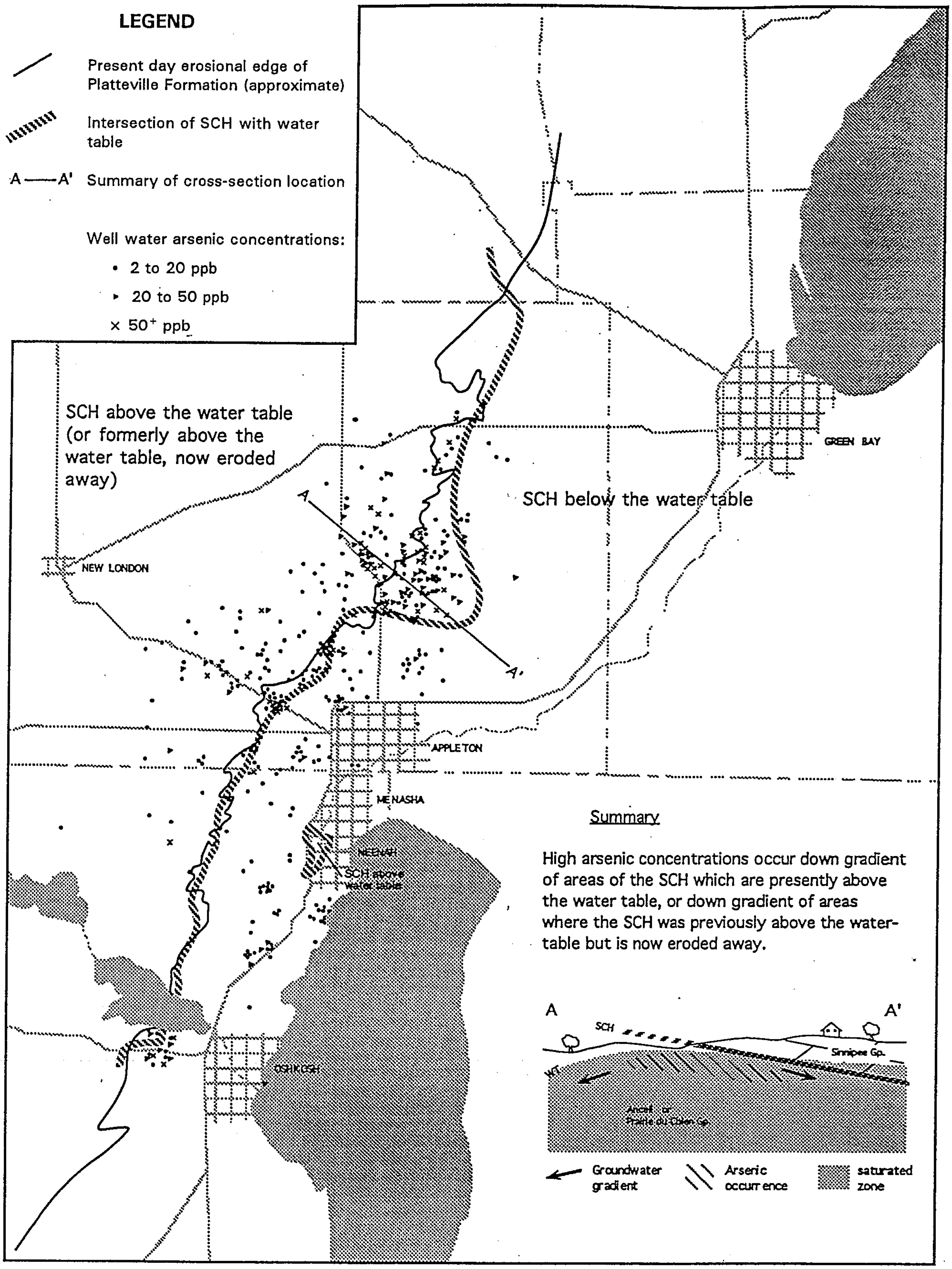


Figure 15. Lateral relationship of the SCH above and below the water table, the present erosional edge of the Platteville Formation, and localities of high arsenic concentrations in groundwater.

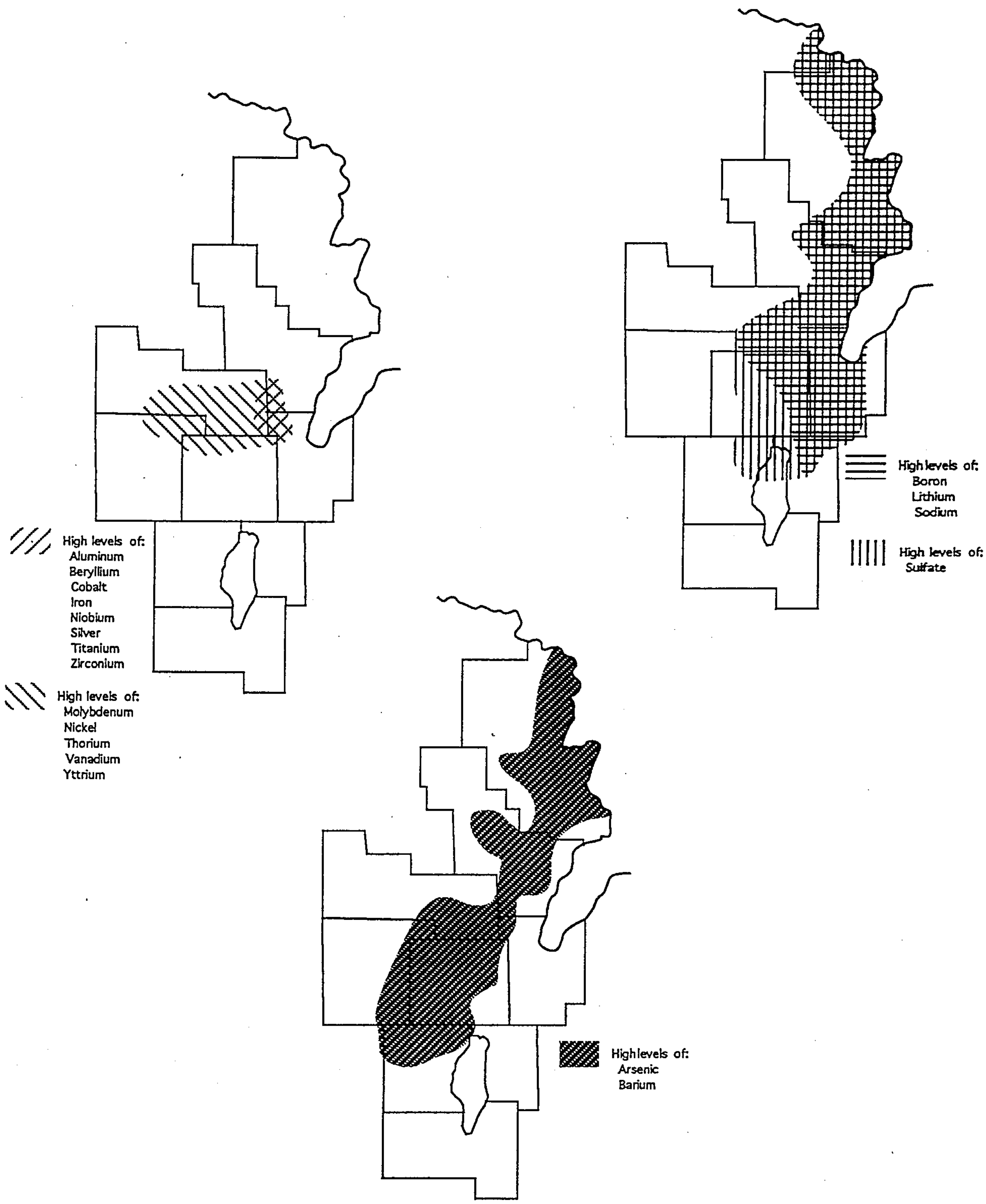


Figure 16. Occurrences of high levels of elements in groundwater with areal extents similar to arsenic contamination. Boron, lithium, and sodium distributions coincide with a known occurrence of saline water in the subsurface, and may be a relict of hydrothermal brines that may have originated in the Michigan Basin. Note similarity to arsenic and boron distribution. Data show areal distribution only; stratigraphic location is not determined. (From Mudrey and Bradbury, 1992.)

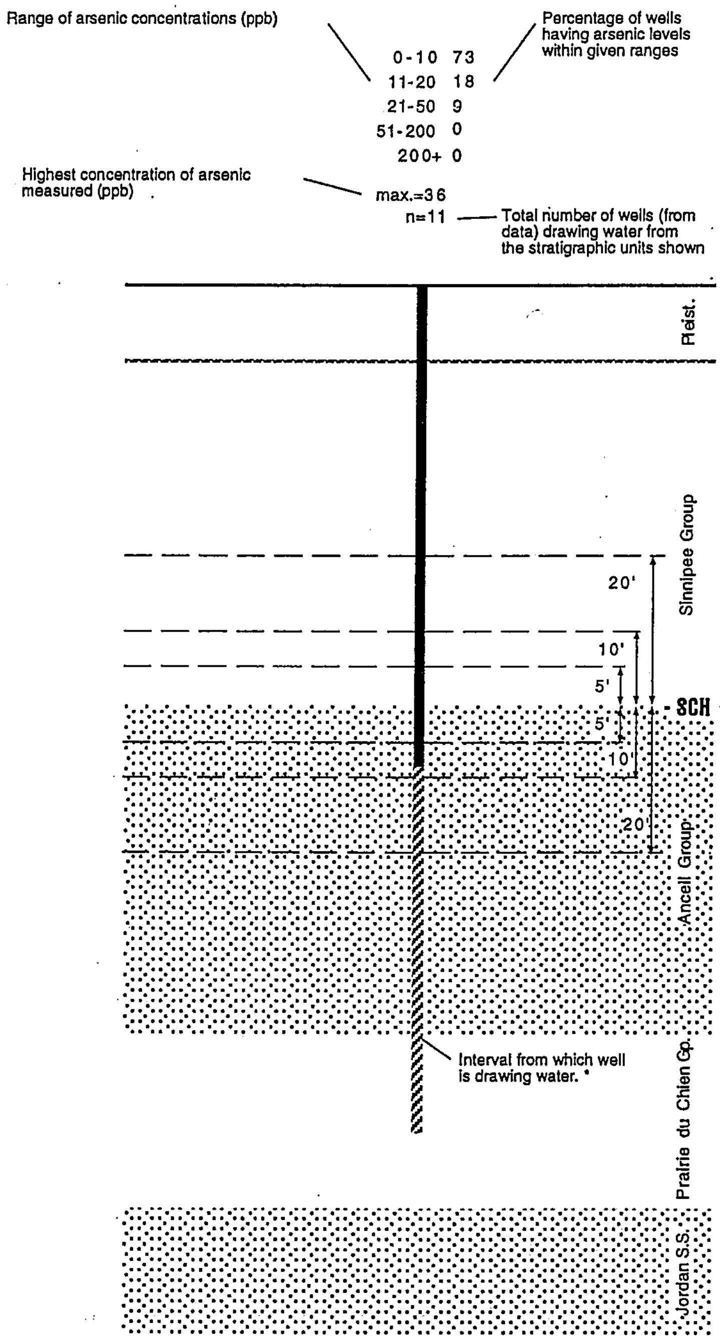
CORRELATION OF THE SULFIDE CEMENT HORIZON WITH KNOWN ARSENIC CONTAMINATION

Private well data collected by the Wisconsin Department of Natural Resources (Lake Michigan District) were used to determine the correlation between high arsenic concentrations in groundwater and the strata (containing the SCH or not) that water is drawn from, and the relationship of the water table to the top of the St. Peter Formation (where the SCH is located). Data were insufficient to determine a correlation between the water table and the top of the Prairie du Chien Group (where the SCH is located).

In the first case, wells were grouped according to the stratigraphic interval (which may consist of a single stratigraphic unit or multiple stratigraphic units) from which they draw water. Only stratigraphic intervals that had five or more wells drawing water from them were used in the analysis. Stratigraphic units used were: the Jordan Formation; the Prairie du Chien Group; the Ancell Group to within 20 feet (6 m) of the top; 10 to 20 feet (3 to 6 m), 5 to 10 feet (1.5 to 3 m), and 0 to 5 feet (0 to 1.5 m) from the top of the Ancell Group (base of the Sinnipee Group); 0 to 5 feet (0 to 1.5 m), 5 to 10 (1.5 to 3 m), and 10 to 20 feet (3 to 6 m) above the base of the Sinnipee Group; the remainder of the Sinnipee Group; and the Pleistocene (see Figure 17 for explanation). The highest arsenic content of each well group was noted, along with the percentage of wells in the group that had groundwater arsenic concentrations of 0 to 10 ppb, 11 to 20 ppb, 21 to 50 ppb, 51 to 200 ppb, and >200 ppb. The analysis is shown in Figures 17-19. Stratigraphic information for these wells is from constructors' reports and was not verified. Although the interval that the well is open to the saturated zone is known, it is unknown which strata contribute the majority of water to the well.

Figures 17-19 show no obvious correlation between arsenic concentration and stratigraphy. However, seven of the 10 wells with highest arsenic concentrations are open to the saturated zone from 10 to 20 feet (3 to 6 m) below the SCH. Five of the wells with highest arsenic concentrations are open to the saturated zone from 0 to 5 feet (0 to 1.5 m) below the SCH to at least 10 to 20 feet below the SCH. Though the exact strata from which groundwater is drawn are unknown, these data support the idea that the SCH is the source of arsenic contamination. Packer tests should be done around the SCH to more accurately determine which intervals the wells are drawing groundwater from.

A comparison was made between high arsenic concentrations in wells and the distance the water table was above or below the top of the St. Peter Formation in those wells. There is a strong correlation between arsenic concentrations and the distance the water table is above or below the top of the St. Peter Formation (Figure 20). The five highest arsenic concentrations (12,000, 5,900, 5,890, 1,200, and 888 ppb) (Wisconsin Preventative Action Limit is 5 ppb; Enforcement Standard is 50 ppb) are found in wells in which the water table is 0 to 15 feet (0 to 4.5 m) below the top of the St. Peter Formation. Eleven of the 12 highest arsenic concentrations (ranging from 12,000 to 550 ppb) are found in wells in which the water table is 0 to 21 feet (0 to 4.6 m) below the top of the St. Peter Formation. And of the 16 wells with arsenic concentrations exceeding 200 ppb, 12 are wells in which the water table is 0 to 21 feet (0 to 4.6 m) below the top of the St. Peter Formation.



For example, this figure shows data for wells that are drawing water from 0 to 5 feet below the top of the Ancell Group (SCH) to within the Prairie du Chien Group. This figure shows that 11 wells are drawing water from these stratigraphic units, with 73% of the wells having between 0 and 10 ppb arsenic, 18% of the wells having between 11 and 20 ppb arsenic, and 9% of the wells having between 21 and 50 ppb. The highest arsenic concentration of any of these wells is 36 ppb.

* Interval from which the well is drawing water extends from the bottom of the well to the bottom of the casing or the static water level, whichever is lowest.

Figure 17. Schematic showing the relationship of wells to stratigraphic units and arsenic concentrations in those wells. (Explanation for Figures 18 and 19.) Data courtesy of Wisconsin Department of Natural Resources, Lake Michigan District.

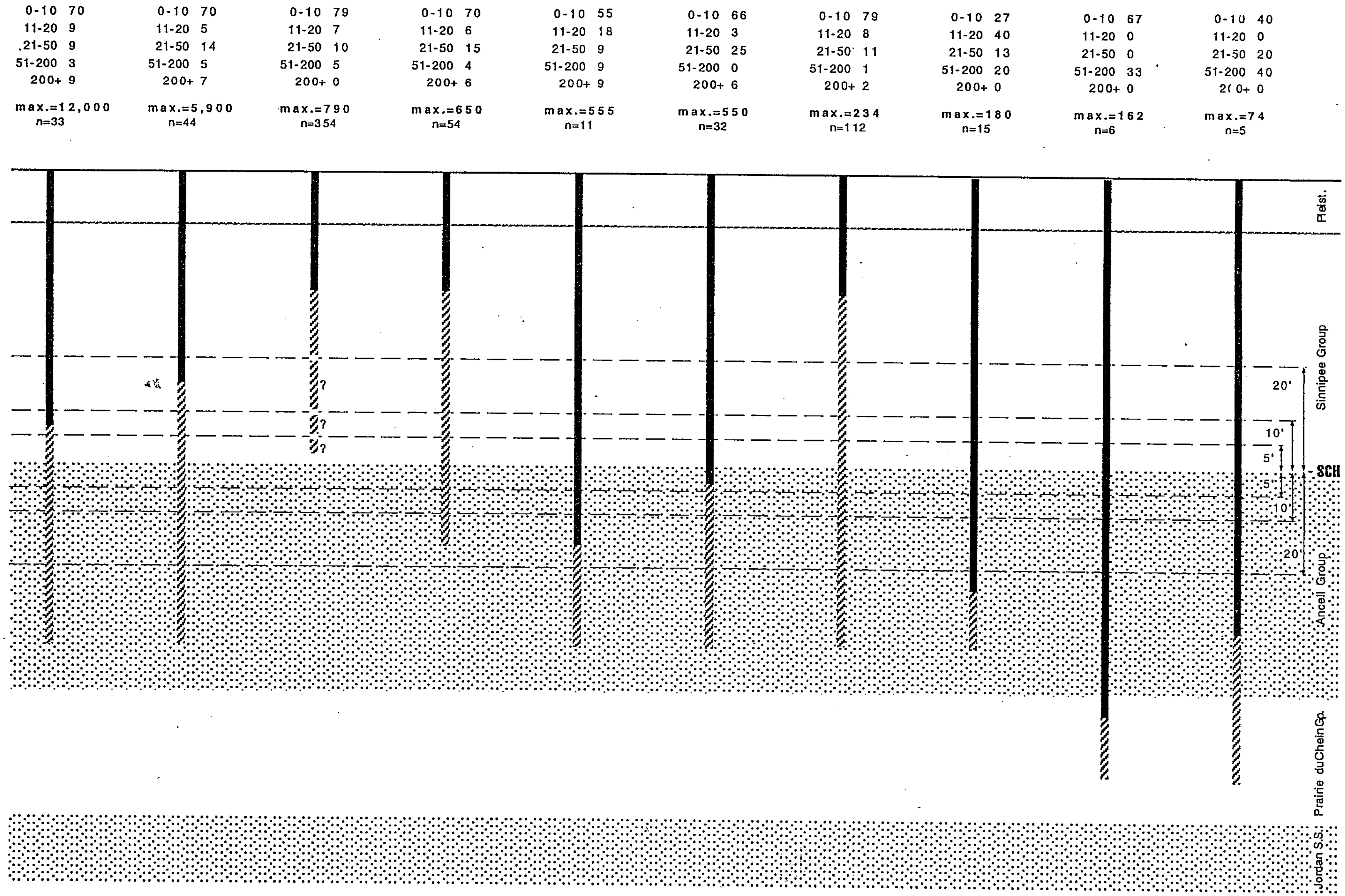


Figure 18. Schematic showing the relationship of wells to stratigraphic units and arsenic concentrations in those wells; wells with arsenic concentrations from 74 to 12,000 ppb. Data courtesy of Wisconsin Department of Natural Resources, Lake Michigan District. (See Figure 17 for explanation.)

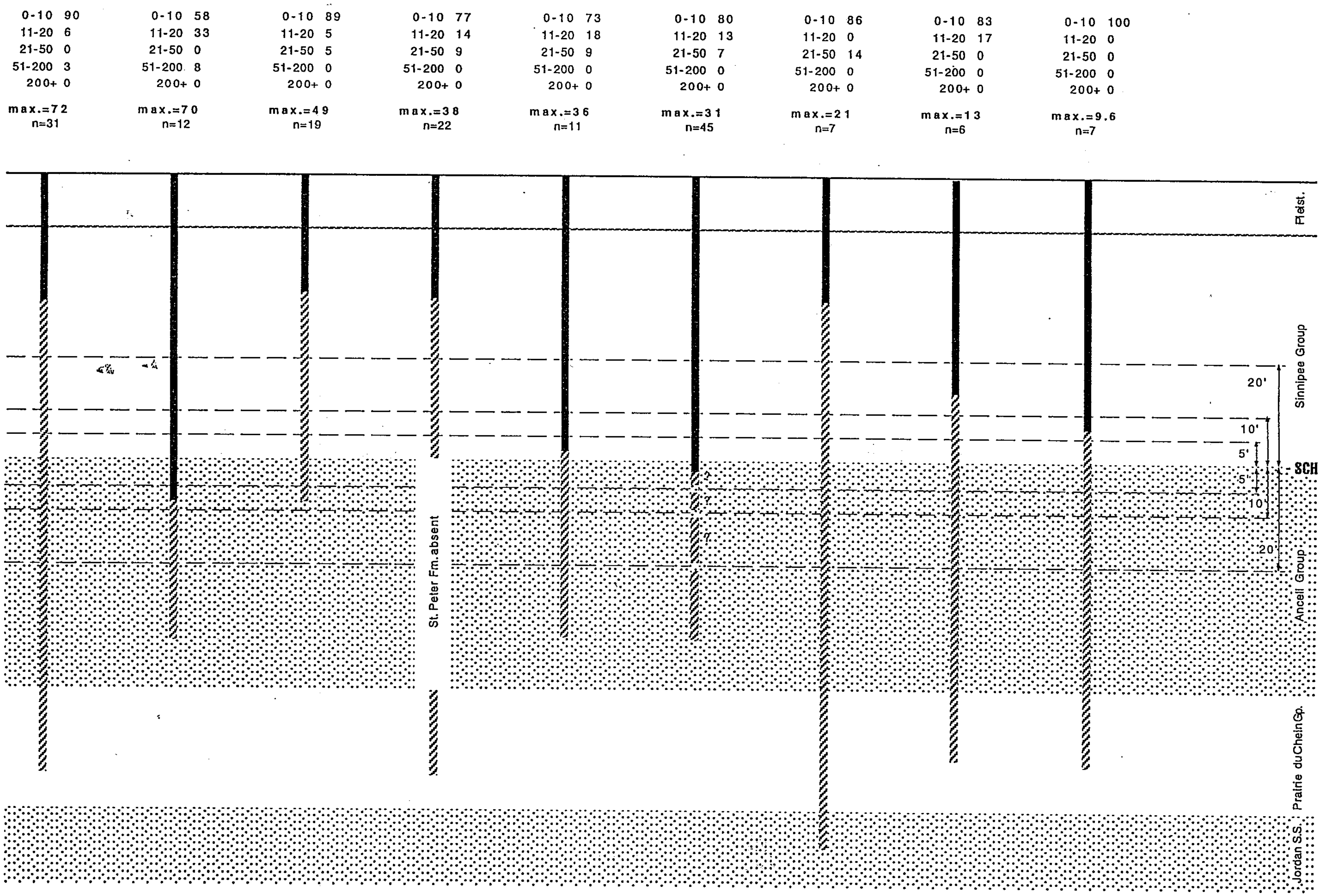


Figure 19. Schematic showing the relationship of wells to stratigraphic units and arsenic concentrations in those wells; wells with arsenic concentrations up to 72 ppb. Data courtesy of Wisconsin Department of Natural Resources, Lake Michigan District. (See Figure 17 for explanation.)

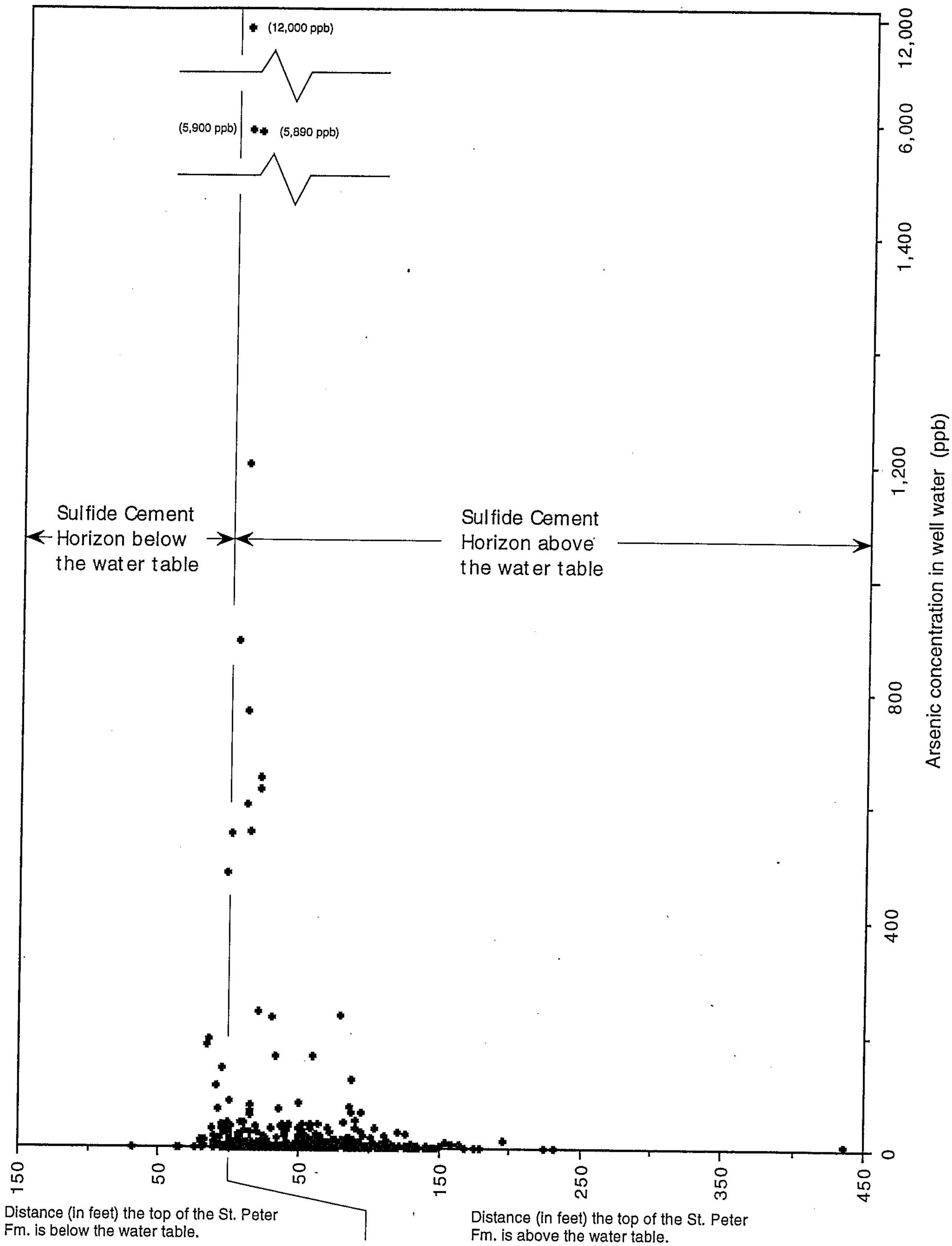


Figure 20. Relationship of arsenic concentrations in well water to the distance the water table is above or below the top of the St. Peter Formation (SCH) in those wells. Figure constructed from private well data provided by the Wisconsin Department of Natural Resources, Lake Michigan District.

These relationships support the idea that the SCH is the source of arsenic contamination and that arsenic concentrations are controlled by the relationship of the water table to the SCH. This suggests that redox conditions are important controls on the concentrations of arsenic in groundwater.

RECOMMENDATIONS

Although the SCH appears to be the source of the high arsenic concentrations in groundwater in the region, more research is needed to understand how the arsenic contamination occurs. Further research should concentrate on:

1) Geochemical reactions between the mineralization and groundwater, including determining the role of redox conditions; and
2) Groundwater flow modeling to determine more precisely which strata wells in the region are drawing from, which strata may be acting as local aquifers for arsenic-contaminated groundwater, and how drawdown caused by well use affects groundwater levels and redox conditions across or near the mineralization zone.

Until the geochemistry and groundwater flow conditions are better known, we recommend avoiding use of water from the strata in the upper Ancell Group (St. Peter and Glenwood Formations). This can be accomplished by drilling wells so that they reach no closer than 10 feet (3 m) above the bottom of the Sinnipee Group (Platteville Formation). If drilling through or into the Ancell Group strata (Glenwood and/or St. Peter Formation) is necessary because the Sinnipee Group is too thin, or because insufficient water is available in the Sinnipee Group, we support the WDNR's current guidance of casing through at least 80 feet of the uppermost Ancell Group strata. At best, the casing should extend as far below the top of the Ancell Group as is financially and mechanically feasible. If Ancell Group strata are absent, and drilling into the Prairie du Chien Group is necessary, casing of the well should extend at least 10 feet (3 m) below the top of the Prairie du Chien Group to avoid possible mineralization. These recommendations are preliminary and the distances stated are approximations. Further research is needed to better define the stratigraphic intervals in which wells may be safely screened or open.

Stratigraphic location can be more accurately determined during the drilling process by the use of gamma ray logging to determine, at least, boundaries of the stratigraphic packages described in this report and, at best, boundaries of lithostratigraphic units also described in this report to more precisely determine the stratigraphic position of the well.

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