

## NATIONAL DRINKING-WATER STANDARDS

National Drinking Water Regulations and Health Advisories (U. S. Environmental Protection Agency, 1993) list concentration limits of specified inorganic and organic chemicals in order to control amounts of contaminants in drinking water. Primary regulations list maximum contaminant levels (MCLs) for inorganic constituents considered toxic to humans above certain concentrations. These standards are health-related and legally enforceable. Secondary maximum contaminant levels (SMCLs) cover constitu-

ents that may adversely affect the aesthetic quality of drinking water. The SMCLs are intended to be guidelines rather than enforceable standards. Although these regulations apply only to drinking water at the tap for public supply, they may be used to assess water quality for privately-owned wells. The table below lists selected inorganic constituents of drinking water covered by the regulations, the significance of each constituent, and their respective MCL or SMCL. Fluoride and nitrate are the only constituents listed which are covered by the primary regulations.

Constituent	Secondary Maximum Contaminant Level (SMCL) (ppm)	Maximum Contaminant Level (MCL) (ppm)	Remarks
Total Dissolved Solids (TDS)	500	*	Levels above SMCL can give water a disagreeable taste. Levels above 1000 mg/L may cause corrosion of well screens, pumps, and casings.
Iron	0.3	*	More than 0.3 ppm can cause staining of clothes and plumbing fixtures, encrustation of well screens, and plugging of pipes. Excessive quantities can stimulate growth of iron bacteria.
Manganese	0.05	*	Amounts greater than 0.05 ppm can stain laundry and plumbing fixtures, and may form a dark brown or black precipitate that can clog filters.
Chloride	250	*	Large amounts in conjunction with high sodium concentrations can impart a salty taste to water. Amounts above 1000 ppm may be physiologically unsafe. High concentrations also increase the corrosiveness of water.
Fluoride	2.0	4.0	Concentration of approximately 1.0 ppm help prevent tooth decay. Amounts above recommended limits increase the severity and occurrence of mottling (discoloration of the teeth). Amounts above 4 ppm can cause adverse skeletal effects (bone sclerosis).
Nitrate**	*	10	Concentrations above 20 ppm impart a bitter taste to drinking water. Concentrations greater than 10 ppm may have a toxic effect (methemoglobinemia) on young infants.
Sulfate	250	*	Large amounts of sulfate in combination with other ions (especially sodium and magnesium) can impart odors and a bitter taste to water. Amounts above 600 ppm can have a laxative effect. Sulfate in combination with calcium in water forms hard scale in steam boilers.
Sodium	NL	NL	Sodium salts may cause foaming in steam boilers. High concentrations may render water unfit for irrigation. High levels of sodium in water have been associated with cardiovascular problems. A sodium level of less than 20 ppm has been recommended for high risk groups (people who have high blood pressure, people genetically predisposed to high blood pressure, and pregnant women).
Calcium	NL	NL	Calcium and magnesium combine with bicarbonate, carbonate, sulfate and silica to form heat-retarding, pipe-clogging scales in steam boilers. For further information on calcium and magnesium, see hardness.
Magnesium	NL	NL	
Hardness	NL	NL	Principally caused by concentration of calcium and magnesium. Hard water consumes excessive amounts of soap and detergents and forms an insoluble scum or scale.
pH	-	-	USEPA recommends pH range between 6.5 and 8.5 for drinking water.

NL No Limit Recommended.

\* No MCL or SMCL Established by USEPA.

\*\* Nitrate concentrations expressed as equivalent amounts of elemental nitrogen (N).

(Adapted from USEPA, 1993a)

Note: 1 part per million (ppm) = 1 mg/L.

## CHEMICAL CLASSIFICATION OF GROUND WATERS USING TRILINEAR DIAGRAMS

Trilinear plotting systems were used in the study of water chemistry and quality as early as 1913 (Hem, 1985). The type of trilinear diagram used in this report, independently developed by Hill (1940) and Piper (1944), has been used extensively to delineate variability and trends in water quality. The technique of trilinear analysis has contributed extensively to the understanding of ground water flow, and geochemistry (Dalton and Upchurch, 1978).

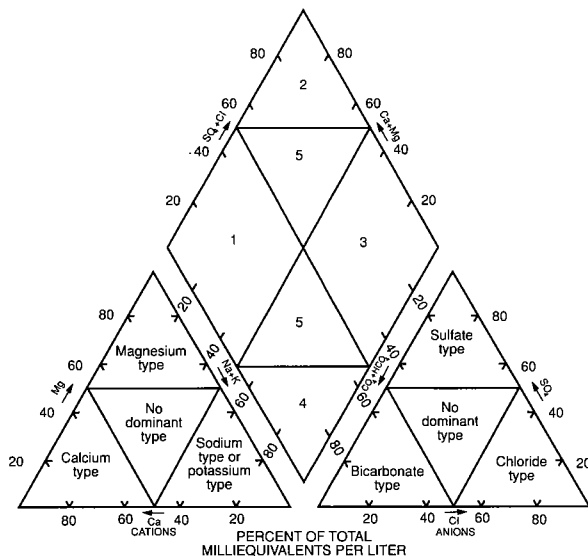
On conventional trilinear diagrams sample values for three cations (calcium, magnesium and the alkali metals- sodium and potassium) and three anions (bicarbonate, chloride and sulfate) are plotted relative to one another. Because these ions are generally the most common constituents in unpolluted ground waters, the chemical character of most natural waters can be closely approximated by the relative concentration of these ions (Hem, 1985; Walton, 1970).

Before values can be plotted on the trilinear diagram, the concentrations of the six ions of interest are converted into milliequivalents per liter (meq/L), a unit of concentration equal to the concentration in milligrams per liter divided by the equivalent weight (atomic weight divided by valence). Each cation value is then plotted, as a percentage of the total concentration (meq/L) of all cations under consideration, in the lower left triangle of the diagram. Likewise, individual anion values are plotted, as percentages of the total concentration of all anions under consideration, in the lower right triangle. Sample values are then projected into the central diamond-shaped field. Fundamental interpretations of the chemical nature of a water sample are based on the location of the sample ion values within the central field.

Distinct zones within aquifers having defined water chemistry properties are referred to as hydrochemical facies (Freeze and Cherry, 1979). Determining the nature and distribution of hydrochemical facies can provide insights into how ground-water quality changes within and between aquifers. Trilinear diagrams can be used to delineate hydrochemical facies, because they graphically demonstrate relationships between the most important dissolved constituents in a set of ground-water samples.

A simple but useful scheme for describing hydrochemical facies with trilinear diagrams is presented by Walton (1970) and is based on methods used by Piper (1944). This method is based on the "dominance" of certain cations and anions in solution. The dominant cation of a water sample is defined as the positively charged ion whose concentration exceeds 50 percent of the summed concentrations of major cations in solution. Likewise, the concentration of the dominant anion exceeds 50 percent of the total anion concentration in the water sample. If no single cation or anion in a water sample meets this criterion, the water has no dominant ion in solution. In most natural waters, the dominant cation is either calcium, magnesium, or alkali metals (sodium and potassium), and the dominant anion is either chloride, bicarbonate, or sulfate (see figure above).

Distinct hydrochemical facies are defined by specific combinations of dominant cations and anions. These combinations will plot



in certain areas of the central, diamond-shaped part of the trilinear diagram. Walton (1970) described a simple but useful classification scheme which divides the central part of the diagram into five subdivisions (see figure above). Five basic hydrochemical facies can be defined with this criteria:

1. Primary Hardness; Combined concentrations of calcium, magnesium and bicarbonate exceed 50 percent of the total dissolved constituent load in meq/L. Such waters are generally considered hard and are often found in limestone aquifers or unconsolidated deposits containing abundant carbonate minerals.
2. Secondary Hardness; Combined concentrations of sulfate, chloride, magnesium and calcium exceed 50 percent of total meq/L.
3. Primary Salinity; Combined concentrations of alkali metals, sulfate and chloride are greater than 50 percent of the total meq/L. Very concentrated waters of this hydrochemical facies are considered brackish or (in extreme cases) saline.
4. Primary Alkalinity; Combined sodium, potassium and bicarbonate concentrations exceed 50 percent of the total meq/L. These waters generally have low hardness in proportion to their dissolved solids concentration (Walton, 1970).
5. No specific cation-anion pair exceeds 50 percent of the total dissolved constituent load. Such waters could result from multiple mineral dissolution or mixing of chemically distinct ground waters.

This chemistry reflects the dissolution of carbonate minerals and is typical of waters in limestone terranes and common in ground waters from midwestern glacial deposits (Freeze and Cherry, 1979). In the Lacustrine

Plain Aquifer system underlying the Calumet, bicarbonate is the dominant *anion* in 73 percent of all samples, but sodium and potassium appear to be the dominant *cations* in this aquifer. In the Bedrock Aquifer

fer system, approximately 50 percent of all water samples were dominated by calcium, magnesium and bicarbonate, while the remaining samples were either sodium-potassium-bicarbonate dominated or had no dominant cation-anion pair.

Although waters in the Region are predominately calcium and bicarbonate dominated, numerous samples are chemically dominated by other anions or cations. That is, the concentrations of these ions exceed 50 percent of the sum of cation or anion concentrations. This indicates that, locally, there can be considerable variation in the nature of water chemistry in the Lake Michigan Region. The amount of chemical variability in an aquifer system is reflected in the scatter of points within the trilinear diagram.

The least amount of chemical variability is observed in the Valparaiso Moraine Aquifer system (appendix 10). The majority of samples from this aquifer are calcium-bicarbonate dominated, but some samples contain considerable amounts of sulfate (as high as 49 percent of total anion concentration).

A large degree of variation is observed in the ground-water chemistry of the Calumet Aquifer system (appendix 10). Forty-one percent of all samples have no dominant cation, and 24 percent have no dominant anion. Some samples from the Calumet Aquifer system are sodium dominated (3 percent); and a considerable number of samples have chloride or sulfate as the dominant anion (13.5 percent and 11 percent, respectively). Other samples from the Calumet Aquifer system plot within the fields of secondary hardness, primary salinity or no dominant chemistry (see insert on preceding page).

The Lacustrine Plain Aquifer system underlying the Calumet and the Silurian and Devonian Bedrock Aquifer system both display variability in water chemistry (appendix 10). However, since only a small number of samples are available from each system, these diagrams may not reflect all chemical conditions in these aquifers.

## Assessment of ground-water quality

### Alkalinity and pH

Alkalinity, the capacity of water to neutralize acid, is determined from levels of bicarbonate, carbonate, hydroxide, borates, and certain organic compounds in the water. In the Lake Michigan Region, alkalinity is

due primarily to the presence of bicarbonate ( $\text{HCO}_3$ ), the dominant anion in most samples from wells completed in both unconsolidated deposits and bedrock. Rosenshein and Hunn (1968a, 1968b) have noted that bicarbonate concentrations are generally higher in aquifers confined between thick tills, where water generally has more contact with carbonate minerals dispersed within the till sediments.

The highest median alkalinity level (330 mg/L) is detected in the Valparaiso Moraine Aquifer system (figure 57). The high median value for this aquifer system may reflect a relatively long ground-water residence time in low-permeability tills overlying the aquifer system. The lowest median alkalinity level (195.5 mg/L) was measured in the Calumet Aquifer system, which may reflect relatively short residence time in this permeable, sandy aquifer.

The median alkalinity concentration of ground water in the Silurian and Devonian Bedrock Aquifer system (382 mg/L) is considerably higher than median ground-water alkalinity in the unconsolidated aquifer systems. The higher alkalinity may be due to: 1) the limestone and dolomite composition of the bedrock units; 2) bicarbonate production from biochemical sulfate reduction (Freeze and Cherry, 1979); and/or 3) longer residence time in bedrock units.

The pH, or hydrogen ion activity, is expressed on a logarithmic scale (0 to 14), and represents the negative base-10 log of the hydrogen-ion concentration. The neutral value of pH is set at 7. Water is considered acidic when the pH is less than 7 and basic when the pH is greater than 7. Overall, the data indicate that ground water in the Region is predominantly near-neutral; pH values generally occur within the 6-8 range.

### Hardness, calcium, and magnesium

"Hardness" is a term relating to the concentration of certain ions in water, particularly magnesium and calcium, and is usually expressed as an equivalent concentration of dissolved calcite ( $\text{CaCO}_3$ ) in milligrams per liter. Durfor and Becker (1964) developed the following classification of water hardness which is useful for discussion purposes: soft water, 0 to 60 mg/L (calcite equivalent); moderately hard water, 61 to 120 mg/L; hard water, 121 to 180 mg/L; and very hard water, more than 180 mg/L. Hardness is a water-quality concern because hard water consumes excessive amounts of soap and detergents, forms an insoluble

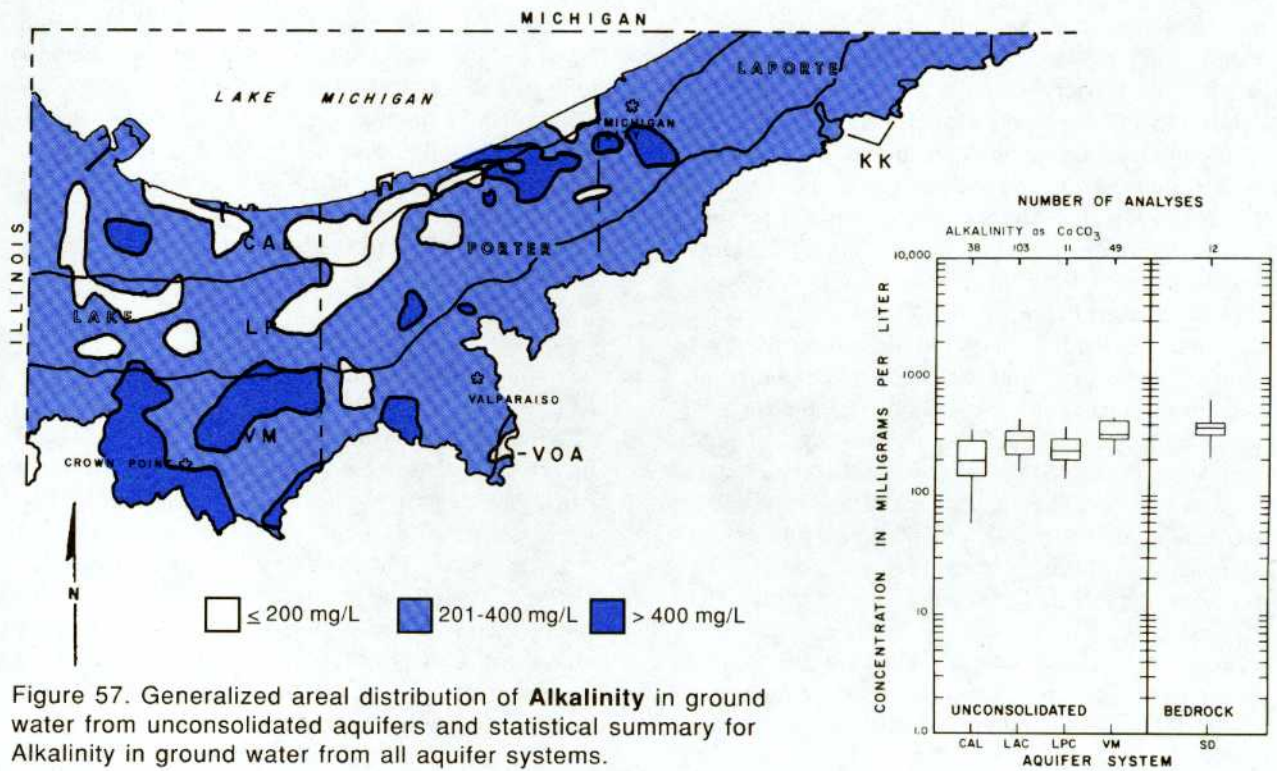


Figure 57. Generalized areal distribution of **Alkalinity** in ground water from unconsolidated aquifers and statistical summary for Alkalinity in ground water from all aquifer systems.

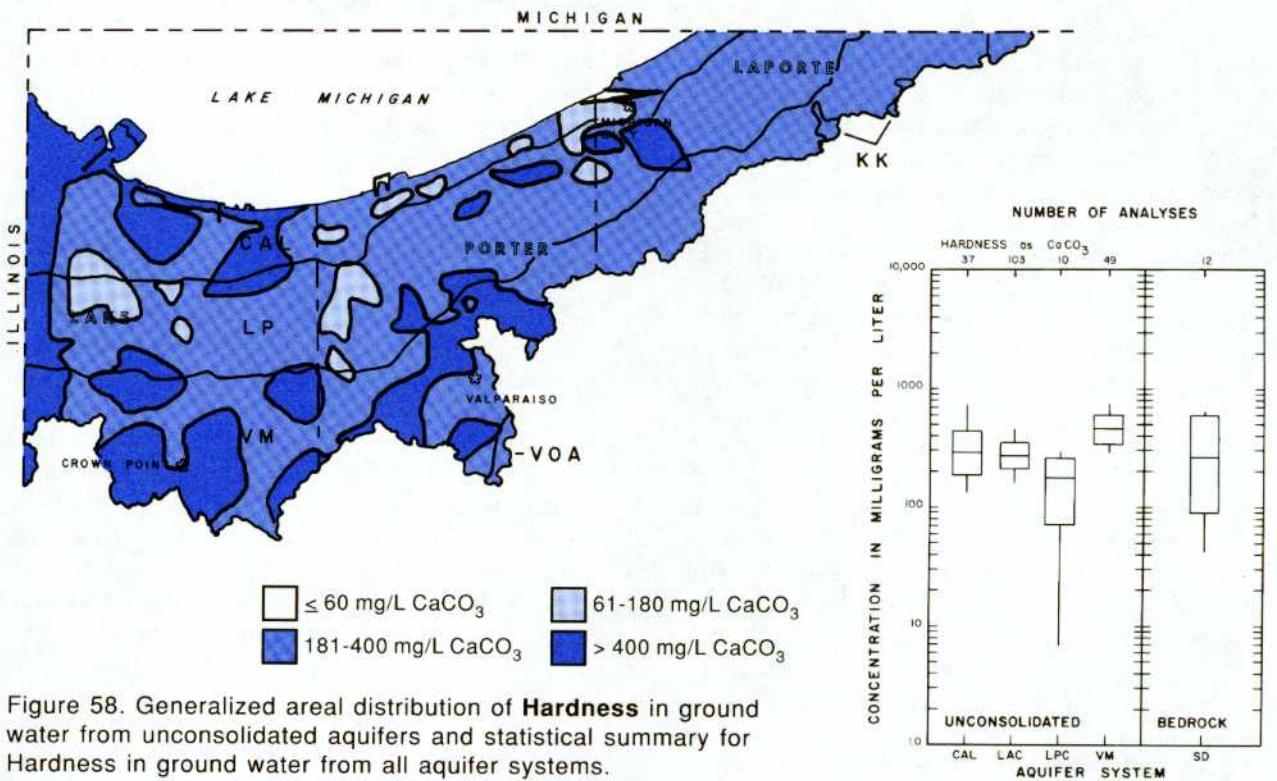


Figure 58. Generalized areal distribution of **Hardness** in ground water from unconsolidated aquifers and statistical summary for Hardness in ground water from all aquifer systems.

ble scum, and causes scale to encrust water heaters, boilers, and pipes, thus decreasing their capacity and heat-transfer properties.

Wells in the unconsolidated aquifers of the Lake Michigan Region generally contain hard to very hard water (figure 58). Very hard water is common in the Valparaiso Moraine Aquifer system, which has a median hardness of 464 mg/L (figure 58). The lowest median hardness, 175 mg/L calcite equivalent, is found in the Lacustrine Plain Aquifer system underlying the Calumet. The hard water in the Valparaiso Moraine Aquifer system may originate from the dissolution of calcium-carbonate and calcium-sulfate minerals.

Having a median hardness of 263 mg/L calcite equivalent, the Silurian and Devonian Bedrock Aquifer system generally contains very hard waters. Some hardness levels in excess of 500-600 mg/L calcite equivalent have been reported in bedrock wells around the town of Dyer in west-central Lake County. The water samples from the Silurian and Devonian Bedrock Aquifer system also have relatively high sulfate concentrations, which may indicate that gypsum ( $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) dissolution is a factor in the elevated hardness.

The hard waters of the Silurian and Devonian Bedrock Aquifers are used in the Dyer area because of changes in the overlying Valparaiso Moraine Aquifer system. This unconsolidated aquifer becomes thinner and less permeable just east of Dyer, which limits its use as a ground-water source in some parts of the southwestern Lake Michigan Region.

Because calcium and magnesium are the major constituents responsible for hardness in water, high concentrations of these ions are generally found in waters with hardness levels above 180 mg/L  $\text{CaCO}_3$  equivalent. The lowest median calcium concentration (31 mg/L) is present in the Lacustrine Plain Aquifer system underlying the Calumet; in contrast, the highest median concentration (115 mg/L) is found in the Valparaiso Moraine Aquifer system (appendix 11). The median magnesium concentrations in the unconsolidated aquifer systems ranged from 21.5 mg/L in the Calumet Aquifer system to 41 mg/L in the Valparaiso Moraine Aquifer system (appendix 11).

In the Silurian and Devonian Bedrock Aquifer system, median calcium and magnesium concentrations are 60 mg/L and 31 mg/L, respectively. These ions also appear to have a wider range of concentrations in bedrock wells relative to concentrations in the unconsolidated aquifer systems (appendix 11). High concen-

trations of magnesium and calcium probably result from the dissolution of carbonate minerals. Some ground-water samples from bedrock wells near Gary and Crown Point, however, have low hardness, calcium and magnesium levels. Compared to other bedrock well samples, these ground waters are sodium-potassium-bicarbonate dominated, have more chloride as part of their total anion percentage, and higher concentrations of fluoride.

### Chloride, sodium and potassium

Wide variation in chloride concentrations are found among the unconsolidated aquifer systems of the Lake Michigan Region (figure 59). The highest median concentration of 31 mg/L is detected in the Calumet Aquifer system. The lowest median chloride concentration (7.0 mg/L) is observed in the Valparaiso Moraine Aquifer system. Some chloride concentrations above the SMCL of 250 mg/L are present in all unconsolidated aquifer systems, except for the Valparaiso Moraine Aquifer system.

The box plots in figure 60 indicate that sodium also has fairly wide concentration ranges in the unconsolidated aquifers. The lowest median concentration of 7.1 mg/L is detected in the Valparaiso Moraine Aquifer system; whereas, the highest median value (76 mg/L) is found in water from the Lacustrine Plain Aquifer system underlying the Calumet. The high sodium content of some waters from the latter aquifer may originate from natural softening. Natural softening is the replacement of calcium and magnesium in solution for sodium and potassium on the surface of a mineral substrate, such as clay particles, by *ion exchange*.

Many chloride concentrations which exceed the SMCL are detected in wells located in or near urban areas and screened at depths from 25 to 65 feet. The high chloride in these wells could originate from anthropogenic sources, such as landfills, industrial chemicals, or deicing salt. Another possible source of this ion could be the upwelling of chloride-dominated waters from the deeper flow system. A few chloride concentrations greater than the SMCL are detected in deep wells (96 to 212 feet) drilled into the Lacustrine Plain Aquifer system underlying the Calumet. The high chloride concentrations in the deeper wells may not reflect contamination, since they occur in isolated, deep wells. Explanations for the high chloride concentrations in water from the deep wells include older,

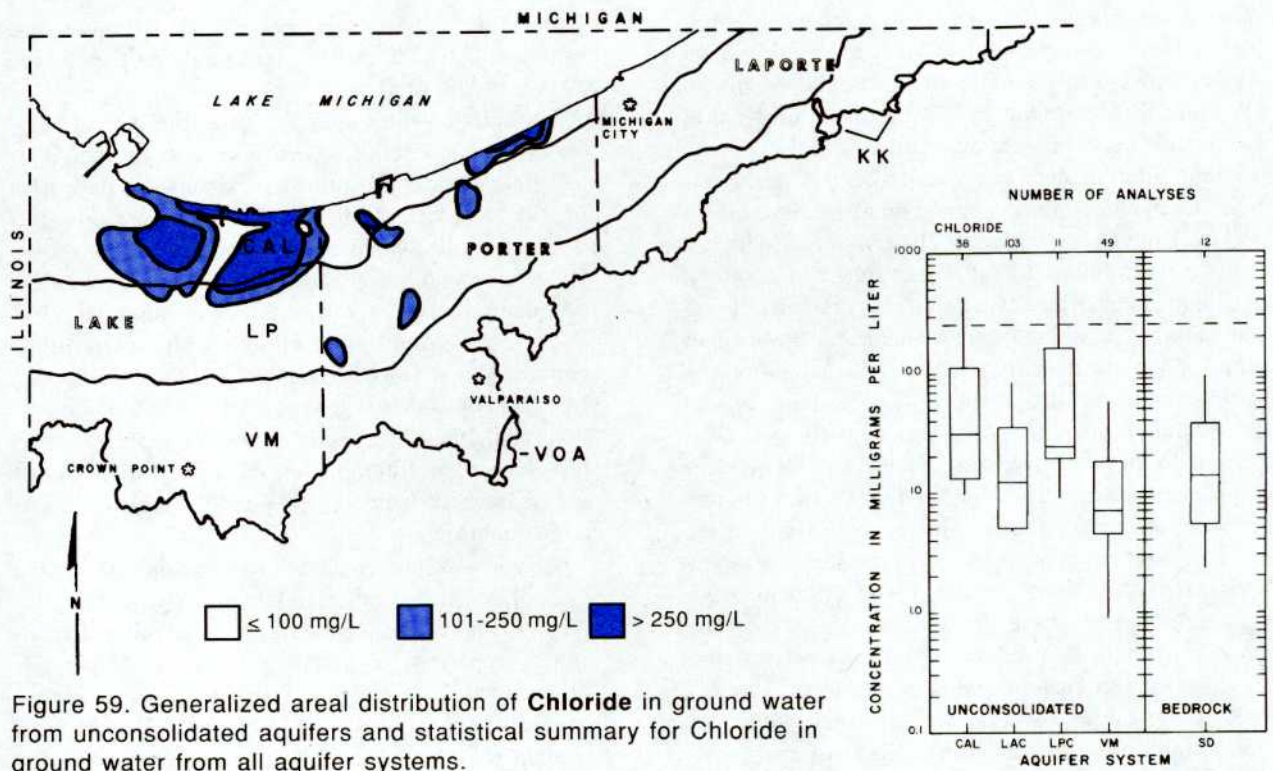


Figure 59. Generalized areal distribution of **Chloride** in ground water from unconsolidated aquifers and statistical summary for Chloride in ground water from all aquifer systems.

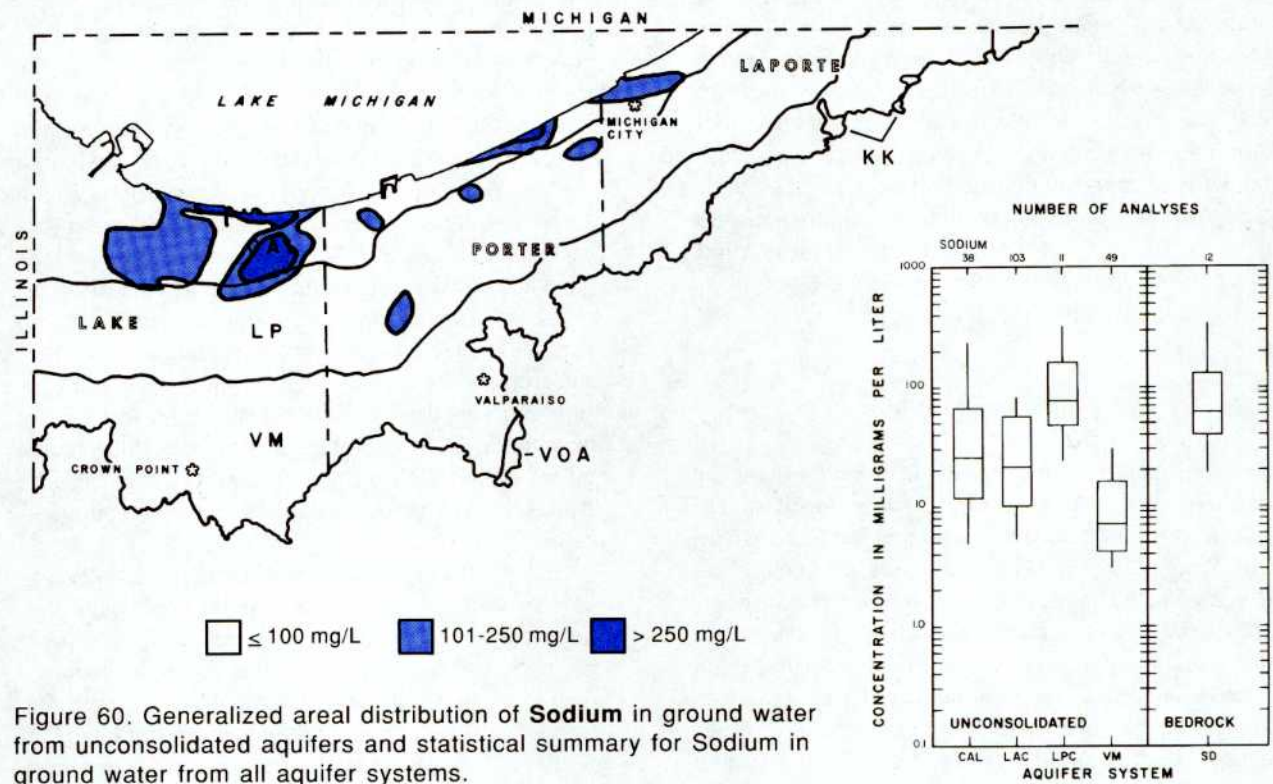


Figure 60. Generalized areal distribution of **Sodium** in ground water from unconsolidated aquifers and statistical summary for Sodium in ground water from all aquifer systems.

more saline waters within the aquifer, and the possibility that these wells are being influenced by more saline waters upwelling from depth into Lake Michigan (William J. Steen, Indiana Department of Natural Resources, personal communication, 1992).

In the Silurian and Devonian Bedrock Aquifer system, the median chloride and sodium levels are 13.5 and 62.1 mg/L, respectively. These values are higher than median values for all unconsolidated aquifers, except the Lacustrine Plain Aquifer system underlying the Calumet. It is important to note that the median value of sodium is nearly five times that of chloride in the Bedrock Aquifer system. The median sodium concentration also exceeds the median chloride concentration in the Lacustrine Plain Aquifer system (figures 59 and 60). The higher sodium concentrations may indicate that salt dissolution is not the only factor affecting sodium concentrations in the Bedrock Aquifer system. Additional sodium could originate from ion-exchange processes in the clay layers of the Lacustrine Plain Aquifer system or in shales overlying the Silurian and Devonian Bedrock Aquifer system.

Relatively little variation is seen in the potassium concentrations of the unconsolidated aquifers (appendix 11). Median values range from 1.7 mg/L in the Valparaiso Moraine Aquifer system to 3.2 mg/L in the Calumet Aquifer system and Lacustrine Plain Aquifer system underlying the Calumet. The median potassium concentration in the Silurian and Devonian Bedrock Aquifer system equaled 5.65 mg/L, which is generally higher than concentrations in the unconsolidated aquifers. Although some potassium concentrations in excess of 10 mg/L are detected, the majority (96.8 percent) of samples from all aquifers have potassium concentrations below this level.

### Sulfate and sulfide

Sulfur generally occurs naturally in ground water in the oxidized form of sulfate ( $\text{SO}_4$ ) and the reduced form of sulfide (S). Sulfate concentrations in the Lake Michigan Region display wide variations throughout the unconsolidated aquifer systems (figure 61). Considerable variability in sulfate concentrations is observed in the Calumet, Lacustrine Plain and Lacustrine Plain Aquifer underlying the Calumet Aquifer systems. The highest median concentration is observed in the Valparaiso Moraine Aquifer system. Every aquifer system in the Region, except the portion of the Lacustrine

Plain Aquifer system underlying the Calumet, has samples in which sulfate concentrations exceed the SMCL of 250 mg/L.

The sulfate values in the Valparaiso Moraine Aquifer system may reflect interactions between percolating ground water and sulfur-based minerals in overlying tills (Hartke and others, 1975). The low permeability of the tills would tend to increase contact time between ground waters and sulfur-based minerals, producing higher overall sulfate concentrations.

There are no apparent depth-related trends in sulfate concentrations, since high and low levels of sulfate are found in both shallow and deep wells. High concentrations could thus, be a result of multiple sources such as dissolution of sulfur minerals, the upward discharge of waters from the bedrock, and possible human-induced contamination.

Very low sulfate concentrations are detected in the Lacustrine Plain Aquifer system underlying the Calumet. As the trilinear diagram for this aquifer demonstrates (appendix 10), sulfate forms an almost negligible percentage of total anions in solution. Sulfate concentrations range from 0.2 to 17 mg/L and have a median value of 1.9 mg/L in the aquifer system. The low sulfate concentrations may result from the reduction of sulfate to sulfide in this deep aquifer.

An extensive degree of variability is observed in the sulfate concentrations of water samples from the Silurian and Devonian Bedrock Aquifer system. Sulfate concentrations range from 3.0 to 343 mg/L and have a median value of 105.5 mg/L in the aquifer system. Approximately 25 percent of all bedrock samples exceed the sulfate SMCL. Many of the samples which have high sulfate concentrations are located in southern Lake County near the Silurian and Devonian bedrock contact. The higher concentrations could result from interactions between ground water and gypsum and anhydrite beds that may be present locally near the Silurian and Devonian contact (Shaver and others, 1986; Doheny and others, 1975; and Curtis Ault, Indiana Geological Survey, personal communication, 1993).

Under reducing, low-oxygen conditions, sulfide is usually the dominant species of sulfur in ground water. Sulfide in ground water can be produced by anaerobic bacteria, which will reduce sulfate during the metabolism of organic matter (Freeze and Cherry, 1979). The form of sulfide in ground water is dependent on pH. In acidic environments (pH less than 7), sulfide generally occurs as dissolved, uncharged hydrogen-sulfide gas

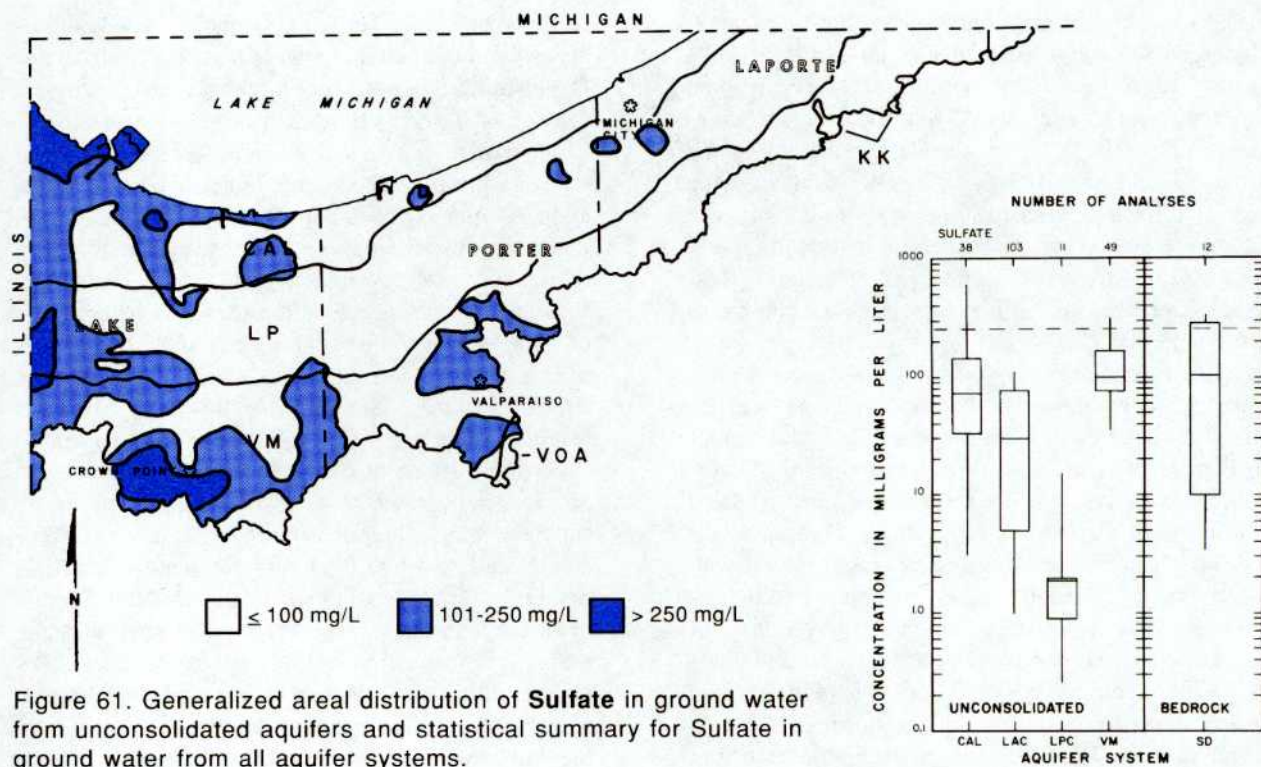


Figure 61. Generalized areal distribution of **Sulfate** in ground water from unconsolidated aquifers and statistical summary for Sulfate in ground water from all aquifer systems.

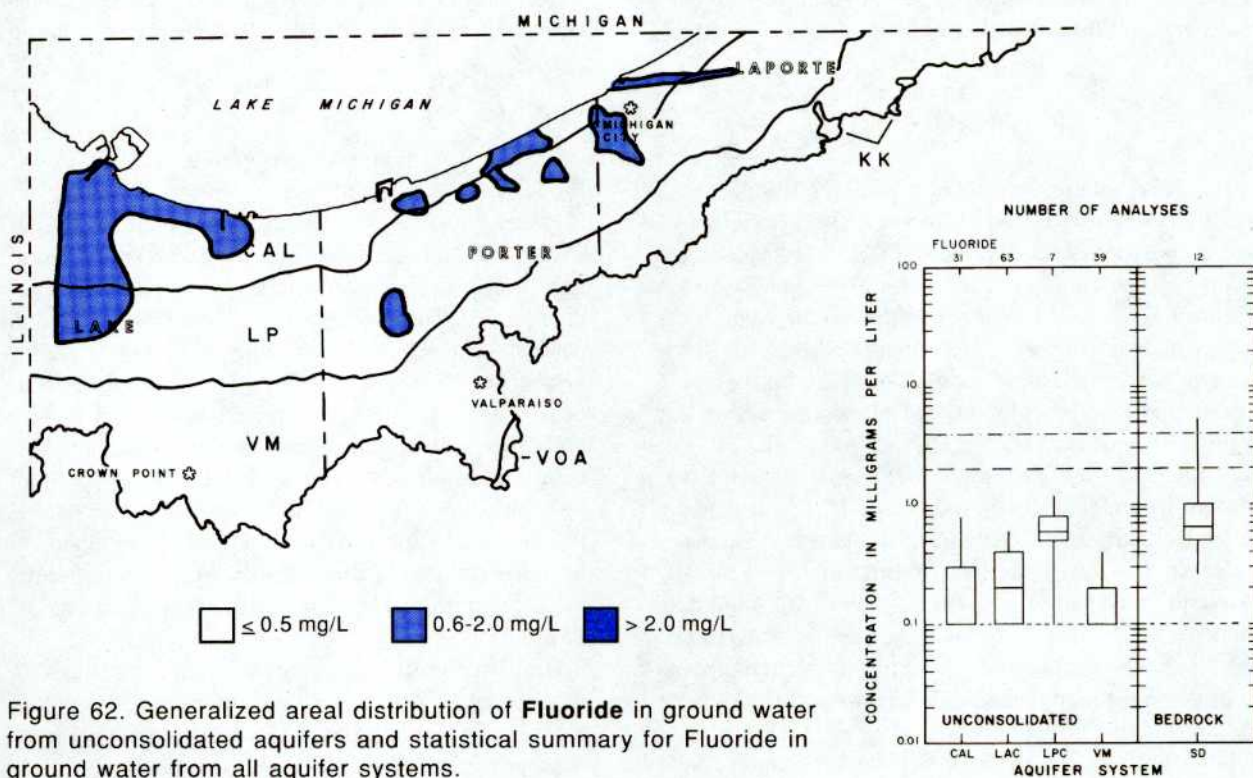


Figure 62. Generalized areal distribution of **Fluoride** in ground water from unconsolidated aquifers and statistical summary for Fluoride in ground water from all aquifer systems.



(H<sub>2</sub>S) while under basic conditions (pH greater than 7) hydrogen-sulfide will disassociate into bisulfide (HS<sup>-</sup>) and hydrogen ions (Freeze and Cherry, 1979; Konrad J. Banaszak, Geraghty and Miller, Inc., personal communication, 1993). Since median pH values in the Region are generally above 7, HS<sup>-</sup> would be the expected form of reduced sulfur in solution. Once out of solution, however, bisulfide and hydrogen recombine to form hydrogen-sulfide gas. (Konrad J. Banaszak, Geraghty and Miller, Inc., personal communication, 1993).

In the Lake Michigan Region, hydrogen sulfide has been encountered in some bedrock wells, particularly in central Lake County (Northwestern Indiana Regional Planning Commission, 1981); however, the occurrence of this gas may not be well documented since disclosure of its presence is voluntary. Hydrogen sulfide is well-known for causing a rotten-egg odor in well water. No SMCL exists for the constituent, but concentrations as low as 1.0 mg/L can render water unfit for human consumption because of odor (Freeze and Cherry, 1979). Hydrogen sulfide is corrosive to metals, and if oxidation to sulfuric acid has occurred, also to concrete pipes. Damage to plumbing and introduction of metals into water supplies are possible results of hydrogen sulfide-induced corrosion.

### Fluoride

The concentration of fluoride in natural waters is usually below 1.0 mg/L (Hem, 1985). This generalization is consistent with the median fluoride levels found in the aquifer systems of the Lake Michigan Region (figure 62). A few samples in the Calumet Aquifer system and the Silurian and Devonian Bedrock Aquifer system, however, exceed the SMCL of 2.0 mg/L; and one sample in the Silurian and Devonian Bedrock Aquifer system exceeds the MCL of 4.0 mg/L.

In the unconsolidated aquifer systems, the highest median fluoride concentration (0.6 mg/L) is detected in the Lacustrine Plain Aquifer system underlying the Calumet. The lowest median concentration was measured in the Calumet Aquifer system (0.1 mg/L). Fluoride in the unconsolidated aquifers of the Lake Michigan Region may originate from weathering of fluoride-based minerals, such as apatite and fluorapatite, in tills and moraine deposits.

In general, higher levels of fluoride are detected in waters from the bedrock aquifer relative to waters from

the unconsolidated aquifer systems. The median concentration of fluoride in waters from the Silurian and Devonian Bedrock Aquifer system is 0.65 mg/L, and the highest observed fluoride concentration (6.0 mg/L) is detected in ground water from a bedrock well near Crown Point in Lake County. Fluoride in the Silurian and Devonian Bedrock Aquifer system probably originates from the dissolution of fluorite in the bedrock or fluorapatite in evaporite deposits.

Problems with excessive fluoride in the water supply of an area near the Region have resulted in disputes over water diversion out of the Lake Michigan Region. In Lake County, just south of the Lake Michigan Region boundary, high concentrations of naturally-occurring fluoride are found in bedrock wells which provide the town of Lowell with its municipal water supply. Because fluoride levels have, at times, exceeded the MCL, the USEPA has imposed an Administrative Order on the town to reduce the levels of fluoride in the public water supply. A recent attempt was made, through the "prior approval" process of the Great Lakes Charter discussed in **Water Resource Development, Legal and political constraints**, to divert water from the Lake Michigan Region to supply Lowell with water. The diversion effort failed, however, because agreement could not be reached among the negotiating parties.

### Iron and manganese

Excessive iron is undesirable in ground water because it can stain clothing and bathroom fixtures, cause taste problems, and result in clogged well screens if precipitated. The box plots in figure 63 indicate that a percentage of ground-water samples from each aquifer system have iron concentrations that exceed the SMCL of 0.3 mg/L. In the Lacustrine Plain Aquifer system underlying the Calumet, the calculated median iron concentration is below the detection limit, and cannot be readily quantified. The highest median iron concentration of 2.4 mg/L is detected in the Valparaiso Moraine Aquifer system. Median iron concentrations in all other aquifer systems in the region exceed the SMCL.

High, naturally-occurring iron concentrations in ground water can originate from several potential sources (see box on page 162). The weathering of iron-bearing minerals in surficial tills is probably a significant source of iron in the Valparaiso Moraine Aquifer

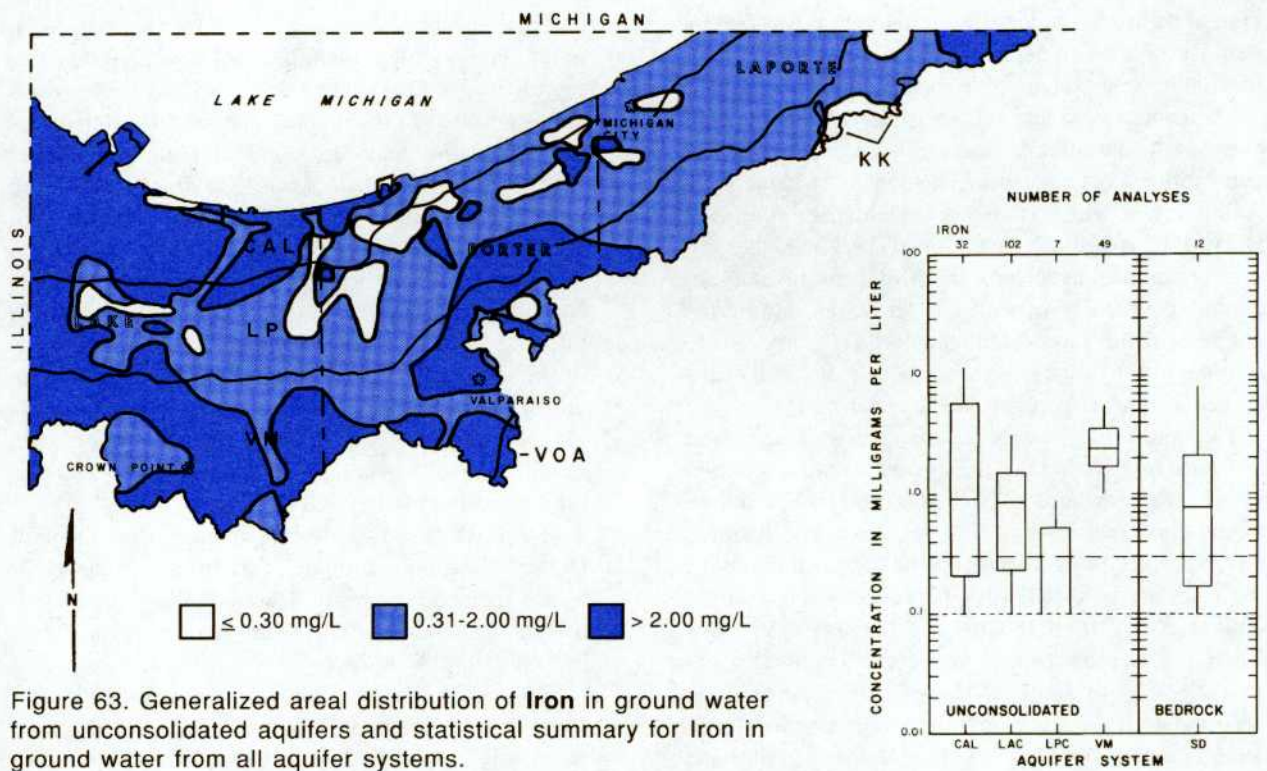


Figure 63. Generalized areal distribution of **Iron** in ground water from unconsolidated aquifers and statistical summary for Iron in ground water from all aquifer systems.

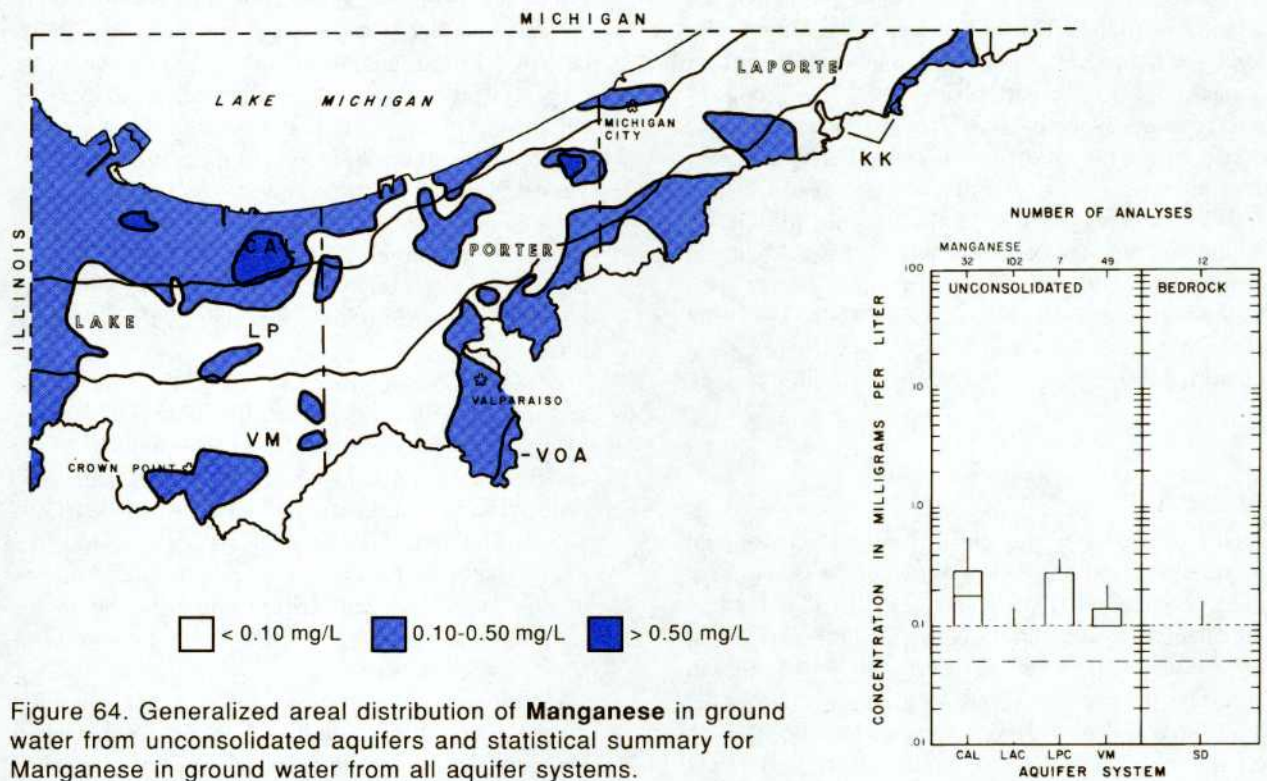


Figure 64. Generalized areal distribution of **Manganese** in ground water from unconsolidated aquifers and statistical summary for Manganese in ground water from all aquifer systems.

system. Lower iron concentrations may result from a scarcity of iron minerals in the aquifer material or metabolic reduction of iron by bacteria.

Manganese is undesirable in drinking water because even small quantities can cause objectionable taste and deposition of black oxides. The SMCL of manganese is 0.05 mg/L, which is only half the detection limit of DOW-IGS analytical techniques. Therefore, the percent of samples exceeding the SMCL in this data set cannot be readily quantified. However, all of the aquifers in the Lake Michigan Region have some samples with manganese concentrations above the detection limit (figure 64 and appendix 9).

The concentration map for manganese is displayed in figure 64. Note that the lowest contour interval indicates areas where the concentration is inferred to be below the detection limit. It is therefore, possible that ground water with manganese concentrations above the 0.05 mg/L SMCL may be encountered in areas delineated by these contours. Manganese in Lake Michigan Region ground water can originate from several different sources. Manganese oxide tends to accumulate in bog or wetland environments (Hem, 1985). In the eastern portion of the Valparaiso Moraine Aquifer system and the Calumet Aquifer system in the vicinity of Indiana Dunes National Lake Shore, relatively high manganese concentrations of 0.10 mg/L or greater appear to be partially associated with bogs or poorly-drained, organic soils. Higher manganese in the northwest portion of the Calumet Aquifer system may also reflect the influence of poorly-drained, organic soils as well as possible anthropogenic influences. Additional sources of manganese in Lake Michigan Region ground waters include manganese oxides associated with stream and lake deposits (Hem, 1985) and manganese-rich Antrim shale gravels which have been identified in the Valparaiso Moraine Aquifer system.

### Nitrate-nitrogen

Nitrate ( $\text{NO}_3$ ) is the most common contaminant found in Indiana drinking water (Indiana Department of Environmental Management, [1990]), as well as the prevalent form of naturally-occurring nitrogen in most ground waters (Freeze and Cherry, 1979). In order to delineate the possible origin of ground-water nitrate, Madison and Brunett (1984) presented a concentration criteria for determining if nitrate (as an equivalent amount of nitrogen) originates from natural or poten-

tially, anthropogenic sources; Using these criteria, nitrate levels of less than 0.2 mg/L are considered to represent natural or background levels. Concentrations ranging from 0.21 to 3.0 mg/L are considered to represent a transition between natural and human influences. Concentrations between 3.1 and 10.0 mg/L are interpreted to indicate possible human influences, such as agricultural runoff or seepage from septic tanks and livestock corrals. Above 10 mg/L, the MCL for this constituent, nitrate can cause *methemoglobinemia* in infants.

The sample detection limit for DOW-IGS samples in this study is 0.3 mg/L, so the occurrence of "background" nitrate levels, based on the criteria above, cannot be readily quantified. Fortunately, the detection limit is far below the MCL.

In addition to the nitrate data obtained from the joint DOW-IGS sampling project, data from a nitrate study by the Indiana University School of Public and Environmental Affairs (SPEA) were used for the analyses of nitrate in this study.

The median concentration of nitrate in ground water from Lake Michigan Region Aquifers can not be accurately determined, because many samples have nitrate levels below the detection limit. In the unconsolidated aquifer systems, some concentrations in excess of 3.1 mg/L are present in the data (appendix 9), possibly indicating contamination of the aquifer by septic tank leakage, nitrate fertilizers or other sources. Median nitrate concentrations in the Silurian and Devonian Bedrock Aquifer system are also below the detection limit, and the maximum concentration detected in the bedrock wells is only 0.8 mg/L. None of the ground-water samples in the DOW-IGS data set had nitrate concentrations exceeding the 10 mg/L MCL.

Aquifers and depths were not delineated in the ground-water nitrate data from the Indiana University SPEA study, and most of the data are limited to the eastern part of the Lake Michigan Region. However, concentration patterns are similar to those of the DOW-IGS data set, with most concentrations at or near 0.3 mg/L. Therefore, the majority of nitrate concentrations in the Lake Michigan Region appear to be in the transition range between natural and human-influenced levels.

Data from a private well testing program sponsored by the Farm Bureau, Soil and Water Conservation Districts, County Health Departments, Extension Service, and Resource Conservation and Development

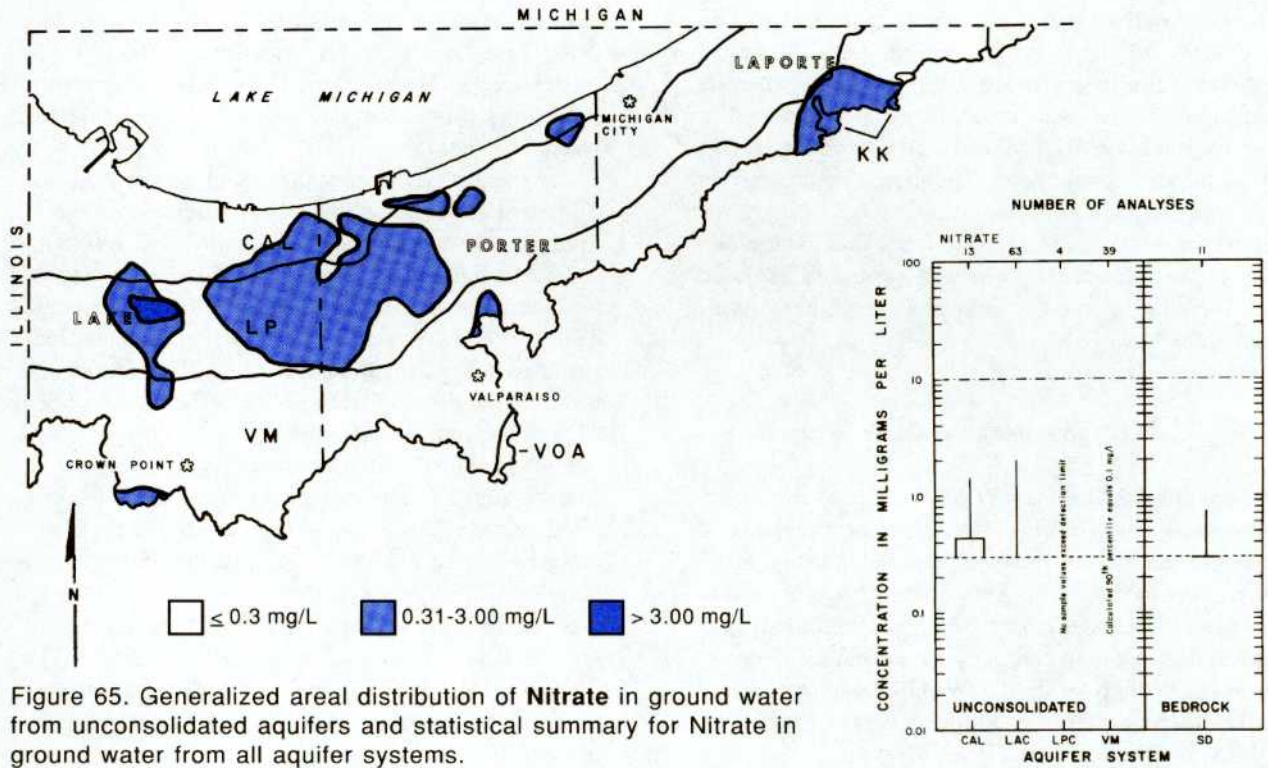


Figure 65. Generalized areal distribution of **Nitrate** in ground water from unconsolidated aquifers and statistical summary for Nitrate in ground water from all aquifer systems.

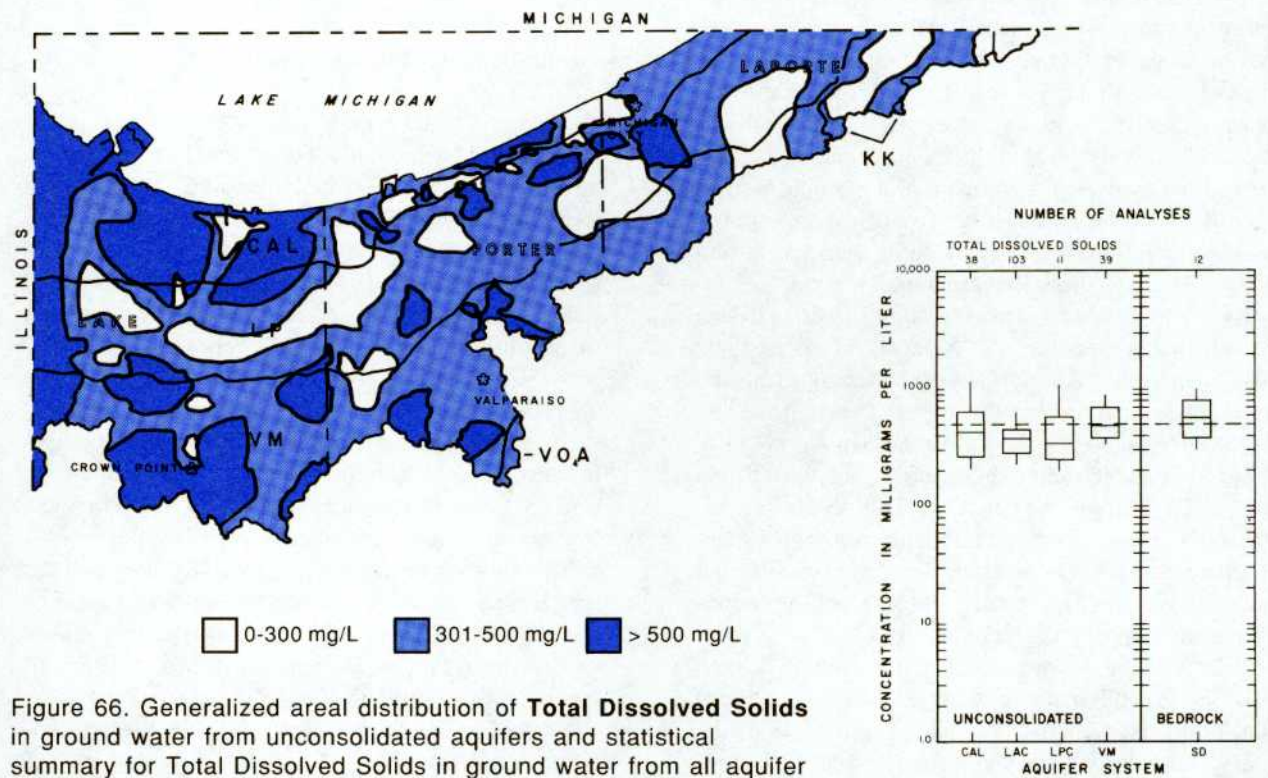


Figure 66. Generalized areal distribution of **Total Dissolved Solids** in ground water from unconsolidated aquifers and statistical summary for Total Dissolved Solids in ground water from all aquifer systems.

Districts indicate that a few nitrate concentrations in excess of 10 mg/L are present in Lake Michigan Region wells in northwest LaPorte County. Nitrate concentrations above the MCL are also detected in nearby Kankakee River Basin wells. In general, however, the data for the Lake Michigan Region seem to indicate that nitrate concentrations above 3.1 mg/L are found in a few, widely-scattered wells. Therefore, the higher concentrations are probably isolated occurrences that are not indicative of regional nitrate contamination.

### **Total dissolved solids**

Total dissolved solids (TDS), the sum of concentrations of all detected ions in solution, are a measure of the concentration of dissolved mineral constituents in water. In general, if the ground water has a high TDS concentration, the levels of the major constituents such as calcium, sodium, chloride, sulfate and bicarbonate, are usually high. Some DOW-IGS samples from all Lake Michigan Region aquifer systems exceed the SMCL of 500 mg/L for TDS.

Total dissolved solids levels in ground water are influenced by various natural and anthropogenic processes. In general, ground waters with long residence times have high TDS levels. Longer residence times result in more interaction between ground water and soluble minerals; thus, high concentrations of dissolved minerals are often found in old ground waters. High TDS levels can also result from the dissolution of very soluble minerals, such as halite or gypsum, and from anthropogenic influences on an aquifer.

Because different factors can influence TDS in ground water, the high TDS levels in some Lake Michigan Region Aquifers (figure 66) are probably the result of several distinct processes. The high median TDS concentrations in the Valparaiso Moraine Aquifer system may be a result of slow infiltration through the Valparaiso Moraine till cap. High TDS levels in some areas of the Calumet Aquifer system wells may reflect discharge from the bedrock or deeper unconsolidated deposits (Shedlock and others, 1992) or local anthropogenic impacts on the water chemistry.

Total dissolved solids can be increased on a local scale by ground-water contamination. In the western portion of the Calumet Aquifer system, some of the areas which have TDS levels greater than 500 mg/L appear to be clustered in urban areas (figure 66), and

several shallow wells (less than 50 feet deep) in this area have TDS levels exceeding 1000 mg/L (appendix 9). These elevated TDS levels may reflect local impacts of industrial and municipal activities on water chemistry.

The median TDS concentration of waters from the Silurian and Devonian Bedrock Aquifer system is 573 mg/L. In addition to exceeding the median levels of all Lake Michigan unconsolidated aquifer systems, this concentration exceeds the SMCL. The higher average TDS concentration in the Silurian and Devonian Bedrock Aquifer system probably reflects longer residence time and the dissolution of soluble evaporite minerals such as gypsum and anhydrite.

Beneath the Silurian limestones, highly mineralized, saline waters in Cambrian and Ordovician sandstones are detected. TDS levels as high as 30,000 mg/L are noted by Hartke and others (1975) in these formations. In general, TDS concentrations in these sandstones increase with greater depth and further distance from their inferred recharge areas in northern Illinois. The high TDS concentration and depth to these aquifers makes them impractical ground-water sources at the present.

### **Ground-water contamination**

A ground-water supply that, under natural conditions, would be acceptable for a variety of uses can be adversely affected by contamination from human activities. Contamination, as defined by the Indiana Department of Environmental Management [1988a], occurs when levels of contaminants are in excess of public drinking-water standards, proposed standards, or health protection guidance levels promulgated by the USEPA.

Over the past 100 years, the intensive settlement and the industrial and agricultural practices that accompany development have created ample opportunity for ground-water contamination in the Lake Michigan Region. In the Area of Concern alone (see page 99 for a discussion on Areas of Concern), there are five sites which are on the EPA's National Priorities List (NPL) of "Superfund" sites and 150 known leaking underground storage tanks (Indiana Department of Environmental Management, 1991).

Numerous potential sources of ground-water contamination exist in the Lake Michigan Region, including sanitary landfills, sewage treatment plants, indus-

trial facilities, septic and underground storage tanks, and road-salt storage facilities. Some cases of actual or potential ground-water contamination have already been identified in the Region. For example, in four of five NPL sites in the northwest portion of the Region, ground-water contamination was considered severe enough to justify treatment of the contaminated aquifers (Indiana Department of Environmental Management, 1991).

### Ground-water sampling studies

Inorganic and organic substances contaminating ground water in Indiana can include petroleum and petroleum products; metals; chlorides and salts; nitrates; pesticides; and *chlorinated, non-halogenated, or aromatic volatile organic compounds* (VOCs). Numerous cases of ground-water contamination within the Lake Michigan Region have been documented by the Indiana Department of Environmental Management (IDEM). A registry of case histories is maintained by the IDEM and provides additional details on chemical contamination.

In the early eighties, concern about ground-water quality in northwest Indiana led to development of a ground-water strategy study for Lake and Porter Counties (Indiana State Board of Health, 1983b). The purpose of the study was to collect and analyze ground-water quality information, delineate aquifer systems, and review the adequacy of Indiana's existing ground-water laws, regulations, and policies for ground-water protection.

Ground water in eight different areas in Lake and Porter Counties was sampled, including water from five areas within the Lake Michigan Region. One ground-water sampling site within the Region is located adjacent to an industrial complex near the lakeshore; the other four sites are near landfills close to the towns of Gary, Griffith, Pines, and Valparaiso. Ninety of the 155 total samples were included in the strategy document for the in-basin portion of the two counties. Ground-water samples were tested for total organic carbon (TOC), chemical oxygen demand (COD), and common inorganic constituents and physical parameters.

The sampling revealed several areas of potential or actual ground-water contamination. Of the 83 in-basin COD samples reported in the ground-water strategy document, seven contained elevated levels, ranging

from 17 to 72 mg/L. Eight of the 90 in-basin TOC samples contained more than 5 mg/L TOC; the highest level was reported to be 19.5 mg/L (Indiana State Board of Health, 1983b). No cause for the elevated levels was obvious from the chemical tests conducted, and several areas were recommended for additional study. The data from Gary and the lakeshore area showed extensive areas of actual or potential ground-water contamination. The highest chloride, COD, TOC, and barium levels reported in the document were found in water from wells near the Wheeler area (Indiana State Board of Health, 1983b).

The detection of barium concentrations exceeding 1 mg/L in several domestic water wells near Wheeler prompted a detailed area-wide investigation into the impact of a nearby landfill on ground-water quality in 1990 (Koelpin and Duncan, 1992). Evaluation of more than 130 domestic and monitoring-well samples revealed a statistically significant association between well depth and water quality. No barium concentrations in excess of the MCL were detected in water from wells less than 100 feet deep. High barium concentrations were, however, detected in samples from deep wells completed in glaciofluvial deposits just above the Antrim Shale. The Wheeler site ground-water samples were subsequently analyzed by Stiff diagram; a graphical technique which can demonstrate similarities and differences in solute chemistry among water samples (Walton, 1970; Hem, 1985). The Stiff diagram analysis revealed that water samples with high barium concentrations were chemically similar to samples from deep bedrock wells and dissimilar to wells completed in shallow unconsolidated deposits. In addition, tritium dating revealed that the barium contamination in the samples pre-dated landfill activities. Bedrock was, therefore, implicated in the study as the most probable source of barium in ground water near Wheeler (Koelpin and Duncan, 1992).

Volatile organic compounds (VOCs) have been the focus of numerous monitoring activities within recent years. VOC occurrences in ground water in Indiana have been detected through monitoring efforts and studies conducted by the USEPA, the IDEM, and Indiana University.

Since 1981, the USEPA has been conducting a survey in Indiana on the occurrence of 26 volatile organic compounds in the ground-water supplies of more than 400 community water systems each serving more than 25 persons year-round. In the Lake Michigan Region, detectable levels of at least one VOC were

found in *raw water* of four public supplies for in-basin portions of Lake, Porter, and LaPorte counties (Gregg LeMasters IDEM, personal communication, 1993). If VOC levels were above USEPA standards in both raw and *finished water*, corrective action was taken such as well abandonment, mixing of water supplies, or use of treatment systems. For other water supplies, the water utilities were advised to continue monitoring if there were detectable levels of VOCs.

Beginning in 1989, the USEPA has required communities serving more than 3300 residents to monitor their finished water supplies for 59 VOCs and other organics. In the future, results from this monitoring could provide information on the occurrence of VOCs in some ground-water supplies.

While VOCs often are associated with point-source pollution, pesticides and herbicides are more typically involved in nonpoint-source impacts on ground water. In Indiana, however, there is generally less information on pesticide and herbicide contamination than for other substances in ground water.

A major focus of a recent private well-water testing program in Indiana is to collect information on the effects of two widely-used agricultural chemicals, atrazine and alachlor, on rural water supplies. LaPorte County is the only county within the Lake Michigan Region which currently has available data from this program. In addition, nitrate levels in rural water supplies were also examined; a brief discussion of findings for LaPorte County may be found on previous pages of this section under the heading of **Nitrate-nitrogen**.

The private testing program, which is sponsored by the Farm Bureau, Soil and Water Conservation Districts, County Health departments, Resource Conservation and Development Districts, County Extension and other local entities, makes use of *immunoassay* techniques to screen for triazine and alachlor.

The results of the triazine and alachlor screening were assessed in terms of two standards; the *detection limit* (DL) and the *health advisory* (HA). Samples were categorized into one of the following four groups: 1) no triazine or alachlor detected; 2) concentrations above DL, but less than one-half HA; 3) concentrations above one-half HA, but less than HA; 4) concentrations above HA. The detection limits for triazine and alachlor for this study are reported at 0.05 micrograms per liter ( $\mu\text{g}/\text{L}$ ) or parts per billion (ppb) and 0.2  $\mu\text{g}/\text{L}$ , respectively.

The triazine immunoassay screen indicates the presence of common triazine herbicides including atrazine

(AAtrex), cyanozine (Bladex), and simazine (Princep). Atrazine is the herbicide most often found in private water supplies. Triazine is not considered by EPA to be a carcinogen (cancer-causing agent); but because of other health effects related to triazine, EPA has set a lifetime health advisory (HA) level for Atrazine in drinking water at 3.0  $\mu\text{g}/\text{L}$ .

One well in the Lake Michigan Region contained detectable levels of atrazine which were below one-half the Health Advisory level. All the wells sampled in LaPorte County that had triazine detected in them were less than 50 feet deep, and most wells were driven, not drilled.

The alachlor screen indicates the presence of alachlor (Lasso), metalachlor (Dual), or metalaxyl (Ridomil). The test for pesticides provides a relatively low-cost, highly sensitive technique to detect the presence of various groups of pesticides in water. The procedure does not indicate which specific pesticide(s) within a group is (are) present, but it will confirm the absence of pesticides within the group tested at concentrations above the method of detection limit (MDL). The immunoassays may also indicate the presence of some of the breakdown products (metabolites) of pesticides within a particular group.

Alachlor is considered to be a probable human carcinogen. EPA has set a Lifetime Health Advisory level for alachlor in drinking water at 2.0 micrograms per liter. EPA has estimated that if an individual consumes water containing alachlor at the Health Advisory level over a lifetime, there is a theoretical chance of not more than five-in-a-million of the individual developing cancer as a direct result of drinking water containing this pesticide.

Most of the wells within the Region that were sampled as part of the cooperative water well testing project had no detectable concentrations of alachlor or metabolite. One well within the Region did contain alachlor or a metabolite at detectable levels, but not in excess of the Health Advisory levels. Some ground-water samples from LaPorte County did contain alachlor or metabolite concentrations above the Health Advisory level. However, these samples originated from wells located south of the Lake Michigan Basin boundary.

Throughout the entire state, most ground waters from wells sampled as a part of this study contain no detectable amounts of alachlor. Only a small percentage of all well samples had alachlor or metabolite concentrations above the Health Advisory level. As

with triazine, most of these samples with excessive alachlor originated from wells less than 50 feet deep that were driven, not drilled. This could indicate that shallow, poorly-constructed wells are more vulnerable to pesticide contamination.

Recent ground-water quality studies in the Grand Calumet River/Indiana Harbor Canal Area of Concern (AOC) have been conducted by the United States Geological Survey. These studies were performed to characterize the general quality of ground water in the Calumet aquifer, assess the extent of aquifer contamination in the AOC, and quantify the effects of ground-water seepage on surface-water resources. Some of the information and interpretations from these studies were utilized by IDEM in developing the Stage 1 RAP for this Area of Concern (Indiana Department of Environmental Management, 1991).

Although relatively few people in northwest Indiana depend on the Calumet aquifer for drinking water, ground-water contamination is a major concern in the AOC because of the subsequent impacts it may have on local streams and wetlands (Indiana Department of Environmental Management, 1993). Computer modeling studies (Watson and Fenelon, 1988; Watson and others, 1989) determined that the Calumet aquifer often discharges ground water into the Indiana Harbor Canal, a large reach of the Grand Calumet River, Lake Michigan, the Silurian bedrock, local wetlands and municipal sewers. Ground-water discharge from the Calumet aquifer is believed to contribute a significant portion of the total pollutant load in some area streams (Indiana Department of Environmental Management, 1991; Fenelon and Watson, 1993).

Ground-water samples for chemical analysis were obtained from a network of 35 USGS wells located along the Grand Calumet River, the Indiana Harbor Canal and Lake Michigan. Fifteen wells were screened at the mid-section or near the bottom of the aquifer to increase the likelihood of intercepting dense contaminant plumes. Some of the wells were emplaced in the discharge zones of flow from suspected sources of contamination; providing information on the extent ground-water seepage could contaminate surface-water resources (Banaszak and Fenelon, 1988).

In July and August 1987, ground-water samples from the well network were collected for chemical analysis. Field analysis was used to determine temperature, alkalinity, dissolved oxygen levels, pH, and *specific conductance* of the samples. Laboratory analysis was subsequently conducted for twenty-four inorganic and

eighty-eight organic chemicals. For a complete list of all water quality variables considered in this study, see Banaszak and Fenelon (1988).

Correlations between ground-water quality and land use were interpreted from the 1987 chemistry data. Specific conductance, which is generally proportional to TDS (Hem, 1985), was found to be higher in some wells screened in steel mill slag or contaminated by petroleum products. A few wells had concentrations of mercury, arsenic, lead, chromium or fluoride which exceeded their respective MCLs (see appendix 6). All but one of these wells were located on or near land used for heavy industry (Banaszak and Fenelon, 1988).

The analysis also revealed apparently higher average concentrations of certain organic chemicals in wells around industrial land. Twenty-one of the eighty-eight organic chemicals under consideration were detected in at least one sample, but only phenols and benzene were present in enough samples to facilitate statistical comparisons of concentration between groups of wells. This comparison indicated that the median concentrations of phenols and benzenes were significantly higher in samples from wells in or near industrial areas. Benzene in ground water is often associated with two other organic compounds: toluene and xylene. Two, or all three of these chemicals were simultaneously detected in some samples from industrial areas. This was interpreted by the authors as possibly indicating multiple anthropogenic sources for these VOCs (Banaszak and Fenelon, 1988).

Apparent relations between well depth and certain chemical constituents were also detected. Ground-water temperatures were significantly higher in wells screened in the upper part of the aquifer, while barium concentrations were significantly higher in deeper wells screened in the lower part of the aquifer (Banaszak and Fenelon, 1988).

A second USGS study of ground-water quality in the AOC was recently concluded by Fenelon and Watson (1993). This study includes a more detailed analysis of water-quality and land use relationships, and an assessment of the impact ground-water discharge has on surface water resources in the AOC. Data came from additional chemical analyses, for volatile organic chemicals and cyanide, of ground-water samples gathered in 1988 from the well network used in the 1987 study. This new data was analyzed along with the data from the 1987 water-quality study (Joseph M. Fenelon, U.S. Geological Survey, personal communication, 1993).



### **Land use and ground-water quality in the Calumet Aquifer system**

The Indiana Dunes State Park and Indiana Dunes National Lakeshore (IDSP-IDNL) are two of the most popular nature preserves in the State. These parks protect some unique natural features on the Lake Michigan coast of Indiana, including sand beaches, active sand dunes, and dune ridges that mark former shorelines of ancient glacial lakes. The beaches in the IDSP-IDNL are utilized for recreational purposes, and the forests and interdunal wetlands within the parks provide habitats for various forms of wildlife.

The IDSP-IDNL parks are protected by various state and federal conservation statutes designed to minimize human impacts on the environment of designated nature preserves. However, extensive industrial and municipal development has significantly altered the environment of some areas adjacent to the IDSP-IDNL. This development has consequently created various potential sources of pollution in close proximity to the IDSP-IDNL.

One possible environmental threat to the IDSP-IDNL is ground-water pollution because most of the IDSP-IDNL area is underlain by the Calumet Aquifer system. The unconfined Calumet Aquifer is relatively susceptible to contamination, because it is composed predominately of sand which provides relatively little resistance to ground-water flow. The parks are also down-gradient from several potential contaminant sources including industrial sites, residential communities and highways. Because the Calumet Aquifer is hydraulically connected to interdunal wetlands, streams and ditches in some areas of the Region (Rosenshein and Hunn, 1968b; Arihood, 1975; Shedlock and others, 1992), ground-water pollution in these areas could eventually threaten aquatic ecosystems and wildlife.

Considering the differences in land-use practices, it appears more probable that human-induced changes in water quality of the Calumet Aquifer will be observed in water-quality data collected outside the IDSP-IDNL boundaries than in water-quality data from inside the IDSP-IDNL boundaries. To assess possible differences of ground-water quality related to land use practices inside and outside park boundaries, median values of relevant chemical constituents in ground water from Calumet Aquifer wells inside the IDSP-IDNL were compared with median values in ground water from Calumet aquifer wells outside the parks. Comparisons were made by using two separate box plots for each chemical constituent, one plot for ground water chemistry data inside the IDSP-

IDNL, and the other for ground-water chemistry data outside the park boundaries (appendix 12).

Overall, higher median values of TDS, hardness, calcium, sulfate, alkalinity, fluoride, chloride, manganese, sodium and potassium are observed in ground waters from wells outside the boundaries of the IDSP-IDNL, when compared to wells within the boundaries. Median magnesium concentrations are nearly equal in both data sets; and only iron displays a higher median concentration within the IDSP-IDNL. Differences in ground-water chemistry of the two data sets examined, therefore, may reflect differences in land-use practices outside and inside the IDSP-IDNL.

Some wells inside the boundaries of the IDSP-IDNL however, have concentrations of certain constituents that exceed recommended SMCLs. The excessive concentrations of these constituents may reflect geologic and/or human influences on ground-water chemistry.

One geologic factor that can influence the chemistry of ground water is the nature of the ground-water flow patterns. Differences in flow patterns can bring ground water into contact with different geologic material which, through processes such as mineral dissolution and cation exchange, may give the water a distinct chemical character.

Shedlock and others (1992) distinguish three separate flow systems that make up the overall ground-water flow regime in the IDSP-IDNL and surrounding area. The systems vary in lateral extent and are controlled by local and regional variations in topography and geology. The ground waters in each flow system have distinct chemical characteristics which can be used to help locate the discharge areas of the different systems. However, some mixing of waters from the three flow systems occurs in certain wetland areas (Shedlock and others, 1992).

Following the classification scheme of Toth (1963), Shedlock and others (1992) describe a local, an intermediate and a regional flow system. The local flow system receives recharge in the dune-beach complexes and discharges into interdunal wetlands and streams. The ground waters in the local flow system are often calcium and bicarbonate dominated. The intermediate ground-water flow system is recharged at the Lake Border Moraine and discharges south into the Little Calumet River and north into wetlands and streams in the IDSP-IDNL. Ground waters in the intermediate flow system are chemically dominated by calcium, magnesium and bicarbonate. The intermediate flow system is not present in the western half of the region, since the Lake Border Moraine pinches out at the surface around the Burns Harbor area.

In the 1993 study, ground-water quality was compared for five different categories of land-use: heavy industry, light industry, commercial, residential and parks. The comparison determined that ground-water samples from wells in heavy industry areas generally had the highest median concentrations of inorganic ions, while ground water from wells in residential areas and parks generally had the lowest median concentrations of inorganic ions. Concentrations of organic chemicals were generally low; only twenty-four of the eighty-eight different types of organic chemicals under consideration were detected in at least one sample. However, the set of ground-water samples from the

industrial areas had the most detections of organic compounds (Fenelon and Watson, 1993). Cyanide was detected in some samples, but no pattern to the distribution of cyanide in ground water could be determined (Joseph M. Fenelon, U.S. Geological Survey, personal communication, 1993).

Subsequent calculations indicate that ground-water seepage may account for some chemical loads in the Grand Calumet River. It is estimated from the data that ground-water discharge could account for 10 percent of the total load of ammonia, chromium, and cyanide; two to six percent of the total load of chloride, fluoride, sulfate, hardness, copper, iron and lead; and small

The regional flow system, which receives recharge in the Valparaiso Moraine south of the study area, flows down to the upper layers of Silurian-Devonian bedrock and discharges into interdunal wetlands and/or to Lake Michigan. In general, waters in the regional flow system are chemically dominated by sodium, calcium, magnesium and bicarbonate at wetland discharge areas, and by sodium, chloride, calcium and bicarbonate at areas closer to the Lake Michigan shore (Shedlock and others, 1992).

In the IDSP-IDNL, many ground-water samples containing low TDS levels are from wells screened at relatively shallow depths (less than 25 feet from the land surface) and in close proximity to the sand-dune complexes. Water samples from many of these wells are relatively dilute and have calcium and bicarbonate as their dominate ions in solution. These shallow wells seem to reflect influence of the local flow system.

The chemistry of shallow ground waters in the wetlands of the IDSP-IDNL appears to be influenced by the discharge of waters from the intermediate and regional flow systems. Ground waters from the intermediate and regional flow system mix with shallow ground waters in wetlands areas, which creates a variable hydrochemical environment (Shedlock and others, 1992). Shallow ground waters that are chemically dominated by magnesium or sodium are present in these wetland areas. Furthermore, these waters generally appear to have higher TDS levels than ground waters in the local flow system.

In addition to the nature of the ground-water flow system, another geologic factor that can affect ground-water chemistry is the amount of organic matter in an aquifer. In particular, organic matter can influence the chemistry of iron in ground water. Decaying plant debris can be a source of organic chemicals which can form complexes with iron that tend to retain iron in solution (Hem, 1960; Oborn and Hem, 1961; Hem, 1985). Furthermore, certain types of bacteria can utilize iron during metabolic processes under anaerobic conditions, which may increase the content of ferrous iron in solution (Oborn and Hem, 1961; Hem, 1985).

Organic matter in swamps and wetlands may account for the higher median iron concentration in waters from wells inside the IDSP-IDNL boundaries. Much of the IDSP-IDNL, especially between Burns Harbor and Michigan City, is wetland or marsh area. Many of the water samples with iron concentrations above the SMCL were taken from shallow USGS wells in or near the wetland areas. Therefore, although there may be numerous site-specific or process-related causes for high iron concentrations in ground water, interaction between ground water and organic matter is

probably one of the principal causes (Shedlock and others, 1992).

Although ground-water chemistry inside the IDSP-IDNL appears to be affected by many natural geologic processes, high concentrations of certain dissolved constituents in some samples may reflect human influences on ground-water chemistry. For example, iron and sulfate concentrations in excess of SMCL and elevated levels of trace elements are detected in ground water from wells near the IDSP-IDNL boundaries and down-gradient from coal fly-ash settling ponds. A previous study (Hardy, 1981) concluded that ground waters down-gradient of these ponds were relatively enriched in iron, sulfate and other constituents. It is therefore, possible that seepage from these ponds may be contributing some iron and sulfate into the ground-water flow system up-gradient of the IDSP-IDNL. Another example of potential human impact on ground-water quality in the IDSP-IDNL sited from Shedlock and others (1992) is the occurrence of some sodium-chloride-bicarbonate dominated well samples along the southern boundary of the IDSP-IDNL. These samples may be the result of deicing salt infiltration.

As previously stated, median TDS, median hardness and median concentrations of many ions are higher in ground-water samples from outside the IDSP-IDNL boundaries relative to samples from wells inside the park boundaries (appendix ). As with the ground-water quality data from inside the IDSP-IDNL, many of the high levels of chemical constituents in the developed areas may relate to natural variations in the ground-water flow regime or composition of the aquifer. However, the area outside the IDSP-IDNL includes industrialized and developed portions of the Calumet Aquifer system. Thus, the presence of higher median concentrations in the developed areas is suggestive of human-induced changes in ground-water chemistry. Anthropogenic effects would most likely be observed in the developed, western part of the Calumet Aquifer system, where sources of potential ground-water pollutants are located.

The difference in median concentrations between the two sets of wells (see appendix 12) is probably not the exclusive results of contamination in developed parts of the Calumet Aquifer. Natural variations in the geology and hydrology in the Calumet Aquifer system will cause local variations in water quality throughout the aquifer. However, the extent to which the differences in median concentrations reflect anthropogenic influences and the extent they represent natural factors cannot be quantified.

amounts of nitrate, mercury, zinc and phenol in the Grand Calumet River. Actual pollutant loads in the river due to contaminated ground water, however, may be much higher than calculated loads since the discharge of localized, but highly contaminated waters into the Grand Calumet River, was not accounted for in this study.

Additional estimates indicate that the East Branch of the Little Calumet River and Indiana Harbor Canal generally receive the greatest pollutant load from direct ground-water discharge. The Silurian bedrock and the sewer system receive intermediate loads, while Lake Michigan receives the smallest relative contam-

inant load from direct ground-water discharge (Fenelon and Watson, 1993). Contaminated ground water in the AOC, however, is still an environmental hazard to Lake Michigan because of the direct discharge of the Indiana Harbor Canal into the Lake.

### **Susceptibility of aquifers to contamination**

Since contaminants can be transmitted to the ground-water system by infiltration from the surface, the susceptibility of an aquifer system to contamination from surface sources depends, in part, on the type of

material that forms the surface layer above the aquifer. In general, sandy surficial layers can easily transmit water from the surface, but provide negligible filtering of contaminants. Clay-rich surface deposits, such as glacial till, generally have lower permeability than sand and gravel which limits the movement of contaminated water. The presence of fractures, however, can locally decrease the effectiveness of a till in protecting ground water. The different basic hydrologic properties of sands and clays make it possible to use surficial geology to estimate the potential for ground-water contamination.

Plate 2 briefly summarizes the susceptibility to contamination of the six unconsolidated aquifers in the Lake Michigan Region. The Calumet, Kankakee and Valparaiso Outwash Apron Aquifer systems are all highly susceptible to contamination from the surface, because they all generally lack surficial clay or till deposits. Susceptibility to contamination of the Valparaiso Moraine Aquifer system and Lacustrine Plain Aquifer system varies considerably with location because of variability in the thickness of overlying tills and aquifer stratigraphy.

In addition to geologic factors, the susceptibility of an aquifer to contamination also depends on local land-use practices. The particular activities occurring up-gradient from or directly above an aquifer can influence the potential for contamination and determine what types of contaminants will enter the flow system. Industrial land use, as in the northwest and Burns Harbor areas of the Region, can result in an increased risk of spills or other accidents which may contaminate ground water in the area. Another concern in the industrialized areas is the wide variety of chemicals used in, or produced by, different manufacturing processes, which could result in ground-water pollution by multiple contaminants. Agriculture, a dominant activity in the eastern and southern part of the Lake Michigan Region, may result in ground-water contamination by nitrate fertilizers, pesticides and other agricultural chemicals. Transportation is another land-use activity that may result in ground-water contamination. De-icing salts used on the extensive network of interstate and state highways in the region could contaminate ground- and surface-waters. Furthermore, other chemicals could enter the aquifer systems if accidentally spilled in transit. Despite present environmental regulations and practices, the potential for continued ground-water contamination in the Lake Michigan Region still exists because of the diverse

geological nature of the aquifer systems and the intense, varied land-use practices.

### **Protection and management of the ground-water resource**

Major ground-water management and protection activities in Indiana are administered by the IDEM, IDNR, and ISDH. An expanded cooperative effort in the form of the Indiana Inter-Agency Ground-Water Task Force involves representatives of these three agencies as well as the State Chemist, State Fire Marshal, and members of local government, labor, and the business, environmental, and agricultural communities. The Task Force was first formed in 1986 to develop a state ground-water quality protection and management strategy and is mandated by the 1989 Ground Water Protection Act (IC 13-7-26) to coordinate the implementation of this strategy. The strategy is an agenda of state action to prevent, detect, and correct contamination and depletion of ground water in Indiana (Indiana Department of Environmental Management, 1988c). The 1989 act also requires the IDEM to maintain a registry of contamination sites, operate a clearinghouse for complaints and reports of ground-water pollution, and investigate incidents of contamination that affect private supply wells.

Developing a program plan for delineating and managing wellhead protection (WHP) zones for public water supplies is one priority action designated by the State Ground-Water Strategy. The federal Safe Drinking Water Act Amendments of 1986 established the program for protection of wellhead areas for public supply systems from contamination, but requires a state to complete a program plan in order to be eligible for federal financial assistance. As part of the program development plan for wellhead protection, the IDEM identified 218 public water supply systems in Indiana as priority sites for wellhead protection. Nine of the priority sites are located in the Lake Michigan Region. The sites will be used to phase-in delineation and management of WHP Zones during program implementation (Indiana Department of Environmental Management, 1988d).

Determining the relative vulnerability of geographic areas to ground-water contamination is important to developing a management and protection program because of the broad spectrum of potential protection, monitoring, management, and regulatory activities

which need to be implemented on a state-wide basis.

Indiana's 92 counties were evaluated by the IDEM to determine the vulnerability of ground-water resources to contamination. Counties which might benefit most from earliest implementation of ground-water management activities were considered as priorities. The priority counties were determined by summing weighted factor scores for 11 criteria. The criteria include numbers of public water wells, private water wells, non-community water wells, ground-water contamination sites, hazardous material spills, underground storage tanks, hazardous waste facilities, sanitary landfills, and abandoned waste sites, as well as county population and geological susceptibility to contamination. Four of the 16 designated priority counties in Indiana lie partly within the Lake Michigan Region and include Lake, Porter, LaPorte, and St. Joseph Counties.

Numerous ground-water protection activities are in progress in the Lake Michigan Region. The U.S. Geological Survey (USGS) has been contracted by the U.S. Environmental Protection Agency (USEPA) for a 2-phase study within the EPA's Geographic Enforcement Initiative Area in the Region. The USGS study area is bounded on the north by Lake Michigan in Indiana and 80th Street in Illinois, on the south by the Little Calumet River, on the east by Mineral Springs Road in Porter County, and on the west by Crawford Avenue in Illinois.

Phase 1 of the USGS project consists of ground-water level measurement in 500 wells, including over 300 in Indiana; production of regional ground-water flow maps for the unconsolidated and bedrock aquifers; and publication of results. Phase 2 of the project includes ground-water chemistry sampling and char-

acterization of the ground-water chemistry for the area. Water-level maps have been produced and the report of results has been completed. Additional water-level measurements may be repeated in 130 wells. Ground-water sampling for phase 2 of the project was completed in the summer of 1993 and a draft report has been completed (Richard Duwelius, U.S. Geological Survey, personal communication, 1994).

Another USEPA activity within the Area of Concern is the incorporation of relevant information into a Geographic Information System (GIS). Pertinent activities include completing and digitizing topographic map revisions for the area by the USGS in 1991; digitizing historic ground-water level information; mapping man-made fill; and a contract from USEPA and IDEM to computerize water-well logs for Lake and Porter Counties by the Indiana Geological Survey (IGS).

The USEPA and IDEM have also funded a project with the Indiana Geological Survey to define ambient ground-water chemistry in Porter County. The analysis was based on samples from 30 recently-drilled water wells that have well-defined geology developed from gamma-ray log analysis. Chemical analyses of the waters include inorganics, trace metals, methane, and radon. In addition, local entities within Porter County have contracted the IGS to provide aquifer sensitivity analysis for the County.

The LaPorte County Health Department has funded the IGS to define ambient ground-water quality for the county. Similar chemical analyses to that used for Porter County will be used for this county. Twenty wells have been sampled in LaPorte County and another 10 are planned.