

Figure 42. Explanation of piper trilinear diagrams and box-and-whisker plots

## Analysis of data

Percentages of the major *cations* and *anions* in ground water were plotted on Piper trilinear diagrams for major unconsolidated and bedrock aquifer systems in the Kankakee River Basin (appendix 14). These diagrams are useful for showing differences in major-ion chemistry. Ground-water types are designated by specifically defined domains on the Piper trilinear diagram segments (figure 42a, appendix 14). Cation ground-water types include sodium and potassium, calcium, magnesium, and no dominant cation. Anion ground-water types include bicarbonate, sulfate, chloride, and no dominant anion. Cation and anion water types combined define the major-ion character of the ground water.

Box plots (figure 42b) were prepared for selected ground-water constituents. Box plots are useful for depicting descriptive statistics, showing the overall variability in constituent levels occurring in an aquifer system, and making general comparisons among aquifer systems.

The areal distributions of some major constituents were mapped according to aquifer system. The maps presented throughout the following discussion show only estimated contour lines because data are widely distributed and because the chemical composition of ground water depends on many complex factors that can change with depth and over short distances. The box on the next page discusses natural factors which affect ground-water quality.

Although the data from well-water samples in the Kankakee River Basin are treated as point values, they represent the average concentration of an unknown water volume in the aquifer. The extent of aquifer representation depends mostly on the depth of the well, hydraulic conductivity of the aquifer, and rate of pumping. For example, the chemistry of water sampled from high-capacity wells may represent average ground-water quality for a large cone of influence (Sasman and others, 1981). Water collected from deep bedrock wells can be a mixture of water from different production zones.

The chemistry of original aquifer water may be altered by contact with plumbing, residence time in a pressure tank, method of sampling, and time elapsed between sampling and laboratory analysis. Because the degree to which these factors affect original aquifer water is unknown, ground-water analyses generally typify the quality of water at the tap rather than the

### **Factors affecting ground-water chemistry**

The chemical composition of ground water varies because of many complex factors that change with aquifer depth and over geographic distances. Ground-water quality can be affected by the composition and solubility of rock materials in the soil or aquifer, water temperature, partial pressure of carbon dioxide, acid-base reactions, oxidation-reduction reactions, loss or gain of constituents as water percolates through clay layers, and mixing of ground water from adjacent strata. The extent of the effect will be determined in part by the residence time of the water within the different environments.

Rain and snow are the major sources of recharge to ground water. As precipitation infiltrates the soil, biologically-derived carbon dioxide reacts with the water to form a weak solution of carbonic acid. The reaction of oxygen with reduced iron minerals such as pyrite is an additional source of acidity in ground water. The slightly acidic water dissolved soluble rock material, thereby increasing the concentrations of chemical constituents such as calcium, magnesium, chloride, iron, and manganese. As ground water moves slowly through an aquifer, the composition of water continues to change, usually by the addition of dissolved constituents (Freeze and Cherry, 1979). Ground water in recharge areas typically has a short residence time and therefore contains lower concentrations of **dissolved solids** than water occurring deeper in the same aquifer or in shallow discharge areas.

Dissolved carbon dioxide, bicarbonate, and carbonate are the principal sources of **alkalinity**, or the capacity of solutes in water to neutralize acid. Carbonate contributors to alkalinity include atmospheric and biologically-produced carbon dioxide, carbonate minerals, and biologically-mediated sulfate reduction. Non-carbonate contributors to alkalinity include hydroxide, silicate, borate, and organic compounds. Alkalinity helps to buffer natural water so that the **pH** is not greatly altered by addition of acid. The pH of most natural ground waters in Indiana is neutral to slightly alkaline.

**Calcium** and **magnesium** are the major constituents responsible for **hardness** in water. Their presence is the result of dissolution of carbonate minerals such as calcite and dolomite.

The weathering of feldspar and clay is a source of **sodium** and **potassium** in ground water. Sodium and **chloride** are produced by the solution of halite (sodium chloride) which can occur as grains disseminated in unconsolidated and bedrock deposits.

Cation exchange is often a modifying influence of ground-water chemistry. The most important cation exchange processes are those involving sodium-calcium, sodium-magnesium, potassium-calcium, and potassium-magnesium. Cation exchanges occurring in clay-rich semi-confining layers can cause magnesium and calcium reductions which result in natural softening.

Concentrations of **sulfate**, **sulfide**, **iron**, and **manganese** depend on the geology and hydrology of the aquifer system, the amount

of dissolved oxygen, pH, minerals available for solution, the amount of organic matter, and microbial activity. In particular, the chemical behavior of sulfate and sulfide is strongly related to oxidation-reduction reactions.

Sulfate generally occurs under oxidizing conditions and can be abundant where sulfur-containing minerals are found. Mineral sources of sulfate can include pyrite, gypsum, barite, and celestite.

Sulfide is derived from reduction of sulfate when dissolved oxygen concentrations are low and *anaerobic* bacteria are present. Sulfate-reducing bacteria derive energy from oxidation of organic compounds and obtain oxygen from sulfate ions (Lehr and others, 1980). Hydrogen sulfide gas, a common reduced form of sulfide, has a distinctive rotten egg odor which can be detected in water containing only a few tenths of a milligram per liter of sulfide (Hem, 1985).

Reducing conditions which produce hydrogen sulfide typically occur in deep wells completed in carbonate and shale bedrock. Oxygen-deficient conditions are more likely to occur in deep wells than in shallow wells in Indiana because permeability of the carbonate bedrock decreases with depth, and solution features and joints become smaller and less abundant (Rosenshein and Hunn, 1968a; Bergeron, 1981; Basch and Funkhouser, 1985). Consequently, deeper portions of the bedrock are not readily flushed by ground water with high dissolved oxygen.

Oxidation-reduction reactions also constitute an important influence on concentrations of both iron and manganese. High dissolved iron concentrations can occur in ground water when pyrite is exposed to oxygenated water or when ferric oxide or hydroxide minerals are in contact with reducing substances (Hem 1985). Sources of manganese include manganese carbonate, dolomite, limestone, and weathering crusts of manganese oxide.

Sources of **fluoride** in bedrock aquifer systems include fluorite, which may be associated with Devonian limestone, and fluoroapatite, which can occur in New Albany Shale. Both rock types are found in the Kankakee River Basin. Fluorite and fluoroapatite may also be found in unconsolidated deposits as disseminated grains.

Natural concentrations of **nitrate-nitrogen** in ground water originate from the atmosphere and from living and decaying organisms. High nitrate levels can result from leachates of industrial and agricultural chemicals or decaying organic matter such as animal waste or sewage.

The chemistry of **strontium** is similar to that of calcium, but strontium is present in ground water in much lower concentrations. Natural sources of strontium in ground water include strontianite (strontium carbonate) and celestite (strontium sulfate). Naturally-occurring **barium** sources include barite (barium sulfate) and witherite (barium carbonate). Areas associated with deposits of coal, petroleum, natural gas, oil shale, black shale, and peat may also contain high levels of barium.

composition of in-situ aquifer water. Despite these limitations, results of sample analyses can provide basic information on ground-water quality characteristics of aquifer systems.

### **Assessment of ground-water quality**

Major chemical constituents of ground water in the Kankakee River Basin include calcium, magnesium,

### National drinking-water standards

National Interim Primary Drinking Water Regulations (U.S. Environmental Protection Agency, 1986a, 1986c) and National Secondary Drinking Water Regulations (U.S. Environmental Protection Agency, 1979) list concentration limits of specified inorganic and organic chemicals for the purpose of controlling amounts of contaminants in drinking water. Primary regulations list maximum contaminant levels (MCLs) for inorganic constituents considered toxic to humans if present above certain concentrations. These standards are health-related and are legally en-

forceable. Secondary maximum contaminant levels (SMCLs) are recommended concentration limits for constituents 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 systems, 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 the respective MCL or SMCL. Fluoride and nitrate are the only constituents listed which are covered by the primary regulations.

Constituent	Remarks	Constituent	Remarks
Sulfate	Concentrations greater than 250 mg/l, the secondary maximum contaminant level, in combination with ions (especially sodium and magnesium) can impart odors and a medicinal or bitter taste to water. Amounts above 600 mg/l may have a laxative effect for people unaccustomed to sulfate-rich water.	Iron	Concentrations exceeding 0.3 mg/l, the secondary maximum contaminant level, cause staining of laundry, utensils and fixtures and may impart a metallic taste to water. Concentrations above 0.5 mg/l may cause well screens to become encrusted. Large quantities stimulate the growth of iron bacteria.
Chloride	Concentrations in excess of 250 mg/l, the secondary contaminant level, in combination with high sodium may impart a salty taste. Amounts above 1000 mg/l may be physiologically unsafe. Large amounts may accelerate corrosion.	Manganese	Concentrations above 0.2 mg/l discolors food during cooking and stains laundry utensils and fixtures black. Food and water may have metallic taste at amounts above 0.5 mg/l. Amounts as low as 0.1 mg/l stimulate growth of certain bacteria. Manganese tends to precipitate at concentrations above 0.05 mg/l, the secondary maximum contaminant level, and may form a filter clogging sludge or slime.
Fluoride	Fluoride concentrations ranging from 0.7 to 1.4 mg/l help prevent tooth decay. Amounts above 2.0 mg/l, the secondary maximum contaminant level, may cause mottled teeth. Crippling skeletal defects may occur with concentrations above 4.0 mg/l, the maximum contaminant level.	Total Dissolved Solids	Water with concentrations greater than 500 mg/l, the secondary maximum contaminant level, may have a disagreeable taste. Amounts greater than 1000 mg/l may accelerate corrosion of well screens, pumps and casings and cause foaming and scaling in boilers.
Nitrate as nitrogen	Concentrations above 20 mg/l impart a bitter taste to drinking water. Concentrations greater than 10 mg/l, the maximum contaminant level, may cause infant methemoglobinemia, a disease characterized by cyanosis or a bluish coloration of the skin.		

References: Hunn and Rosenshein, 1969; Governor's Water Resource Study Commission, 1980; Lehr and others, 1980; Todd, 1980; and U.S. Environmental Protection Agency, 1986a.

sodium, potassium, bicarbonate, chloride, and sulfate (appendix 14). Less abundant components include iron, manganese, fluoride, nitrate, strontium, and barium. Additional information is on file at the Division of Water for bromide, zinc, phosphate, and silica.

About 85 percent of the analyses in the unconsolidated aquifer systems of the Kankakee River Basin can be classified as the calcium-bicarbonate ground-water type (appendix 14), which is characterized by high alkalinity, high hardness, and generally basic pH. The three most common ground-water types among the remaining 15 percent are bicarbonate, calcium, and sodium-potassium bicarbonate.

In bedrock aquifer systems, nearly all of the samples contain bicarbonate as the dominant anion (appendix 14). Nearly half of the samples have no dominant ca-

tion and most other samples are classified as either calcium bicarbonate or sodium-potassium bicarbonate ground-water types.

Where applicable, ground-water quality is assessed in the context of national primary and secondary drinking-water standards (see box on this page). General water-quality criteria for irrigation and livestock and standards for public supply are given in appendix 6.

### Alkalinity and pH

Alkalinity, or 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 Kankakee River Basin, alkalinity is due mostly to the presence of bicarbonate, which is the dominant anion in nearly all water samples from wells completed in both unconsolidated deposits and bedrock. The bicarbonate is derived primarily from the atmosphere, carbon dioxide produced in the soil zone, and the solution of carbonate minerals such as calcite and dolomite (Hem, 1985).

Alkalinity as  $\text{CaCO}_3$  generally is high in the unconsolidated aquifer systems of the Kankakee River Basin (figure 43) and typically increases with well depth. Very high alkalinity (greater than 400 mg/L) occurs only in the Valparaiso Moraine Aquifer System whereas low alkalinity (less than 200 mg/L) occurs mostly in the Eolian Sands, Kankakee, and Valparaiso Outwash Apron Aquifer Systems. The four intratill systems (Maxinkuckee Moraine, Nappanee, Iroquois Moraine, and Iroquois Basin) are similar to each other in terms of degree of alkalinity.

The high alkalinity in the morainal and intratill aquifer systems may be caused by long residence time of ground water in low-permeability till and the increased solution of carbonate minerals. Abundance of carbonate materials in the till cap may be contributing to the notably high alkalinities in the Valparaiso Moraine Aquifer System.

Low alkalinity in the Eolian Sands Aquifer System and the outwash deposits may be the result of the ground water's short residence time in the permeable sands and gravels. Low alkalinities, particularly in the Eolian Sands system, also may be explained by 1) reduced amounts of carbonate minerals in the surficial sand, 2) release of carbon dioxide from porous sands to the atmosphere, and 3) low carbon dioxide production which is due to reduced amounts of organic material.

Alkalinity is high in all bedrock systems of the basin (figure 43), and is highest in the shale-capped Silurian and Devonian carbonates. Alkalinity is lowest in the Devonian and Mississippian shales.

Alkalinity of less than 200 mg/L or greater than 400 mg/L occurs only in scattered areas in the basin. Because unconsolidated deposits often supply recharge to underlying Silurian and Devonian carbonates, alkalinity tends to be similar in the two types of systems (Rosenshein and Hunn, 1968a). In some areas underlying the Kankakee Aquifer System, however, alkalinity is higher in bedrock units than in overlying deposits and may be caused by bicarbonate production from biochemical sulfate reduction (Freeze and Cherry,

1979) or longer residence time in the bedrock units.

The pH of water, or hydrogen ion activity, is expressed on a logarithmic scale (0-14) which represents the negative base-10 log of the hydrogen ion concentration. Water is acidic when the pH is less than 7 and basic when the pH is greater than 7. Ground water in the basin is predominantly basic, but median pH values in the unconsolidated aquifer systems range from 6.9 to 7.7. Median values in bedrock aquifer systems range from 7.1 to 7.6.

### Hardness, calcium and magnesium

Hard water and soft water are relative terms because water considered hard in one region might be considered soft in another region. For discussion purposes the following classification is commonly used: soft water, 0-60 mg/L (as  $\text{CaCO}_3$ ); moderately hard water, 61-120 mg/L; hard water, 121-180 mg/L; and very hard water, more than 180 mg/L (Durfur and Becker, 1964). Hardness is a water-quality concern because hard water consumes excessive amounts of soap and detergents, forms an insoluble scum, and causes scale to encrust water heaters, boilers, and pipes, thus decreasing their capacity and heat-transfer properties.

Unconsolidated deposits in the Kankakee River Basin generally contain hard to very hard water. Very hard water is especially common in the Valparaiso Moraine Aquifer System, which has a median hardness of 406 mg/L (figure 44). Ground water having less than 180 mg/L of hardness occurs mainly in the Eolian Sands Aquifer System, but also can be found in the Kankakee, Iroquois Moraine, Valparaiso Outwash Apron, Iroquois Basin, and Iroquois Valley Aquifer Systems.

Water from bedrock units is more variable in its hardness than water from unconsolidated deposits, and more samples may be classified as soft or only moderately hard. The softest water occurs in parts of Newton County. In general, water is moderately hard in the shale-capped Silurian and Devonian carbonates and the Devonian and Mississippian shales, but very hard in the Silurian and Devonian Aquifer System and the Mississippian Aquifer System (figure 44). The hardest water occurs in southeastern Jasper County and Lake County in the Silurian and Devonian system.

Because calcium and magnesium are the major constituents responsible for hardness in water, their medians and ranges of concentrations correspond closely to degree of hardness for most aquifer systems (figures

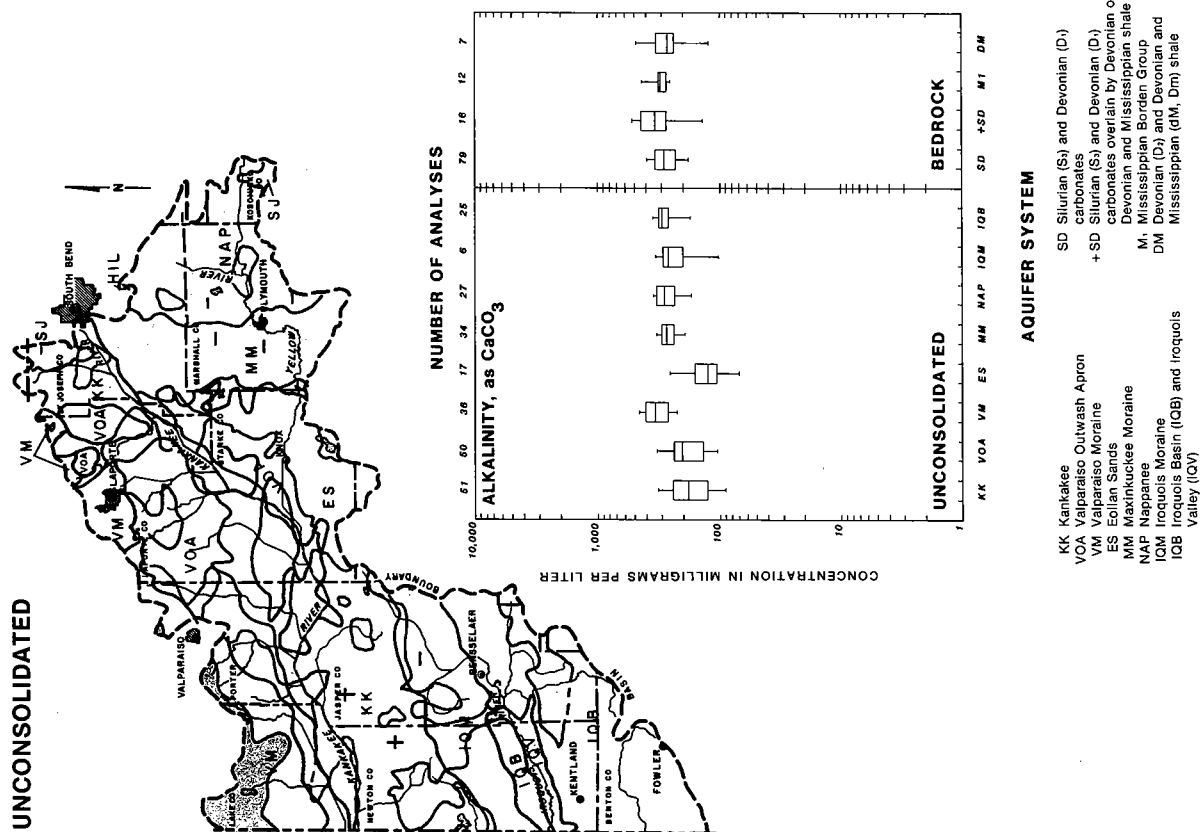
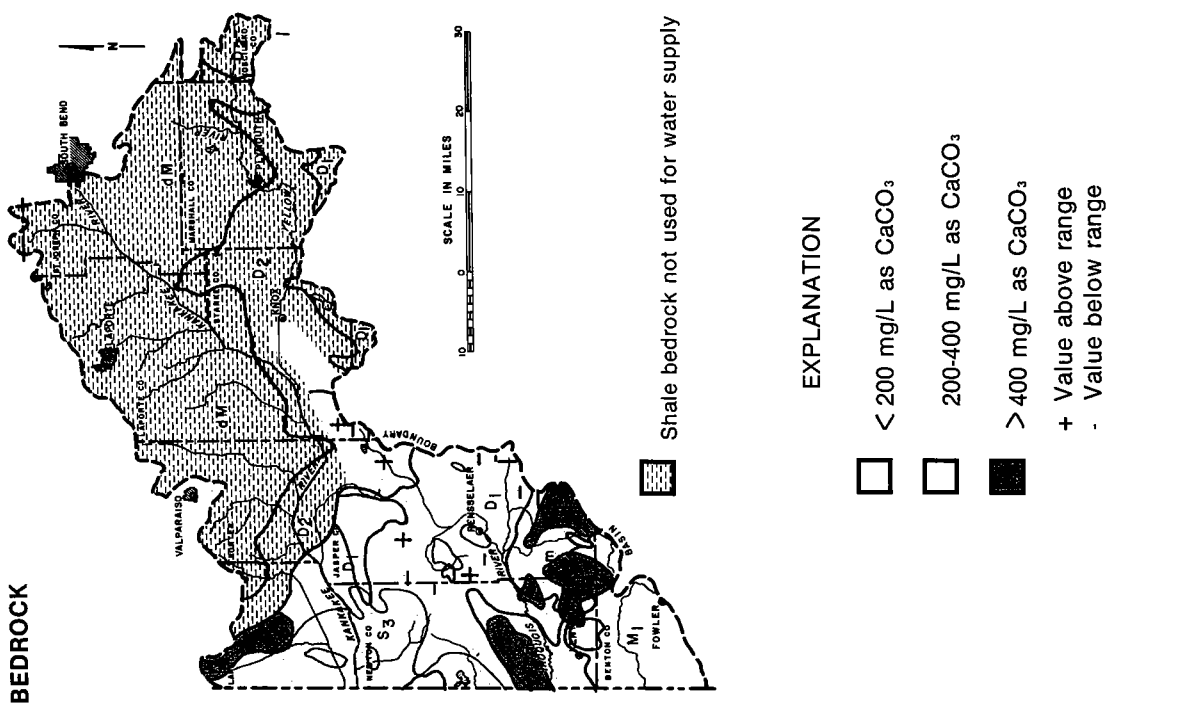


Figure 43. Generalized areal distribution and statistical summary for alkalinity

**BEDROCK**

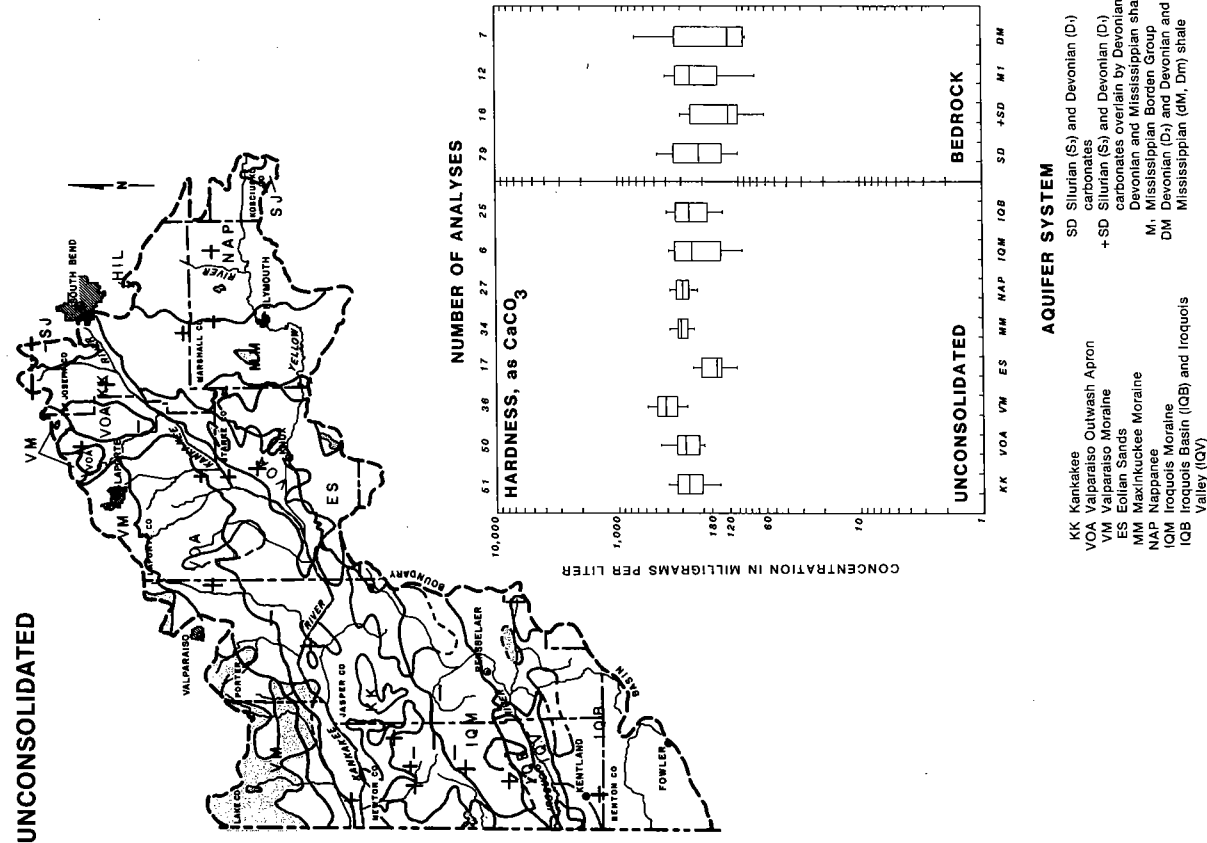
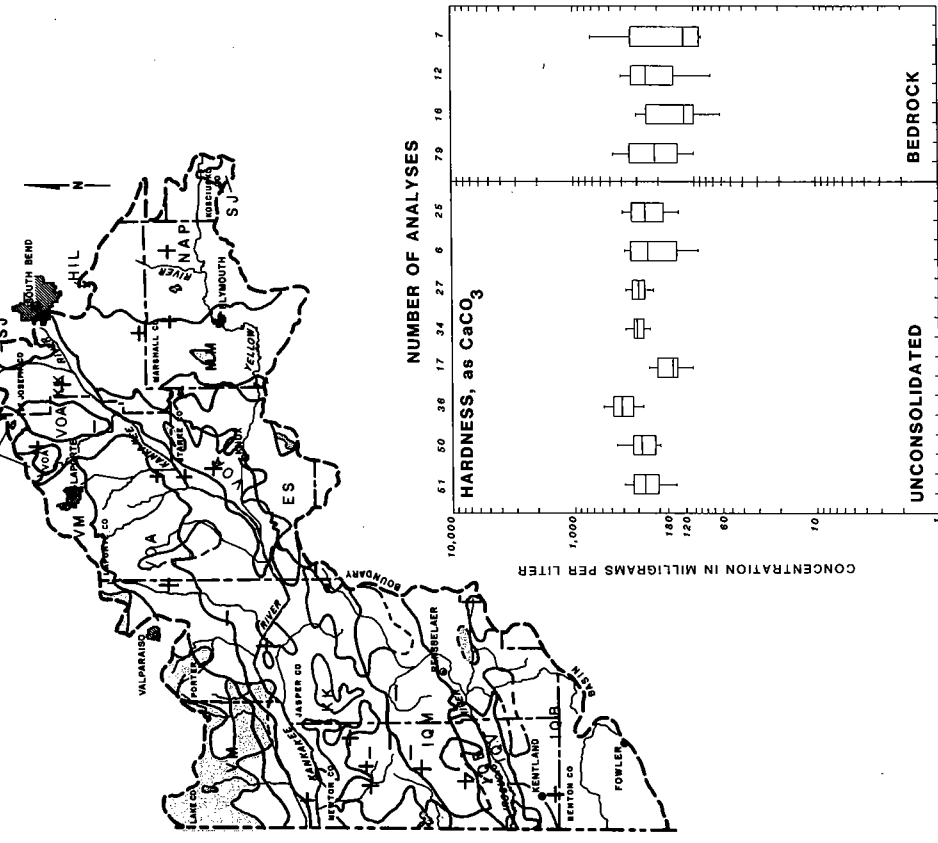


Figure 44. Generalized areal distribution and statistical summary for hardness

**UNCONSOLIDATED**



44, 45). In unconsolidated deposits, median calcium and magnesium concentrations are highest in the Valparaiso Moraine Aquifer System and lowest in the Eolian Sands Aquifer System. In bedrock, the highest concentrations are in the Mississippian Aquifer System and lowest in the shale-capped Silurian and Devonian carbonates and in the Devonian and Mississippian shales.

Low median hardness, calcium, and magnesium levels in the Eolian Sands Aquifer System may be attributed to the same factors which cause low alkalinity. Factors such as short residence time, low carbon-dioxide production, and scarcity of carbonate materials can limit solution of carbonate materials. The very hard water and high calcium and magnesium concentrations in the Valparaiso Moraine Aquifer System may be explained by abundant carbonate minerals in the till cap.

The low hardness, calcium, and magnesium levels in bedrock aquifers is probably caused by cation-exchange processes occurring in the semi-confining clay, till, and shale beds overlying the carbonate rocks. Because recharge water from the glacial material is saturated with calcium and magnesium, little dissolution of carbonate materials occurs in the bedrock (Rosenshein and Hunn, 1968a).

### Chloride, sodium and potassium

Chloride concentrations vary widely in the unconsolidated deposits, as shown by the large percentile ranges in figure 45. The lowest chloride concentrations (generally less than 10 mg/L) are found mainly in the Nappanee, Maxinkuckee Moraine, Eolian Sands, Iroquois Moraine, and Iroquois Basin Aquifer Systems. High chloride levels (between 100 and 250 mg/L) occur locally, but concentrations are less than the secondary maximum contaminant level (SMCL) of 250 mg/L in all water samples from unconsolidated deposits.

In general, chloride concentrations decrease with depth in each unconsolidated aquifer system. Median chloride concentrations are greater in water from wells less than 50 feet deep than in water from wells greater than 100 feet deep. Two wells having high chloride concentrations also contain elevated sodium concentrations. Because both wells are shallow, the high sodium and chloride concentrations may be due to surface contamination.

Bedrock systems also have wide variability in chloride levels, but all median concentrations are less than 20 mg/L (figure 45). Locally high chloride levels (ranging from 88 to 240 mg/L) can be found in three of the bedrock systems. Chloride concentrations in two wells, one each in the Silurian and Devonian System and the shale-capped Silurian and Devonian carbonates, exceed the SMCL of 250 mg/L.

Sodium levels are moderately variable in unconsolidated aquifer systems. Concentrations are highest in the Iroquois Moraine and Iroquois Basin Aquifer Systems, where at least half of the samples in each system have sodium levels exceeding 20 mg/L. Sodium levels in most samples from the other unconsolidated systems are less than 20 mg/L.

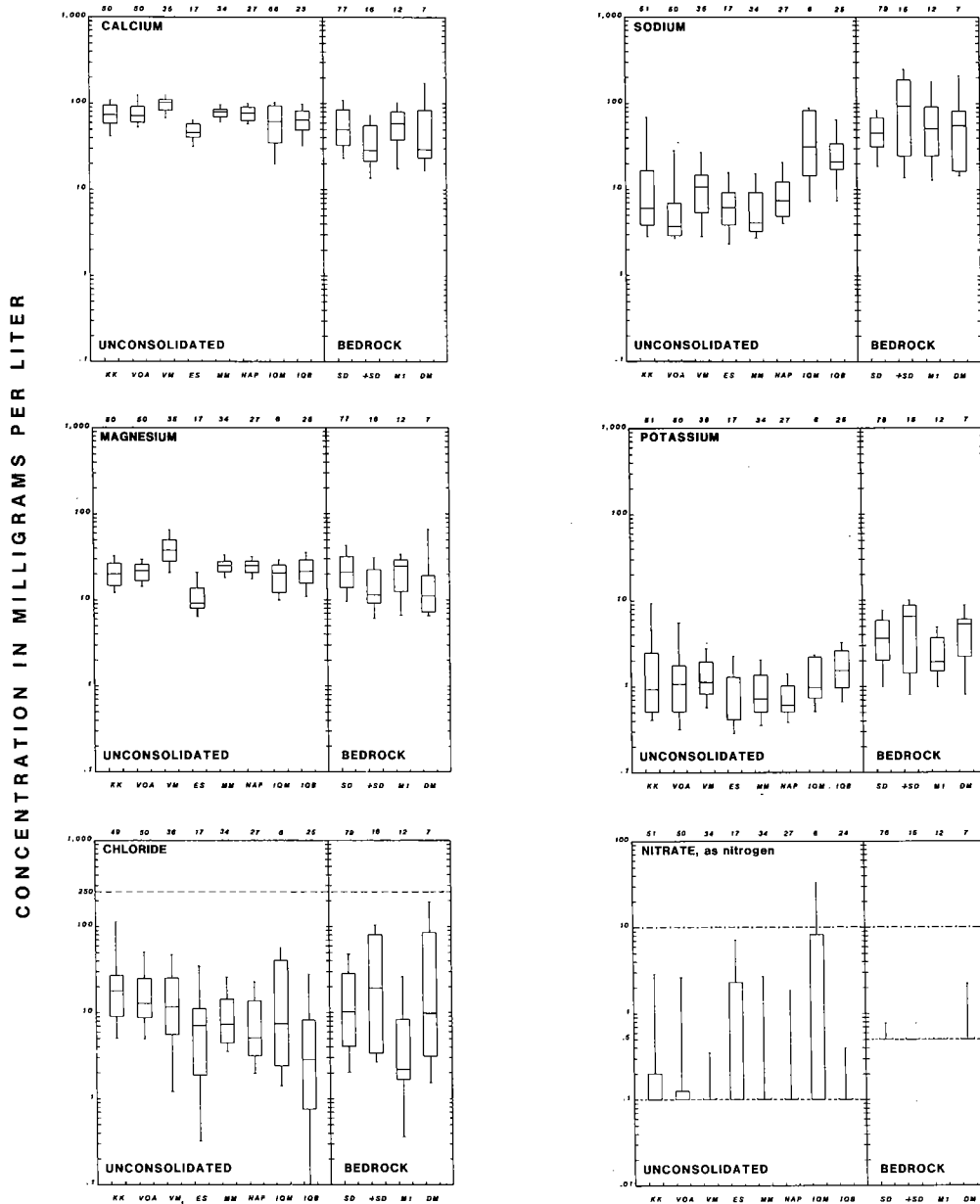
Median sodium levels in bedrock systems generally are several times higher than median levels in overlying unconsolidated systems, and range from nearly 50 mg/L to nearly 100 mg/L (figure 45). Seven bedrock wells containing high sodium concentrations (ranging from 90 mg/L to 695 mg/L) also have elevated chloride levels.

Median potassium levels in all unconsolidated systems are less than 2 mg/L (figure 45). The Eolian Sands Aquifer System has the lowest median potassium concentration (0.4 mg/L), but potassium concentrations also are low in other parts of the upper basin, including the Maxinkuckee Moraine and Nappanee Aquifer Systems. In the Iroquois Basin and Iroquois Moraine Aquifer Systems, the moderately high sodium and potassium levels may reflect natural softening.

Like sodium, median potassium levels are noticeably higher in bedrock systems than in unconsolidated deposits (figure 45). Conversely, calcium and magnesium are generally higher in the unconsolidated deposits than in bedrock units, except in the Mississippian Borden Group. These patterns probably are the result of natural softening caused by cation exchange of sodium-calcium, sodium-magnesium, potassium-calcium, and potassium-magnesium in shale, clay, and till overlying the bedrock.

An example of natural softening occurs in the Silurian and Devonian Aquifer System in Lake County near Lowell. In this area water is softer, calcium and magnesium concentrations are much lower, and sodium and potassium concentrations are much higher in the bedrock units than in water from the overlying unconsolidated aquifer systems. High-capacity pumping may be increasing the recharge of naturally softened water from overlying clays. Sources of chloride, sodium, and

NUMBER OF ANALYSES



AQUIFER SYSTEMS

- |  |   |
|--|---|
| KK Kankakee  | SD Silurian (S <sub>1</sub> ) and Devonian (D <sub>1</sub> ) carbonates   |
| VOA Valparaiso Outwash Apron                       | +SD Silurian (S <sub>1</sub> ) and Devonian (D <sub>1</sub> ) carbonates overlain by Devonian or Devonian and Mississippian shale |
| VM Valparaiso Moraine                              | M <sub>1</sub> Mississippian Borden Group   |
| ES Eolian Sands                                    | DM Devonian (D <sub>2</sub> ) and Devonian and Mississippian (DM, Dm) shale   |
| MM Maxinkuckee Moraine                             |   |
| NAP Nappanee                                       |   |
| IQM Iroquois Moraine                               |   |
| IQB Iroquois Basin (IQB) and Iroquois Valley (IQV) |   |

Figure 45. Statistical summaries for selected ground-water quality constituents



potassium and the modifying influence of cation exchange were discussed in the previous section.

### Sulfate and sulfide

Ground water in the Kankakee River Basin contains sulfur in the oxidized form of sulfate and the reduced form of sulfide. Sulfate concentrations are typically highest in unconsolidated systems and upper portions of the Silurian and Devonian carbonates where oxidizing conditions result from active flushing of ground water. Sulfide is found more commonly in deeper bedrock wells where reducing conditions are most likely to occur.

DOW-IGS sampling in 1986 included field testing for sulfide occurrence in the Kankakee River Basin. During subsequent data analysis, however, it was discovered that a procedural error made during field measurements had invalidated the results. Analyses for the determination of sulfate concentrations were not affected by the erroneous field measurements.

Sulfate concentrations are moderately to highly variable in four of the unconsolidated systems in the Kankakee River Basin, as seen by the large percentile ranges in figure 46. In the Kankakee, Valparaiso Moraine, and Valparaiso Outwash Apron Aquifer Systems, sulfate concentrations are less variable and generally higher than in the other unconsolidated deposits, but very few samples contain elevated sulfate levels (more than 100 mg/L). The SMCL of 250 mg/L is exceeded in water from only one well. Possible sources of sulfate in these systems include organic decay in poorly-drained soils (Rosenshein and Hunn, 1968a, 1968b) and broken crystals of pyrite and shale fragments, especially in the Valparaiso Moraine. High sulfate in the Valparaiso Moraine also may be due to slow percolation of the ground water and increased contact with the till (Hartke and others, 1975). *Gypsiferous* material has been known to originate from Devonian bedrock and may influence sulfate chemistry locally.

In unconsolidated systems sulfate concentrations generally decrease with depth. Water from wells less than 50 feet deep typically has higher sulfate concentrations than water from wells greater than 100 feet deep (appendix 12). The higher sulfate concentrations in shallow wells may be due to greater prevalence of oxidizing conditions.

Sulfate occurrence is highly variable in bedrock systems, especially in the shale-capped Silurian and Devonian carbonates and Devonian and Mississippian shales. These two systems generally contain the lowest sulfate levels, as shown by the low median values in figure 46. Although a few samples contain more than 100 mg/L sulfate, mainly in the Silurian and Devonian system, the SMCL is exceeded in only two samples. Sources of sulfate in Devonian carbonates (figure 46) may include trace pyrite and shale beds, which have been found in a quarry near Rensselaer (GeoTrans, Inc., 1983). Reduction of sulfate to sulfide may be the reason for low sulfate levels in some areas of the bedrock.

Hydrogen sulfide gas is known to occur in detectable levels in portions of the basin, especially in wells completed in Silurian and Devonian carbonates. Drillers often note on water-well records the occurrence of "sulfur water". This observation usually indicates the presence of hydrogen sulfide gas in the well water.

Well-record data in Jasper, Newton, and Lake Counties indicate occurrence of hydrogen sulfide odor in about 25 percent of bedrock wells (Rosenshein, 1961; Rosenshein and Hunn, 1964c, 1964d). Hydrogen sulfide occurrence was geographically widespread, but more common in wells deeper than 75 feet. Hydrogen sulfide was rarely reported for wells completed in unconsolidated deposits.

Occurrence of hydrogen sulfide gas may be under-reported because this type of information is reported only on a voluntary basis on water-well records. The gas, or conditions favorable for gas production, can still be present even when the odor is not detected. Moreover, hydrogen sulfide may occur more frequently in unconsolidated deposits than is reported. For example, a 100-foot test well recently drilled near Kingsbury in the Valparaiso Outwash Apron Aquifer System contained water with a detectable sulfide odor.

The vertical distribution of hydrogen sulfide gas in aquifer systems in the Kankakee River Basin has not yet been completely documented, although IDNR investigators have noticed a general trend of increasing hydrogen sulfide with well depth in the Silurian and Devonian carbonates in Jasper and Newton Counties (Basch and Funkhouser, 1985). Determining the lateral and vertical movement of hydrogen sulfide in response to changing aquifer conditions requires further research. The response of hydrogen sulfide to changing chemical conditions, such as the length of time it

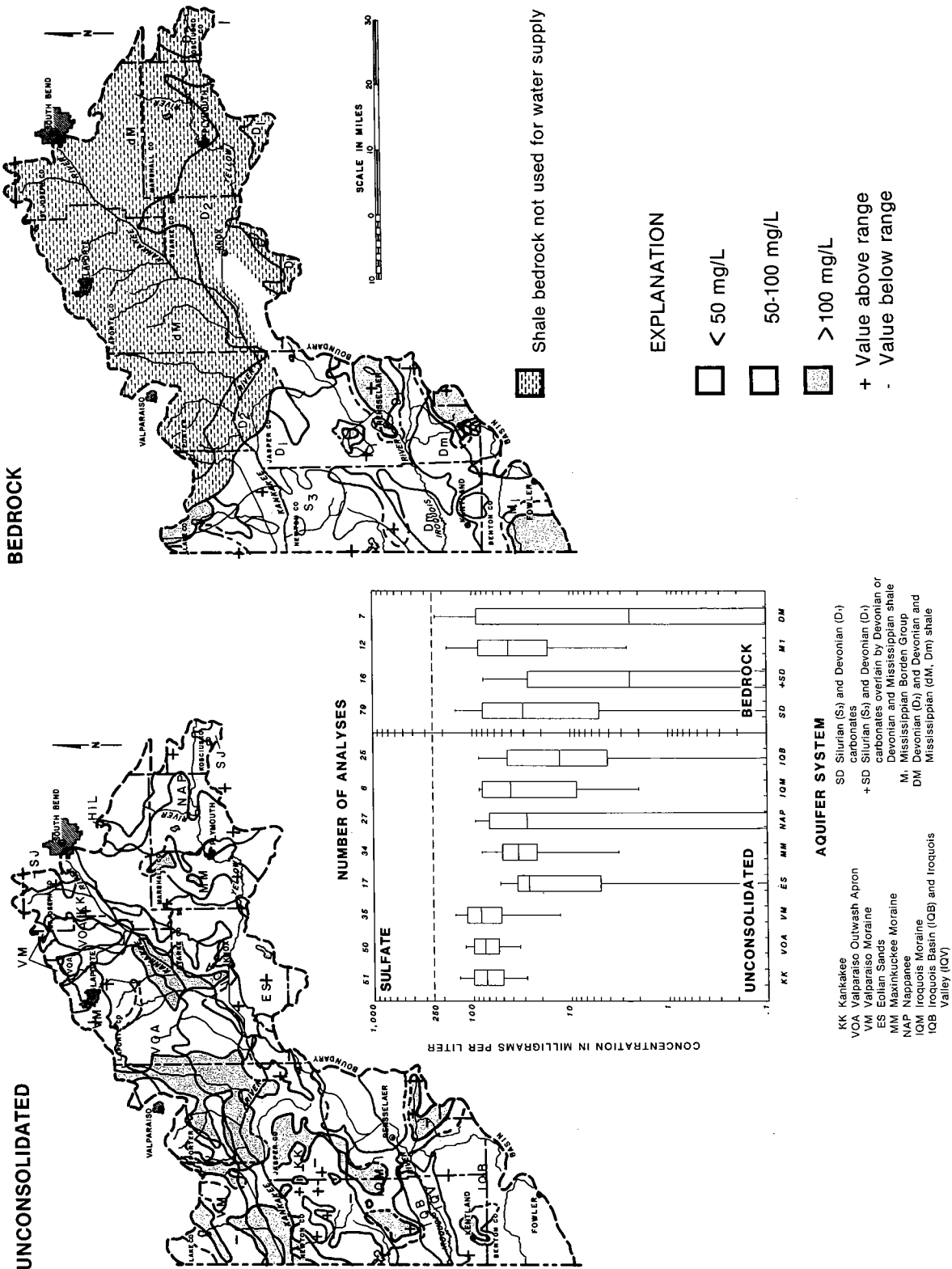


Figure 46. Generalized areal distribution and statistical summary for sulfate

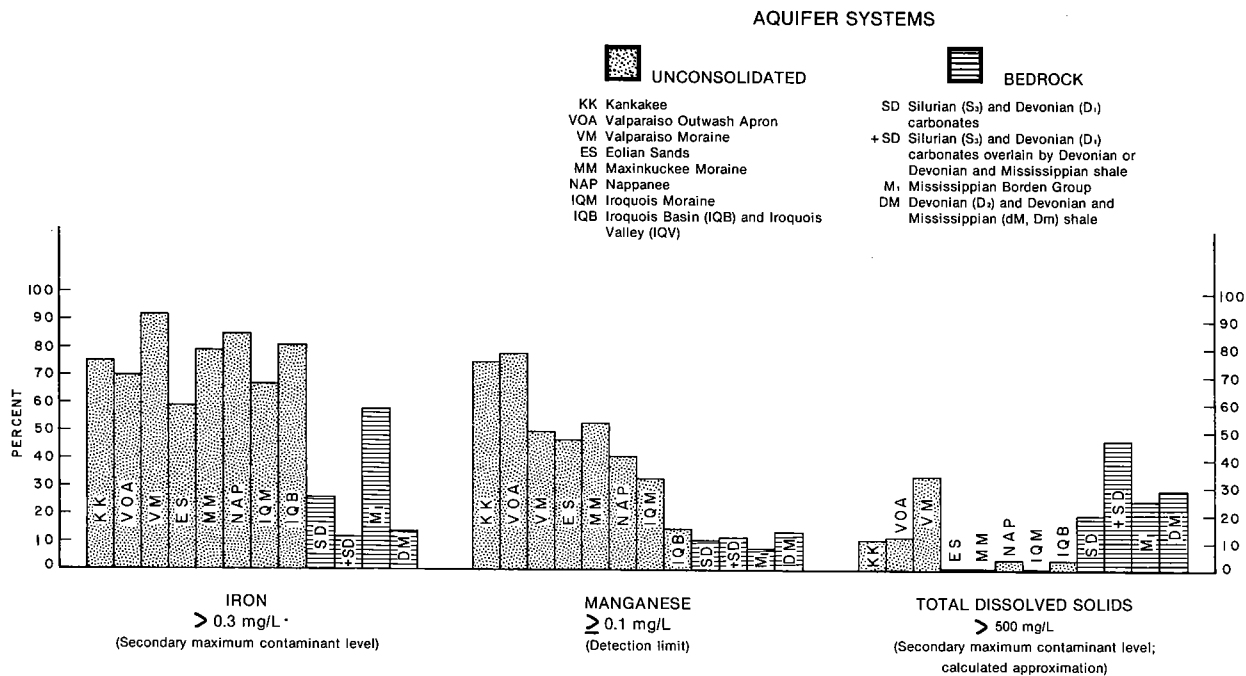


Figure 47. Percent of ground-water samples exceeding selected concentration limits

takes hydrogen sulfide to alter to sulfate when brought into an oxidizing aquifer, has yet to be fully quantified.

### Iron and manganese

Iron concentrations commonly exceed the SMCL of 0.3 mg/L in unconsolidated aquifer systems (figures 47 and 48). Median concentrations range from 0.4 mg/L in the Eolian Sands Aquifer System to 2.2 mg/L in the Valparaiso Moraine Aquifer System.

Oxidation of pyrite may produce high iron concentrations in the Kankakee, Valparaiso Moraine, and Valparaiso Outwash Apron Aquifer Systems. The occurrence of high sulfate concentrations in many samples containing high iron concentrations is one indication that pyrite may be a source of dissolved iron.

In the Valparaiso Moraine, Eolian Sands, Nappanee, and Maxinkuckee Moraine Aquifer Systems, iron concentrations often are higher in deep wells than in shallow wells. Reducing conditions in deep, confined aquifers may have increased the solubility of ferric hydroxide minerals, thus producing dissolved iron (Hem, 1985). Several other sources of iron, however, may be present in a single aquifer system.

The SMCL for iron is less commonly exceeded in bedrock systems than in unconsolidated deposits (figures 47 and 48). Although more than half of all samples in the Mississippian Borden Group have iron concentrations exceeding the SMCL, median iron concentrations in the other three bedrock systems are less than the detection limit of 0.1 mg/L. Iron concentrations, however, can be locally high, as indicated by the 90th percentiles in figure 48. High iron concentrations are known to occur locally in the Silurian and Devonian carbonates in southern Lake County (Hartke and others, 1975).

Low iron concentrations in the bedrock systems may be explained by precipitation of iron minerals from activity of reducing bacteria (Hem, 1985) or by the loss of iron from cation-exchange processes occurring in the semiconfining clay, till or shale which overlies bedrock (Rosenshein and Hunn, 1968a).

Manganese typically is less abundant than iron in natural waters (Hem, 1985) and rarely exceeds 1.0 mg/L in the Kankakee River Basin. Manganese has a low SMCL (0.05 mg/L) because even in small quantities this constituent can cause objectionable taste and deposition of black oxides. Because the analytical detection limit of 0.1 mg/L is twice the SMCL, the

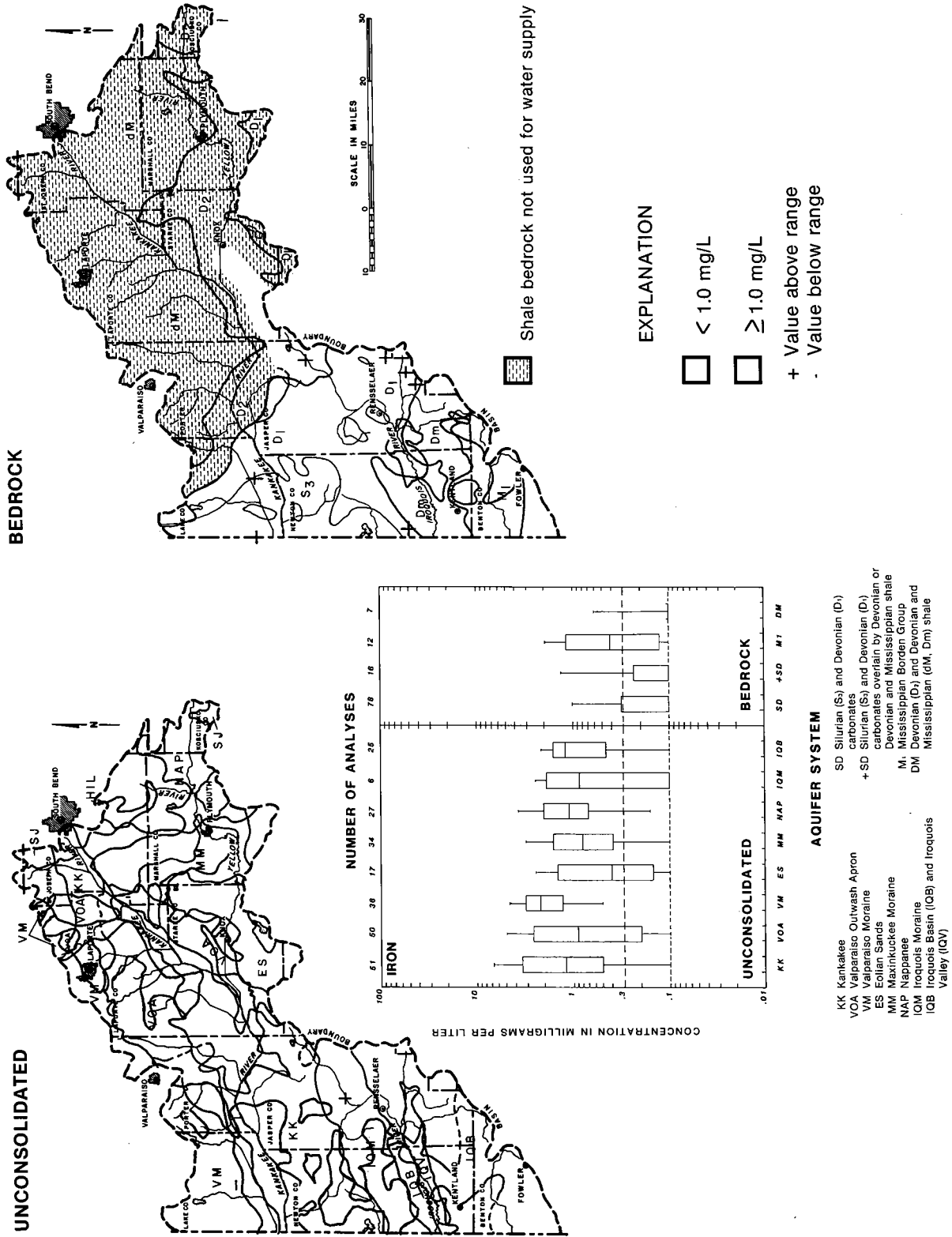


Figure 48. Generalized areal distribution and statistical summary for iron

percentage of samples exceeding the standard cannot be quantified for DOW-IGS samples. In some unconsolidated systems, exceedance of the detection limit and therefore the SMCL is common, especially in the Kankakee and Valparaiso Outwash Apron Aquifer Systems (figure 47). Manganese concentrations greater than 0.1 mg/L are less common in the Iroquois Basin, Iroquois Moraine, and Nappanee Aquifer Systems.

Manganese concentrations are generally lower in bedrock systems than in unconsolidated systems. Less than 15 percent of samples in any bedrock system contain manganese levels greater than 0.1 mg/L and all median values are below the detection limit.

### Fluoride

Fluoride levels in unconsolidated systems of the Kankakee River Basin are generally less than 1.0 mg/L, and in DOW-IGS samples of 1986 there are no exceedances of either the SMCL (2.0 mg/L) or the MCL (4.0 mg/L). The highest fluoride levels (generally between 0.5 mg/L and 1.0 mg/L) occur in the Iroquois Basin, Iroquois Moraine, and the Nappanee Aquifer Systems.

The bedrock systems generally have higher fluoride concentrations than do most of the unconsolidated systems, and portions of all bedrock units contain fluoride levels greater than 0.5 mg/L. Samples from six bedrock wells (four in the Silurian and Devonian System and two in the shale-capped Silurian and Devonian carbonates) contain fluoride concentrations above the SMCL. Groundwater from two of the four Silurian and Devonian wells also exceed the MCL.

Areas of high fluoride concentrations in the bedrock tend to coincide with areas of low hardness and calcium (figures 45 and 49). This relationship of fluoride, calcium, and hardness may be due to processes affecting the solubility of fluorite and other sources of calcium (Hem, 1985).

High fluoride levels and reduced water hardness occur along the Indiana-Illinois state line in Newton County. In Lake County, fluoride concentrations increase and calcium levels and hardness decrease toward the pumping center for Lowell's municipal water supply. To achieve the MCL for fluoride in drinking water, the municipality of Lowell mixes ground water from several sources (A. Viere, Indiana Department of Environmental Management, personal communication, 1989).

### Nitrate-nitrogen

Nitrate-nitrogen data from a study by Indiana University (1985) and the joint DOW-IGS basin assessment are evaluated in the context of concentration ranges as defined by Madison and Brunett (1984). These ranges reflect background levels and varying degrees of human influence. The concentration categories include 1) less than 0.20 mg/L, which represents natural, or background levels; 2) 0.21 to 3.0 mg/L, which represents concentrations considered to be transitional between natural levels and those due to human influence; 3) 3.1 mg/L to 10.0 mg/L, which indicates human activity such as the presence of leachates of industrial and agricultural chemicals or decaying organic matter such as animal waste or sewage; and 4) concentrations exceeding the MCL of 10 mg/L, the level associated with *methemoglobinemia* in infants.

Because analytical detection limits vary among laboratories it was difficult to evaluate the occurrence of background concentrations using data from several agencies. For this report, the detection limit of 0.30 mg/L was selected to represent near-background levels.

In most areas of the basin, nitrate concentrations are at or below the near-background level of 0.30 mg/L in both unconsolidated and bedrock systems. Of all 733 samples in the DOW-IGS and Indiana University data sets combined, more than three-fourths of the samples contain nitrate levels less than 0.30 mg/L. Median nitrate concentrations in DOW-IGS samples from unconsolidated systems are less than 0.02 mg/L, (figure 50) and median concentrations from bedrock aquifers are less than 0.5 mg/L.

Nearly 20 percent (140 wells) of all DOW-IGS and Indiana University samples show elevated nitrate levels, but most of these analyses (98 wells) are in the range considered as transitional between near-background levels and human influence (0.31 mg/L to 3.0 mg/L). DOW-IGS data reveal that transitional nitrate levels in bedrock units are found mostly in the Silurian and Devonian Aquifer System but can occur in almost all unconsolidated deposits.

About 3 percent (24 wells) of the analyses show nitrate levels between 3.0 mg/L and 10.0 mg/L. According to DOW-IGS data, five of 10 unconsolidated wells are located in the Kankakee Aquifer System, which has been designated as susceptible to contamination (Indiana Department of Environmental Management, [1988]).

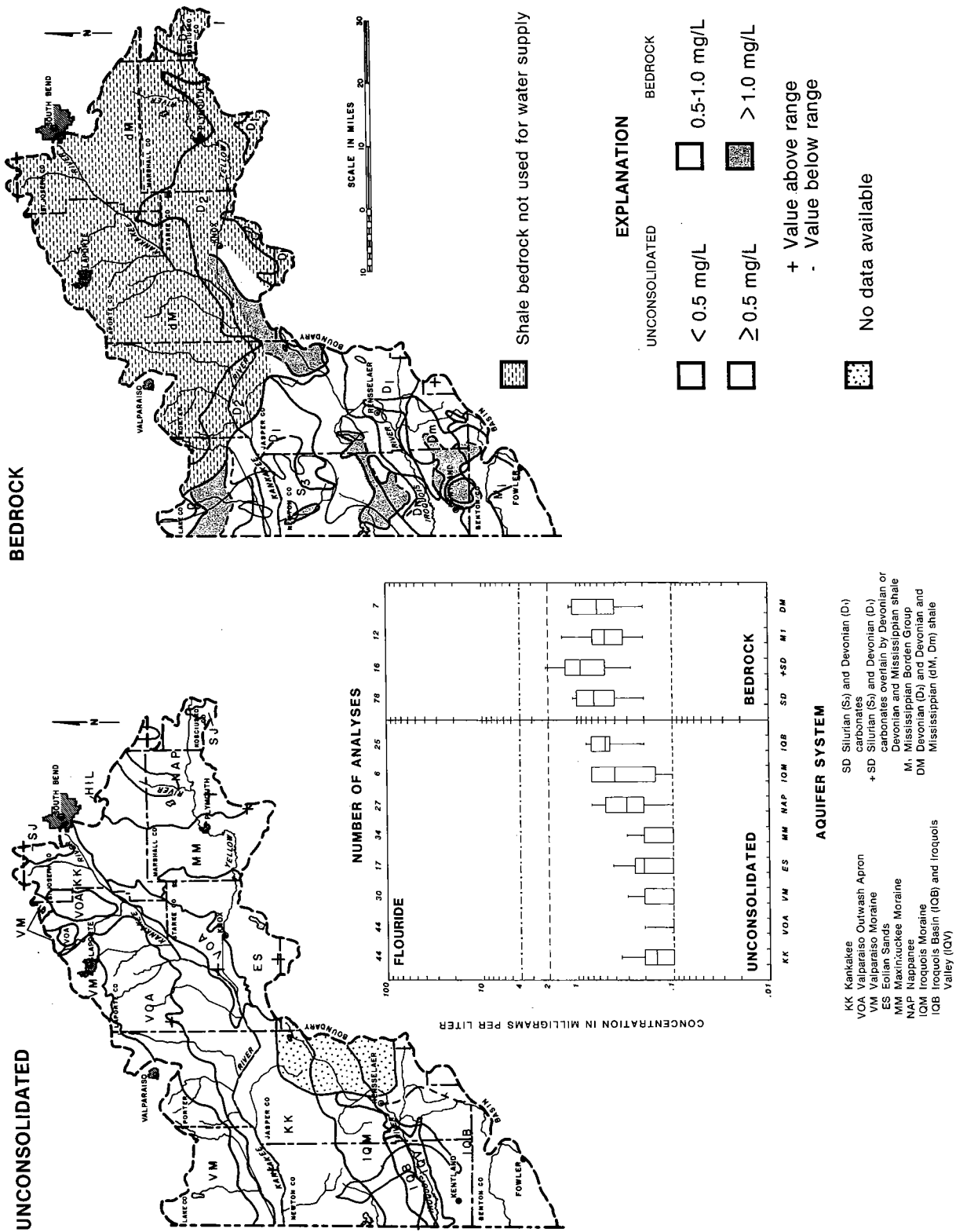


Figure 49. Generalized areal distribution and statistical summary for fluoride

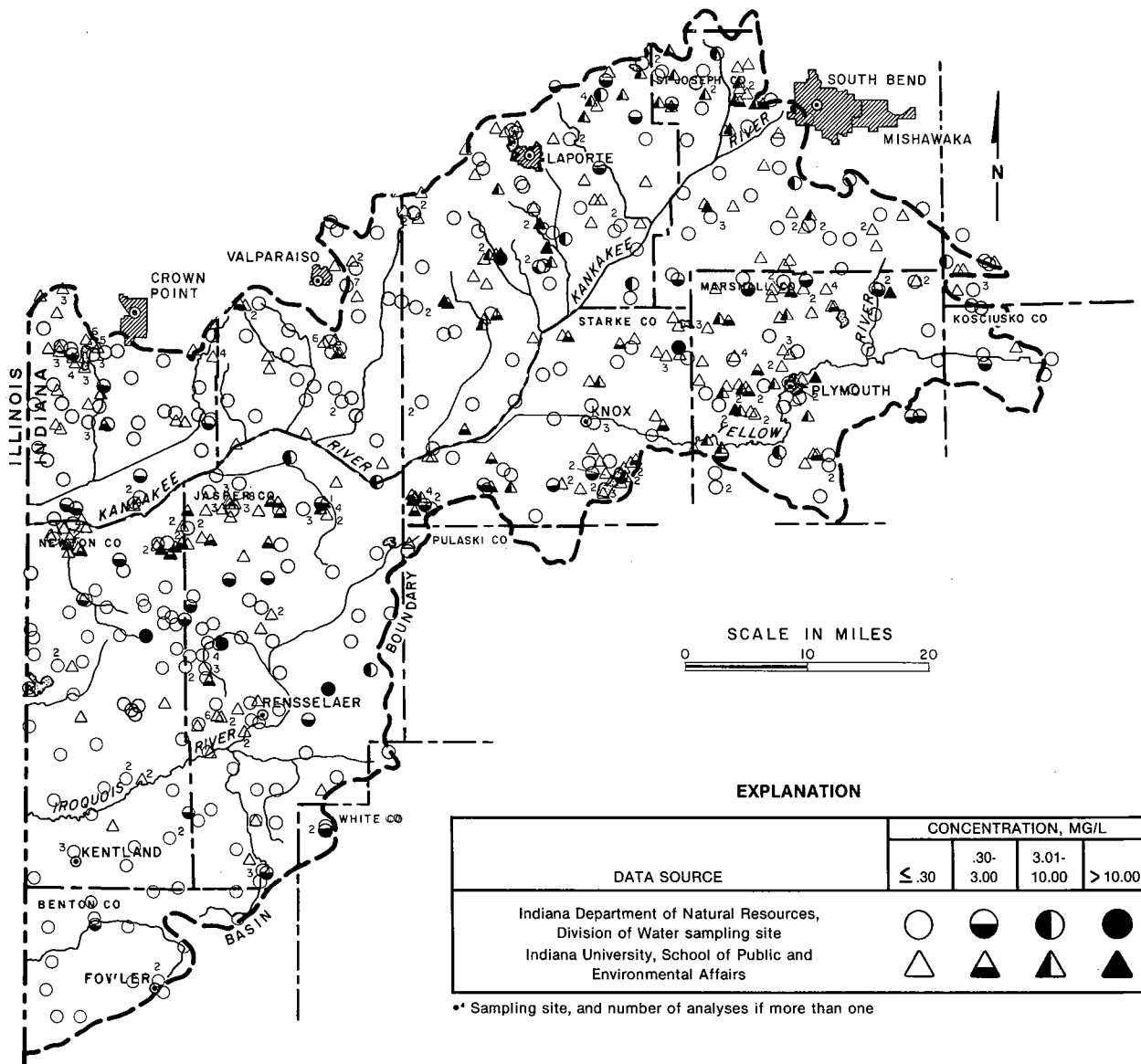


Figure 50. Distribution of nitrate-nitrogen concentrations for wells sampled in bedrock and unconsolidated deposits

About 2 percent (18 wells) of all DOW-IGS and Indiana University analyses show nitrate levels above the MCL of 10 mg/L. According to DOW-IGS data, MCL exceedances occurred in water from five wells, one each in the Kankakee, Valparaiso Outwash Apron, Eolian Sands, and Iroquois Moraine Aquifer Systems and the Silurian and Devonian System (figure 50).

### Strontium and barium

Strontium, one of the less common alkaline-earth metals, rarely exceeds 1.0 mg/L in ground water of the Kankakee River Basin. In unconsolidated deposits, median strontium concentrations are at or near the detection limit of 0.1 mg/L except for the Iroquois

Moraine and Iroquois Basin Aquifer Systems, where the median concentration is 0.7 mg/L. In bedrock units, strontium is generally slightly higher than in unconsolidated systems. All median levels are above the detection limit, and range from 0.4 mg/L to 0.7 mg/L.

Barium is a minor ground-water constituent in the Kankakee River Basin and generally is present in much lower concentrations than strontium. For both unconsolidated and bedrock systems, median levels are at or below the detection limit of 0.1 mg/L. In bedrock systems, barium levels can be locally high, but exceed the MCL of 1.0 mg/L in only two samples.

### Total dissolved solids

Total dissolved solids (TDS), a measure of the concentration of dissolved mineral constituents in water, typically are present in unconsolidated systems in concentrations less than 700 mg/L. The lowest TDS concentrations are found primarily in the Eolian Sands Aquifer System (figure 51), but low TDS levels also occur locally in other unconsolidated systems. There are no exceedances of the 500 mg/L SMCL standard in the Eolian Sands, Maxinkuckee Moraine, and Iroquois Moraine Aquifer Systems; however, concentrations exceeding 500 mg/L can be found occasionally in other unconsolidated deposits (figure 47). In the Valparaiso Moraine Aquifer System, the most highly mineralized of all the unconsolidated deposits, about one-third of the samples have TDS concentrations exceeding the SMCL.

The Valparaiso Moraine has the highest median TDS concentration (449 mg/L) and the highest median hardness, alkalinity, calcium, magnesium, potassium, iron, and sulfate concentrations. In contrast, median levels for these constituents (except sulfate) are lowest in the Eolian Sands. The differing concentrations indicate that the amount of carbonate materials and ground-water residence time exert substantial control over the levels of chemical constituents in ground water.

TDS levels generally are higher in the bedrock systems than in the unconsolidated deposits but are still mostly less than 700 mg/L. SMCL exceedances occur in localized areas of all bedrock aquifer systems (figure 51). In the shale-capped Silurian and Devonian carbonate system, nearly half of the samples contain TDS concentrations exceeding the SMCL (figure 47). Water from one livestock well contains more than 2000 mg/L TDS.

Of the bedrock systems, the shale-capped Silurian and Devonian carbonate system contains the highest median TDS levels and also the highest median alkalinity, chloride, potassium, sodium, and fluoride concentrations. The high TDS levels are probably due to cation-exchange processes in the shale cap or overlying glacial deposits. The exchange of calcium for sodium results in high sodium levels, and total dissolved solids increase in ground water when calcium ions are exchanged for sodium ions (Freeze and Cherry, 1979).

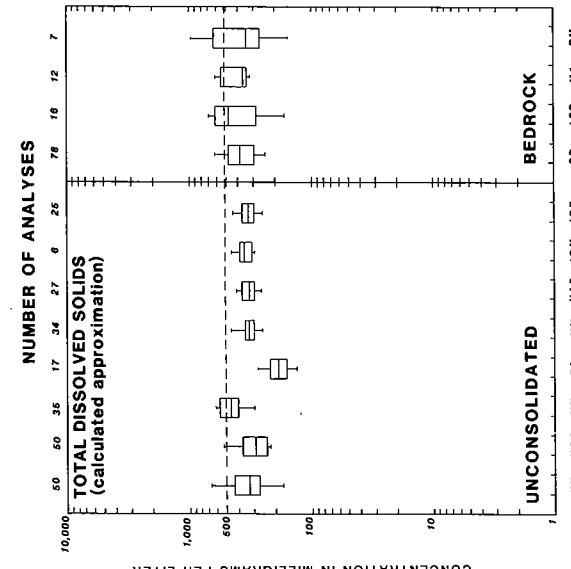
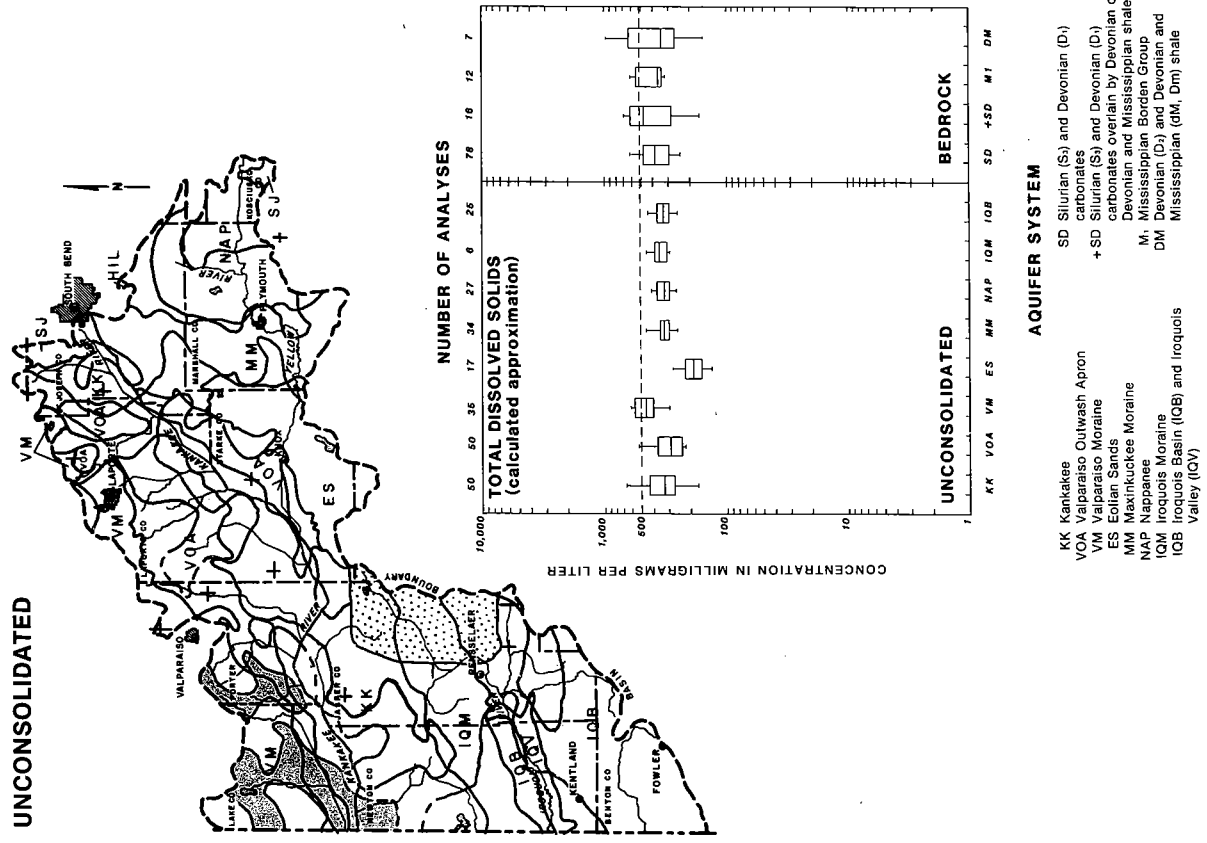
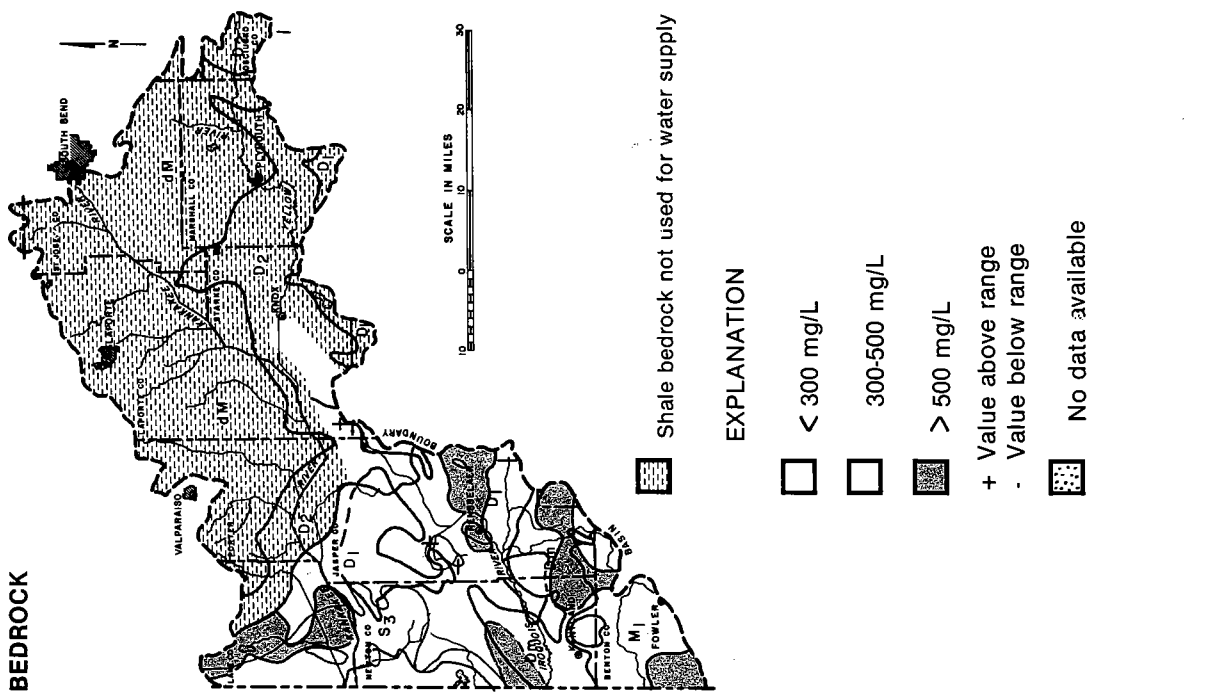
Wells completed in bedrock aquifers and used for drinking water in the Kankakee River Basin are rarely deeper than 400 feet and generally contain TDS concentrations less than 1000 mg/L. Water in much deeper bedrock aquifers, however, is saline, containing TDS levels greater than 10,000 mg/L (J. Rupp, Indiana Geological Survey, personal communication, 1989). In the Kankakee River Basin, saline water is encountered in Cambrian and Ordovician rock units. Brines, or water having chloride concentrations greater than 100,000 mg/L, occur in the basal sandstone unit of the Cambrian system (Hartke and others, 1975). Ground water in these deep systems is highly mineralized from temperature, pressure, age, and natural filtering mechanisms (Freeze and Cherry, 1979). Because concentrations of chloride and total dissolved solids can exceed U.S. EPA standards substantially, use of water from these formations for public supply is restricted.

### Ground-water contamination

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

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, and aromatic *volatile organic compounds* (VOCs). About two dozen cases of ground-water contamination within the Kankakee River Basin have been documented by the IDEM in the mid-1980s. A registry





- AQUIFER SYSTEM**
- KK Kankakee
  - VOA Valparaiso Outwash Apron
  - VM Valparaiso Moraine
  - ES Eolian Sands
  - MM Maxinkuckee Moraine
  - NAP Napanee
  - IQM Iroquois Moraine
  - IOB Iroquois Basin (IOB) and Iroquois Valley (IOV)
  - SD Silurian (S) and Devonian (D) carbonates
  - +SD Silurian (S) and Devonian (D) carbonates overlain by Devonian or Devonian and Mississippian shale
  - M. Mississippian Borden Group
  - DM Devonian (D) and Devonian and Mississippian (dM, Dm) shale

Figure 51. Generalized areal distribution and statistical summary for total dissolved solids

of these case histories is maintained by the IDEM and provides additional details on chemical contamination.

### Recent studies

VOCs have been the focus of numerous monitoring activities. VOC occurrences in ground water in the Kankakee River Basin 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 (VOCs) in the ground-water supplies of more than 400 community water systems each serving more than 25 persons year-round. In the Kankakee River Basin, detectable levels of at least one VOC were found in the raw water of public supplies for Newton, Jasper, and in-basin portions of Porter and Marshall Counties (Indiana Department of Environmental Management, [1988]). 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.

From a subset of the wells selected for DOW-IGS sampling in 1986, the IDEM analyzed 23 well-water samples for 18 halogenated, two non-halogenated, and four aromatic VOCs. None of the wells sampled contained concentrations of these VOCs above the detection limit.

Other well-water samples were collected in the summer of 1988 for VOC analysis during the second phase of an USEPA-funded study on non-community water systems conducted by Indiana University. Data will be available for approximately 47 sampling sites in the in-basin portions of Marshall, St. Joseph, LaPorte, Starke, Jasper, Newton, Lake, Porter, and Elkhart Counties.

While VOCs often are associated with point-source pollution, pesticides are more typically involved in nonpoint-source impacts on ground water. In Indiana,

however, there is generally less information on pesticide contamination than for other substances in ground water. The IDEM analyses of samples from 23 wells selected for DOW-IGS basin assessment and a study by Purdue University (Turco and Konopka, 1988) provide some information on pesticide occurrence in the Kankakee River Basin.

The IDEM analyzed water samples for 10 pesticides from the subset of 23 wells which were tested for VOCs. One well contained Lasso (Alachlor) levels close to the USEPA health advisory of 1.5 mg/L (U.S. Environmental Protection Agency, 1985a). Ground-water conditions may vary over time at this site, as indicated by the fluctuation of alachlor concentrations in duplicate samples taken at different times. The presence of Alachlor may be due to improper well construction or a Lasso application washed into the well by rain, but there was insufficient information to determine the exact cause of contamination. No pesticides were detected in any of the other sampled wells.

In 1987-1988 Purdue University studied the effects of agricultural activities such as pesticide applications and confined feedlots on ground-water quality (Turco and Konopka, 1988). A total of 19 farm wells in Newton and Jasper Counties were monitored for various chemicals including five pesticides and nitrate-nitrogen. Well placement, well depth, soil types, and results of seasonal sampling were evaluated in an attempt to determine patterns of agricultural contamination.

Pesticide contamination of wells was not extensive in the Purdue study area. Of the 153 samples collected in Newton and Jasper Counties over a one-year period, only one well exhibited contamination by the pesticides Atrazine, Alachlor, and Metolachlor. Pesticide occurrence was considered transient and localized because 1) most concentrations were detected briefly in August, and 2) a nearby deeper well did not contain detectable levels of any of the three pesticides (Turco and Konopka, 1988). Because Metolachlor is considered nonleachable, its occurrence may reflect activity at the well head.

Analyses of samples collected as part of the Purdue study showed some occurrence of elevated nitrate levels in the Kankakee River Basin. One well each in Newton and Jasper Counties contained average nitrate-nitrogen concentrations above the MCL of 10 mg/L. In addition, three wells (two in Newton County and one in Jasper County) contained average nitrate-nitrogen concentrations greater than 1 mg/L, a level

that is indicative of the potential for the development of human and animal health problems (Turco and Konopka, 1988; also see Madison and Brunett, 1984).

The Purdue study did not directly trace elevated nitrate-nitrogen levels to either feedlot waste or fertilizer application as the major contributing factor in their study area. However, the study suggested that factors contributing to variability in nitrate concentrations include drainage characteristics of soil and horizontal and vertical separation distances from potential nitrate sources.

A 1989 pesticide survey conducted by the IDEM revealed detectable levels of nitrate occurring at least once in each of 25 wells completed in or passing through the Kankakee Aquifer System in Newton County (Indiana Department of Environmental Management, [1990]). The MCL for nitrate was exceeded in four of these wells. In addition, eight pesticides were detected in three wells.

In a 1977 ground-water survey conducted by the Michiana Area Council of Governments, it was found that 72 out of 1055 water-well samples contained nitrate-nitrogen concentrations in excess of 10 mg/L. In the area encompassed by the survey, including Elkhart, LaPorte, Marshall, and St. Joseph Counties, many of these exceedances were clustered in localized areas (Michiana Area Council of Governments, 1978).

Information pertaining to potential agricultural impacts on ground-water was obtained during a 1981 ground-water strategy study in Lake and Porter Counties (Indiana State Board of Health, 1982). The purpose of the study was to evaluate the circumstances surrounding ground-water contamination in urban and rural settings so that the adequacy of Indiana's laws, regulations and policies for ground-water protection could be ascertained. Two agricultural areas in this study that are located in the Kankakee River Basin include the Schneider-Shelby area in Lake County and the Kouts area in Porter County. Both areas have similar land-use patterns such as confined feeding and irrigation.

Samples were tested for total organic carbon (TOC), chemical oxygen demand (COD), and common inorganic constituents and physical parameters. Six out of 30 wells sampled in the Shelby-Schneider area contained more than 5 mg/L TOC. Four out of these six wells also contained elevated COD (ranging from 17 to 25 mg/L). The study recommended additional testing in the two wells containing the highest TOC levels to identify specific organic substances and to determine

the cause for contamination. In the Kouts area, one out of 13 wells sampled contained high COD and TOC, but no cause for the elevated levels was obvious.

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

The susceptibility of an aquifer system to contamination from surface sources depends in part on the type of material that forms the unsaturated layer above the water table. Contaminants can be transmitted from the surface through the unsaturated zone by percolating water. A sand-rich surficial layer can easily transmit water from the surface. A clay-rich surface deposit can limit the movement of water and contaminants carried by the water. Plate 2 briefly summarizes the susceptibility to contamination of eight unconsolidated aquifer systems in the Kankakee River Basin. The degree of protection of bedrock aquifers from contamination depends on the thickness of overlying till or clay.

The unconfined outwash aquifers of the Valparaiso Outwash Apron, Kankakee, St. Joseph, Maxinkuckee, and Hilltop Aquifer Systems and the surficial sands of the Eolian Sands Aquifer System are highly susceptible to surface contamination. These aquifer systems are particularly vulnerable where the water table is near the surface, as it is in most of the Kankakee Aquifer System.

Aquifer systems with variably thick surficial clay deposits are susceptible to surface contamination where the clay layer is absent or discontinuous. For example, the Valparaiso Moraine Aquifer System is susceptible to surficial contamination near the upper reaches of the Little Kankakee Valley where the surficial clay layer is thin or absent. West of Valparaiso, however, the intratill aquifers may be only slightly susceptible because they are overlain by consistently thick surficial clay deposits.

In some areas along the extent of the Eolian Sands Aquifer System, deep sand and gravel lenses are overlain by a thick till. This low-permeable layer restricts migration of contamination from surficial deposits. Thick clay deposits also protect the intratill aquifers of the Nappanee, Iroquois Moraine, and Iroquois Basin Aquifer Systems and the Iroquois Buried Valley Subsystem.