TIME-SERIES ANALYSIS OF GROUNDWATER CHEMISTRY IN THE WEST TENNESSEE SAND AQUIFERS

T. MARGUERITTE WILSON, ALBERT E. OGDEN, AND H. H. MILLS, III

Tennessee Valley Authority, 400 West Summit Hill Drive, Knoxville, TN 37902 (TMW)
Center for the Management, Utilization, and Protection of Water Resources and Department of Earth Science, Box 5033, Tennessee Technological University, Cookeville, TN 38505 (AEO, HHM)

ABSTRACT--In West Tennessee, nearly all municipalities, industries, and rural residents rely on groundwater. To understand water quality changes caused by mans' activities, it is first important to establish background ionic concentrations from a time-series analysis of past data for wellhead protection purposes. For this analysis, well-water quality data from a 1964-1965 survey by the Tennessee Stream Pollution Control Board was compared to precipitation data. In all of the aquifers studied, calcium increased with depth probably due to the continual solution of calcium minerals as water moved downgradient. Iron also increased with depth to the aquifer associated with a change from oxidizing to reducing conditions downdip. A spatial analysis of nitrate and iron levels was made using data from the Tennessee Division of Water Supply for the period 1982 through 1987. Nitrate and chloride concentrations were higher in recharge areas possibly due to surface contamination sources. The significant variability of chemical constituents was found to be related to recharge events, depth to the aquifer, spatial changes in aquifer lithology, and mans' activities in the recharge areas. The inter-relationships of these factors must be understood for determining site-specific ambient quality conditions before implementing a wellhead protection program.

Groundwater is one of our nation's most important resources. It is estimated that aquifers in the United States contain quantities of water 50 times that of all the surface water sources. In Tennessee, nearly half of the population relies on groundwater, varying from rural private springs and wells to municipal water systems. Memphis, the state's largest city, depends completely on groundwater from the West Tennessee aquifer system. Congress recently reauthorized the Safe Drinking Water Act and requested that the United States Environmental Protection Agency (1988) prepare guidelines for municipalities to implement a "wellhead protection" plan. Three factors necessary to implement such a plan are delineation of recharge areas, determination of groundwater travel times, and documentation of ambient groundwater quality conditions. This paper addresses the latter factor by investigating the groundwater quality changes with time in the West Tennessee sand aquifers.

STUDY AREA AND HYDROGEOLOGY

The State of Tennessee has been divided into six groundwater provinces by the United States Geological Survey (Bradley and Hollyday, 1985) on the basis of areal extent of bedrock units, regional groundwater movement and divides, and physiography. A geologic cross-section of the aquifers involved in the present study is shown on Fig. 1. Each groundwater province has one or more principal aquifers on which municipalities, industries, and rural residents depend. In West Tennessee, more municipalities depend on groundwater than any other region in the state. This groundwater province has been named the Coastal Plain Province after Miller's (1974) naming of the physiographic regions. The Coastal Plain Groundwater Province includes the Mississippi River Valley, the West Tennessee Plain, and the West Tennessee Uplands. The region has abundant rainfall with records of the United States Weather Bureau showing an average annual precipitation of about 127 cm (1988).

Western Tennessee is situated within the Mississippi Embayment of the Gulf Coastal Plain. The dip of all the post-Paleozoic deposits is generally toward the axis of the Mississippi Embayment. Near the outcrops of these formations, the dip is about 6.6 m/km and decreases considerably toward the west, reaching a minimum of about 2.8 m/km (Wells, 1933).

In the Coastal Plain Province, the important aquifers are the unconsolidated sand formations. The principal aquifers of this groundwater province are the Cretaceous Sand Aquifer, Tertiary Sand Aquifer, and Alluvial Aquifer. These aquifers are mainly sand formations interbedded with gravel, clay, silt, marl, and lignite. These highly permeable aquifers contain abundant porosity and permit storage of large quantities of water; these characteristics allow movement of water over long distances and easy withdrawal of water from wells. These sand aquifers are the most productive water-bearing formations in Tennessee, commonly yielding 378.5 to 189.6 l/min and sometimes exceeding 378.2 l/min (Bradley and Hollyday, 1985). The water in the sand formations is confined in the downdip direction and becomes unconfined in the outcrop area.

MATERIALS AND METHODS

The data used in the time-series analysis were obtained from samples taken from 18 municipalities in West Tennessee during the period between August 1964 and July 1965 by the Tennessee Stream Pollution Control Board. During this period, these municipal groundwater sources were sampled on a monthly basis for 22 parameters on raw (untreated) water. Seasonal variability in 13 of the 22 measured monthly parameters was analyzed by Wilson (1988), but only calcium, chloride, nitrate, and iron will be discussed in this paper.

The time-series analysis involved selecting municipalities that have wells pumping from the confined and unconfined segments of the same aquifer. Post-Paleozoic formations were chosen because these

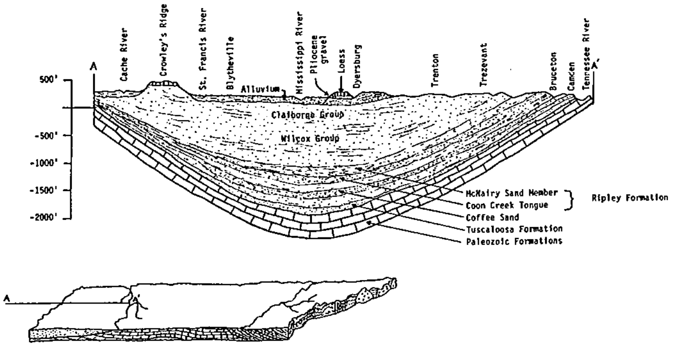

FIG. 1. Idealized geologic cross-section of West Tennessee/East Arkansas (modified from Wells, 1933).

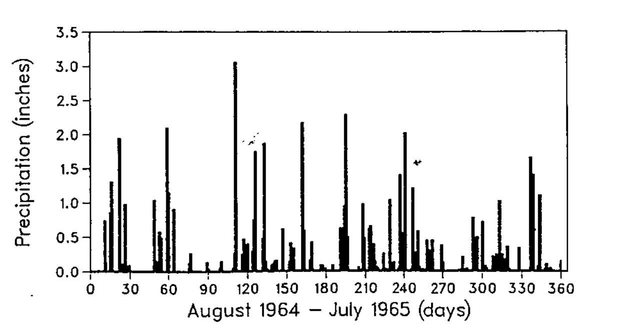

FIG. 2. Precipitation events between August 1964 and July 1965.

formations are somewhat similar in lithologic characteristics, are generally uniform, and occur over broad regions. Thirteen municipalities were selected using the following criteria: the producing aquifer had to be known; it had to be of post-Paleozoic age; pumpage had to from one aquifer only. These municipalities were separated by aquifer and further divided into recharge (outcrop) areas and confined areas. The data from the 13 municipalities were plotted by considering each water quality parameter versus time for each city. These plots were studied in groups by well depth and by geographical location and on an individual basis. The three aquifers studied were the Ripley Formation (Cretaceous), Wilcox Formation (Tertiary), and Claiborne Formation (Tertiary). Two municipalities for each aquifer were chosen to demonstrate the water quality in typical wells pumping from that aquifer. One municipality is located in (or near) the recharge-outcrop area, and the other is located downdip in the confined area. A spatial analysis of nitrate and iron concentrations was made utilizing data from the Tennessee Division of Water Supply for the period 1982 through 1987. Precipitation data were acquired from the United States Weather Bureau (1965) for the study period of August 1964 through July 1985 (Fig. 2).

RESULTS AND DISCUSSION

Ripley Formation, Cretaceous Age--The major municipalities pumping from the Ripley Formation are from north to south: Paris, Bruceton, Huntingdon, and Lexington. Lexington and Paris were chosen to represent municipalities pumping from the Ripley Formation. Lexington represented municipalities pumping from shallow wells with well depths ranging from 46.9 to 52.1 m and static water levels from 15.8 to 18.9 m below the land surface. Paris was the representative deep well with well depths ranging from 137.2 to 140.2 m and static water levels from 34.8 to 41.2 m below the land surface. Yearly average water temperatures for all the municipalities ranged from 17.7 to 18.8°C.

The plots of calcium hardness (Fig. 3A) show somewhat of a seasonal trend with lower values occurring during the winter and higher values in the summer. Although not plotted, similar trends were seen for alkalinity, magnesium, and carbon dioxide. The concentrations tended to decrease when the precipitation increased which may have been due to dilution. Also, the pH tended to increase with depth in the Ripley Formation. The increase in pH is caused by the continued dissolution of carbonate minerals as water moves slowly downdip.

Chloride levels were lower during the summer months when precipitation decreased (Fig. 3B). Apparently, chloride is very mobile in this aquifer system and moves rapidly during high rainfall periods. Chloride concentrations tended to be higher in the shallower wells located in the outcrop area and lower in deeper, confined wells downdip. This may have been caused by contamination sources of sodium chloride, such as from septic systems.

The plots of nitrate concentration are given in Fig. 3C. The shallow wells located in the recharge area have values considerably higher than the deeper wells. The peak values during April in the recharge zone may have been caused by application of fertilizers. These peaks are seen in the deeper wells by late summer. It is equally likely that spring rains moved septic system waters downward. Lexington and Bruceton have shallow wells, and their waters occasionally exceed the limit of 10 mg/l (Hem, 1989).

The time-series plots of iron concentration are shown in Fig. 4D. Iron concentrations correspond to major rainfall periods but do not show marked seasonal trends. Lexington's groundwater exceeded the health limit of 0.03 mg/l (Hem, 1989) during May and July; yet, the yearly average was below the limit. Paris had the highest values of iron concentration. During 11 of 12 months, Paris' iron concentrations far exceeded the health limit. The yearly average for Paris was 2.1 mg/l. Iron pyrite in the aquifer material and conditions of low pH and oxidation-reduction potential likely enable the iron to be mobile.

Wilcox Formation, Tertiary Age--The municipalities pumping from the Wilcox Formation are from north to south: Dresden, Dyersburg, Alamo, Jackson, and Brownsville. Jackson and Dyersburg were chosen for graphic display of the geochemical data. Jackson was selected to represent the municipalities pumping from shallow wells with depths ranging from 45.7 to 48.8 m, while Dyersburg was chosen as the representative deep well, with depths ranging from 194.2 to 219.5 m. The yearly average groundwater temperatures for all municipalities ranged from 17.3 to 18.3°C.

When the plots of calcium (Fig. 4A) are compared to those of precipitation, calcium tended to decrease with the increase in precipitation during winter months. Although not presented here, the trends for alkalinity and magnesium are similar to that for calcium as predicted by the calcite and dolomite dissolution equations. Calcium, alkalinity, magnesium, and pH increased in concentration towards the axis of the Mississippi Embayment probably due to the solution of calcium and magnesium minerals as water moves downdip.

Chloride concentrations rose during the wet season as recharge dissolved salts that had accumulated in soils from evaporative times during the hot summer (Fig. 4B). The Jackson city shallow wells had significantly higher levels of chloride suggesting the influence of pollution sources.

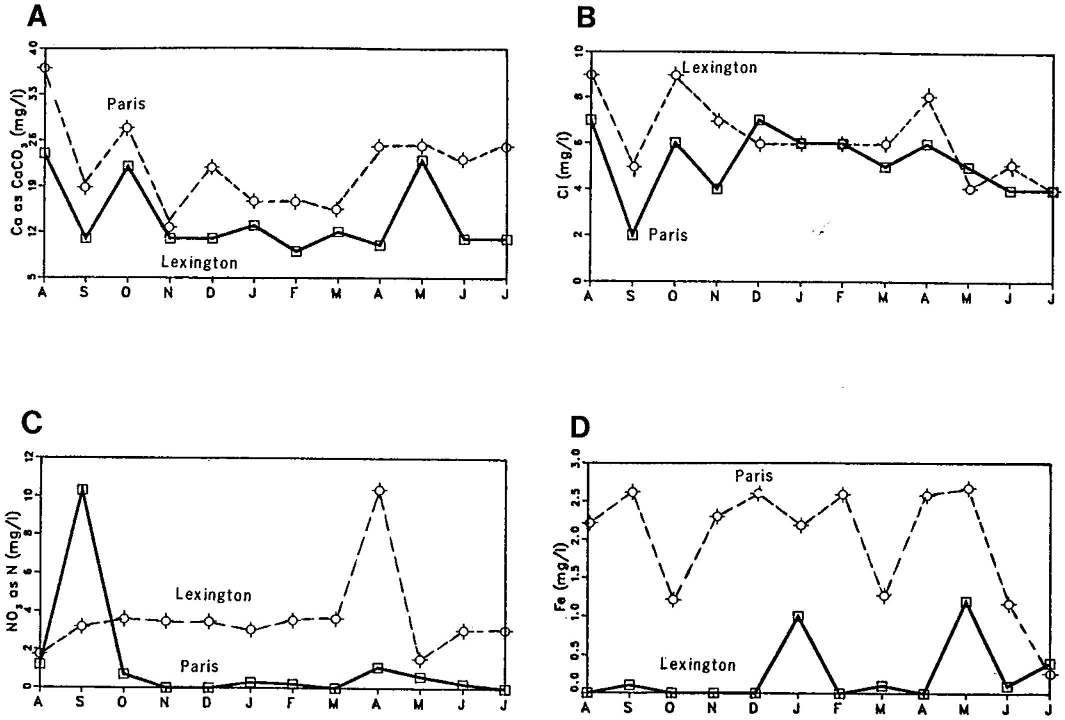

FIG. 3. Time-series plot of (A) calcium, (B) chloride, (C) nitrate, and (D) iron concentrations for Lexington and Paris wells in the Ripley Formation (1964-1965).

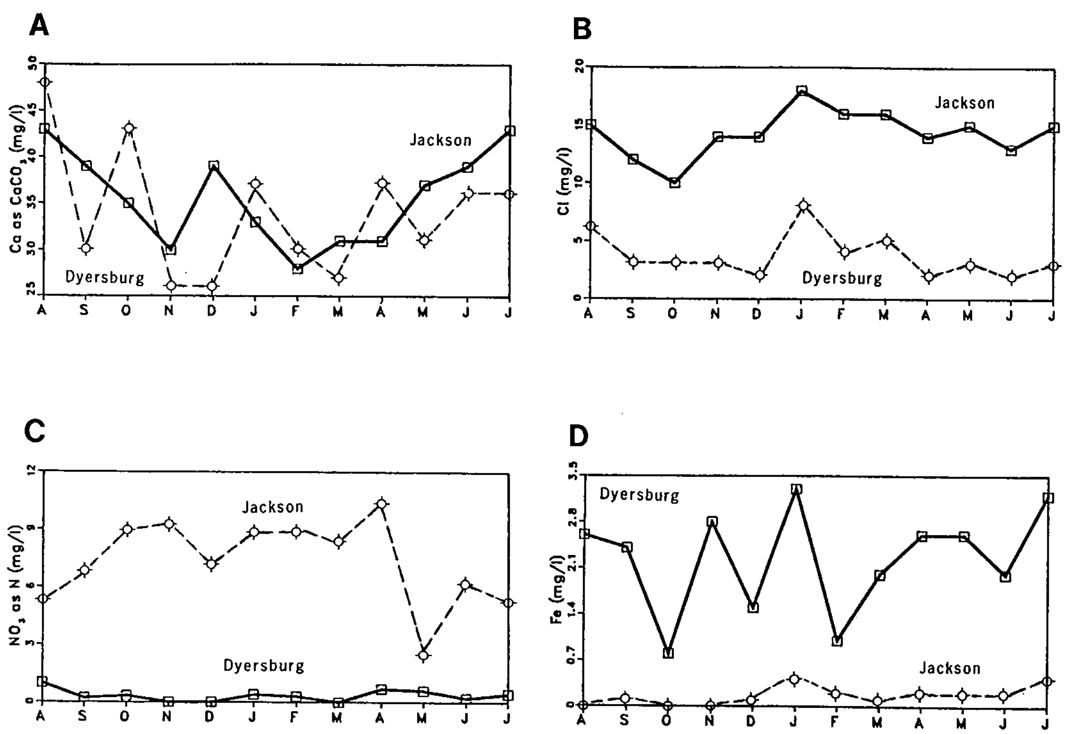

FIG. 4. Time-series plot of (A) calcium, (B) chloride, (C) nitrate, and (D) iron concentrations for Jackson and Dyersburg wells in the Wilcox Formation (1964-1965).

The plots of nitrate concentration are shown in Fig. 4C. The yearly average values for the municipalities with shallow wells (Alamo, Brownsville, and Jackson) had significantly higher levels than the deeper wells in Dresden and Dyersburg. Alamo exceeded the nitrate limit throughout the year. Shallow wells showed significantly greater nitrate concentrations than the deeper wells. The source of nitrate contamination may be from a combination of fertilizers spread on fields, falling septic tank systems, and leaky sewer lines.

Figure 4D shows plots of iron concentration. The yearly average for Jackson did not exceed the health limit; yet, the town had values that exceeded the limit twice during the year. Dyersburg, with the deepest wells, had values that exceeded the limit every month for the entire study period. The yearly average concentration for Dyersburg was 2.2 mg/l which far surpasses the drinking water limit. There is a definite downdip increase in iron concentration similar to that in the wells in the Ripley Formation.

Claiborne Formation--Four municipalities that pump from the Claiborne Formation in West Tennessee (Ripley, Somerville, Trenton, and Union City) were analyzed. Somerville was selected as the municipality representing those in the recharge area. The city's well depths range from 25.9 to 26.5 m, and static water levels are 0.2 to 4.0 m below the land surface. Ripley was chosen to represent municipalities with wells located in the confined zone. Ripley's wells range in depth from 121.9 to 243.8 m with static water levels 43.6 to 47.9 m below the land surface. The average yearly water temperatures ranged from 17.2 to 18.3°C for all municipalities. Calcium concentrations tended to increase in depth with soft water in the outcrop area and a moderately hard water downdip (Fig. 5A). Alkalinity, hardness, magnesium, and pH values also showed increases between the shallow wells and the downdip deep wells as predicted by the carbonate dissolution equation. Chloride and nitrate concentrations (Fig. 5B,C) are higher in the shallow wells. The Somerville wells sometimes exceeded the 10-mg/l health limit for nitrate. Nitrate is lower during the warm growing seasson, related to plant use and less recharge to carry nitrate down to the water table. Available nitrate from both natural and man-derived sources is driven downward during winter and spring months when recharge is highest.

The plots of iron concentrations for the Somerville and Ripley city wells (Fig. 5D) markedly demonstrate the differences between water quality in the recharge areas versus in the confined portion of the Claiborne Aquifer. All of the wells in the town of Ripley had iron levels that exceeded the 0.03-mg/l health limit. Iron concentration increased with depth to producing horizon, similar to the trend for the Ripley and Wilcox formations.

Spatial Analysis--A spatial analysis of nitrate concentrations from all aquifers in West Tennessee showed a range from 0.01 mg/l to 4.46 mg/l with a median of 0.22 mg/l (Fig. 6A). The higher nitrate concentrations tended to be in the northern portion of the study area, possibly related to fertilizer application in this highly cultivated region. The larger towns also tended to have higher values likely caused by contamination from septic tanks and leaky sewer lines (Miller and Gonthier, 1984).

The spatial distribution of iron data (Fig. 6B) shows that many municipalities in West Tennessee utilize groundwater that exceeds the health limit; thus, treatment is often necessary. There is an increase in concentration with depth. The increase in iron concentration downdip could be due to a shift from an oxidizing environment near the outcrop to a reducing environment at depth causing mobilization of the metals. Iron in the Cretaceous and Tertiary formations of Tennessee is dissolved from oxides and sulfides of iron. Iron oxides laid down with the sediments during deposition were probably dissolved when the formation was buried and reducing conditions existed. The sulfides of iron are associated with the carbonaceous and pyritic clays of these formations.

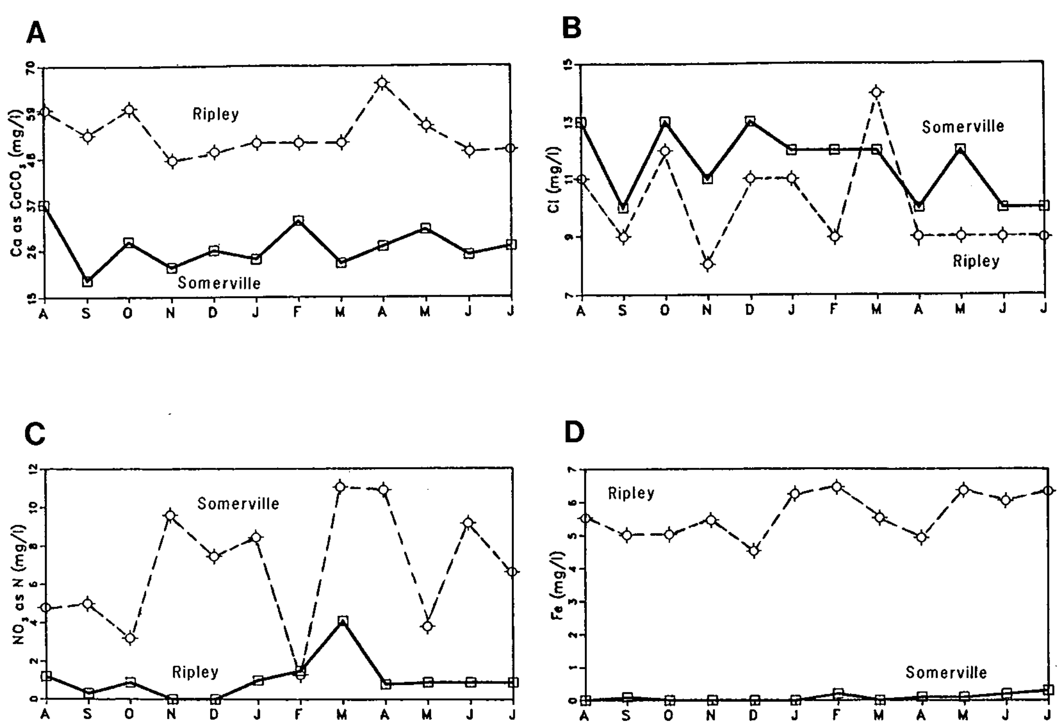

FIG. 5. Time-series plot of (A) calcium, (B) chloride, (C) nitrate, and (D) iron concentrations for Somerville and Ripley wells in the Claiborne Formation (1964-1965).

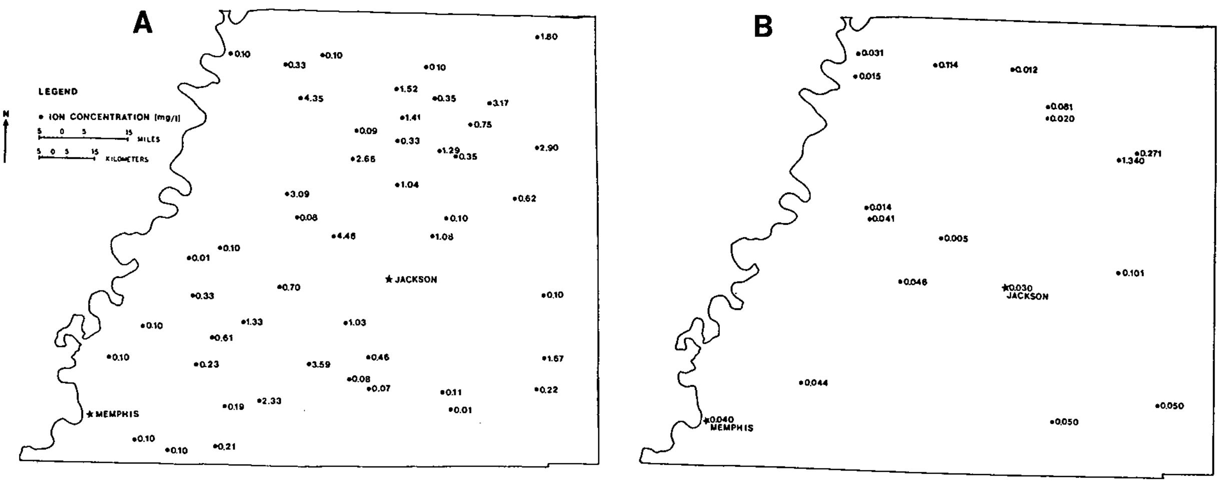

FIG. 6. Spatial distribution of (A) nitrate and (B) iron concentrations in West Tennessee wells.

Moore (1962) concluded that the water from the Memphis Sand (Claiborne Formation) increases in calcium, magnesium, and bicarbonate probably from the slow solution of carbonate minerals as the water moves downdip. This process would also account for the downdip increase in pH, assuming there was no addition of carbon dioxide to the water. The increase in iron concentration downdip is probably due to the shift from an oxidizing environment near the outcrop area to a reducing environment closer to the Mississippi River. In the pH range of these waters, the solubility of iron is dependent on the oxidation-reduction potential of the water in the aquifer. Hydrogen sulfide has been found in some wells pumping from the Memphis Sand near the axis of the embayment which is evidence of a reducing environment, thus explaining many of the observed spatial changes in the aquifer.

CONCLUSIONS

The results of the research demonstrate that significant spatial and time variability of water quality data occurs in the unconsolidated sand aquifers of West Tennessee. Change from oxidizing to reducing conditions in a downdip direction from the recharge areas causes higher levels of iron. Continued dissolution of carbonate minerals as groundwater moves downgradient results in increases of calcium concentrations and pH. Nitrate and chloride levels are greater in the recharge areas versus confined portions of all three aquifer systems demonstrating the high groundwater pollution susceptibility of the shallow groundwater. Due to the great variability of ambient water quality both seasonally and spatially, it is essential that the natural and man-induced factors affecting these changes be understood when developing a wellhead protection plan. Also, by understanding seasonal and spatial differences of groundwater quality, false positives can be avoided when comparing monitoring well data at RCRA, Superfund, UST, and solid waste facilities.

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