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Heterogeneities in ground-water geochemistry in a sand aquifer beneath an irrigated field

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Abstract

The contamination of shallow aquifers by elevated nitrate concentrations is a common problem in many rural regions of the world. Aquifers under irrigated land are especially susceptible to this type of contamination. An intensive three-dimensional investigation of water chemistry was undertaken in a shallow unconfined sand aquifer in an area of intensive irrigation in Mason County, Illinois, in order to investigate processes affecting water quality. Results reveal considerable heterogeneity in the aqueous chemistry in three spatial dimensions and temporally. Recharge is rapid in this system and the water chemistry of the recharge water is variable both spatially and temporally, being especially influenced by agricultural practices. Nitrate concentrations are elevated in a zone between about 6 and 10 m beneath the surface, although in certain areas and at certain times this zone was not found. The maximum nitrate concentrations in this zone were slightly greater than 20 mg l^{-1} as N, well above the US Environmental Protection Agency's maximum contaminant level (MCL) of 10 mg l^{-1}. Nitrate was generally absent both above and below this depth in the aquifer. Water relatively depleted in nitrate recharges the aquifer from the surface at the site, producing a zone of dilute water near the water table. Beneath the plume, denitrification reactions are responsible for removing nitrate from solution, probably mainly coupled to oxidation of sulfide minerals; tritium data suggest that vertical movement of solutes is rapid and thus there has been enough time to transport surface-applied fertilizer to depths in excess of 30 m in the aquifer. This rapid vertical movement is almost certainly enhanced by intensive irrigation in the county. A number of aqueous species and chemical parameters (Ca, Mg, Sr, Fe, Si, dissolved inorganic carbon (DIC), dissolved oxygen, total dissolved solids, and pH) are correlated with nitrate concentrations, primarily because, like nitrate, they are either a significant fraction of fertilizers or are redox-sensitive. Drinking water quality is generally not degraded by fertilizer applications in this area, because almost all drinking-water wells are screened well below the zone of elevated nitrate concentrations.

1. Introduction

Agricultural chemicals, i.e. fertilizer-nitrate and pesticides, are being detected with

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increasing frequency in rural water supplies and are an international health concern. Nitrate is probably the most widespread contaminant in ground water in the world (Hallberg and Keeney, 1993). The US Environmental Protection Agency (USEPA) has set a maximum contaminant level (MCL) for nitrate of 10 mg l^{-1} as nitrogen (N) for drinking water (USEPA, 1991).

Elevated concentrations of nitrate in soil and ground water are almost always the result of intense land-use activities, especially large-scale fertilizer applications, high density animal operations, and septic systems (Keeney, 1986). The application of fertilizers to crops is the most widespread of these sources. Corn accounts for much of the nitrogen fertilizers applied in the United States. For example, in 1993 about 44% of the fertilizer applied in the US was for corn, although only 22% of the cropland was in corn (Taylor, 1994). In addition, because much of the fertilizer nitrogen applied to cornland is not removed in harvested crops, a significant fraction is available for leaching (Aldrich, 1980).

Aquifers beneath irrigated land are especially susceptible to contamination by agricultural chemicals. Multiple and high value crops are grown with higher inputs of fertilizer, pesticides, and irrigation water (Pratt, 1984). Soils in the Midwestern United States that are under irrigation are often sandy and have low moisture-holding capacities, thus percolation rates through the unsaturated zone tend to be rapid. Leaching tends to be enhanced in irrigated systems, thus the potential for nitrate contamination of ground water is high in these areas (Keeney, 1982; Hubbard et al., 1984, 1986). High concentrations of nitrate have been observed in shallow ground water beneath irrigated areas in many regions of the United States (e.g. Saffigna and Keeney, 1977; Spalding et al., 1978). The amount of irrigated land has increased substantially in the last few decades. In Illinois, irrigated cropland increased from less than 400 ha in 1960 to greater than 130 000 ha in 1992 (US Department of Commerce, 1994).

The movement of nitrate in the subsurface is primarily controlled by sorptive processes and microbiological activity. Nitrate adsorption in soils and aquifer sediments is most strongly controlled by the organic matter content (Starr and Gillham, 1993). In sandy soils and aquifers, nitrate is usually poorly adsorbed. Denitrification is an important process in many systems where oxygen is depleted, but is generally also controlled by the amount and reactivity of organic matter. Thus in systems with low amounts of organic matter, nitrate may behave conservatively.

Nitrate is typically not found at depth in aquifers. Nitrate applied at the surface in the past several decades has not had time to migrate to depths greater than a few tens of meters in most aquifers. Also, ground water tends to be anoxic at depth, thus favoring denitrification and other nitrate-reduction reactions. For example, Postma et al. (1991) did not detect nitrate in samples taken from depths greater than 15 m, which they correlated with a change in redox conditions with depth. Many investigators have observed that nitrate concentrations are elevated near the water table and decrease with depth. Trudell et al. (1986) report nitrate-N concentrations between 8 and 10 mg l^{-1} near the water table (about 1 m below the surface), decreasing to less than 0.1 mg l^{-1} at depths greater than 2 m. Ritter and Chirnside (1984), Hallberg (1989), Pedersen et al. (1991), Bjerg and Christensen (1992), and Geyer et al. (1992) found similar patterns at other sites, with nitrate levels highest near the water table and decreasing to below detection with depth.

This pattern is not always observed, however. Nitrate concentrations have been reported

to be depleted near the water table. Postma et al. (1991) found relatively depleted levels of nitrate near the water table in multi-level samplers that were emplaced in forested land, as opposed to arable land. In this aquifer, a plume of elevated nitrate concentrations in a fairly well-defined zone several meters below the water table was attributed to recharge from farmland hydrologically up-gradient. The nitrate-depleted zone near the water table was presumed to be from recharge from the non-cultivated and thus non-fertilized land. Kalkhoff et al. (1992) report similar results from a site where seven nested wells were emplaced. Nitrate concentrations were relatively low near the water table, increased with depth, then decreased rapidly with increased depth (>5 m below the water table). They attributed the vertical differences to preferential flow in heterogeneous aquifer material.

Seasonal changes in nitrate concentrations have been documented in some shallow unconfined aquifers (e.g. Hallberg, 1986, 1987). Nitrate concentrations tend to increase when recharge through the soil occurs. Littke and Hallberg (1991) observed annual peak concentrations during the spring–early summer and/or fall recharge periods. Annual minima occurred during the spring snowmelt.

Management practices and weather patterns also strongly influence nitrate concentrations in ground water. Changing crop types, fertilization rates, or application methods, and periods of drought and unusually wet conditions may affect nitrate concentrations (Hallberg and Keeney, 1993). The most notable and widespread temporal trend in nitrate concentrations, however, is the long-term increase since the 1950s and 1960s (e.g. Exner and Spalding, 1974; Spalding et al., 1978; Hallberg, 1986; Strebel et al., 1989). There is little doubt that the rapid increase in fertilizer applications is being reflected in the shallow ground-water quality in many parts of the world.

Spatial and temporal variability in nitrate concentrations among individual wells is also commonly observed (Hallberg and Keeney, 1993). Significant spatial variability can occur over very small distances. For example, Bjerg and Christensen (1992) calculated correlation ranges of less than 10 m for horizontal variations in a farm field. Temporal variability is especially pronounced in shallow aquifers in which variable inputs can be expected. This temporal variability is a reflection of the complex interactions between land use practices, recharge characteristics, soil and aquifer hydraulic properties, and microbial activity, among other things. Because movement of water and solutes through soils and the saturated zone is often very slow, the application of fertilizer at the land surface may not be reflected in the ground water for several years. Thus the time frame for sampling ground water is an important consideration (Hallberg and Keeney, 1993).

The potential for significant volumes of ground water beneath irrigated land to be contaminated by agrichemicals is large and growing. The fate and transport of agrichemicals in these systems is thus of considerable concern. Knowledge of the transport of these contaminants from the application site to the regional ground-water flow system is essential in planning future water well locations and evaluating existing water supplies. It is important to know how the ground-water chemistry has been affected by irrigation and fertilizer application and if there is cause for concern regarding drinking water quality. In addition, an understanding of the aqueous chemistry of contaminated aquifers will help in predicting contaminant fate and designing remediation schemes. In this paper, results are presented from a field study investigating spatial and temporal variability of water chemistry in an aquifer in an irrigated area, with a special emphasis on nitrate.

2. Field site

The field site for this study is located on the property of the Mason State Tree Nursery in Mason County, Illinois, USA, approximately 50 km southwest of Peoria (Fig. 1). The field site is located in the southeast corner of the nursery property. The private fields near this corner of the tree nursery were planted in field corn during both years of this study. The tree nursery and the surrounding fields all have irrigation systems.

The main aquifer in this region is in the unconsolidated sand and gravel deposits of Pleistocene age overlying Pennsylvanian bedrock valleys. The water table is generally less than 5 m below the surface and frequently less than 3 m. The area is located at the confluence of the ancient Mississippi and Teays Rivers (Bowman and Kimpel, 1991). The unconsolidated deposits were deposited by glacial meltwaters and are more than 30 m thick in most of the region. The uppermost sands are Wisconsinan outwash deposits and may reach thicknesses of about 30 m. These deposits consist of 60–75% quartz, 10–20% feldspar, and 20–30% sedimentary and crystalline rocks and minerals, with a light brown to yellowish brown color (Walker et al., 1965).

At the study area, all wells and multi-level samplers were finished in the Wisconsinan outwash deposits. The top 50 to 100 cm below the land surface consist of dark brown clayey sand, followed by 50 to 100 cm of dark brown clay. Beneath this clay zone is reddish-brown, medium-grained sand to a depth of 12–15 m. At greater depths, the deposits become coarser and have a gray color, with some pebbles. The change in color from reddish-brown to gray may represent a change in redox conditions resulting in

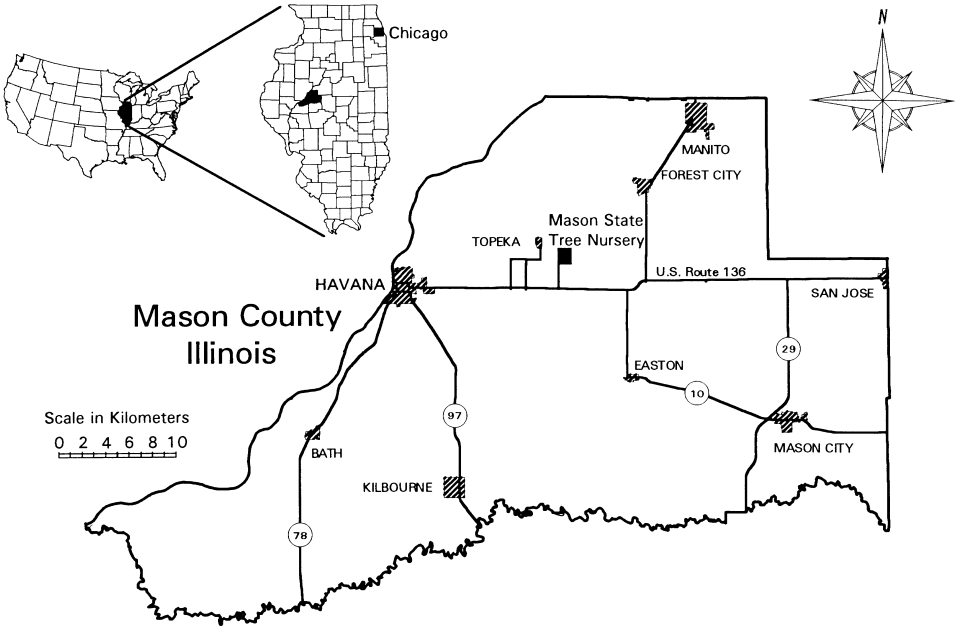

Fig. 1. Location of the field site at the Mason State Tree Nursery in Mason County, Illinois, USA.

reduction of iron oxyhydroxide coatings. Gravel-sized pieces of coal were found in a number of zones, and are especially abundant 10–12 m beneath the surface.

The primary characteristic of the soils in Mason County is their low moisture-holding capacity. Surface drainage is poorly developed in the region and there is little overland runoff during rain events because the high permeabilities of these soils facilitate rapid percolation to the underlying sand and gravel aquifer (Bowman and Kimpel, 1991). As a result, Mason County is the most intensely irrigated county in Illinois. Nearly 36 000 ha were irrigated in the County in 1989, which is about 25% of the total land in the county and more than a third of the state's total land under irrigation (Bowman and Kimpel, 1991).

3. Methods

Multi-level samplers (MLSs) were constructed using methods modified from LeBlanc et al. (1991). MLSs were prepared in ten-foot (3 m) sections of 1.5-inch-diameter (3.81 cm) PVC pipe and were installed using a 4.25-inch-ID (10.8 cm) hollow stem auger and standard augering techniques. There were between eight and 11 sampling ports per MLS with intervals between ports varying between 0.3 and 3 m.

Sixteen MLSs were emplaced within a 7- by 9-m rectangular plot (Fig. 2). MLS-11 was installed about 20 m east of this plot and MLS-18 was installed at the southeast corner of the tree nursery, hydraulically up-gradient about 235 m away from the other MLSs and about 5 m from private fields. Observation wells were also installed at the site using standard augering techniques.

All the wells, MLSs, and the irrigation well were surveyed using both traditional optical techniques, which determine relative elevations, and a Leica Wild System 200 Global Positioning System (GPS), which determined absolute spatial locations in three dimensions. The precision of the GPS is approximately $\pm$10–20 mm.

Complete chemical analyses were performed approximately quarterly from July 1993 to July 1994 for all producing ports of MLSs 3, 7, and 11. MLSs 16 and 18 were sampled once each during the study period. Samples were collected from various MLSs on three other occasions solely for nitrate analysis.

Samples were collected using a multi-channel peristaltic pump and silicone tubing and tubing connectors. Water from an individual port was pumped through a flow cell containing temperature, pH, conductivity, and redox probes until these parameters had stabilized. A dissolved oxygen (DO) measurement was then made by continually filling a bottle holding a DO probe. Samples were then collected through a 0.45-μm filter and appropriately preserved for transport back to the analytical laboratories.

Chemical analyses were performed at the Illinois State Water Survey Laboratories using standard methods. Anions were analyzed by ion chromatography, cations and metals by inductively coupled plasma, ammonium colorimetrically, alkalinity by gran titration, and non-volatile organic carbon (NVOC) by UV-promoted oxidation. Total dissolved solids (TDS) were determined on samples dried at 180°C. Samples for tritium analysis were shipped to the Alberta (Canada) Environmental Centre.

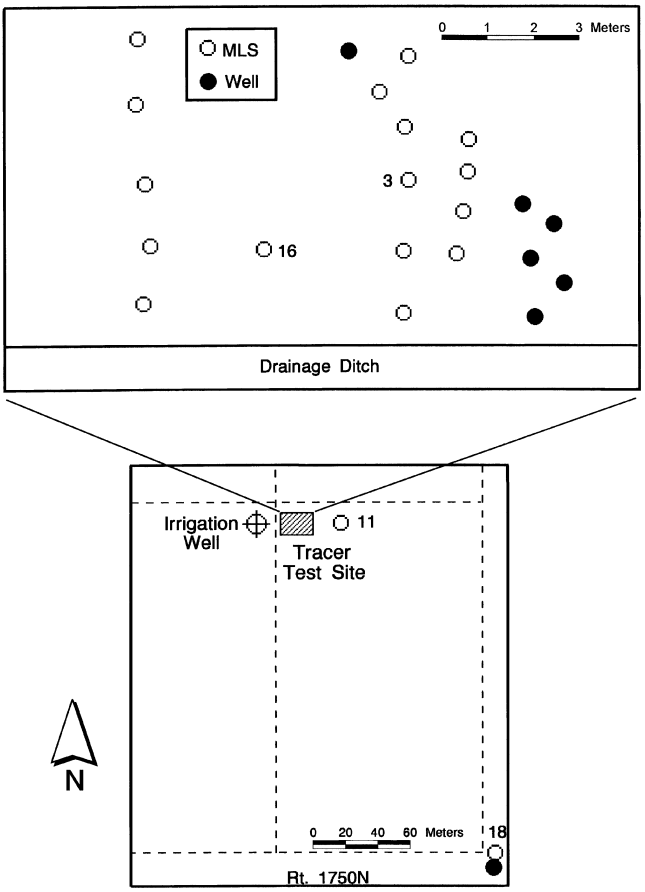

Fig. 2. Location of wells and MLSs on Mason State Tree Nursery property. Filled circles represent wells and open circles represent MLSs; those discussed in the text are identified by number.

4. Results and discussion

Vertical migration of solutes is quite significant in this aquifer. Because percolation is rapid in these soils, the water table is sensitive to precipitation patterns. Ground-water levels were very high during 1993, a year of record rainfall, and in fact considerable amounts of land in Mason County were inundated in 1993 and into 1994 as the water table intersected the land surface. Peak ground-water levels were measured at the site in September and October 1993, and generally fell throughout the remainder of 1993 and all of 1994. Hydraulic heads varied by about 2.5 m at the site during the 18-month study period. Because of the fluctuation of the water table, the top two ports in MLSs 1 through 10 were sometimes located in the unsaturated zone, especially during the latter period of the study. The chemical data (discussed below) reinforce the observation that the water table is sensitive to precipitation patterns.

4.1. Depth profiles

MLSs 3, 7, and 11 were sampled quarterly from July 1993 to July 1994. MLS-16 was also sampled in July 1994 and MLS-18 was sampled in April 1994. Profiles for some of the chemical parameters analyzed for MLSs 3, 11, and 16 from the July 1994 sampling date and MLS-18 from the April 1995 sampling date are shown in Fig. 3. While concentrations varied for the different sampling times, the trends of the vertical profiles were similar for the duration of the project. The following discussion will focus on the July 1994 data unless otherwise specified. Complete results are reported in Kelly and Ray (1997).

The nitrate profile can be divided into three zones (Fig. 3(a)). Near the water table, concentrations were low. Between about 6 and 10 to 12 m below the surface, concentrations were elevated, occasionally exceeding the MCL. Below 10 to 12 m, nitrate was generally below detection. These three zones represent areas where recharge and/or chemical and biochemical reactions are different. The chemical signatures of each zone will be discussed in separate sections below.

4.1.1. Near the water table

The relative depletion of nitrate near the water table, which is atypical in agricultural settings, is hypothesized to be because of mixing with recharge from the nursery, which is depleted in nitrate due to the application of minimal amounts of fertilizer. Irrigation and fertilization practices at the tree nursery are typically much less than for surrounding agricultural fields; for example, no fertilizer was applied here in 1993. To test this hypothesis, MLS-18, hydraulically up-gradient from the other MLSs and about 5 m down-gradient from fields planted in corn or soybeans, was sampled during April 1994 along with MLSs 3, 7, and 11.

Nitrate concentrations in the shallower ports of MLS-18 tended to be greater than in the comparable ports of MLS-3, but the depth at which nitrate disappears is similar for both (Fig. 4(a)). As expected, elevated concentrations of nitrate are found near the water table beneath fertilized fields at MLS-18, but recharge on the tree nursery fields low in nitrate causes a lens of water relatively depleted in nitrate to form near the water table. These results are similar to observations made by Postma et al. (1991), who found nitrate to be depleted near the water table beneath wooded land that was down-gradient from fertilized fields. In fact, plumes containing many types of contaminants are commonly observed to exhibit this behavior in unconfined aquifers.

The fact that this lens has a thickness on the order of 3 m less than 250 m from the agricultural fields up-gradient indicates how substantial recharge from precipitation to the aquifer is in this area. The nitrate profiles for MLSs 3 and 18 are similar if the data from MLS-18 are plotted 3 m deeper, to simulate the addition of low-nitrate recharge water found at MLS-3 (Fig. 4(b)). Assuming a ground-water velocity of about 0.18 m day^{-1}, determined in tracer tests at the site (Kelly and Ray, 1997), it would take approximately 3.6 years for a particle to travel from MLS-18 to MLS-3. During the 3.6 years prior to the April sampling date, approximately 400 cm of precipitation fell at the tree nursery. If the 3-m-thick lens is due solely to recharge from precipitation (irrigation is ignored), then approximately 75% of the precipitation water that fell during the period recharged the aquifer. There is no evapotranspiration data for the tree nursery, but the average rate for

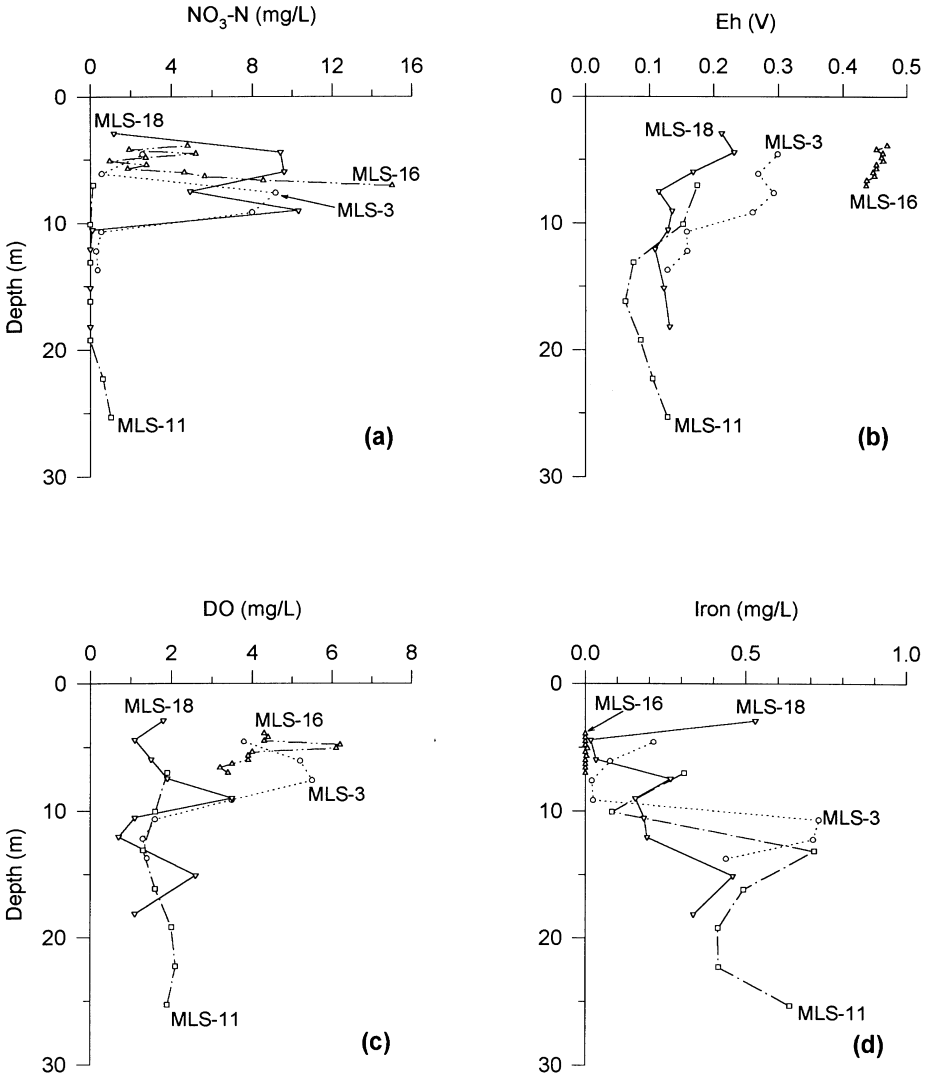

Fig. 3. Concentrations of chemical parameters vs depth from surface for MLSs 3 (○), 11 (□), and 16 (△) in July 1994 and MLS-18 (▽) in April 1994: (a) nitrate, (b) Eh, (c) DO, (d) total iron, (e) sulfate, (f) calcium, (g) chloride, (h) DIC.

soybeans in Mason County is around 20 cm year^{-1} (Bowman and Kimpel, 1991), which approximately accounts for the remaining 25% of the precipitation. There is very little overland runoff in the sandy soils in Mason County, thus the estimated recharge percentage of 75% seems reasonable.

This dilution at the water table between MLSs 3 and 18 is also observed for most of the other inorganic species. For many species, concentrations near the water table are much higher in MLS-18 than MLS-3. Calcium, magnesium, sulfate, DIC, TDS, and strontium

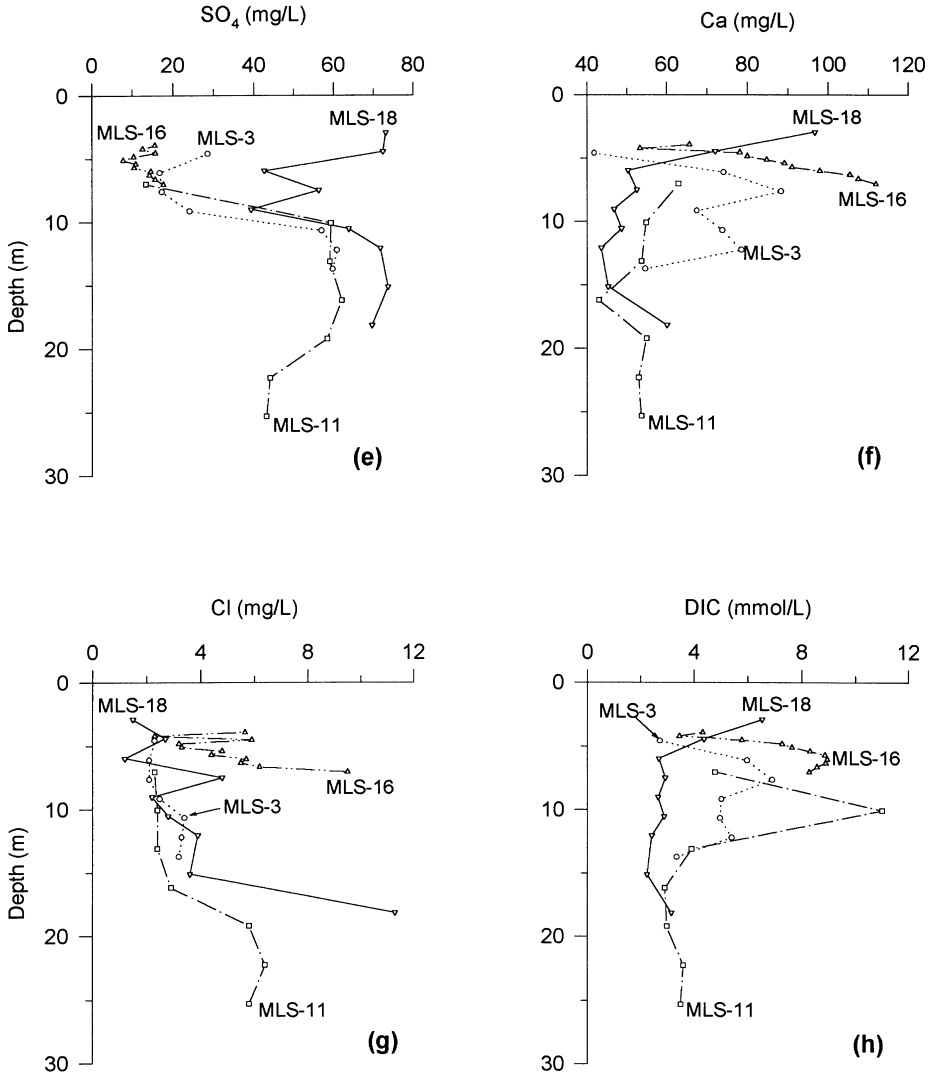

Fig. 3. Continued.

are all approximately twice as high in the uppermost port of MLS-18 versus MLS-3. Iron and manganese are about five and ten times higher, respectively. NVOC concentrations are ten times higher and the pH is higher by about 0.5 pH units. On the other hand, Eh and DO are lower in MLS-18. While the decrease in concentrations for most of the species is likely due to dilution by dilute recharge water, the increase in DO between MLS-18 and MLS-3 may contribute to the loss of iron and manganese from solution by promoting precipitation of iron- and manganese-bearing phases.

These results suggest several things. First, conditions are more reducing near the water table next to the agricultural fields found up-gradient from the tree nursery. This may

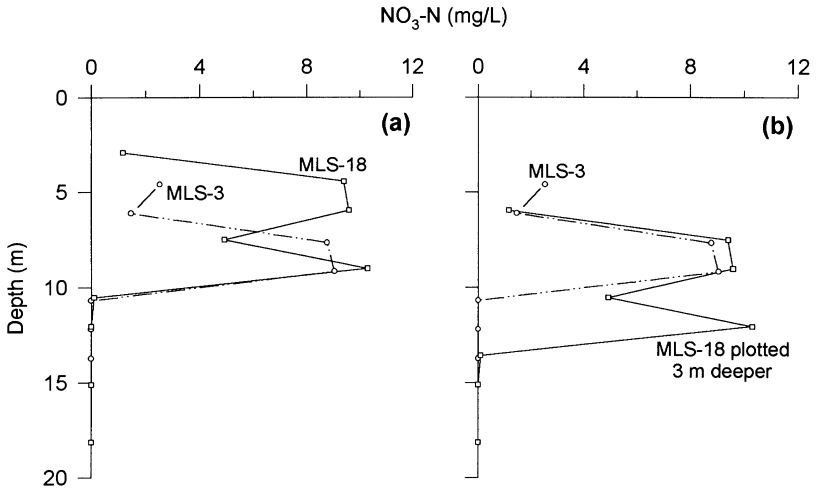

Fig. 4. Nitrate concentrations for MLSs 3 (◦) and 18 (□) in April 1994: (a) actual data, (b) MLS-18 data plotted 3m feet deeper than actual.

reflect more intense biological activity in the agricultural fields up-gradient of the field site, due to denser plantings and greater applications of fertilizer. Increased amounts of organic matter and nutrients stimulate microbiological activity, which depletes oxygen and makes conditions more reducing. Second, in addition to there being a source for nitrate in this area, there are also sources for many other major ions. Possible sources include fertilizers (S. Panno, unpublished data, 1994), irrigation water, and/or reactions in the unsaturated zone. Finally, it should be noted that the vertical profiles for many of the parameters do not match well between MLSs 3 and 18, even when the MLS-18 data are plotted 3 m deeper, as with the nitrate data. It is obvious that there are mechanisms other than dilution affecting water quality in the aquifer, including redox reactions, mineral dissolution/precipitation reactions, spatial and temporal variability in the chemistry of the recharging water, and physical heterogeneities in the aquifer.

At the tree nursery, water recharging the aquifer should have the composition of rainwater that has reacted with materials in the unsaturated zone. In the agricultural fields, the recharge-water composition should include a significant component of deep ground water. Water recharging most unconfined aquifers starts out as precipitation that migrates through the unsaturated zone. In this region, however, a significant portion of the recharging water starts out as irrigation water that has been pumped up from depth, generally greater than 20 m beneath the land surface (Bowman and Kimpel, 1991). In Mason County, an average of 38 cm of water is applied to the fields annually by irrigation; thus almost 30% of the water striking the land surface in irrigated fields during a year with average precipitation (94 cm) is from irrigation. This percentage is quite variable, being higher during drought years and lower during wet years. For example, during the drought year of 1988, the average amount of irrigation water applied was 58 cm (Bowman and Kimpel, 1991), while in the flood year of 1993, many farmers did not irrigate.

Precipitation water is very dilute, with most constituents typically having

concentrations less than 1 mg l^{-1} (Table 1). In addition, it is undersaturated with respect to most common minerals. The irrigation water, on the other hand, which usually comes from fairly deep parts of the aquifer (>20 m below land surface), has greater concentrations of most chemical constituents. Water samples taken from the deepest port of MLS-11 (24 m below the land surface) have an average chemical composition shown in Table 1.

The composition of the water striking the land surface is important because the composition controls the identity and rates of chemical and biochemical reactions that occur in the subsurface, such as mineral dissolution, ion exchange, biodegradation, etc. The fact that the composition of the recharge water is variable complicates interpretation of the ground-water quality data.

The geochemical reaction-path code PHREEQE (Parkhurst et al., 1980) was used to simulate mixing of 30% deep aquifer water with 70% rainwater, to produce recharge water that includes the average annual input from irrigation. Chloride, which behaves conservatively in sand and gravel aquifers, has a mixed concentration of approximately 2.3 mg l^{-1}, which is close to the concentration found in the upper ports of MLS-18 (between 1.5 and 2.7 mg l^{-1}). Sodium, which may also behave conservatively in this system, has a mixed concentration around 1 mg l^{-1}, slightly less than observed in MLS-18 (between 1.85 and 2.47 mg l^{-1}). For the rest of the parameters, however, the simulation underpredicts the concentrations found in the uppermost ports of MLS-18. Therefore, simple mixing of

Table 1
Average water chemistries and results from PHREEQE simulations. Precipitation data are from Illinois State Water Survey sampling station in Monmouth, Illinois, about 50 miles northeast of the study site. PHREEQE simulations are 30% composition from MLS11-1 mixed with (1) 70% precipitation and (2) 70% composition from top port of MLS-3. Data reported as mg l^{-1} unless otherwise noted

Parameter	Precipitation	MLS-11 bottom	PHREEQE		MLS-18 top
			70% precipitation + 30% MLS11-1	70% MLS3 + 30% MLS11-1	
pH[a]	4.70	7.30	7.26	7.15	7.45
Ca	0.26	62.8	19.0	58.2	84.4
Mg	0.031	17.1	5.15	16.0	24.9
Na	0.056	3.07	0.96	3.38	2.16
K	0.018	1.03	0.32	1.39	0.84
Cl	0.11	7.47	2.32	4.24	2.10
SO_4	2.10	40.5	13.6	35.2	72.8
DIC[b]	n.r.	4.15	1.24	4.02	5.46
NO_3-N	0.34	0.30	0.33	3.16	5.28
NH_4	0.45	0.04	0.33	0.32	< 0.02
Fe	n.r.	0.49	0.15	0.29	0.274
Mn	n.r.	0.22	0.07	0.21	1.40
Si	n.r.	5.98	1.80	5.23	5.04
Sr	n.r.	0.09	0.03	0.12	0.18
NVOC	n.r.	1.5	0.45	0.40	3.0

[a] pH units.
[b] mmol l^{-1}.
n.r., not reported.

irrigation water and rainwater cannot account for the observed composition of water near the water table at the tree nursery.

Simulations were also run using the water composition from the top port of MLS-3, which should have little input from irrigation, instead of rainwater. The rationale for this was that rainwater composition is altered during migration through the unsaturated zone and thus a water composition from MLS-3 would be more representative of the composition of water recharging the aquifer without irrigation contributions. The mixed water more closely resembles MLS-18 for this simulation, but still underpredicts the concentrations of most parameters (Table 1). It appears that some other mechanisms must account for the observations. An obvious source of ions not considered in these simulations is fertilizers, which could account for increases in the concentrations of nitrate, calcium, magnesium, sulfate, and DIC, among others. Additional explanations are that there is considerable variability in the water chemistry in the aquifer, even at depths of 25 m, and biodegradation reactions may be more significant near MLS-18, where higher levels of organic carbon in the ground water were measured (Fig. 5), which would affect redox-sensitive species and alkalinity. The mixed solutions from both simulations are calculated to be undersaturated with respect to calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$).

Saturation indices were also calculated for other water compositions using the thermodynamic geochemical code WATEQF (Plummer et al., 1976). The water sample from the shallowest port in MLS-3 is undersaturated with respect to calcite and dolomite. All other samples from MLS-3 are saturated with respect to these minerals. Similar results were found for MLS-18, except the shallowest port was undersaturated only with respect to dolomite. Thus in the unsaturated zone and/or a narrow zone just below the water table, enough calcium and magnesium are put into solution that dissolution of calcite and dolomite is no longer thermodynamically favored.

4.1.2. Nitrate plume

The only significant source of nitrate in this area is from fertilizer. The results from

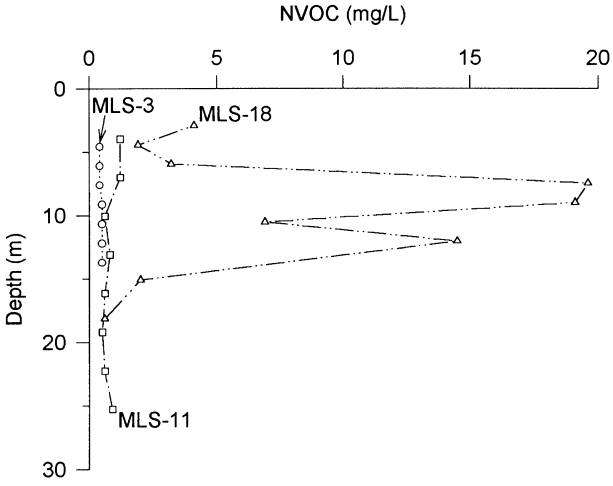

Fig. 5. NVOC concentrations vs depth from surface for MLSs 3 (∘), 11 (□), and 18 (△) in April 1994.

MLS-18 indicate that applications in fields up-gradient from the study site account for the nitrate plume found in the ground water.

Correlations between nitrate and the other chemical parameters were calculated to determine if the concentrations of the other parameters could be related to nitrate. Because nitrate concentrations were below detection in some of the samples, a non-parametric test, the Spearman rank order correlation, was used (Helsel and Hirsch, 1992). Fairly strong positive correlations ($r_s > 0.6$) were found between nitrate and magnesium, strontium, calcium, DIC, silicon, DO, and TDS for the July 1994 samples (Table 2). Nitrate had fairly strong negative correlations ($r_s < -0.6$) with pH and iron. Poor correlations were found between nitrate and NVOC, sodium, potassium, and sulfate. Similar results were found for all sampling dates.

Some of these correlations are readily explained. As mentioned above, fertilizers can include a number of ions other than nitrate. In addition, nitrate is a redox-sensitive species, and thus it would be expected to be correlated to some extent with other redox-sensitive species, such as DO and iron. Nitrate concentrations are also influenced by biodegradation reactions, and thus its correlation with DIC and pH, which are often affected by biodegradation reactions, is not unexpected. On the other hand, nitrate was not correlated with NVOC, another parameter affected by biodegradation.

4.1.3. Deep aquifer

Low levels of nitrate at depth are not unexpected; this observation has been made in most unconfined aquifers. The two most likely explanations are (1) conditions at depth are conducive to denitrification reactions, or (2) there has been inadequate time for nitrate to reach such depths.

The nitrate plume is probably dominated by aerobic bacteria, where detectable levels of DO are present. There is a sharp zonation in the water chemistry at the base of the nitrate plume, where the disappearance of nitrate occurs in conjunction with decreases in DO and Eh values (Fig. 3(b) and (c)) and the appearance of significant concentrations of dissolved iron, manganese, and sulfate (Fig. 3(d) and (e)). These changes indicate a redoxcline, below which the redox conditions are significantly more reducing; below the redoxcline, nitrate is unstable and removed via denitrification or other nitrate reduction reactions. Both

Table 2

Spearman rank correlation coefficients (r_s) and P values for nitrate with other chemical parameters for July 1994 data. Larger absolute r_s values indicate stronger correlations between variables. P values measure the probability of wrongly concluding that there is a true association between the variables (falsely rejecting null hypothesis). P values >0.05 generally indicate there is no significant relationship

Parameter	r_s	P	Parameter	r_s	P	Parameter	r_s	P
pH	–0.67	0.0	DIC	0.66	0.0	Sr	0.67	0.0
Ca	0.66	0.0	Fe	–0.66	0.0	Zn	0.11	0.55
Mg	0.67	0.0	Mn	–0.60	0.0	TDS	0.64	0.0
Na	–0.37	0.04	Al	0.09	0.65	DO	0.21	0.0
K	–0.45	0.01	Ba	0.09	0.63	Eh	0.59	0.0
Cl	0.53	0.0	Si	0.66	0.0	DOC	0.65	0.24
SO_4	–0.43	0.01						

iron and manganese tend to form insoluble oxyhydroxide solid phases under oxidizing conditions, but are much more soluble under reducing conditions. The change in color from reddish-brown to gray sand at depths around 12 m suggests that iron reduction is occurring. Because iron reduction reactions occur under conditions more reducing than nitrate-reduction reactions, the thermodynamics of the system are favorable for denitrification.

Nitrate may be denitrified in the presence of several terminal electron donors, most commonly organic carbon or sulfide (Appelo and Postma, 1993). If organic carbon is the primary electron donor, then the disappearance of nitrate should occur in conjunction with a decrease in NVOC and an increase in CO_2, which in turn might affect other geochemical reactions (e.g. decreased pH and increased solubility of carbonate minerals). If sulfide is the primary electron donor, then increases in iron and sulfate and a decrease in pH should be observed (van Beek et al., 1989).

Denitrification rates in ground water are most commonly limited by a lack of metabolizable organic matter (Starr and Gillham, 1993). This is especially true in well-sorted sand aquifers, where amounts of organic matter tend to be small. While NVOC levels are not high in this aquifer (generally between 0.4 and 3.0 mg l^{-1}), there do appear to be sufficient amounts for denitrification. NVOC concentrations in the shallower ports of MLS-18 were much higher than for any of the other MLSs sampled (Fig. 5). The loss of NVOC as ground water migrates is indirect evidence that biodegradation reactions in which organic matter is oxidized are occurring.

DIC concentrations, a measure of CO_2 production, are also higher down-gradient from MLS-18. There is also a slight increase in DIC beneath the redoxcline in MLS-18. However, there is no increase in DIC at the base of the nitrate plume in MLS-3 at the July 1994 sampling date (Fig. 3(h)), which would be expected if organic carbon was being oxidized to CO_2. DIC concentrations were observed to be slightly higher below the plume at other sampling dates, although concentrations always tended to be relatively low in the deepest ports (>12 m). DIC concentrations tend to be greatest in the nitrate plume and just below it, suggesting there is an active bacterial population in this zone. NVOC and DIC concentrations are correlated (r^2 = 0.48), suggesting increased microbial activity in zones where NVOC levels are greatest. However, DIC is more strongly correlated with calcium and magnesium, having r^2 values of 0.95 and 0.95, respectively. These two cations are highly correlated with each other (r^2 = 0.96) and are commonly associated with one another. The production of DIC decreases the pH and increases the solubility of carbonate minerals, such as calcite and dolomite. Below the nitrate plume, however, there is no increase in calcium and magnesium concentrations (Fig. 3(f)) and there is no significant change in saturation indices for carbonate minerals.

The possibility of denitrification in conjunction with sulfide oxidation is supported by the sulfate data, which increase sharply at the base of the nitrate plume and at a rate consistent with the amount of nitrate removed (Fig. 3(e)). The increase in iron is much smaller (Fig. 3(d)), although it may be removed from solution by precipitation as oxyhydroxide minerals. Using the concept of electron equivalents developed by Postma et al. (1991), sulfide oxidation as measured by production of sulfate can account for between 50 and 95% of the nitrate reduced across the redoxcline for the various MLSs and sampling times.

However, sulfate concentrations decrease between MLS-18 and MLS-3, when they should be increasing if sulfide oxidation is occurring (Fig. 3(e)). Sulfate would not be expected to be sorbed significantly in a sand aquifer. Sulfate reduction is a potential sink for sulfate, but no sulfide was ever detected in these samples and iron concentrations would be expected to be very low at depth if sulfide was being produced. The decrease in sulfate may be due to dilution effects as discussed previously; a significant source of sulfate to the aquifer is likely from impurities in fertilizers applied up-gradient of the tree nursery. Fertilizers commonly used in the area have high levels of sulfate, up to 10% by weight (S. Panno, unpublished data).

Further drawbacks to the sulfide oxidation mechanism are that the pH does not decrease below the nitrate plume, but increases slightly (data not shown), and pyrite has not been identified in the aquifer material in this or other investigations, although the gravel-sized coal that is especially abundant 10 to 12 m beneath the surface, the approximate depth of the redoxcline, could be a source of sulfur, and sulfide minerals are commonly associated with coal.

In sum, there is evidence from the redox data that conditions for denitrification reactions are favorable, but the data are equivocal and exact mechanisms cannot be defined. It is possible that both organic matter and sulfide are being used as terminal electron donors during denitrification. In order to assess the second possibility for absence of nitrate at depth, i.e. that nitrate has had insufficient time to reach depth, tritium analyses were performed. In April of 1994, samples were taken for tritium analysis to determine the relative age of the waters and estimate how rapidly water moves through the aquifer.

Tritium was detected in all samples taken, even to a depth of nearly 25 m below the surface (Fig. 6). Concentrations decrease from the water table to about 6 m below land surface, then tend to increase with depth at greater depths. There is no observable ‘bomb pulse’; based on work by Daniels et al. (1989) in Indiana ground water, present tritium concentrations of ground water that recharged during the early 1960s would be around 75 TU (ritium units) (K. Hackley, personal communication, 1995). It appears that all the samples tested are less than 20 years old, indicating that rapid transport of solutes to considerable depths has occurred in this area. This rapid transport may be facilitated by the widespread irrigation pumping in this region. Forced-gradient tracer tests performed at the site suggest that vertical movement due to irrigation pumping could be important (Kelly and Ray, 1997).

Because tritium is found throughout the water column but nitrate is not suggests that denitrification is the principal factor restricting migration of nitrate to depth in this aquifer. This hypothesis is supported by the redox data. However, elevated levels of other constituents in the plume, such as calcium and magnesium, confound this interpretation. The concentrations at depth for calcium ($\sim$60 mg l^{-1}) and magnesium ($\sim$20 mg l^{-1}) are less than those found in the nitrate plume. If water is rapidly moving vertically through the aquifer as indicated by the tritium results, then either there must be some process removing them at depth or else their presence in the plume represents a fairly recent addition via recharge. The ground water is supersaturated with respect to calcite throughout the water column except near the water table, but it is unclear why calcite precipitation would be enhanced at the base of the plume since the reaction is not directly affected by redox conditions.

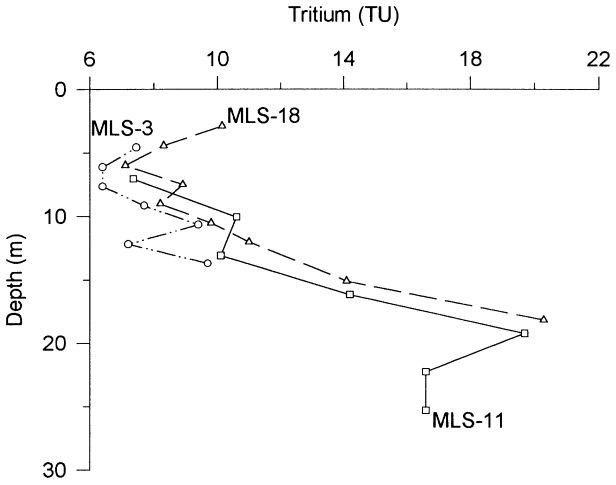

Fig. 6. Tritium concentrations vs depth from surface for MLSs 3 (◦), 11 (□), and 18 (△) in July 1994.

4.1.4. Summary of depth profile data

A simple conceptual model summarizing interpretation of the depth profile data, with special emphasis on nitrate, is illustrated in Fig. 7. Water with elevated levels of most ions resulting from fertilizer applications recharges the aquifer beneath cultivated fields. As the plume migrates down-gradient, recharge at the Tree Nursery is relatively low in solutes due to limited fertilizer application, causing the plume to sink. Once the plume reaches a depth where conditions are reducing enough so that denitrification proceeds, nitrate is removed from solution and is generally not detected below this depth.

4.2. Lateral variability

In addition to the vertical variability in water chemistry, variability among the MLSs was also often quite striking. MLSs were sampled for nitrate in November 1993 (MLSs 1 through 5) and November 1994 (all MLSs). The November 1994 data were plotted in cross-sections to produce two- and three-dimensional pictures of nitrate concentrations (Fig. 8). The high-nitrate zone is readily apparent, but considerable variability can be observed. This is especially apparent in two of the profiles. In Fig. 8(b), three MLSs had no samples above 2 mg l^{-1} while the other two had two each above 4 mg l^{-1}. The absence of elevated levels of nitrate in the other MLSs may be because none of their ports are located in the elevated zone or the nitrate plume, for some reason, is confined to a narrow zone. MLSs 12 through 15 sample every foot (30 cm), and this fine resolution allows considerable variability to be observed (Fig. 8(a)). It seems reasonable to conclude that the migration of solutes is significantly affected by heterogeneities in the aquifer. This conclusion is borne out by tracer studies at the site (Kelly and Ray, 1997).

Four MLSs were sampled in July 1994. Three (MLSs 3, 7, and 16) are within 6 m of each other. The other, MLS-11, is approximately 25 m east of MLS-3. MLSs 3 and 7 have sample ports at approximately the same depths. Chemical trends for these two MLSs were

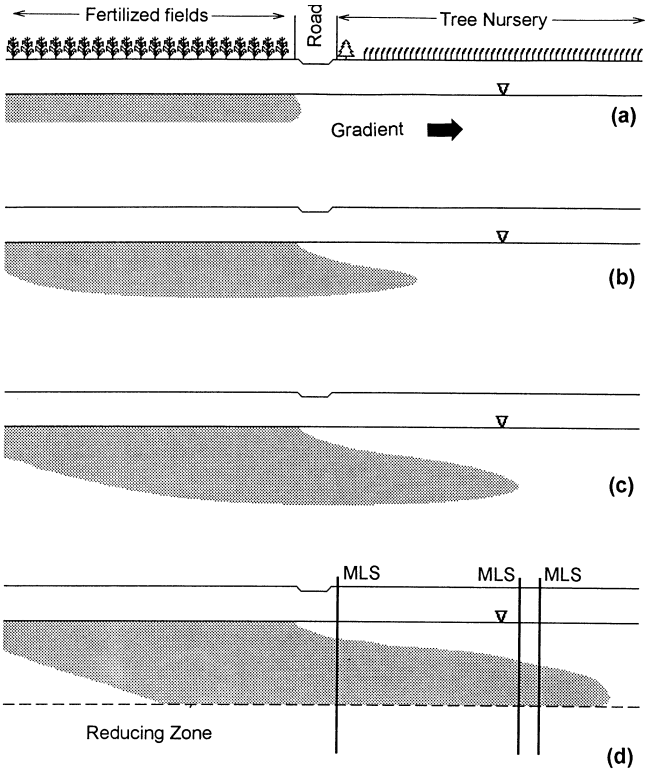

Fig. 7. Cross-sectional view of simple conceptual model of evolution of the water chemistry at the field site: (a) water with elevated levels of many ions recharges aquifer beneath fertilized fields up-gradient from field site; (b) and (c) as the plume migrates down gradient, water with relatively low concentrations of ions recharges the aquifer at the water table; (d) when the plume reaches a certain depth, conditions are favorable for denitrification, and nitrate is removed from solution. Vertical exaggeration is approximately 10 ×.

generally the same, but there are some differences. For example, while nitrate concentrations were greatest for both MLSs between 7.5 and 9 m below land surface, concentrations in MLS-7 were considerably greater for the 3 m below this zone in MLS-7 than MLS-3 (data not shown). Most of the other chemical constituents were similar for the two MLSs.

MLS-16, which is approximately halfway between MLSs 3 and 7, samples the upper part of the aquifer with ports that are closer together than those in MLSs 3 and 7. Chemical trends are similar for MLS-16, although more variability is observed because of the greater depth resolution. For example, between about 3 and 6 m below the surface, nitrate concentrations fluctuate, and a higher peak concentration is observed than for the other two MLSs. This variability is evident for most other constituents as well, and reflects the common observation that the more closely spaced the samples, the more heterogeneities and variability that are observed.

For some constituents, concentrations in MLS-16 were significantly different than for MLSs 3 and 7. For example, NVOC concentrations were higher in MLS-16, sometimes twice the value for MLSs 3 and 7 (data not shown). Peak concentrations were highest in

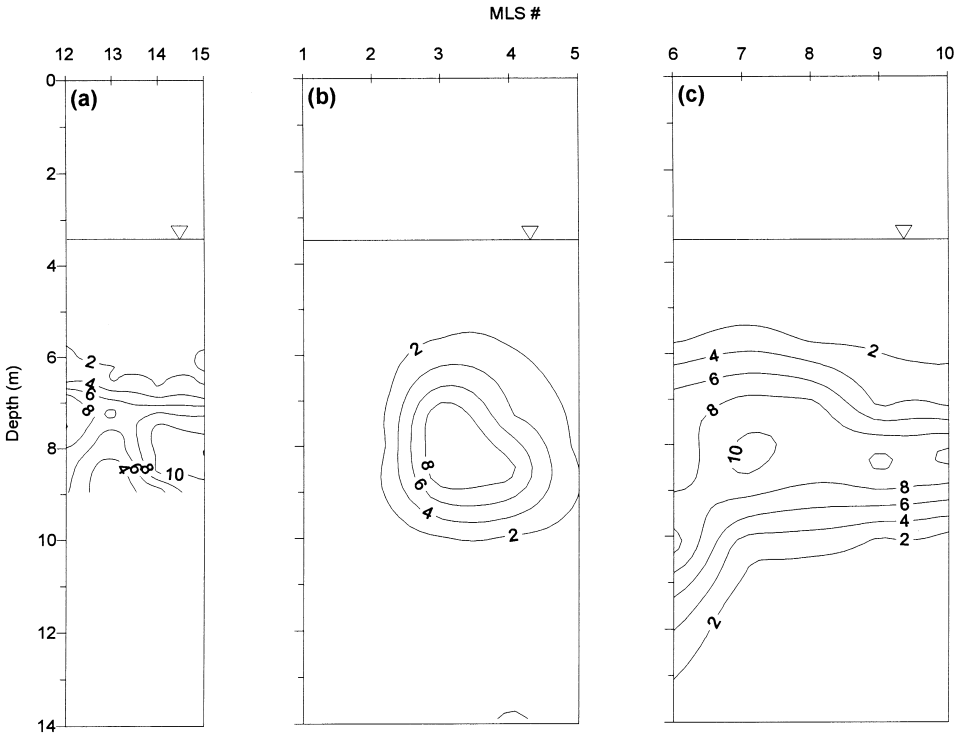

Fig. 8. Vertical cross-section of nitrate concentrations in November 1994 as a function of depth for (a) MLSs 12 through 15, (b) MLSs 1 through 5, and (c) MLSs 6 through 10. Contours in mg l^{-1} NO_3-N. No vertical exaggeration. Ground-water flow is generally from left to right for each section.

MLS-16 for several other parameters, including calcium, magnesium, TDS, and DIC. Eh values were also highest in MLS-16, but DO concentrations decreased at shallower depths than for MLSs 3 and 7 (Fig. 3(b) and (c)).

The water-chemistry differences among MLSs 3, 7, and 16 were relatively minor compared with differences with MLS-11. MLS-11 has deeper and more widely spaced (3 m) ports than the other three. Perhaps the most striking difference is that nitrate was not detected or had very low concentrations in all ports, including those that straddle the nitrate plume found in MLSs 3, 7, and 16 (Fig. 3(a)). The waters from MLS-11 also were significantly more reducing than for the other MLSs, as indicated by Eh and DO values (Fig. 3(b) and (c)). It appears that either denitrification reactions occur at much shallower depths in this region of the aquifer or there is no source for a nitrate plume up-gradient from MLS-11. The latter explanation seems unlikely because the farm field up-gradient of MLS-11 is the same as that up-gradient of MLSs 3 and 7.

Other differences in water chemistry found for MLS-11 included higher pHs and lower calcium, magnesium, TDS, and DIC concentrations. The other chemical parameters had trends similar to the shallower MLSs.

These differences illustrate the chemical and physical heterogeneities found in a system such as this one. While we might expect the chemical composition of precipitation and

irrigation water to be relatively consistent, both temporal and spatial variability in fertilization inputs and irrigation rates will lead to ground-water compositions that are not 'well mixed.' In addition, spatial variability in hydraulic conductivity leads to preferred flow paths and variable ground-water velocities (Kelly and Ray, 1997).

4.3. Temporal changes

Concentration profiles for each MLS were similar for all the constituents throughout the study period, although actual concentrations for some of the constituents varied considerably (Fig. 9). Nitrate in some ports varied by as much as 100% (Fig. 9(a)). Redox conditions and other constituents also varied temporally. Based on the Eh, DO, and dissolved iron data, conditions were most reducing at the February sampling date (Fig. 9(b)–(d)). Calcium, magnesium, TDS, and DIC sometimes varied more than 100% (Fig. 9(f) and (h)). Sodium, chloride, sulfate, and pH all exhibited some temporal variability, although magnitudes were less than for the other constituents (Fig. 9(e) and (g)). Highest concentrations for many of the constituents were measured at the February sampling date.

Little irrigation pumping was done in 1993 because of the extremely wet conditions, thus it cannot be used to explain variability in water chemistry for that year. The significant temporal variability probably is an illustration of the large impact agricultural practices have on ground-water chemistry in this region. For example, fertilizer is applied at specific times of year, and rapid percolation of precipitation and irrigation water to the water table suggests that the input of nitrate to ground water will be quite variable over the course of a year, a function of land use activities and precipitation/irrigation events. Thus one might expect the water chemistry of migrating ground water to be quite variable in composition, especially for constituents that are affected by human activity.

Another possibility for changes in nitrate and redox conditions over time is variations in bacterial activity. Bacterial metabolism is affected by temperature, generally increasing with increasing temperature. Therefore, one would expect greater reaction rates in warmer weather and lower rates in winter. This has been reported in some shallow ground waters (e.g. Hallberg, 1987; Littke and Hallberg, 1991). However, at this site the data are equivocal for this hypothesis. While highest nitrate concentrations are observed for some ports in the winter, highest concentrations are observed in July for others (Fig. 9(a)). The fact that little fertilizer is applied at the tree nursery and recharge is rapid confounds the interpretation. Because sampling was done for only 1 year, seasonal differences cannot be adequately assessed.

5. Summary and conclusions

Water samples taken from MLSs installed in a sand aquifer beneath irrigated fields reveal considerable heterogeneity in the aqueous chemistry both spatially and temporally. Recharge is rapid in this system and the water chemistry of the recharge water is variable both spatially and temporally, and is influenced by agricultural practices. The water chemistry data strongly reflect both the geology of the aquifer, soils, and irrigation and fertilization practices. The lateral and temporal variabilities observed for most of the

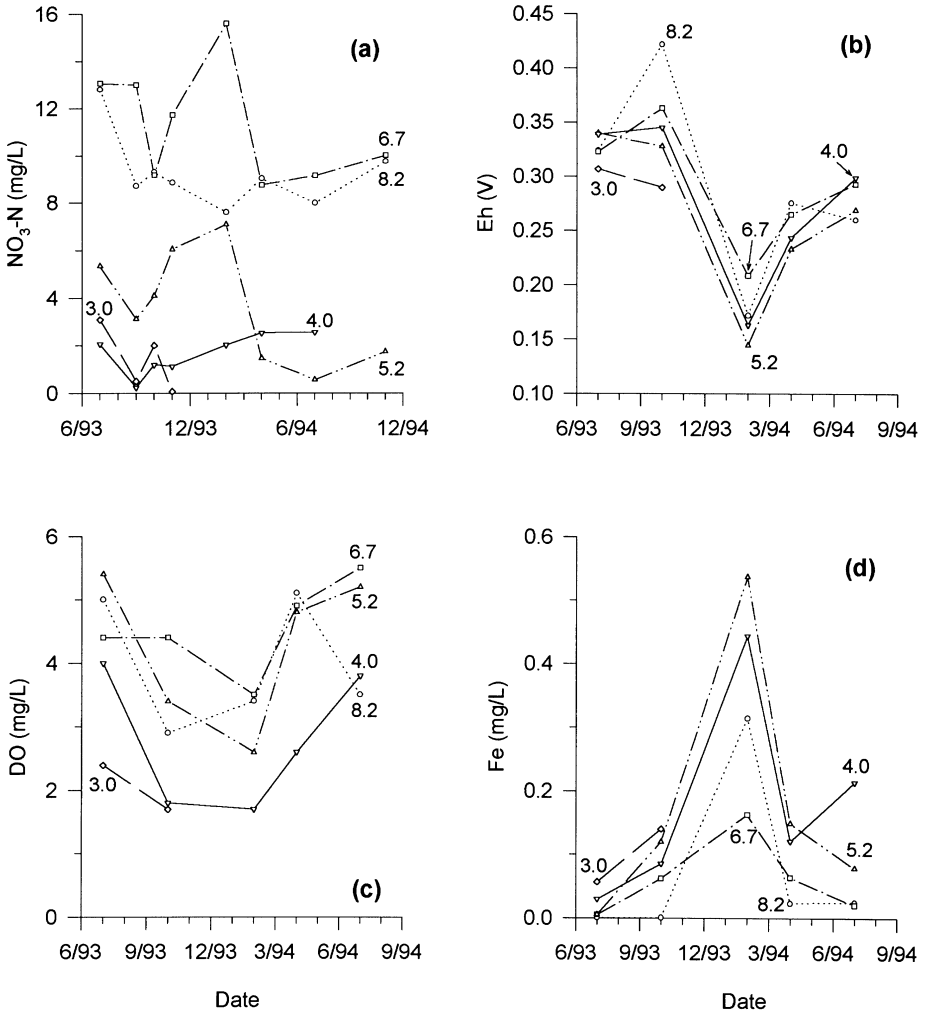

Fig. 9. Temporal variation in chemical parameters for five uppermost ports of MLS-3 for (a) nitrate, (b) Eh, (c) DO, (d) total iron, (e) sulfate, (f) calcium, (g) chloride, (h) DIC. Ports 3.0 (◇), 4.0 (▽), 5.2 (△), 6.7 (□), and 8.2 (◦) m below land surface. Missing data from upper two ports represent times when these ports were in the unsaturated zone. Data from lowest four ports not shown.

chemical parameters are most likely explained by the inconstant application of fertilizer and other agrichemicals at the surface, physical heterogeneities in the aquifer leading to variability in permeability, and the rapid percolation of water to the saturated zone, which in turn is a function of precipitation events and scheduling of irrigation activities.

The lack of nitrate near the water table at the field site is probably because little fertilizer is applied at the tree nursery compared with surrounding agricultural fields and recharge to the aquifer is rapid. Nitrate concentrations are elevated in a zone between about 6 and 10 m beneath the surface, although in certain areas and at certain times this zone was not found.

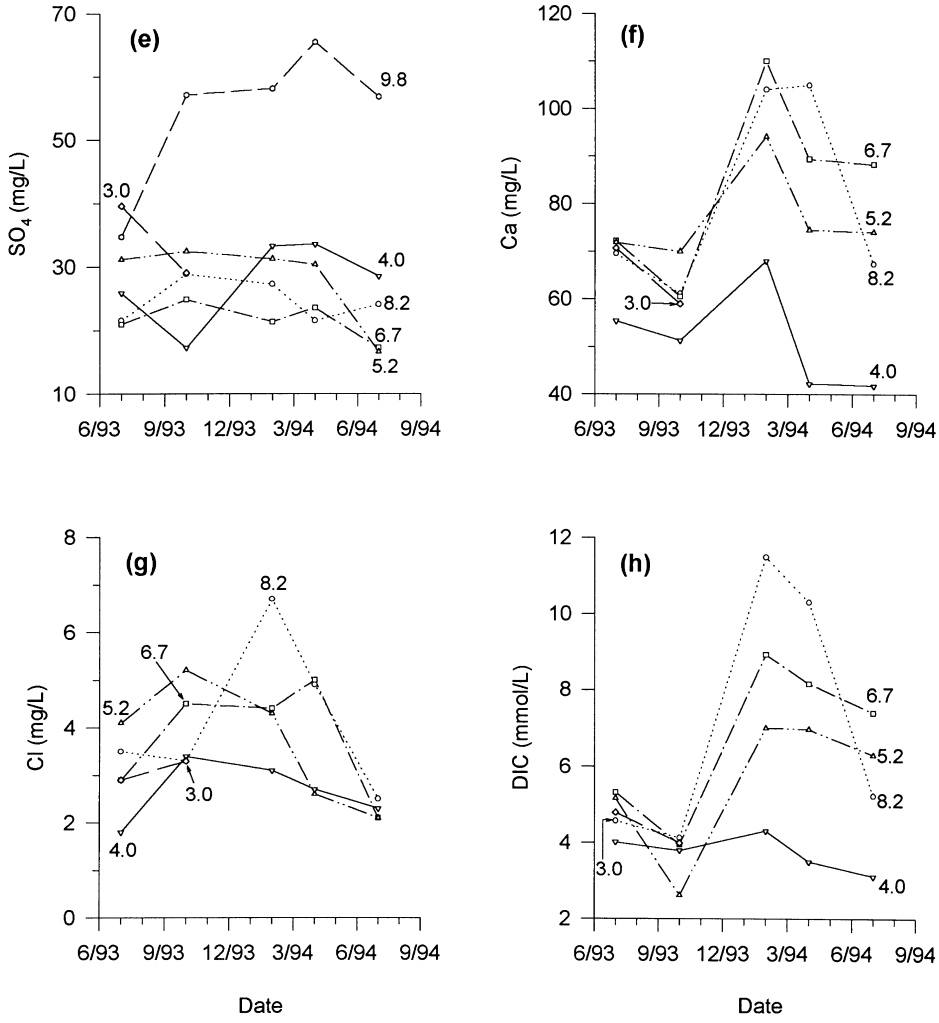

Fig. 9. Continued.

The maximum nitrate concentrations in this zone were slightly greater than 20 mg l^{-1} as N, well above the MCL. Nitrate was generally absent below this depth in the aquifer, probably due to denitrification reactions, probably mainly in conjunction with sulfide oxidation; the tritium data suggest that vertical movement of solutes is rapid and thus there has been enough time to transport fertilizer applied at the surface in the last few decades to depths in excess of 30 m in this area. Reducing conditions are found at depth, indicating conditions are conducive to denitrification. The lateral variability highlights the heterogeneous nature of the microbial activity. In some areas (i.e. near MLS-11), denitrification appears to be important even near the water table. Drinking water quality is not degraded by fertilization in this area, because drinking-water wells are generally screened well

below the zone of elevated nitrate concentrations. Homeowners with a well screened at depths less than 15 m should have their water periodically analyzed for nitrate.

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