SPATIAL AND TEMPORAL NITRATE CONCENTRATION VARIABILITY WITHIN THE MISSISSIPPI RIVER VALLEY ALLUVIAL AQUIFER ON A SMALL SCALE AT SELECTED ARKANSAS, USA SITES

Steele, Kenneth F.[1], Davis, Ralph K.[1] and Kresse, Timothy M.[2]

[1]*Department of Geosciences, University of Arkansas, Fayetteville, AR 72701, USA.*
[2]*Water Division, Arkansas Department of Environmental Quality, Little Rock, AR 72219, USA*

ABSTRACT

Twelve shallow wells at three sites and six deep irrigation wells at two sites were used to evaluate the spatial variability of nitrate concentrations in the Mississippi River Valley alluvial aquifer. Seven of these wells at two sites were used to evaluate the temporal variability. There is significant nitrate concentration variability both spatially and temporally. Spatial variability is as great as 0.04 to 14.45 mg/L NO_3-N, and temporal variability in a well is as great as 0.11 to 14.45 mg/L NO_3-N over a period of 45 days. The deep wells generally have low nitrate concentrations. Transport of nitrate from fertilizer to the ground-water system and subsequent denitrification are considered the major factors causing nitrate variability within the alluvial aquifer.

Keywords: alluvial aquifer, ground water, nitrate, spatial variation, temporal variation, water quality

INTRODUCTION

The objective of this study was to ascertain spatial and temporal variability of aqueous nitrate concentrations on a small scale within the Mississippi River Valley alluvial aquifer at three Arkansas sites (Fig. 1). The eastern third of Arkansas is covered by alluvium deposited by an ancestral Mississippi River and is a major producer of rice and soybeans in the U.S.A. Despite receiving about 1270 mm of rain annually (NCDC, 2003), these sites rely on ground water during the summer when drought conditions are prevalent. During the summer, rain is mostly from short-lived thunderstorms that produce intense rainfall, and there is high evapo-transpiration. The aquifer is composed of alluvium that grades downward from sand, silt and clay at the surface to coarse sand and gravel at the base; however, discontinuous lenses of clay, silt or sandy silt occur within the aquifer (Ackerman, 1989). These discontinuous lenses may pinch out spatially within a short distance, as little as 60 m. The lower portion of the aquifer yields 3,785 to 11,355 liters of water per minute (Petersen *et al.*, 1985) to irrigation wells that are critical for crop production. Overlying much of the aquifer is a unit composed of as much as 6 m of fine silt and clay (in the study area) that can restrict local recharge of the aquifer. The discontinuous lenses and the overlying fine silt and clay could potentially affect composition of local ground water. The aquifer contains carbonaceous material in a form and sufficient quantity to produce reducing conditions in the aquifer (Kresse and Fazio, 2003; Holbrook, 1980).

Figure 1. Map of Arkansas showing site locations in each county. The inset shows the location of Arkansas in the U.S.A.

DESCRIPTION OF SITES

Shallow, closely spaced monitoring wells, originally installed near domestic drinking water wells to investigate pesticide contamination at three sites, were utilized for this project. The monitoring wells are approximately 9 m deep, and depth to water ranges from 4.5 to 7.5 m depending on season and site (Kresse and Van Schaik, 1996; Johnston, 2001). Information suggests that the domestic wells have similar depths and water levels to those measured in the monitoring wells. Maximum distance between wells is 212 m at each site. Because of the relatively flat water table, flow directions are subject to change based on local usage and recharge variability. Three irrigation wells also were sampled at each of two the sites. The irrigation wells are 30 ± 6 m deep (Kresse and Van Schaik, 1996; Johnston, 2001) and are about 0.13 km from each other at each site. Each is about 0.8 km from the monitoring wells at each site.

Site characteristics are summarized in Table 1. The soils vary among sites as well as on site for the closely spaced monitoring wells. As noted above, lenses of sandy silt to clay occur sporadically within the soil and alluvium Crops are rotated periodically among soybean, milo, wheat and some vegetables at the Pulaski County site (personal communication, Mark Luebke, 2003) and rice at the Monroe County site. The crops listed in Table 1 are those grown during the sample collection periods in 2002.

Table 1. Characteristics for the study sites.

Site	Crops	Soil Mapping Unit	Relief m	Nitrate Sources	Well Depth m	Water Depth m
Pulaski County	Soybeans vegetables	Keo - well drained Rilla - well drained Perry - clayey	~ 0.45	Septic tank Fertillizer	Shallow 9 – 10 Deep 24 - 30	Shallow 7 - 9 Deep ~8
Monroe County	Soybeans Rice	Foley - poorly drained Dundee - poorly drained	~ 0.3	Septic tank Pig pen Fertillizer	Shallow 8 - 9 Deep 30 - 34	Shallow 4 - 5 Deep ~5
Woodruff County	Soybeans	Dubbs - permeable Amagon - more clay than Dubbs	~0.3	Septic tank Fertilizer	Shallow 9 - 15 Deep 24 - 30	Shallow ~6

METHODS

Well Descriptions

Twelve shallow monitoring and domestic wells at three sites and six deep irrigation wells at two of the sites were used for this study. The distribution of the wells among the three sites are: (1) three monitoring wells, a domestic well and three irrigation wells in Pulaski County, (2) three monitoring wells and three irrigation wells in Monroe County and (3) four monitoring wells and a domestic well in Woodruff County. The monitoring wells were constructed of five-centimeter diameter PVC casing (Johnston, 2001); whereas, the domestic wells were completed with galvanized steel casing and plumbing. The casing for the 40.6 and 61.0 cm diameter irrigation wells is galvanized steel.

The Pulaski County site was sampled on June 24 and August 12, 2002, and the Monroe County site was sampled on June 25 and August 11, 2002. These water samples were analyzed for major ions including iron using standard methods. In addition, these two sites had been sampled periodically (8 - 10 times) from 1999 to 2002 for nitrate analysis. The Woodruff County site was sampled only once on June 18, 1996 and thus can be only used to investigate spatial variability. Three well volumes were removed from each well prior to sampling, at which time the pH, specific conductance and temperature had stabilized. On August 11 and 12, 2002, three irrigation wells were sampled at the sites in Pulaski and Monroe counties. Water had been flowing from the irrigation wells for at least one hour prior to sample collection.

Designation of Recharge Conditions.

In this area of Arkansas, the recharge period is typically from October through June, with the possibility of recharge occurring during the rest of the year from septic tank effluent, irrigation water return flow and random abnormally large rains. Only one shallow well appears to be impacted by septic tank effluent and the return flows are diverted away from the shallow wells. Thus the impact of septic tank effluent and irrigation water return flows are considered to be minimal. The wells were classified as having been collected under “recharge” or “non-recharge” conditions based the month of collection and, when justified, modified using scientific judgment based on depth to the water table and amount of recent rainfall (NCDC, 2003). Use of rainfall amounts for designation of recharge conditions must be done cautiously because of lag times for the recharge water to reach the ground-water table. Differences in ground-water table depths also must be used with caution because of the effect of drawdown and rebound brought about by heavy irrigation pumpage. Wells with consecutive collection dates (one to seven months separation) and having different recharge classifications were paired as recharge or non-recharge to investigate the impacts of recharge on the water chemistry. On the same date and at the same site, a few wells were classed with different recharge conditions using the protocol described above. This situation indicates that there are lag times for water to reach the water table at some sites.

RESULTS AND DISCUSSIONS

There are not sufficient data to carry out statistical analyses of the data but qualitative interpretations are possible and meaningful as a first step in evaluating the variability of nitrate concentrations.

Source of Nitrate

Atmospheric deposition and soybeans (a legume) can be sources of nitrate (Steele and Brye, in press); however, the atmospheric input is typically minor (0.37 mg/L inorganic-nitrogen) (NADP, 2003 for Warren AR site) relative to fertilizer. Nitrate fixation by soybeans will be classed with fertilizer, which is discussed below. There are three major nitrate sources at all sites: (1) crop fertilizer, (2) lawn fertilizer and (3) septic tank effluent, and a fourth source at the Monroe County site—a pig pen. Ground-water chemistry can be used to constrain and perhaps identify the major nitrate sources.

Septic tank effluent often has relatively high total nitrogen, sulfate, chloride, and total phosphorus concentrations (Tchobanoglous, 1987; Wollach, 1994). The ranges (mg/L) for these ions during recharge conditions for the three shallow wells at the Monroe County site are: NO_3-N (1.03-14.45), chloride (5.23-35.28), sulfate (7.20-29.79) and PO_4-P (0.114 – 0.133). It is noteworthy that the highest nitrate concentration for this study occurs with the highest concentrations of these ions in well M-R at the Monroe County site. Well M-R is the well closest to both the septic tank drain field and to the pigpen at the Monroe County site.

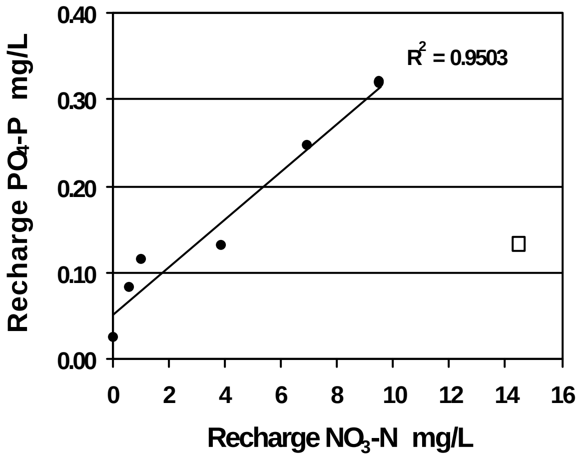

Figure 2. Plot of nitrate versus phosphate concentrations under recharge conditions for shallow wells at the sites in Monroe and Pulaski counties. The strong correlation indicates a similar source.

The two sites where temporal data were analyzed show a positive correlation (R^2 = 0.35 and 0.95—see below) between nitrate and phosphate during *recharge* conditions, suggesting that the source of these two ions is from fertilizer applied nearby. The lack of high nitrate, chloride, and sulfate values suggest that septic tank effluent is not a major component of recharge water, except for well M-R described above. If the water migrated very far from the source, one would expect more scatter of the points in Figure 2 because of retardation of phosphate transport by adsorption and precipitation. Based on the large amount of the fertilizer used on crops versus that used on lawns, and the poor quality of the lawns at the sites, it is assumed that agricultural fertilizer is the source of most of the nitrate. Well (M-R), with the highest nitrate concentration, plots noticeably off the regression line for nitrate versus phosphate (Fig. 2), which indicates that the source of nitrate for this sample is different from the other samples; i.e., septic tank effluent and/or pig manure. If the 14.45 mg/L NO_3-N value is omitted, the R^2 value for nitrate versus phosphate increases from 0.35 to 0.95 (Fig. 2). A very poor correlation is noted for nitrate and phosphate during *non-recharge* conditions (R^2 = 0.003) with a shift toward decreasing nitrate/phosphate ratios. These observations suggest nitrate and phosphate from agricultural application of fertilizer were transported to the ground-water system during recharge periods (Fig. 2) and later likely underwent denitrification (see discussion under the heading Temporal Variation), thus destroying the correlation with phosphate during non-recharge conditions.

No Variation

Ideally, if there is no spatial or temporal variation of nitrate all of the data for the two different recharge conditions would plot at one point. Because of the variation due to analytical error and variation in sampling errors, the data would plot as a circle.

Spatial Variation

If there is only variation in the concentration of an ion from site to site (spatial variation) then recharge and non-recharge data pairs having a ratio of 1:1 plot as a straight line; i.e., the slope of the line is 1.00. Chloride is a conservative ion and would be expected to behave in this manner and indeed does form a 1:1 line (Fig. 3) similar to the idealized relationship for spatial variation only. There is considerable scatter of data points for a plot of recharge and non-recharge nitrate concentrations; i.e., there is temporal as well as spatial variation of nitrate concentrations (Fig. 4). Spatial variation at a site (Monroe County) is as much as 0.04 to 14.45 mg/L NO_3-N.

Temporal Variation

If nitrate behaves conservatively and only spatial variability accounts for differing nitrate concentrations at each site, a plot of nitrate versus nitrate for recharge and non-recharge conditions would produce a straight line. Temporal variation is indicated as deviation from the 1:1 line (Fig. 5). The temporal variation can be attributed to: (1) introduction of additional nitrate from fertilizer, (2) dilution of existing nitrate, or (3) denitrification of existing nitrate. Non-recharge water is expected to be more anoxic than recharge waters and could support denitrification. The first two processes, addition or dilution, are not compatible with *non-recharge* conditions. Nonetheless, it is possible that septic tank effluent could increase nitrate concentrations in ground water during non-recharge events (process 1), but is diluted during recharge events (process 2). However, ground-water flow direction and proximity to a septic tank are not reflected in the ground water chemistry at two sites. Only well M-R has ground water chemistry consistent with contamination by septic tank effluent (and pig manure). Under *recharge* conditions, addition of nitrate from fertilizer is very likely (process 1). Denitrification (process 3) is not compatible with the inferred oxic state of the recharge waters. Process 2, dilution, can occur if the nitrate source has been "flushed" or if the non-recharge source has been removed.

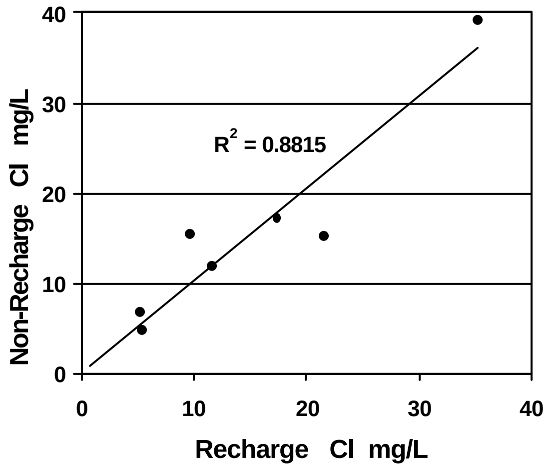

Figure 3. Recharge versus non-recharge chloride concentrations for shallow wells at the sites in Monroe and Pulaski counties exhibiting a near 1:1 relationship.

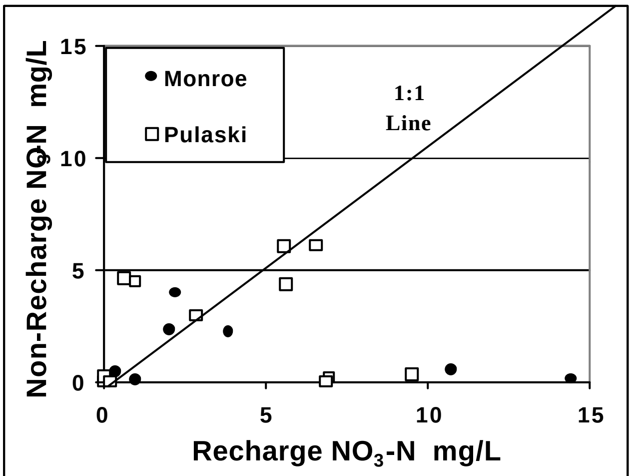

Figure 4. Plot of nitrate concentrations for recharge and non-recharge conditions for shallow and deep wells at the sites in Monroe and Pulaski counties. Data points below the line indicate addition of nitrate under recharge conditions and/or denitrification under non-recharge conditions. The points above the line indicate dilution. See Figure 5 and text.

Based on the discussions above and Figure 5, the points above the 1:1 line in Figure 4 are interpreted as dilution of nitrate concentrations under recharge conditions. The points below the 1:1 line in Figure 4 are interpreted as nitrate transport to the ground-water system during *recharge* and/or denitrification during *non-recharge*. The correlation of nitrate and phosphate during *recharge* (Fig. 2) is also consistent with transport of surface-derived nitrate during recharge events. The fact that a correlation for nitrate versus phosphate does not exist (R^2 = 0.003) during *non-recharge* conditions suggests that denitrification is occurring in the aquifer. Additional support for denitrification is provided by the near 1:1 relationship and strong correlation (R^2 = 0.89) for phosphate under recharge and non-recharge conditions (Fig. 6), which demonstrates no substantial loss or gain of phosphate in the ground-water system. Therefore, the positive correlation between nitrate and phosphate during the recharge events (suggesting common source) (Fig. 2) and the fact that phosphate concentrations are not affected during transport (Fig. 6) strongly indicates that nitrate is lost from the ground water by denitrification.

Further evidence for denitrification and reducing conditions required to drive the denitrification process is provided by the relationship between iron and nitrate (Fig. 7). Deep wells would be expected to have ground water that is relatively more reducing than shallower wells (Spalding and Exner, 1993; Steele *et al.*, 1996). Most of the irrigation wells (deeper wells) in this study have the highest iron concentrations and lowest nitrate concentrations (indicative of reducing conditions); whereas, most of the high nitrate samples have relatively low iron concentrations (indicative of oxidation conditions). Because high iron and nitrate concentrations are essentially exclusive, the data points cluster along the x and y axes in

Figure 7. These observations are collaborated by unpublished data for hundreds of wells in the alluvial aquifer that show data points plotting very close to the x and y axes on nitrate versus iron graphs. There are two points in Figure 7 that have relatively high iron and nitrate, which can be explained as the result of mixing two different redox waters in the wells (Smedley and Kinniburgh, 2002; Kresse and Fazio, 2003).

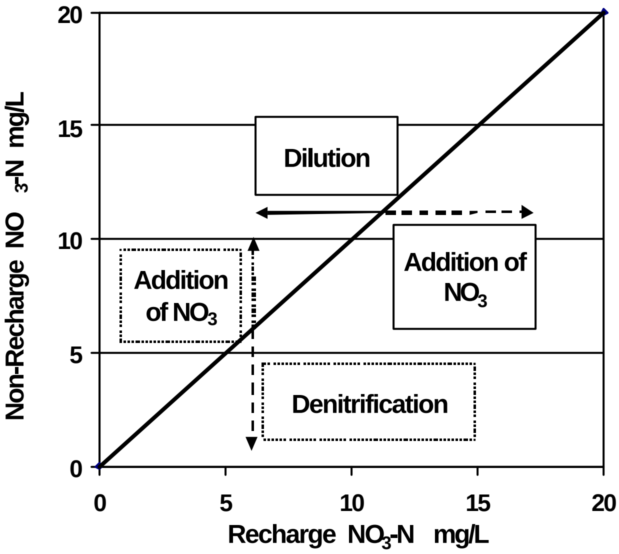

Figure 5. Schematic diagram showing processes affecting nitrate concentrations under recharge and non-recharge conditions.

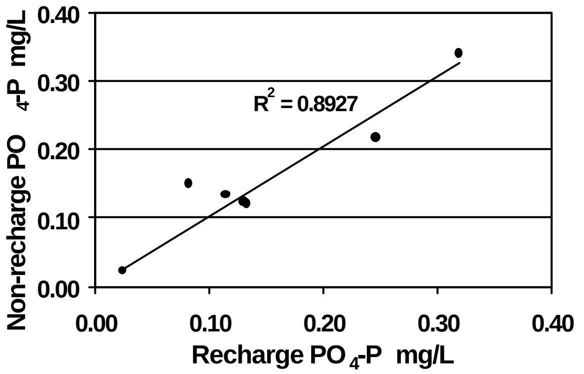

Figure 6. Recharge versus non-recharge phosphate concentrations for shallow wells at the sites in Monroe and Pulaski counties. The close similarity of the regression line to a 1:1 line argues against gain or loss of phosphate for these samples and indicates phosphate has not been retarded significantly.

The highest nitrate-nitrogen concentration of 14.45 mg/L was reduced to 0.11 mg/L in less than 45 days. The rate of denitrification is apparently rather rapid, and undoubtedly the carbonaceous material in the alluvium enhances denitrification. The highest nitrate concentration might be attributed to a plug movement of a nitrate contamination plume. However, the possibility of a plume is not likely, because the slow rate of ground-water movement (3 to 8 cm/day) (Kresse and Van Schaik, 1996; Johnston, 2001) would dictate total breakthrough of the plume within 45 days, during a period in which ground water movement was only a maximum of 3.5 m over the same period. In addition, wide ranges in concentration have occurred previously (well M-R in Fig. 8) and it is difficult to envision periodic plumes developing and dissipating within a few months. Figure 8 indicates that there have been two periods of rapid decrease in nitrate concentration (denitrification) within a period of three months or less and an intervening period of about nine months for recharge. This intervening recharge period corresponds with the regional recharge period of October through June.

Depth Variation

Nitrate contamination is generally greater in water from shallow wells because of the ease of contamination (Helsel, 1995) and because of limited vertical dispersion and the fact that deeper wells generally have greater reducing conditions that favor denitrification (Spalding and Exner, 1993; Steele *et al.*, 1996). With the exception of one shallow well, the higher iron concentrations are all from deep wells. The domestic well at Monroe County had an iron concentration of about 16 mg/L; however, this is thought to be due to plumbing contamination because this well is used infrequently and rust flakes could be seen in the water samples. One deep well had 1.8 mg/L NO_3-N and the others had less than 0.3 mg/L NO_3-N. With the exception of this well, these data are consistent with the inferred redox and contaminant transport for these sites.

CONCLUSIONS

There is significant nitrate variation both spatially and temporally for shallow wells and spatial variability for deep wells in the alluvial aquifer. There were no samples representing temporal variability collected from the deep wells. Agricultural fertilizer is the main source of nitrate, but one well apparently has septic tank effluent and/or pig manure as its source of nitrate. Transport of nitrate from fertilizer occurs during periods of recharge. Differences in the rate of ground-water recharge and flow directions combined with variable denitrification rates cause rapid changes in nitrate. Sufficient spatial and temporal data must be collected for ascertaining the sources and fate of nitrate contamination within the alluvial aquifer.

These conclusions are based on qualitative analysis of the data and are not conclusive based on these limited data. Additional temporal sampling, additional wells, and nitrogen and oxygen isotope analyses are required for definitive interpretations.

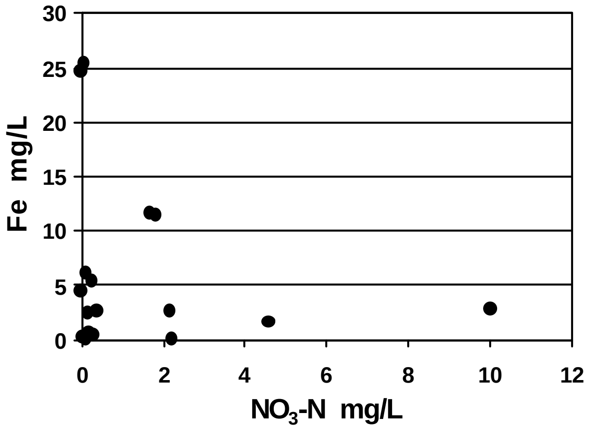

Figure 7. Plot of Fe versus NO_3-N for shallow and deep wells during the non-recharge period for all sites.

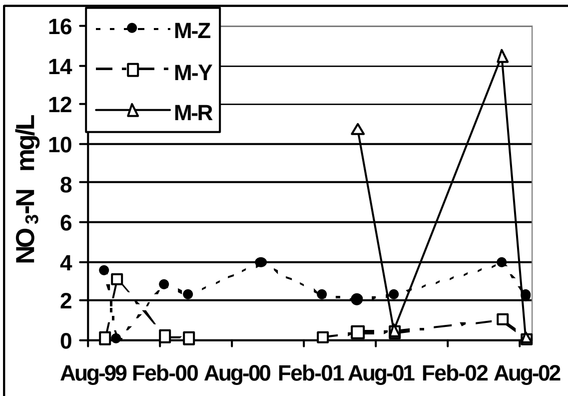

Figure 8. Plot of NO_3-N concentration versus collection date for the Monroe County site. The high concentrations for Well M-R are for recharge conditions and the low concentrations are for the non-recharge conditions.

REFERENCES

Ackerman D.J. (1989). Hydrology of the Mississippi River Alluvial aquifer, south-central United States – A preliminary assessment of the regional flow system. U.S. Geological Survey Water-Resources Investigations Report 88-4028.

Helsel D.R. (1995). Nitrate in the nation's waters: A summary of recent studies. Water Resouces, Issue 101, 12-17.

Holbrook D. F. (1980). Arkansas Lignite Investigation, Preliminary Report. Misc. Pub. 16, Arkansas Geological Commission, Little Rock, Arkansas.

Kresse T. and Fazio J. (2003). Occurrence of Arsenic in Ground Waters of Arkansas and Implications for Source and Release Mechanisms. Arkansas Department of Environmental Quality, Little Rock, Arkansas.

Kresse T. and Van Schaik E. (1996). Preliminary Results of Pesticide Investigation Augusta, Arkansas. Arkansas Department of Pollution Control & Ecology, Little Rock, Arkansas.

Johnston, J.S. (2001). Implementation of BMPs to Protect Ground Water Quality in Coastal Plain Aquifers of Eastern Arkansas, Final Report for Task 97-400. Arkansas Soil and Water Conservation Commission, Little Rock, Arkansas.

Petersen, J.C., Broom M.E. and Bush W.V. (1985). Geohydrologic Units of the Gulf Coastal Plain in Arkansas. U.S. Geological Survey Water-Resources Investigations Report 85-4116.

NADP (National Atmospheric Deposition Program). (2003). http://nadp.sws.uiuc.edu/ Rain chemistry for Warren, Arkansas.

NCDC (National Climatic Data Center). 2003). http://www.srcc.lsu.edu/index.html Rainfall data for Augusta, Arkansas station for use with the Monroe County site and Little Rock, Arkansas station for use with the Pulaski County site.

Smedley, P.L. and Kinniburgh D.G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry. 17, 517-568.

Spalding, R.F. and Exner M.E. (1993). Occurrence of nitrate in ground water – A review. Journal of Environmental Quality. 22, 392-402.

Steele, K.F. and. Brye K.R. (in press). Nitrogen. Encyclopedia of Water, John Wiley and Sons Publishers, New York.

Steele, K.F., Hill S.S., Nichols T., Scott, H.D., Vendrell, P.F. and Lin, H.S. (1996). Impact of Agricultural Chemicals of the Alluvial Aquifer, Lower Mississippi River Delta. In: Proceedings of the University Council on Water Resources Meeting 1996, Carbondale, IL, pp. 50-59.

Tchobanoglous, G. and Schroeder E.D. (1987). Water Quality. Addison-Wesley Publishing Company, Reading, Massachusetts.

Wallach, R. (1994). Goundwater Contamination by Sewage Irrigation. In: Groundwater Contamination and Control, U. Zoller (ed.), Marcel Deckker, Inc., New York, pp. 189-202.