A RELATIONSHIP BETWEEN NITRATE AND IRON IN GEORGIA'S GROUNDWATER

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Abstract. A mutually exclusive relationship exists between iron and nitrate-N in the ground waters of Georgia. No high nitrate was detected in the presence of high iron and no high iron in the presence of high nitrate. The proposed mechanism for this relationship is that anaerobic microbial activity causes a process of reduction in which first nitrate is denitrified and then ferric iron is reduced to ferrous iron. The consequence of this relationship is that groundwater contamination by nitrate-N is not widespread in Georgia, due in part to reducing conditions in at least a portion of the aquifer system. Nitrate-N is commonly used as an environmental indicator to trace the impact of agricultural land-use activities on groundwater. In cases where agricultural chemicals or wastes have the potential to leach into groundwater and iron levels are high in the groundwater, the absence of nitrate would not rule out other impacts.

INTRODUCTION

As in other states, many of the intensive agricultural activities in the state of Georgia have been implicated as being the sources of nitrate contamination of groundwater. Confined animal operations in northern Georgia and high yielding row crops of the south have not yet caused widespread nitrate problems. Other less humid regions of the United States with similar production levels have extensive groundwater contamination from nitrate. However, dilution from higher rainfall is likely not the only process that protects ground waters of the humid southern United States.

Frequently, soil nitrate is lost due to denitrification during periods when rainfall or irrigation water saturates the soil and microbial respiration causes the depletion of oxygen at a rate far in excess of replenishment. This anaerobic condition causes the soil microbes to use nitrate-ions as the electron acceptor during respiration. In the process, nitrate is converted to nitrogenous gas. Upon the depletion of nitrate, the microbial populations turn to the next available electron acceptor, manganese. When available manganese is reduced, iron becomes the next element to be reduced. This results in conversion of insoluble oxidized states to the soluble reduced states.

High iron concentrations, >0.3 mg L^{-1}, in water indicates that this water has gone through sufficient reduction to produce reduced iron and conceptually nitrate would have been denitrified prior to the iron reduction.

RELATED WORK

Groundwater studies in the humid southern United States have identified a relationship between iron and nitrate concentrations (Steele et al., 1996 and Nolan, 1999). Nitrate and iron concentrations are inversely correlated or mutually exclusive. Authors have concluded that this relationship indicates a process of nitrate removal or attenuation by biologically mediated nitrogen transformations such as denitrification and dissimilatory nitrate reduction. However, reports of studies in Georgia (Nolan, 1999) concluded that nitrate reduction was not a great influence to ground waters of the Georgia Coastal Plain, the Apalachicola Basin, the Chattahoochee Basin, or the Flint River Basin. The results of this report suggest that there are exceptions to these conclusions.

In a prior report of the nitrate concentrations in Georgia's groundwater (Bush, et al., 1997), nitrate-N greater than 10 mg-N L^{-1} occurred more frequently in

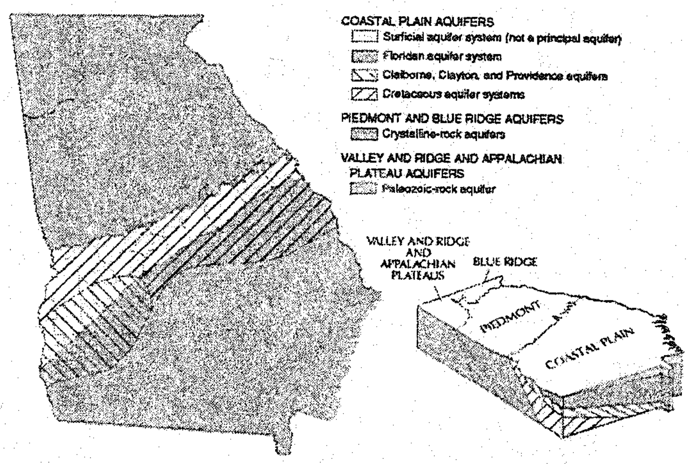

Figure 1. Groundwater aquifers in the provinces of Georgia (produced and provided by the U.S. Geological Survey).

wells that were less than 100 ft deep. These authors reported that nitrate in Coastal Plain wells was low regardless of well depth; whereas, the Piedmont province had higher and more frequent occurrence of nitrate above their background level of 3 mg N L^{-1}, and nitrate was more prevalent in the shallower wells. Their conclusions attributed the higher nitrates to more long-term confined animal agriculture in the Piedmont compared to the Coastal Plain. However, attenuation of nitrate in the Coastal Plain ground waters by reduction or other processes was not considered. Therefore, the objective of this report is to determine if a relationship exists between nitrate and iron in well waters of Georgia's Piedmont and Coastal Plain.

METHODS

The University of Georgia Agricultural and Environmental Services Laboratories (AESL) provide analytical services to the public through the Cooperative Extension Service. One of the many services provided is testing the quality of the water from wells used to supply single-family houses or used on farms for irrigation or watering livestock. Groundwater was analyzed from aquifers throughout Georgia from 1992 through June 2000. Well water samples were tested from all the major Georgia provinces that are the Valley and Ridge, Blue Ridge, Piedmont, and Coastal Plain (Figure 1.) There were 2368 well water samples analyzed that had both iron and nitrate-N measurements. Only data from the Piedmont and Coastal Plain wells will be used in this report and there were 1754 and 544 samples analyzed, respectively.

Twenty-five other water quality parameters were measured during this testing period but only iron and nitrate are presented in this report. For information of these other parameters refer to the report by Bush et al., 1997.

Iron concentrations were measured using an inductively coupled plasma emission spectrophotometer (ICPES) and nitrate-N was measured using an ion chromatograph. References for the methodologies used by the AESL can be found on the web at *http://aesl.ces.uga.edu/methods/stl-water.html*.

CONCLUSIONS

The Piedmont and Coastal Plain relationship between nitrate-N and iron is presented in Figure 2. There is a definite relationship between iron and nitrate-N measured in wells from Georgia's Piedmont and Coastal Plain. The Piedmont province produced a relationship similar that for the Coastal Plain. The relationship is best described as mutual exclusion: no high nitrate was detected in the presence of high iron and no high iron in the presence of high nitrate. The most likely mechanism generating this relationship is nitrate reduction occurring in the Piedmont and Coastal Plain soils, regolith, or aquifers and this same anaerobic process is also responsible for iron reduction and higher solubility. It is not suggested that iron is directly responsible for nitrate reduction, but that iron is serving as an indicator of microbial denitrification process that initially reduced nitrate and then left behind a residual iron signature.

High iron concentrations, greater than 0.3 mg L^{-1}, occurred in 17% of the samples tested. Whereas, 16% of the samples tested had high nitrate-N levels in excess of the background level of 2 mg L^{-1}.

Nitrate reducing processes in the Coastal Plain and Piedmont provinces of Georgia is contrary to conclusions of a more defendable monitoring effort (Nolan, 1999). Nolan used National Water Quality Assessment (NAWQA) data that was collected according to strict criteria for well construction and that the well water collected was from targeted aquifers. Our study used water samples submitted by the general public collected from wells of unknown

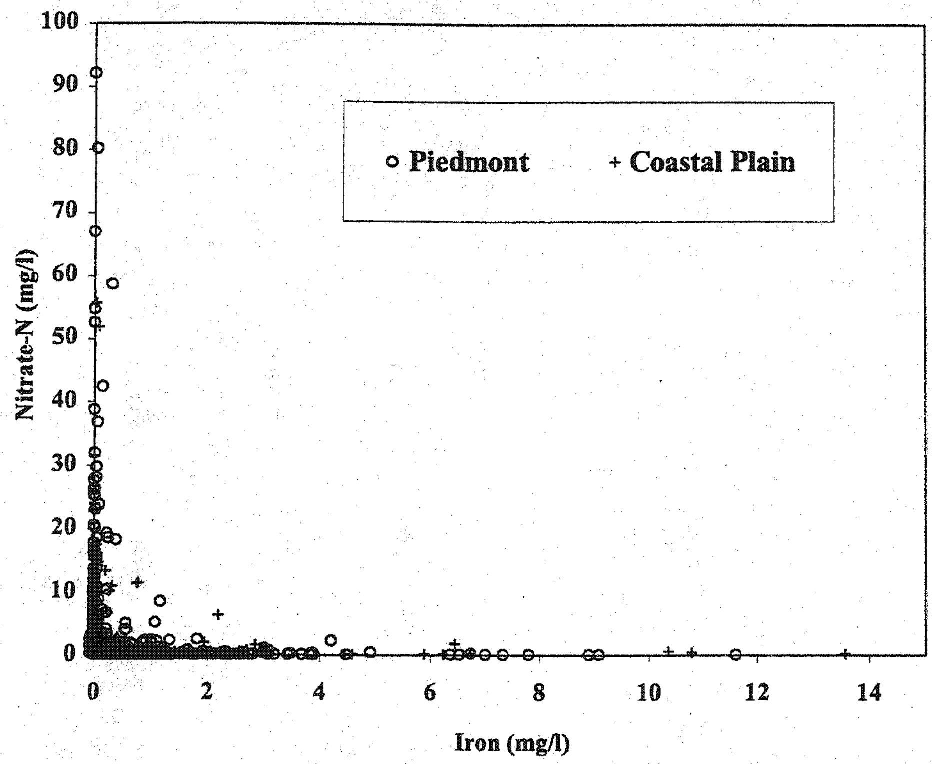

Figure 2. A mutually exclusive relationship between nitrate-N and iron in wells from the Piedmont and Coastal Plain of Georgia.

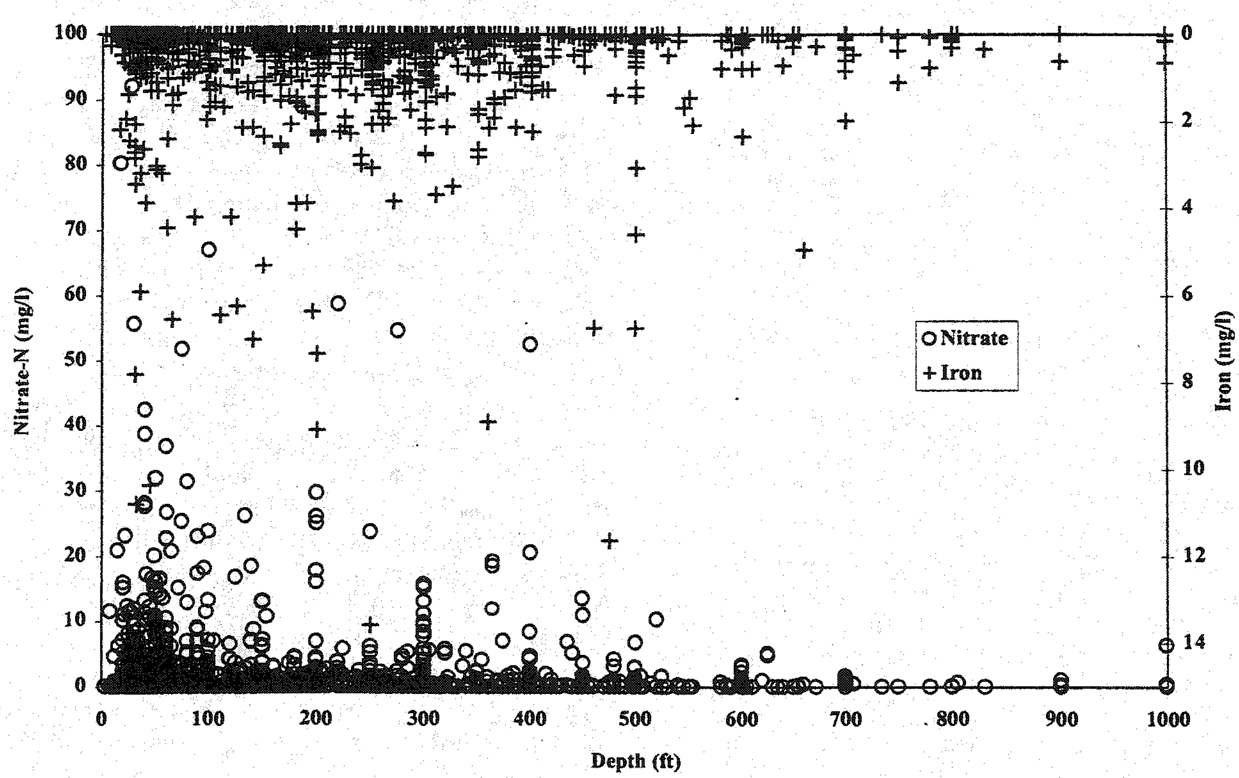

Figure 3. Relationships among nitrate-N, iron, and well depth in well waters of Georgia.

construction and unverified depths. Therefore, the most plausible explanation for the discrepancies between the report by Nolan and these results is that nitrate attenuation is occurring at depths shallower than those sampled by the NAWQA program. These shallower ground waters are then mixing with deeper groundwater due to leaks in corroded casing or failed grout seals. In support of this explanation, the relationship among nitrate, iron and well depth are presented in Figure 3.

Both nitrate and iron levels increase as well depth decreases. These relationships with depth indicate that nitrate originates at the surface and that the process that reduce and dissolve iron are also more active at shallower depths.

DISCUSSION

Indications are that Georgia's groundwater is being protected from widespread nitrate contamination due in part to anaerobic processes that both denitrify nitrate and reduce iron. This process is occurring in both Piedmont and Coastal Plain provinces, appears to occur primarily at shallow depths, and probably does not occur in deep or confined aquifers. Availability of organic substrates and increased microbial populations at shallow depths are likely the cause for increased microbial activities.

Nitrate is commonly used as a tracer to determine if activities such as on-site wastewater disposal, intensive crop production, vegetable production, animal waste storage structures, or lagoons are impacting groundwater. When nitrate attenuation is occurring, the absence of nitrate in monitoring wells does not eliminate the possibility that other impacts are occurring. The recommendation for avoiding this type of mistake is to use a more stable tracer such as chloride.

Further understanding of this nitrate reduction process could lead to agricultural nutrient management strategies that capitalize upon this process to protect groundwater. Logically, the first step may be to identifying the location of this process, either within the soil, regolith, or aquifer.

LITERATURE CITED

Bush, P. B., A. W. Tyson, R. Perkins, and W. Segars, 1997. Results of Georgia domestic well water testing program. In: *Proceedings of the 1997 Georgia Water Resources Conference*, held on March 20-22, 1997, at the University of Georgia. Kathy J. Hatcher, editor, Institute Ecology, The University of Georgia, Athens, GA.

Nolan, B. T., 1999. Nitrate behavior in ground water of the Southeastern USA. *Journal of Environmental Quality*. 28:1518-1527.

Steele, K. F., S. S. Hill, T. J. Nichols, H. D. Scott, P. F. Vendrell, and H. S. Lin, 1996. Impact of agricultural chemicals on the alluvial aquifer, lower Mississippi River delta. *Proceedings of the University Council of Water Resources*. Austin, TX. 50-59.