WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: A Geochemical Investigation of the Source of Nitrate Contamination in Groundwaters in the Vicinity of Albany, Georgia

Focus categories: NC, NPP, GW

Keywords: nitrate, dissolved organic carbon, isotopes, groundwater quality, karst hydrology (4) Duration: 1 year, March 1, 1999 to February 29, 2000

Federal Funds Requested: 14,000 14,000 Total Direct Indirect

Non-Federal (matching) funds pledged: 28,000 19,244 8,756 Total Direct Indirect

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Congressional District: 11th of Georgia

Water Problem, Need for Research

The objective of the proposed study is to determine the source of nitrate pollution in groundwater recently identified in an area southwest of Albany, Georgia. Nitrates in drinking water have been linked with methemoglobinemia ("baby blue" disease) in infants and chronic toxicity in adults, and pose a possible cancer risk through the formation of nitrosamines (Vigil et al, 1965; US EPA, 1976; Safe Drinking Water Committee, 1977). Because untreated groundwater from domestic wells is the primary source of drinking water for a growing residential community in the affected area, it is essential to ascertain what the source of nitrate contamination is and to determine its mechanism of groundwater infiltration. This information is vital for remediation and future protection of this resource. A hydrogeologic investigation by the Georgia Environmental Protection Division (EPD, 1997) identified a disused feedlot and/or adjacent sinkhole drainage ponds on the Shamrock Ranch as probable site of nitrate contamination. This assessment implied that the sinkhole drainage ponds served as point sources of contamination, permitting a rapid and direct conduit for surface contamination to reach the underlying aquifer. The EPD report de-emphasized but was unable to exclude other non-point sources of pollution. The ranch contains other local drainage features, residences, and has used a wide variety of fertilizers over a long period of time. Materials used for this purpose include synthetic inorganic nitrogen fertilizers, chicken litter, and biosolids derived from sewage sludge from the city of Albany. The latter has produced heated criticism in the community. In reaction to this criticism, EPD placed a restraining order on further application of biosolids at this site. In light of this situation, information is vitally needed to further identify the source or sources of nitrate contamination and in particular to examine the question of whether biosolids are a contributing source. This information is vitally needed so that informed decisions concerning its agricultural use can be made in other locations.

Expected Results, Benefits, Other Information, etc.

This proposal requests funds to support a detailed geochemical and stable isotope study of nitrate and related contaminants in groundwater in the Albany area. The overall goal of the research is to more fully identify the source of contamination and possibly elucidate the mechanism of nitrate transport into the underlying aquifer. Many recent studies (see Clark and Fritz, 1997, and numerous references therein) have successfully used stable isotopes to identify sources of nitrate pollution in a variety of geologic settings. As discussed in more detail below, we plan to use the nitrogen isotopic composition of nitrate and carbon isotopic composition of associated dissolved organic carbon (DOC) contamination to identify the source or sources of the contaminant plume. We specifically want to see if these data provide a means for distinguishing biosolids, feedlot runoff, and inorganic nitrate fertilizers as potential sources of groundwater nitrate contamination. Additionally, hydrogen and oxygen isotope studies of water will be used to assess the role that sinkholes and other similar topological features serve as conduits for transport of water and dissolved contaminants into the subsurface. In addition to its local significance, this will be the first study of its kind performed in a karstic region of the southeast. This region serves as an important recharge zone to the Floridan Aquifer. Since agricultural practices such as sewage sludge applications and concentrated-waste-producing animal husbandry practices (confined feedlots, holding pens, etc) are becoming widespread throughout the southeast, this study will help assess the potential impact that such practices have on regional groundwater resources.

Nature, Scope, and Objectives of Research

Summary of EPD studies. In 1997, the Dougherty County Health Department, in cooperation with the Georgia Environmental Protection Division (EPD), identified a nitrate-contamination plume in groundwater with concentrations greater than 10 mg/L (the MCL for nitrate-nitrogen) covering an area of approximately 4 square miles southwest of Albany, Georgia. The center of the plume appears to be centered within and on the southeast side of Shamrock Ranch (see Figure 1). After discovery of this plume and generation of considerable controversy in the community, EPD conducted a hydrologic assessment to identify potential sources for the nitrate contamination. On the basis of the hydrogeological setting and the location of the plume with respect to a number of potential sources, the study concluded that the most likely source of nitrate pollution was runoff from an old feedlot on the ranch that drained into nearby sinkholes (EPD, 1997). However, other nitrate-generating materials such as municipal biosolids, poultry waste, and commercial synthetic inorganic fertilizers were also used on the ranch and remain possible non-point-source contributors of nitrate contamination.

Preliminary isotope studies. In June of 1997, the PI (Wenner) initiated a reconnaissance study to determine whether nitrate concentrations in combination with stable isotope data might provide more specific information about the source of groundwater contamination.

This project was undertaken in cooperation with Kristen Lekrone, a postdoctoral student at UGA, and Susan Reyher, director of environmental health for the Dougherty County Health Department. Groundwater samples were collected from nine sites and analyzed for their nitrate concentrations and nitrogen isotopic compositions (expressed as d15N values in ‰). This approach is predicated on numerous studies indicating that different sources of nitrates have different ranges of nitrogen isotope ratios. Typically nitrates derived from inorganic fertilizers range from -5‰ to + 3.5, soil organic material, from + 3.5‰ to + 7.5‰, and manure and septic system effluent, from +10‰ to +20‰.

Two samples were collected from monitoring wells on the Shamrock Ranch and five from homeowner drinking water wells in the surrounding area (see Figure 1). All seven samples are from the contaminated area. Since the EPD report suggested that organic waste was a likely source, these same samples were also analyzed for dissolved organic carbon (DOC) concentrations and carbon isotopic compositions (expressed as d13C values in ‰). The results from the nitrogen isotope study will soon be published in the upcoming proceedings of the 1999 Georgia Water Resources Conference.

Our reconnaissance studies suggest the following conclusions.

1. 1. The nitrogen isotope data do not appear to support the hypothesis that a cattle feedlot is the primary source of nitrate contamination. The d15N values of dissolved nitrate from the plume range from +2.3‰ to +5.5, significantly different than values reported for nitrates derived from animal wastes. Numerous studies in other areas indicate that nitrates in groundwaters from such sources range from +10 to +22‰, with a mean +14‰ (Clark and Fritz, 1997 and numerous references therein). In fact, the observed d15N values are more characteristic of nitrates derived from mineralization of plant-derived organic matter in soils (Kreitler and Browning, 1983; Daplan and Magaritz, 1986). Such a source seems possible, but requires further investigation. Another possibility is that the nitrates formed from a mixture of materials that includes both inorganic and organic substances. Such materials can potentially account for the observed isotopic data, since synthetic inorganic fertilizers typically have d15N values < +5‰ and organic wastes have values > +10‰. Both materials were use d as fertilizers at the Shamrock Ranch. Such a mixed source has been inferred in other studies (e.g., Exner and Spalding, 1994).
2. 2. The d15N value of a groundwater sample contaminated by a point source of inorganic fertilizers is isotopically distinct (-0.7‰). The value confirms that inorganic fertilizers used at the ranch are probably not the sole source of the contamination. More importantly, this value is typical of the nitrogen isotopic composition of fertilizer itself, suggesting that denitrification is probably not an important process in this environment. Denitrification, where extensive, can alter the d15N value of nitrate and thus invalidate using nitrogen isotopic data to identify the sources of contamination.
3. 3. The concentration of DOC in two monitoring wells on the Shamrock Ranch (1.70 mg C/L and 1.38 mg C/L) were distinctly higher than any of the homeowner wells in the community. DOC concentrations in seven off-site wells ranged from 0.40 to 0.62 mg C/L, and generally declined with distance from the ranch. These data suggest that the Shamrock Ranch site may be a source of dissolved organic carbon as well as nitrate to the groundwater, and that dilution may lower the DOC concentration away from the ranch. An elevated DOC content is consistent with an organic (either feedlot or biosolids) or mixed nitrate source, but not solely with an inorganic nitrogen fertilizer source.
4. 4. The carbon isotope data for the DOC proved to be ambiguous. The data appear to support only a very limited contribution from the feedlot as a source of the contamination. Although d13C values of DOC from a monitoring well (-24.7‰) and pond (-23.5‰) adjacent to the feedlot encompassed the range of values observed for domestic wells outside the ranch (-23.5‰ to -24.6‰), these values are only slightly enriched in d13C relative to groundwater DOC reported for

other, nonagricultural regions (e.g. Schiff et al, 1997, report values averaging -27‰). This enrichment, however, is smaller than anticipated for a carbon source derived from feedlot waste. Such materials were expected to have a strongly enriched d13C value from the corn in the feed (-8 to -12‰ for corn, compared to an average of -27‰ for most other terrestrial plants).

Proposed studies. It is clear from these preliminary conclusions that a number of unanswered questions remain. The studies summarized below are expected to address some of these questions.

Although the old feedlot on the Shamrock Ranch appears on the basis of hydrogeological factors to be the source of the nitrate contamination of groundwaters in the region, the d15N values (ranging from +2.3‰ to +5.5‰) do not fall in the same range reported at other locations where similar sources of contamination have been identified. A major question remains as to why these differences exist. Additionally, no nitrogen isotope data were obtained from the biosolids applied at the Ranch. In other studies, d15N values for such materials are distinctly enriched (e.g., Kaplan and Magaritz, 1986, report values from +19‰ to +29‰). If the biosolids used at the Ranch have these kind of nitrogen isotopic compositions, then we can be more positive in asserting that their application is not contributing to the nitrate contamination. Finally, we have no idea what the nitrogen isotope compositions of nitrates in groundwaters from true "background" sources are where no animal or other fertilizer sources of nitrate were used. Potential sites for the latter include areas being reclaimed from virgin forest growth and swampland.

To address these questions, samples of the each of the source materials will be sampled where possible. These include solid samples from the feedlot and the biosolids. Other materials such as chicken litter will need to be sampled off-site since they no longer exist at the ranch. We also plan to sample shallow groundwaters both on and off the Ranch. Several approaches will be used. Waters from the saturated zone can be sampled from an existing network of 15 monitoring wells on the ranch, from over 300 homeowner wells in the residential community, and from monitoring wells currently being drilled in the area. Some of the monitoring wells on the Ranch are located in critical areas where only the biosolids or manure have been applied. It is also deemed critical to sample waters from the unsaturated zone directly beneath clearly identifiable sources of contamination. One approach that can be used for measuring nitrogen isotope compositions will be to sample grasses growing directly on an identified contaminate source. This approach can be used because plant uptake does not fractionate the nitrogen isotopes and thus the d15N of the plant will directly reflect the d15N value of the dissolved nitrate in the unsaturated zone. A second approach requires the instillation of suction lysimeters. It is envisioned that several will be installed on the ranch in critical areas.

Although we have tentatively concluded that the d13C values of DOC from the high nitrate plume is slightly enriched, and thus compatible with perhaps a small contribution from a corn-based cattle feed, we really don't know what the isotopic composition of other "background" sources of DOC are in the region. A few studies elsewhere suggest that d13C values may be more isotopically depleted (e.g., Schiff et al., 1997, report values averaging -27.0‰), although no such data are know to exist in southwest Georgia. Accordingly, both solid and groundwater samples will be taken from the animal feedlot, from sites where biosolids were applied, and from pristine wetlands areas for measurement of d13C on DOC. These data will be compared to data from drinking water wells outside the Ranch.

Finally, oxygen and hydrogen isotopic data will be acquired from both surface and ground waters both on the Ranch and from the residential community. Surface waters, which typically occupy sinkholes in the region, would be expected to show a strong seasonal isotopic variation due to enhanced summer evaporation. If these variations are imparted to groundwaters, then it could concluded that such surface water bodies provide an important mechanism for recharge to the aquifer. This part of the study will further test the hypothesis of whether sinkholes adjacent to the old animal feedlot may be a source of groundwater nitrate contamination in the residential community adjacent to the Ranch. The area is particularly susceptible to groundwater contamination because of its hydrogeological environment. Although most of the region consists of mantled karst with a 20 to 40 ft. thick residuum of undifferentiated sand and clay overlying limestone of the Upper Floridan Aquifer (Hicks et al., 1995), some sinkholes provide a direct connection to the subsurface bedrock.

Although the principal focus of this investigation will be directed towards obtaining geochemical data for identification of the source or sources of nitrate contamination, it is recognized that this can be best interpreted in conjunction with basic hydrologic information. Since this project is projected to last for only one year, much of that kind of data will have to be obtained from other investigators. A number of organizations are currently or have in the recent past worked in this area, including the Georgia Geological Survey, the U.S. Geological Survey and Geosciences, Inc., an independent environmental company employed by the City of Albany. All these organizations have installed or are currently installing monitoring test wells in the area. The P.I. has in the past obtained samples from some of these wells and will again seek permission to take samples for this project. We hope to work with these other investigators so as to obtain basic hydrologic data at the time of sampling. Where possible, we plan to measure water levels in the monitoring wells that are sampled for geochemistry. This will not be possible for most homeowner wells. We recognize, however, that it is important to obtain data from these other studies. With this information, we hope to be able to delineate hydrologic gradients. Such information, when combined with other basic hydrologic data (hydraulic conductivity, porosity) should allow us to construct a basic groundwater flow model. Although hydrologic modeling is not the expertise of the two principal P.I.'s, most of our graduate students specializing in hydrogeology take basic groundwater modeling courses and have proved capable of performing this kind of modeling under the supervision of Dr. John Dowd, a physical hydrogeologist in the Department of Geology. The principal P.I. has worked closely with Dr. Dowd for a number of years. It is envisioned that the final story resulting from this investigation will include an integration of both the geochemical results and physical flow modeling.