INVESTIGATION OF THE SOURCE OF NITRATE CONTAMINATION IN THE UPPER FLORIDAN AQUIFER NEAR ALBANY, GEORGIA

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Abstract. An area of nitrate contamination was detected in the Upper Floridan aquifer in a 20 square mile area southwest of Albany, Georgia. This area appears to originate on the Shamrock Ranch, a site where a wide variety of potential nitrate sources were used. These sources include cattle manure, synthetic inorganic fertilizers, poultry litter and municipal biosolids. Although a disused cattle feedlot was suspected of being the most probable source of groundwater contamination, questions concerning the contributions from other materials remain.

To further evaluate the source of contamination, an investigation was undertaken to measure the nitrogen isotopic composition of dissolved nitrates in groundwater both on and off the ranch. This approach potentially provides a means for distinguishing different sources of nitrate-producing materials. Measurements of both nitrate concentrations and nitrogen isotopic compositions in groundwater were made of one sample from an inorganic fertilizer source, one background sample, and seven samples from within the contaminated area. Although some ambiguities remain, it appears that the disused cattle feed lots are not a major source of contamination. Rather, the nitrogen isotopic data are most consistent with a mixed source of contaminants. One of the important components of this mixture appears to be synthetic inorganic fertilizers that were used in the past.

INTRODUCTION

In 1997, the Dougherty County Health Department, in cooperation with the Georgia Department of Natural Resources - Environmental Protection Division (EPD), identified a zone of nitrate contamination in groundwater in the Upper Floridan aquifer southwest of Albany, Georgia. In this region, approximately 60% of the wells had nitrate-nitrogen concentrations in excess of background (> 4 mg/L) and 12% of these were greater than 10 mg/L (the MCL for drinking water). This zone of contamination extends over an area of approximately 20 square miles. The highest nitrate concentrations are centered on the southeast side of the Shamrock Ranch in a residential community that obtains its water from private homeowner wells that tap the Upper Floridan aquifer (Figure 1). The ranch is a site where inorganic fertilizers, poultry litter, and municipal biosolids were used as fertilizers. In addition, several disused cattle feed lots exist on the site and a number of individual septic systems serve residences on the property. A preliminary investigation conducted by EPD (EPD, 1997) identified one of the cattle feedlots as the most probable source of nitrate contamination.

The area is particularly susceptible to groundwater contamination because of its hydrogeological environment. The region consists of mantled karst with a 20- to 40-ft. thick overburden of undifferentiated sand and clay overlying the Ocala Limestone of the Upper Floridan aquifer (Hicks et al., 1987). The regional hydraulic gradient within the aquifer is from northwest to southeast (Hicks et al., 1987), accounting for the attention focused on the Shamrock Ranch.

Because so many potential sources of nitrate contamination exist on this site, an investigation was initiated employing the measurement of the nitrogen isotope composition (expressed as $\delta^{15}N$ values in per mil or ‰ relative to atmospheric nitrogen) of nitrate in groundwater. This was done in an attempt to distinguish among the potential sources. This approach is predicated on numerous studies indicating that different nitrate

sources produce different ranges of $\delta\ ^{15}N$ values for dissolved nitrate (see Clark and Fritz, 1997, and numerous references therein). 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‰.

MATERIALS AND METHODS

Nine groundwater samples were collected in 1.0 Liter neoprene containers during June 1997, and shipped frozen to Coastal Sciences Laboratories (Austin, TX) for nitrogen isotopic analysis. Sample splits were submitted to the Agricultural Services Laboratory of the University of Georgia for nitrate concentration determination using ion chromatography. The nitrogen isotope data have a precision better than ±0.5‰ as indicated by duplicate analysis of two samples. Nitrate concentrations are given in mg/L, with an estimated precision of ±1.6% based on duplication of one sample.

A sampling strategy was adopted to evaluate isotopic variations in different hydrogeological environments within and outside the known nitrate contamination plume. The distribution of samples, shown in Figure 1, include:

(1) one sample from a homeowner well that was known to be contaminated by synthetic inorganic fertilizers;
(2) two samples within the contaminated zone on the Shamrock Ranch from shallow (< 40 ft.) monitoring wells;
(3) five samples within the contaminated zone from homeowner wells southeast and east of the Shamrock Ranch; and
(4) one background sample from a homeowner well west of the Shamrock Ranch.

The monitoring wells were drilled into the weathered residuum part of the overburden, whereas homeowner wells are typically cased through the overburden and the very uppermost parts of Upper Floridan aquifer to depths of greater than 100 ft.

RESULTS AND CONCLUSIONS

Nitrate concentration and isotopic data are presented in Figure 1. The following tentative conclusions can be deduced from this limited data set.

- One sample, identified with an inorganic fertilizer source, is clearly anomalous. The nitrate concentration (89 mg/L) is distinctly higher than any other reported groundwater sample in the region (EPD, 1997; Geosciences, Inc., 1997) and the $\delta^{15}N$ value of –0.7‰ is distinctly low. This isotopic value is consistent with data reported in other studies where nitrate is derived from synthetic inorganic fertilizers. This isotopic composition implies that there is no process such as denitrification operating in the groundwater environment that subsequently alters the $\delta^{15}N$ value of the nitrates. It is known, for example, that denitrification can produce isotopic enrichment (thus increasing the $\delta^{15}N$ value) of the residual nitrate (Clark and Fritz, 1997). Such processes, if present, can invalidate the whole isotopic approach for identifying the source of nitrate contamination. The assertion that denitrification is probably not an important process in the groundwater environment in this area is independently confirmed by observations that virtually all samples from the homeowner wells contain a substantial amount of dissolved oxygen (most are > 50% saturation at ambient conditions). Such conditions exclude denitrification processes, which occur only under anaerobic conditions.
- One sample taken from outside the plume of contamination has a low nitrate concentration (1.1 mg/L) and a relatively low $\delta^{15}N$ value of +1.1‰. This sample may represent a background chemical and isotopic composition for the area. This is in part supported by a reconnaissance study indicating that of 33 groundwater samples taken from Dougherty County outside the contaminated area, all have nitrate concentrations less than 3.0 mg/L (Shellenberger et al., 1996).
- Seven samples from the contaminated zone both within and outside the Shamrock Ranch have a wide range of nitrate concentrations from 42 mg/L to 4.0 mg/L, and yet their $\delta^{15}N$ values are relatively restricted, ranging from +5.5‰ to +2.3‰. It is noteworthy that $\delta^{15}N$ values of two samples from the monitoring wells (+4.2‰ and +3.5‰) fall within the

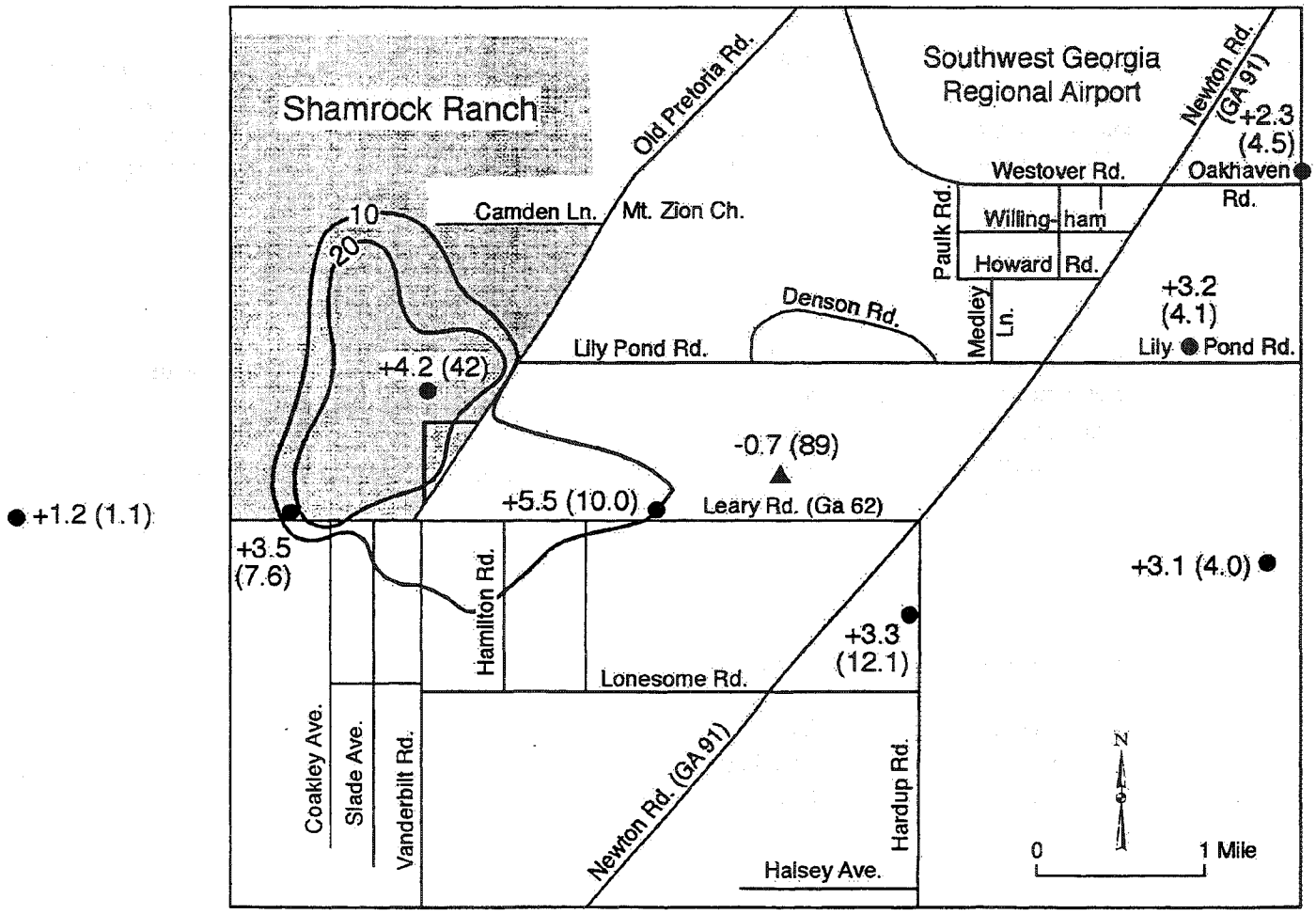

Figure 1. Map of the nitrate contaminated area southwest of Albany, Georgia. The contours show nitrate concentrations (mg/liter nitrate-nitrogen) in groundwaters (EPD 1997). Also shown are our reconnaissance chemical (in paratheses) and nitrogen isotopic data (expressed as $\delta^{15}N$ value in 0/00). The location of one sample derived from synthetic inorganic fertilizers is identified by the triangle.

range of values (+2.3‰ to +5.5‰) displayed by homeowner wells east and southeast of the ranch. This adds further support to the hypothesis that the Shamrock Ranch may be the source of nitrate contamination.

- The isotopic values within the plume, however, are not compatible with the inference (EPD, 1997) that an old animal feedlot may be the principal source of nitrate contamination. Nitrates derived from animal wastes are invariably much more isotopically enriched, with $\delta^{15}N$ values ranging from +10‰ to +20‰.
- The observed isotopic variation of nitrates within the plume falls within a range of values generally characterized in other studies as having formed from mineralization of decomposed soil organic matter. Although such a contaminate source needs further evaluation, the existence of numerous other nitrate-producing materials raises questions as to the likelihood that just this one source is responsible for all the groundwater contamination in the area.
- Serious consideration must be given to the hypothesis that the observed nitrogen isotopic values reflect multiple contamination sources. Among the known nitrate-producing materials on the ranch, most, such as animal and human waste products (cattle manure, poultry litter, sewage system effluent, and municipal biosolids) would be expected to produce nitrates with relatively enriched $\delta^{15}N$ values (> +10‰) whereas synthetic inorganic fertilizers generate nitrates with depleted isotopic values (< +3.5‰). Given the observed range of $\delta^{15}N$ values and relatively high nitrate concentrations observed within the contaminated area, it seems reasonable to propose that past overuse of both synthetic inorganic and organic fertilizers on the Shamrock Ranch may be responsible for the nitrate contamination in the area.

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