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## Nitrate Contamination in Groundwater on an Urbanized Dairy Farm

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Urbanization of rural farmland is a pervasive trend around the globe, and maintaining and protecting adequate water supplies in suburban areas is a growing problem. Identification of the sources of groundwater contamination in urbanized areas is problematic, but will become important in areas of rapid population growth and development. The isotopic composition of  $\text{NO}_3$  ( $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ ),  $\text{NH}_4$  ( $\delta^{15}\text{N}_{\text{NH}_4}$ ), groundwater ( $\delta^2\text{H}_{\text{wt}}$  and  $\delta^{18}\text{O}_{\text{wt}}$ ) and chloride/bromide ratios were used to determine the source of nitrate contamination in drinking water wells in a housing development that was built on the site of a dairy farm in the North Carolina Piedmont, U.S. The  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  compositions imply that elevated nitrate levels at this site in drinking well water are the result of waste contamination, and that denitrification has not significantly attenuated the groundwater nitrate concentrations.  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  compositions in groundwater could not differentiate between septic effluent and animal waste contamination. Chloride/bromide ratios in the most contaminated drinking water wells were similar to ratios found in animal waste application fields, and were higher than Cl/Br ratios observed in septic drain fields in the area.  $\delta^{18}\text{O}_{\text{wt}}$  was depleted near the site of a buried waste lagoon without an accompanying shift in  $\delta^2\text{H}_{\text{wt}}$  suggesting water oxygen exchange with  $\text{CO}_2$ . This water- $\text{CO}_2$  exchange resulted from the reduction of buried lagoon organic matter, and oxidation of the released gases in aerobic soils.  $\delta^{18}\text{O}_{\text{wt}}$  is not depleted in the contaminated drinking water wells, indicating that the buried dairy lagoon is not a source of waste contamination. The isotope and Cl/Br ratios indicate that nitrate contamination in these drinking wells are not from septic systems, but are the result of animal waste leached from pastures into groundwater during 35 years of dairy operations which did not violate any existing regulations. Statutes need to be enacted to protect the health of the

homeowners that require well water to be tested prior to the sale of homes built on urbanized farmland.

### Introduction

Urbanization is a pervasive global trend, and by 2030 over 60% of the world's population and 80% of the U.S. population is expected to live in urban areas (1–3). Groundwater is an important source of municipal water supply for domestic and industrial use in many urban areas, and is the only drinking water supply in areas classified as “critical watersheds” where development utilizing municipal water and sewer service is prohibited. Groundwaters in urban areas are susceptible to nitrate contamination from leaking septic and sewer systems as well as from previous land use when farmland has been developed (2, 3). After World War II fertilizer use increased dramatically, and contamination of groundwater by nitrate in rural areas is now recognized as an evolving public health crisis in many parts of the world (4, 5). Numerous studies have shown that groundwater nitrate concentrations in the U.S. are 3–60 times higher in agricultural areas relative to undisturbed areas (2, 6). Nitrate concentrations in most community water supplies are monitored and are below 10 mg/L  $\text{NO}_3\text{-N}$  which is the maximum contaminant level (MCL) for nitrate in drinking water in the United States (7). Approximately 9–39% of domestic wells test above the nitrate MCL (8) in rural areas of the U.S., and approximately 9% of rural drinking water wells have excess nitrate in North Carolina (9). Urbanized rural areas that use groundwater for drinking water can have high nitrate concentrations as a result of previous land use or from combined urban and agricultural nitrate sources. While these groundwater quality problems are common, identification of the sources of contamination is problematic, and protection of the homeowners is commonly not addressed by municipal or state construction regulations. The health risks of nitrate contamination in drinking water above 10 mg/L  $\text{NO}_3\text{-N}$  are well documented (2, 4, 7, 10), but the risks from long-term exposure are unknown (7, 11). New studies suggest that there is a positive association between nitrate in drinking water and non-Hodgkin lymphoma and colorectal cancer in humans (4). High population densities and the proximity of many potential nitrate sources in urbanized areas make source identification problematic (1), and urbanized farmland may combine exposure to agricultural and urban contaminants, making source identification even more complicated. This study will focus on a new housing development built on farmlands in a critical watershed area that does not permit development with municipal water and sewer utilities.

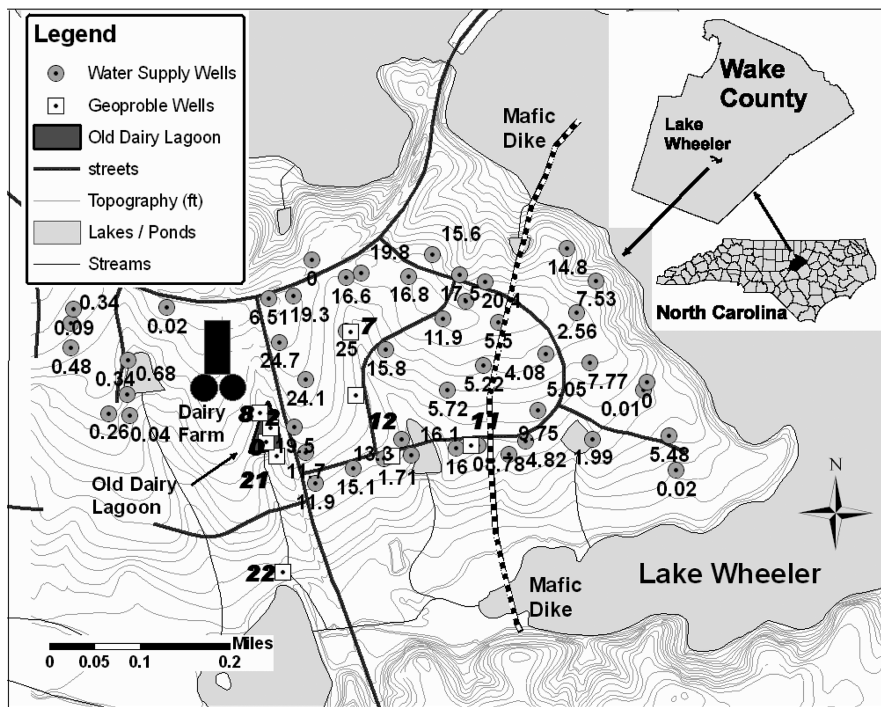
### Materials and Methods

Wake County, North Carolina is an area of rapid population growth where farmlands are quickly being urbanized. The population of Wake County doubled from 1980 to 2000, and is expected to double again by 2030. This study examines the geochemistry of drinking water in a housing site that was developed on an old dairy farm south of Raleigh, N.C. (Figure 1.) The development is located in the upper Swift Creek watershed which is an unincorporated 9246 ha area completely surrounded by rapidly growing municipalities. A Land Management Plan for the Swift Creek Watershed was adopted in 1990 that does not permit development with municipal water and sewer in an effort to protect downstream drinking water reservoirs. Drinking water in this housing development

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**FIGURE 1.** Location map of the study site in Wake County, NC. Nitrate concentrations of drinking water wells (numbers), shallow monitoring Geoprobe wells (**Bold italics**), and location of the mafic dike determined from magnetic anomaly measurements are shown.

is supplied from wells drilled 44–215 m deep into the crystalline rocks of the Crabtree Terrain (12). The hydrogeology is typical Piedmont comprised of an unsaturated soil and regolith zone, a saturated regolith zone, and a transition zone underlain by fractured crystalline bedrock (13). The drinking water wells are cased down to ~80 ft where the casing is sealed into fractured rock. The area is within the Nutbush Creek Fault Zone and is intruded by mafic dikes (14). A dairy farm operated on the site from the 1950s until 1986. The dairy lagoon was drained and buried in 1995, and single-family houses were built after 1993. Homes are located on 0.8–1.2 ha lots with individual well and septic systems. High groundwater nitrate concentrations at the site were first reported by the Wake County Environmental Services Department in 2003. This study examines the geochemistry of shallow and deep groundwater to determine the source of nitrogen contamination at this site.

One-liter water samples were collected in acid washed Nalgene bottles from June 2003 to June 2007 from 50 drinking water wells (Figure 1, Table 1). Nitrate concentrations remained relatively constant during these sampling periods. Nine shallow Geoprobe monitoring wells, screened over the bottom 0.6 m, were installed to a depth of 7–13.4 m in spring 2004 to sample shallow groundwater near the buried waste lagoon and in the septic leach field in the central area of the site where the highest drinking water nitrate levels were found (Figure 1). Rainfall event samples were collected in Raleigh with an Aerochem wet–dry bucket sampler following National Atmospheric Deposition Program guidelines (<http://nadp.sws.uiuc.edu/QA/>). Samples were filtered through a 0.45  $\mu\text{m}$  filter and kept at 4 °C until analysis. Soil samples were collected during Geoprobe well installation at two foot intervals from the Geoprobe coring rods, and were frozen until analysis. Nutrient and ion concentrations in water samples ( $\text{NO}_3$ ,  $\text{NH}_4$ ,  $\text{PO}_4$ ,  $\text{Cl}$ ,  $\text{Br}$ ) were determined by flow injection chromatography (15–18).  $\text{NO}_3$  and  $\text{NH}_4$  concentrations are reported as  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  mg/L. An automated flow injection method for bromide and chloride was modified to increase detection limits by doubling the size of the injection loop from standard techniques (16, 17). Baseline

detection levels were reduced by using >17 megaOhm polished RO water for the carrier liquid and to mix all standards and chemicals. With these modifications, minimum detection levels were reduced from 0.5 to 0.25 mg/L for chloride and 5 mg/L to 40  $\mu\text{g/L}$  for bromide. With the single injection loop, chloride standards had a reproducibility of  $\pm 3\%$  from 5 to 100 mg/L. With a double injection loop, chloride standards were reproducible  $\pm 3\%$  at 5 mg/L and 1.5% at 0.5 mg/L. Bromide standards were reproducible  $\pm 1\%$  at 5 mg/L,  $\pm 5\%$  at 2.5 mg/L, and  $\pm 9\%$  from 1.5 mg/L to 40  $\mu\text{g/L}$ . These techniques allow Cl/Br ratios to be determined in contaminated groundwater samples, but were not sensitive enough to analyze rainwater samples with extremely low Br concentrations (<40  $\mu\text{g/L}$ ). Magnetic field strength at the study site was measured with an EG&G Geometric Proton Precession Magnetometer (model 6856AX). The  $\delta^{15}\text{N}_{\text{NO}_3}$ ,  $\delta^{18}\text{O}_{\text{NO}_3}$ ,  $\delta^{15}\text{N}_{\text{NH}_4}$ ,  $\delta^{18}\text{O}_{\text{wt}}$ ,  $\delta^2\text{H}_{\text{wt}}$ , % $\text{C}_{\text{sed}}$ , and % $\text{N}_{\text{sed}}$  was determined by elemental analysis (EA), pyrolysis (TCEA), and continuous flow isotope ratio mass spectrometry (18, 19). Nitrate and ammonium (~30  $\mu\text{M}$ ) were concentrated from water samples on ion exchange resins (Biorad AG 50-WX8 cation and; AG 2-X8 anion resins). Eluted samples were neutralized and then cleaned of organic contaminants by passing the eluted sample through a column of cation resin, PVP, silica gel, and SPE C-18 (19). The nitrate was then converted to  $\text{AgNO}_3$  with  $\text{AgO}$ , lyophilized, and analyzed by combustion ( $\delta^{15}\text{N}_{\text{NO}_3}$ ) or pyrolysis ( $\delta^{18}\text{O}_{\text{NO}_3}$ ) with a Carlo Erba NC2500 EA, a Thermo TCEA, and a Thermo Delta+<sup>XL</sup> CF-IRMS (18, 19). Ammonium samples were analyzed by EA combustion of the cation resin with a carbon trap placed before the GC column (14).  $\delta^2\text{H}_{\text{wt}}$  and  $\delta^{18}\text{O}_{\text{wt}}$  compositions were determined by pyrolyzing 0.2  $\mu\text{L}$  of sample in a Thermo TCEA and simultaneously measuring the CO and H<sub>2</sub> peaks with a Delta+<sup>XL</sup> CF-IRMS (14). Each water sample was injected five times and the syringe needle was cleaned with methanol, air, and vacuum between each injection eliminating any memory effect between injections. Frozen soil samples were lyophilized, homogenized, and run in triplicate for  $\delta^{15}\text{N}_{\text{sed}}$ ,  $\delta^{13}\text{C}_{\text{sed}}$ , % $\text{C}_{\text{sed}}$ , and % $\text{N}_{\text{sed}}$  with a Carlo Erba NC2500 EA and a Thermo Delta+<sup>XL</sup> CF-IRMS (18). Isotopic results were

**TABLE 1. Shallow Geoprobe Monitoring Wells and Drinking Water Wells Results**

sample ID	DEPTH (ft)	NO <sub>3</sub> (mg/L)	Cl (mg/L)	NH <sub>4</sub> (mg/L)	δ <sup>15</sup> N <sub>NO<sub>3</sub></sub> (‰)	δ <sup>18</sup> O <sub>NO<sub>3</sub></sub> (‰)	δ <sup>18</sup> O <sub>wt</sub> (‰)	δ <sup>2</sup> H <sub>wt</sub> (‰)	D <sub>EX</sub>
Dairy Lagoon Geoprobe Wells									
mw-10 (b)	42	0.01	124.00	0.33	11.4	6.3	-13.4	-23.9	83.1
mw-11	44	2.25	48.00	1.07	15.4	7.5	-5.1	-20.5	19.9
mw-2	24	22.10	31.50	0.17	11.4	8.8	-9.8	-21.7	57.0
>mw-3 (b)	44	8.10	26.60	0.10	13.5	7.0	-8.2	-21.5	43.9
mw-7	34	21.10	25.50	0.13	10.9	7.2	-2.6	-10.9	10.0
Central Geoprobe Wells									
mw-5	36	14.60	17.10	0.07	9.2	9.0	-6.0	-29.1	18.7
mw-6	37	7.44	4.59	0.03	11.4	2.2	-6.9	-21.7	33.6
mw-8	44	11.70	9.48	0.13	8.6	8.0	-3.5	-18.6	9.4
mw-1	33	11.00	15.30	0.02	7.6	11.3	-5.0	-31.8	8.3
Drinking Water Wells *									
upper area									
average	271	0.26	2.44	0.08	11.8	8.9	-6.3	-44.3	6.5
std dev	43	0.23	0.19	0.07	3.1	2.8	1.1	13.8	8.0
central area									
average	386	15.89	22.50	0.02	8.8	7.6	-6.4	-31.8	19.7
std dev	165	5.46	10.76	0.07	1.8	3.0	0.5	9.3	9.5
lower area									
average	325	5.91	8.13	0.01	6.5	9.1	-6.7	-39.0	14.9
std dev	182	5.08	6.40	0.02	2.0	3.6	0.7	10.7	10.4
Raleigh Rainfall 1997–2007									
average		0.30	1.09	0.26	-0.62	31.44	-5.7	-29.2	16.6
std dev		0.25	0.57	0.27	2.17	8.23	3.4	24.8	14.6

calibrated and corrected to NBS, NIST, and internal laboratory isotope standards (18) and are reported as per mil (‰) deviations from the international standard according to the following equation:

$$\delta^{15}\text{N}, \delta^{18}\text{O} \delta^2\text{H} = \left\{ \left[ \frac{(R)_{\text{sam}}}{(R)_{\text{std}}} - 1 \right] \times 10^3 \right.$$

$$R = {}^{15}\text{N}/{}^{14}\text{N}, {}^{18}\text{O}/{}^{16}\text{O} \text{ or } {}^2\text{H}/{}^1\text{H}. \text{ Std} = \text{Air or VSMOW}$$

Statistical analyses of nutrient and isotopic results were completed using Microsoft Excel, SigmaPlot, and SigmaStat software.

## Results and Discussion

Nitrate concentrations are higher than the MCL in 44% {22 of 50} of the domestic wells, and in 56% {5 of 9} of the shallow monitoring wells at this site (Table 1). This is a significantly higher percentage of contaminated drinking wells than found in other rural areas in North Carolina or other areas of the United States (8, 9). The majority of the contaminated drinking wells {20} are located in the central area between the dairy farm and the position of the mafic dike that bisects the area (Figure 1). Although the feature was identified as a fault on the state geological map (12, 14), a magnetometer survey confirmed that a mafic dike cuts across the housing development with a N–S trend and suggests that the dike dips steeply to the east in the location where groundwater nitrate concentrations decrease eastward toward the lake. Shallow groundwaters in the area have nitrate concentrations that vary from 0.01 to 22 mg/L (Figure 1, Table 1). The lowest nitrate and highest ammonium and chloride concentrations are found near the buried dairy lagoon (Table 1). High nitrate concentrations in the shallow groundwater are found down slope, south of the buried dairy waste lagoon. Most of the wells down slope of the mafic dike have nitrate concentrations <10 mg/L. Two wells that have higher nitrate concentrations {15–20 mg/L} in this lower area are located just east of the dike. It is possible that these two wells pass through the dike at depth and sample groundwaters on the western (upslope) side of the dike.

Based on the nitrate concentrations and the trend of the mafic dike, groundwaters at this site fall into three groups.

The hilltop area west of the former dairy farm has nitrate concentrations below 10 mg/L and chloride concentrations below 3 mg/L. The central area east of the dairy farm and west of the mafic dike has nitrate concentrations that vary from 2 to 25 mg/L and chloride concentrations that vary from 4 to 44 mg/L. The wells that have <10 mg/L nitrate in this central area are either topographically above the dairy farm or more than 600 feet deep. Nitrate concentrations in the lower area, east of the mafic dike, are generally less than 10 mg/L with chloride concentrations below 10 mg/L. Nitrate concentrations have no significant trend with depth, except that wells deeper than 600 feet have low nitrate and chloride concentrations.

The potential sources of nitrate contamination at this site include lawn fertilizers, organic matter in the buried dairy waste lagoon, animal wastes leached from the dairy pastures, and effluent from septic systems. δ<sup>15</sup>N<sub>NO<sub>3</sub></sub> and δ<sup>18</sup>O<sub>NO<sub>3</sub></sub> in groundwater has been used to differentiate between potential nitrogen contamination sources, and can indicate areas of denitrification which can make fertilizer contaminated areas appear to be affected by animal or septic waste (20–24). The δ<sup>15</sup>N<sub>NO<sub>3</sub></sub> in the deep and shallow wells at this site varies from 3 to 15‰, while the δ<sup>18</sup>O<sub>NO<sub>3</sub></sub> varies from 3 to 18‰ (Figure 2.) The δ<sup>15</sup>N<sub>NO<sub>3</sub></sub> to δ<sup>18</sup>O<sub>NO<sub>3</sub></sub> plot of groundwater suggests that denitrification does not affect the majority of wells in this area. This interpretation can be verified by plotting δ<sup>15</sup>N<sub>NO<sub>3</sub></sub> versus the inverse nitrate concentration so that different source mixing lines plot as straight lines and denitrification trends plot as curves (23). Natural soil organic nitrogen varies from +4 to +7‰, fertilizers are near, 0‰, and septic wastes are ~ 8–10‰ (20–24). Dairy lagoons in this region are enriched in <sup>15</sup>N and can have δ<sup>15</sup>N<sub>NH<sub>4</sub></sub> values as high as +20‰, whereas streams draining dairy waste application fields in the area have δ<sup>15</sup>N<sub>NO<sub>3</sub></sub> values that vary from 9 to 16‰ (25). None of the δ<sup>15</sup>N<sub>NO<sub>3</sub></sub> groundwater values at this site plot along end-member mixing or denitrification lines (Figure 3.) This suggests that there has been minimal nitrate attenuation by denitrification, although fertilizer may be present in the low concentration wells with higher δ<sup>18</sup>O<sub>NO<sub>3</sub></sub> values from the lower area. Assuming an original waste δ<sup>15</sup>N<sub>NO<sub>3</sub></sub> value of +7‰, the observed 13–15‰ δ<sup>15</sup>N<sub>NO<sub>3</sub></sub> values in some of the wells could

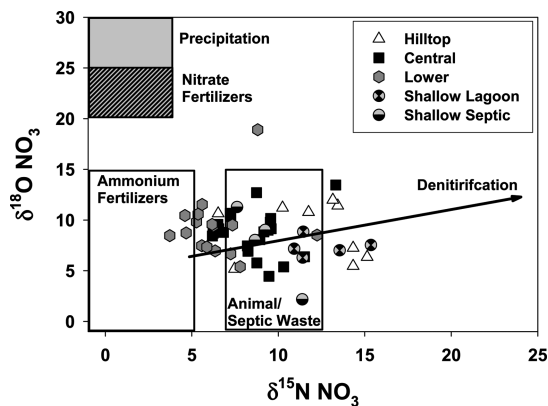


FIGURE 2. Nitrogen and oxygen isotopic composition of groundwater nitrate in the area. The  $^{15}\text{N}$ – $^{18}\text{O}$  dual isotope relationship indicates little amount of denitrification at the site.

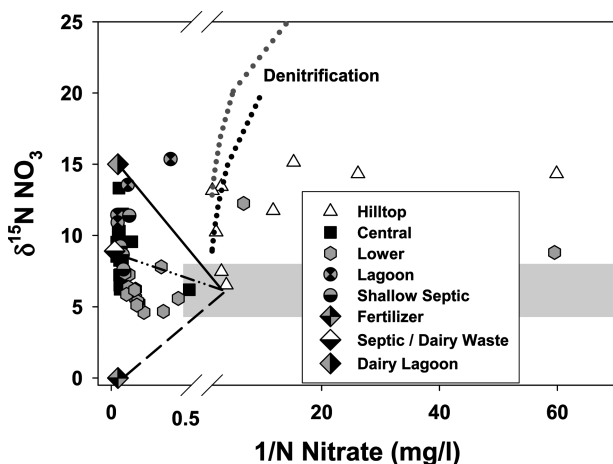


FIGURE 3. Natural  $\delta^{15}\text{N}$  versus inverse nitrate concentration of groundwater. Shaded area shows the isotopic range of soil organic nitrogen. Diamonds represent fertilizer, septic and dairy waste end point values (2023). Mixing lines are straight lines on this inverse plot, and the  $^{15}\text{N}$ /concentration values produced from a Rayleigh fractionation model starting at 1–2 mg/L N- $\text{NO}_3$  are shown as dotted lines.

represent a N loss of 35–75%, calculated from a Rayleigh fractionation model with an  $\epsilon$  of  $-5.7$  and an initial N concentration of 1–2 mg/L (23). Since most highly contaminated wells in the central area have  $\delta^{15}\text{N}_{\text{NO}_3}$  values below  $+10\text{‰}$  and low  $\delta^{18}\text{O}_{\text{NO}_3}$  compositions, denitrification cannot be a significant process in these wells.

Soils at the site are aerobic (nonhydric) soils, while hydric soils occur in wetlands to the south of the area near the lake. Oxidized nonhydric soils are biochemically incapable of sustaining extensive amounts of denitrification. Ammonium derived from septic or animal waste sources will be rapidly nitrified under these conditions, and the resulting nitrate would have  $\delta^{18}\text{O}_{\text{NO}_3}$  compositions within the range observed in the drinking water wells of the central area, but with higher  $\delta^{15}\text{N}_{\text{NO}_3}$  values than observed in the central area (23–27). The fate of nitrate from septic systems has been the focus of many previous studies (24, 26). Raw septic effluent contains labile organic carbon, which should support denitrification in septic leach fields. Previous studies suggest that carbon in the vadose zone degrades during effluent oxidation, leaving DOC levels that are only marginally higher than background levels (26). Denitrification will not significantly attenuate nitrate in these soils if the remaining DOC is refractory or in low concentrations, and if an additional energy source is not present. Nitrogen from septic system effluent and animal wastes leached from pastureland in aerobic conditions should

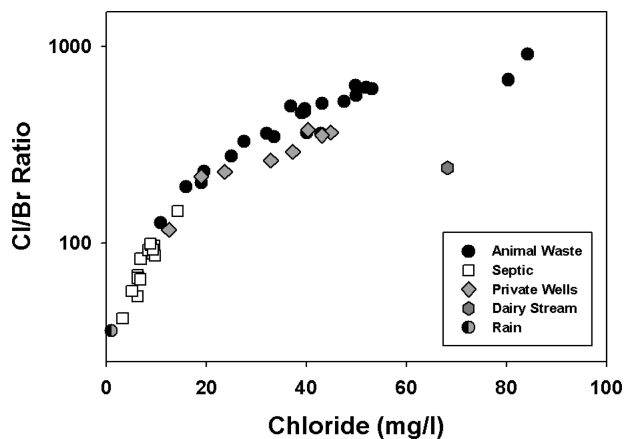


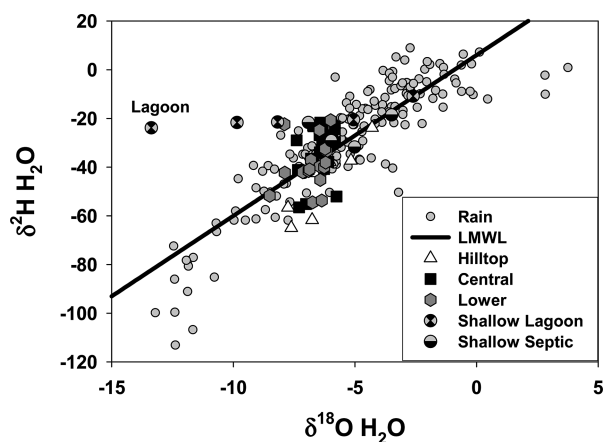
FIGURE 4. Chloride/bromide ratios of private drinking water wells in the central area of the site with high nitrate concentrations, a swine waste application field, a stream draining a dairy farm, and rainfall samples.

have overlapping  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  signatures, whereas waste lagoon  $\delta^{15}\text{N}_{\text{NH}_4}$  should be much higher producing elevated  $\delta^{15}\text{N}_{\text{NO}_3}$  in down slope groundwater areas (20–27).

Chloride concentrations, chloride/bromide ratios, as well as the  $\delta^2\text{H}_{\text{wt}}$ ,  $\delta^{18}\text{O}_{\text{wt}}$  and  $\delta^{11}\text{B}$  of groundwater have been used to separate animal and septic wastes (3, 23, 25, 28–32). Chloride and nitrate concentrations are below 10 mg/L in the hilltop and lower area drinking wells, but are consistently above 10 mg/L in the central area (Figure 4). Chloride concentrations increase with nitrate and  $\delta^{15}\text{N}_{\text{NO}_3}$  in the central area where the highest nitrate concentrations are found. Shallow wells near the buried waste lagoon have the highest chloride {44–124 mg/L}, low nitrate {<3 mg/L}, and highest ammonium concentrations {>1 mg/L} at the site (Table 1). Wells placed in the buried lagoon have high ammonium concentrations and  $\delta^{15}\text{N}_{\text{NH}_4}$  values of  $> +10\text{‰}$ . Down slope from the buried waste lagoon, groundwaters have 20–22 mg/L nitrate and  $\delta^{15}\text{N}_{\text{NO}_3}$  compositions of  $+11$  to  $+13\text{‰}$ . Elemental analysis of the sediments recovered from the cores drilled through the buried dairy waste lagoon indicate that the buried lagoon sediments have high organic carbon concentrations {>2%} at a depth of 12 feet, whereas all the other sediment cores have carbon weight per cents that are  $<0.5\%$ .  $\delta^{13}\text{C}$  of the sediments in most of the Geoprobe cores vary from  $-23$  to  $-27\text{‰}$ . The sediments with the 2% organic carbon concentrations have  $\delta^{13}\text{C}_{\text{sed}}$  values of  $-40\text{‰}$ , indicating extensive microbial activity in the buried organic layer. It is likely that organic reduction in the buried lagoon produces ammonium that is quickly oxidized to nitrate with a small  $\delta^{15}\text{N}$  fractionation (20, 21). That nitrate is then leached into groundwater, resulting in high nitrate concentrations and elevated  $\delta^{15}\text{N}_{\text{NO}_3}$  values observed in shallow groundwaters down slope from the buried lagoon.

Chloride is concentrated in groundwaters affected by animal waste (25, 27, 33). The NCSU dairy farm located 5 km south of this site has chloride concentrations  $>100$  mg/L in the dairy waste lagoons, and chloride concentrations that vary from 30 to 60 mg/L in dairy spray field streams (25). Chloride concentrations are high in wells from the central area with high nitrate concentrations, and in the shallow groundwaters near the buried dairy lagoon. However, previous studies have found that there is no consistent chloride maximum concentration observed in septic leach fields, and that concentrations in septic leach fields appear to vary according to distance from the tank and dilution by groundwater (3, 24, 28, 29).

Chloride and bromide ratios in groundwater behave conservatively and have also been used to separate septic and animal waste sources (31, 32, 34, 35). Cl/Br ratios can



**FIGURE 5. Hydrogen and oxygen isotopic composition of groundwaters at the site with rain collected on the NCSU campus ~6 miles to the northeast.**

vary depending upon the analytical method and the region (32, 35). In the southwest U.S. and Alberta, Canada Cl/Br ratios are generally <50–150 for rainfall, <100 for unaffected soil–water, 100–200 for most groundwaters, 300–600 in domestic sewage, and 1000–10 000 for runoff affected by deep salt brines (31). Cl/Br ratios in groundwaters from the midwest are higher, possibly due to the prevalence of road salt. Groundwater affected by animal waste in the midwest had Cl/Br ratios in between 1250 and 1650 (32). Studies in Texas indicate that oil field brines, which have very high Cl/Br ratios, and were pervasive contaminates in shallow groundwater (34, 35). Cl/Br ratios have to be calibrated for individual regions, because of differences in geology and anthropogenic salt sources that have high Cl/Br ratios (34). Groundwater from this site and from North Carolina locations described in previous studies (18, 19, 25, 27, 33), and were analyzed for Cl and Br concentrations with the flow injection method. In North Carolina Cl/Br ratios are <50 for rain, 50–150 for septic leach fields, and from 150 to 1000 for animal waste application fields. The groundwater in the central area at this site have Cl/Br ratios that vary from 100 to 400 and are similar to ratios found in other animal waste application fields, but not from septic leach fields in North Carolina (Figure 4).

The two potential sources of animal waste at this site are the buried dairy lagoon and pasture waste accumulation over the time. Precipitation in the area over the past 9 years has an isotopic relationship of  $\delta^2H_{wt} = 6.6\delta^{18}O_{wt} + 6.2$  (Figure 5,) which is similar to other published equations for North Carolina (36). The  $\delta^2H_{wt}$  and  $\delta^{18}O_{wt}$  of the groundwaters at the study site fall along this local meteoric water line (LMWL), except for shallow groundwater near the buried lagoon. Groundwaters near the buried lagoon are depleted in  $\delta^{18}O_{wt}$  by up to 10‰, and fall off the LMWL (Figure 5). Organic bacterial reduction and exchange of water oxygen with metabolic  $CO_2$  can produce this type of  $\delta^{18}O_{wt}$  shift, although this has not been observed very often (37, 38). Rain and shallow septic wells at this site have similar average  $\delta^{18}O_{wt}$  and  $D_{ex}$  values ( $D_{ex}$  or deuterium excess is defined as  $D_{ex} = \delta^2H_{wt} - [8 \times \delta^{18}O_{wt}]$  (39), whereas all the deeper wells have a slightly depleted average  $\delta^{18}O_{wt}$  (Table 1). It is not unusual for groundwater in fractured rock systems to be slightly depleted by 1–2‰ compared to rainfall and shallow groundwater, although this phenomenon is not well documented (40, 41). Shallow groundwater collected around the buried waste lagoon has distinctly different  $\delta^{18}O_{wt}$  and  $D_{ex}$  values from the rest of the wells which suggests that the buried dairy waste lagoon is not the source of contamination in the central area wells with high nitrate concentrations. The contaminated drinking water wells at this site have

intermediate  $\delta^{15}N_{NO_3}$  compositions, Cl/Br ratios that are similar to animal wastes, and normal  $\delta^{18}O_{wt}$  values that suggest that these groundwaters were contaminated by dairy waste that leached from pasture land during normal dairy grazing and feeding operations over a 35 year period. No existing environmental regulations were violated during the period of dairy operations or during housing construction.

Low  $\delta^{18}O_{wt}$  values, high,  $D_{ex}$  and  $\delta^{15}N_{NO_3}$  compositions with elevated nitrate concentrations may be an indicator of groundwater contamination by buried waste lagoons. There are currently >4100 animal waste lagoons located in the North Carolina coastal plain and piedmont region (19). Retirement of these lagoons and development of these farms could be an impediment for future urbanization. Ultimately more information is needed about how water is recharged from shallow groundwater reservoirs, which can be easily contaminated, to deeper groundwater reservoirs, which are commonly used for drinking water supplies. More work is also needed to better define Cl/Br ratios of groundwater with different land use in the southeast region of the U.S., which is largely unaffected by road salt or evaporate deposits. Urbanization of farmlands will continue in Wake County and in other areas of the U.S. to accommodate population growth. Most current construction regulations do not address the problem of predevelopment groundwater contamination when farmlands are converted to housing developments. This is especially important in critical watershed areas where development with municipal water and sewer services is prohibited to protect surface water quality downstream. Regulations should be enacted to protect public health in new construction areas by requiring groundwater quality testing of all new construction wells as part of the permitting process.

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### Supporting Information Available

Detailed methods used in this paper as well as drinking well water chemistry and isotopic results, and a figure of the nitrate, chloride and Cl/Br ratio results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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