

Ground Water Quality

Tracing Nitrate Transport and Environmental Impact from Intensive Swine Farming using Delta Nitrogen-15

Jonathan D. Karr,* William J. Showers, J. Wendell Gilliam, and A. Scott Andres

ABSTRACT

Natural-abundance $\delta^{15}\text{N}$ showed that nitrate generated from commercial land application of swine (*Sus scrofa domestica*) waste within a North Carolina Coastal Plain catchment was being discharged to surface waters by ground water passing beneath the sprayfields and adjacent riparian buffers. This was significant because intensive swine farms in North Carolina are considered *non-discharge* operations, and riparian buffers with minimum widths of 7.6 m (25 ft) are the primary regulatory control on ground water export of nitrate from these operations. This study shows that such buffers are not always adequate to prevent discharge of concentrated nitrate in ground water from commercial swine farms in the Mid-Atlantic Coastal Plain, and that additional measures are required to ensure non-discharge conditions. The median $\delta^{15}\text{N}$ -total N of liquids in site swine waste lagoons was $+15.4 \pm 0.2\text{‰}$ vs. atmospheric nitrogen. The median $\delta^{15}\text{N}$ - NO_3 values of shallow ground water beneath and adjacent to site sprayfields, a stream draining sprayfields, and waters up to 1.5 km downstream were $+15.3 \pm 0.2$ to $+15.4 \pm 0.2\text{‰}$. Seasonal and spatial isotopic variations in lagoons and well waters were greatly homogenized during ground water transport and discharge to streams. Neither denitrification nor losses of ammonia during spraying significantly altered the bulk ground water $\delta^{15}\text{N}$ signal being delivered to streams. The lagoons were sources of chloride and potassium enrichment, and shallow ground water showed strong correlation between nitrate N, potassium, and chloride. The ^{15}N -enriched nitrate in ground water beneath swine waste sprayfields can thus be successfully traced during transport and discharge into nearby surface waters.

NITROGEN from animal wastes can enter ground water and surface water through leaking lagoons, inadvertent spills, surface runoff, improper discharge, atmospheric transport, and land application of wastes (Evans et al., 1984; Puckett, 1995; Ackerman and Taylor, 1996; Andres, 1996; Gould, 1996; Hunt et al., 1996; Gilliam et al., 1996; Mikkelsen and Gilliam, 1996; North Carolina Division of Water Quality, 1996a; Sloan et al., 1999). Animal waste ammonium is mobilized in the subsurface by nitrification where conditions are oxidizing. Nitrate has low affinity for anion exchange sites in soils and aquifer matrices and may travel unimpeded unless denitrification occurs (Behnke, 1975; Burt and Trudgill, 1993). Accepted agronomic rates of swine waste application for coastal bermuda grass (*Cynodon dactylon* L.) are approximately 180 to 400 kg/ha/yr plant-available

N applied during the growing season (Zublena et al., 1990). Recommended rates of application have been shown to result in subsurface drainage waters with average annual nitrate N concentrations in the 5 to 30 mg/L range beneath sprayfields, although concentrations greater than 100 mg/L have been reported (Evans et al., 1984; Gilliam et al., 1996; Sloan et al., 1999). Surface runoff total dissolved N at swine waste irrigation sites has been measured at 7 to 13 mg/L (Westerman et al., 1985). Spills from swine and cattle waste lagoons have created runoff containing 40 to 92 mg/L of ammonium N (Ackerman and Taylor, 1996; Mallin et al., 1997; Burkholder et al., 1997).

Swine have experienced a greater percentage increase in head than any other major livestock in North Carolina in recent years (North Carolina Department of Agriculture, 1997), although poultry production is also growing rapidly. As of 1 Dec. 1997, the total state swine inventory was 9.8 million head, up nearly 400% from a decade earlier. Most swine facilities are in the southeastern portion of the state, within the Coastal Plain. Sampson and Duplin counties contain the largest numbers of swine, with 1.8 million and 2.2 million head respectively. In addition, 11.2 million turkeys (*Meleagris gallopavo*) are raised in dry litter operations in both Sampson and Duplin counties (North Carolina Department of Agriculture, 1997). In comparison, the 1990 human populations of Sampson and Duplin counties were approximately 40 000 each (North Carolina Division of Water Quality, 1996b). In these high-animal-density counties, manure provides greater than 100% of crop needs for plant-available N. Land application of swine waste slurry yields only ~17% of the original manure N as plant-available on average, with ~70% of the original N lost to the atmosphere by ammonia volatilization before application and nearly half of the remaining N lost in the field to the atmosphere, runoff, or drainage (Barker and Zublena, 1995). Therefore, the original manure N produced may actually be more than 500% of crop needs in some of these counties, even though commercial fertilizers are also widely used. This excess N is a potential pollutant of surface waters and ground water (North Carolina Division of Water Quality, 1996b).

Eastern North Carolina rivers are under various levels of nutrient stress. The Neuse River basin has received the most attention and was declared a nutrient-sensitive watershed in 1993. Of 3053 stream miles (~4912 km) evaluated (92% of the basin), only 22% were found to

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Abbreviations: $\delta^{15}\text{N}$ - NO_3 , delta nitrogen-15 of dissolved nitrate + nitrite; $\delta^{15}\text{N}$ -total N, delta nitrogen-15 of total dissolved nitrogen; USGS, United States Geological Survey.

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be fully supporting their designated uses. Of the impaired stream miles, 34% were judged as impacted by agriculture (North Carolina Division of Water Quality, 1996a). Nitrogen appears to be the limiting nutrient for algal growth in the lower Neuse River (Paerl, 1983; Paerl et al., 1995), as in many other estuarine and coastal water bodies (Heathwaite, 1993). Recurring and worsening algal blooms, subsequent oxygen depletion, and large fish kills in eastern North Carolina waters have raised concerns about nonpoint-source nutrients (North Carolina Division of Water Quality, 1996a,b; Paerl et al., 1998). The present study was conducted in the adjacent Cape Fear River basin, Black River subbasin, which has a higher concentration of commercial swine operations than the Neuse (North Carolina Department of Agriculture, 1997) but has come under less scrutiny, since the hydrography of the Cape Fear estuary is not as conducive to algal blooms as that of the Neuse. In the Cape Fear basin, 18% of stream miles (1100 of 6300 miles; ~1770 of 10137 km) are classified as impaired. It is estimated that 40% (462) of those stream miles are impacted by agriculture, including intensive livestock operations (North Carolina Division of Water Quality, 1996b). Watersheds in the Black River subbasin are within the highest USDA Natural Resources Conservation Service category of vulnerability to manure N leaching and runoff (USDA Natural Resources Conservation Service, 1997). According to the USEPA (1997), 11 to 25% of surface water sites measured in the Black River watersheds of Sampson and Duplin Counties in recent years were above target levels for conventional pollutants, including nutrients. The Black River has potential for developing algal blooms driven by increased N loading (Mallin et al., 1998).

Stable Nitrogen Isotopes

It is possible to identify a range of natural-abundance stable nitrogen isotope ratios associated with classes of pollutants in a given geographic region. Physical and biogeochemical processes are accompanied by kinetic and equilibrium isotopic fractionations, which lead to nitrogen compounds having different isotopic ratios (Heaton, 1986). Data are expressed as $\delta^{15}\text{N}$, the relative difference in $^{15}\text{N}/^{14}\text{N}$ ratios between samples and atmospheric nitrogen, which is isotopically constant and designated as 0‰ (Mariotti, 1983). The $\delta^{15}\text{N}$ values are given as a per mil (‰) difference from this atmospheric standard, where:

$$\% \delta^{15}\text{N} = \left[\frac{(^{15}\text{N}/^{14}\text{N} \text{ sample} - ^{15}\text{N}/^{14}\text{N} \text{ standard})}{^{15}\text{N}/^{14}\text{N} \text{ standard}} \right] \times 1000$$

The extent to which nitrogen sources can be identified in receiving waters depends upon the isotopic separation between various sources and the degree of isotopic fractionation that affects the nitrogen in transit and during transformations (Shearer and Kohl, 1993). Inorganic fertilizers are synthesized from atmospheric nitrogen and generally are within about $\pm 4\%$ of atmospheric nitrogen (Hübner, 1986). However, fertilizer nitrogen

often is enriched by several per mil $\delta^{15}\text{N}$ in the process of passing through the soil nitrogen pool due to processes such as ammonia volatilization, mixing with nitrate of soil organic origin, biological conversion to organic nitrogen, microbial remineralization involving loss of isotopically light (^{15}N depleted) nitrogen, and partial denitrification (Black and Waring, 1977; Hübner, 1986). Plant uptake of N generally involves a very small fractionation factor relative to other processes (Hübner, 1986). The resulting $\delta^{15}\text{N}$ of nitrate draining from fertilized fields is often similar to that of naturally occurring soil nitrate, which ranges from about +3 to +8‰ (Hübner, 1986; Heaton, 1986). Fertilizer-generated nitrate can be distinguished from natural soil nitrate only when the former approaches the $\delta^{15}\text{N}$ value of the original fertilizer at high ground water nitrate concentrations. (Kreitler, 1979; Heaton, 1986).

In contrast, animal waste-generated nitrate generally takes on a nitrogen isotopic signature greatly enriched in ^{15}N relative to other nitrate sources. The key to this distinction is ammonia volatilization occurring during the storage and application of animal wastes, which preferentially removes ^{14}N and causes a large enrichment of the heavier ^{15}N isotope in the residual ammonium. At high pH, a typical equilibrium isotope fractionation factor between gaseous NH_3 and residual aqueous NH_4^+ is about 1.034 at 25°C (Wada and Hattori, 1991). This means that ammonia molecules bearing ^{14}N would be 3.4% more likely to volatilize in a given period of time under these conditions than those with ^{15}N . The actual isotopic enrichment expressed in the residual ammonium is a function of the fraction of original ammonia lost, which should increase with temperature, pH, and lagoon residence time. The elevated $\delta^{15}\text{N}$ signal of the residual ammonium is transferred to the resulting nitrate in drainage waters when ammonia is oxidized to nitrate by soil bacteria. In the case of spraying swine wastes onto sandy soils of the North Carolina Coastal Plain, complete nitrification generally occurs as little or no ammonium is found in ground waters (Gilliam et al., 1996; Sloan et al., 1999). Nitrate derived from animal waste is generally in the isotopic range of +10‰ to +20‰ or greater (Gormly and Spalding, 1979; Kreitler, 1979; Wassenaar, 1995).

Objectives

The overall objective of the present study was to determine whether nitrate derived from swine waste was being exported from a fairly typical Mid-Atlantic Coastal Plain intensive swine farming site. This required isotopic and concentration monitoring of nitrogen in the site swine lagoon liquids, in ground water beneath sprayfields and riparian buffers, and in nearby surface waters. Denitrification in fields and riparian buffers, as well as ammonia losses during spraying, were also investigated. Nitrate N concentrations, $\delta^{15}\text{N}$, chloride to nitrate N ratios, pH, and dissolved oxygen were used to determine whether denitrification significantly affects the total isotopic signal of any exported nitrate.

STUDY SITE

The study site encompasses two adjacent instrumented commercial swine farms located in the inner Coastal Plain near Turkey, NC. These farms were also the subject of previous and concurrent nutrient transport studies (Gilliam et al., 1996, Sloan et al., 1999). The farms have approximately 110 shallow monitoring wells clustered in nests across sprayfields and in riparian buffers (Fig. 1). Each farm has three transects of well nests traversing fields used for swine lagoon irrigation. Wells are all 5.1-cm-diameter polyvinyl chloride (PVC) construction with a single slotted screen interval over approximately the lower 60 cm of the casing, and the bottom is plugged. Each well nest consists of a shallow, intermediate, and deep well. Shallow well depths are generally ~ 1 m while intermediate and deep wells range from about 2 to 10 m. The well depths were chosen to bracket the expected fluctuation of the water table and to reach the lower limit of the surficial unconfined aquifer (Fig. 2a,b). Screened intervals of wells within individual nests generally do not overlap. The mean water table depth measured in individual wells during the study ranged from 0 to 2.7 m, with a total mean depth of 0.8 m. Average water table contours followed the topography very closely. Streams draining the fields were sampled adjacent to Transects 3 and 6, and Transect 1 (between Nests 3E and 6E, and near Nest 1E; Fig. 2a,b). Stream drainage from between the two farms enters *Stewarts Creek*, an ungauged third-order stream within the Black River subbasin of the Cape Fear River basin. From 1955 to 1971, a United States Geological Survey (USGS) gauging station (Station 02106410, Hydrologic Unit Code [HUC] 03030006) was located near the study site. United States Geological Survey historical data show peak annual discharge averaging $7031 \text{ m}^3/\text{h}$ and ranging from 2242 to $16\,915 \text{ m}^3/\text{h}$. Typical stream depth is 1 m or less. Annual average precipitation at nearby Warsaw is approximately 1300 mm. Surface water samples were taken from *Stewarts Creek* near the downstream limit of each farm and at bridges ~ 3 km upstream and ~ 1.5 km downstream (Fig. 1). There are no other intensive livestock operations or National Pollution Discharge Elimination System (NPDES) permitted point-source dischargers (North Carolina Division of Water Quality, 1996b) along *Stewarts Creek* between these upstream and downstream sites. There are several other intensive livestock operations within the headwaters upstream of the study area. Fields are separated from *Stewarts Creek* by a wide (>30 m) riparian buffer. The *Stewarts Creek* watershed is primarily in Sampson County but has tributaries in Duplin County. This watershed contains the oldest intensive swine farms in North Carolina (G. Upton, North Carolina Agric. Ext., personal communication, 1998). The watershed has a high rating for potential impact from agricultural runoff and leaching (USEPA, 1997; USDA Natural Resources Conservation Service, 1997).

Soil and Aquifer Characterization

The dominant soils within fields are sandy loams of the Blanton series (loamy, siliceous, semiactive, thermic Grossarenic Paleudult), Johnston series (coarse-loamy, siliceous, active, acid, thermic Cumulic Humaquept), and Chipley series (thermic, coated Aquic Quartzipsamment) (Brandon, 1981). Riparian soils are largely Marvyn series (fine-loamy, kaolinitic, thermic Typic Kanhapludult) and Bibb (coarse-loamy, siliceous, active, acid, thermic Typic Fluvaquent) and Johnson series, exhibiting evidence of fluvial deposition of clay and organic matter in surface and subsurface horizons (Brandon, 1981; Sloan et al., 1999). Reconnaissance hydrogeologic and stratigraphic characterizations of the site were performed by

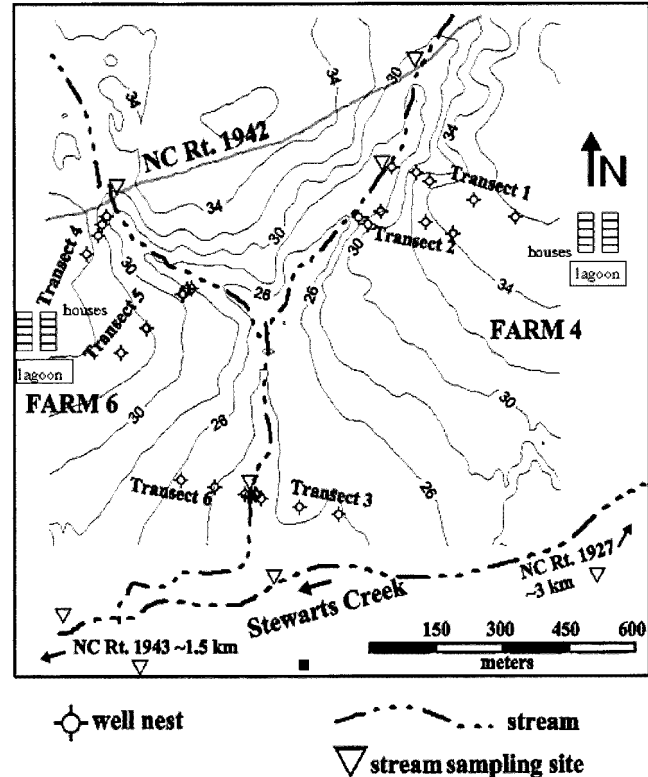


Fig. 1. Study site map with monitoring well transects and stream sampling sites. Swine houses and lagoons are near the northern border of each farm. Well transects traverse sprayfields into riparian buffers. The farms are located within the *Stewarts Creek* watershed, Black River subbasin, Cape Fear River basin, North Carolina. Elevations in meters above sea level. Average water table contours follow the topography very closely.

personnel from the Delaware Geological Survey (Andres, unpublished preliminary hydrogeologic report, 1997). Unconsolidated sediments of Tertiary and Quaternary age unconformably overlie the Cretaceous Black Creek clayey confining unit (Fig. 2a,b). Four deeper wells were also installed into or below the Black Creek clay to depths of 8 to 14 m. The upland portions of the site (elevations >27 m) are dominated by Tertiary sediments, possibly correlating to the Chowan River or Bear Bluff Formations. This unit is dominantly silt and clay with minor amounts of fine quartz sand, with a composition typical of tidal flat deposits. Hydraulic conductivities measured by the Bouwer and Rice slug test ranged from about 0.5 to 1.4 m/d. The lowland portions (elevations <27 m) are underlain by Quaternary fine to medium sands that may correlate with the Waccamaw or Penholoway formations and have a composition indicative of fluvial channel deposits. Hydraulic conductivities ranged from about 1.4 to 90 m/d. Forested riparian buffers on the edge of the application fields vary in width from about 10 to >100 m. The buffers are underlain by organic silts up to 3 m thick, which unconformably overlie either the Tertiary or Quaternary units. Hydraulic conductivities measured in three riparian zone wells in Transect 3 ranged from 1.4 to 39 m/d. On Farm 4, ground water transport appears to be more perpendicular to *Stewarts Creek* than on Farm 6. Based on measured hydraulic conductivities, topographic gradients, and assumed porosities of 0.1 to 0.3, ground water flow velocities were calculated at 0.1 to 0.8 m/d toward the left and right tributary forks and at 0.3 to 1.5 m/d toward the main fork and *Stewarts Creek*. The results of the hydrogeologic survey suggest ground water residence times

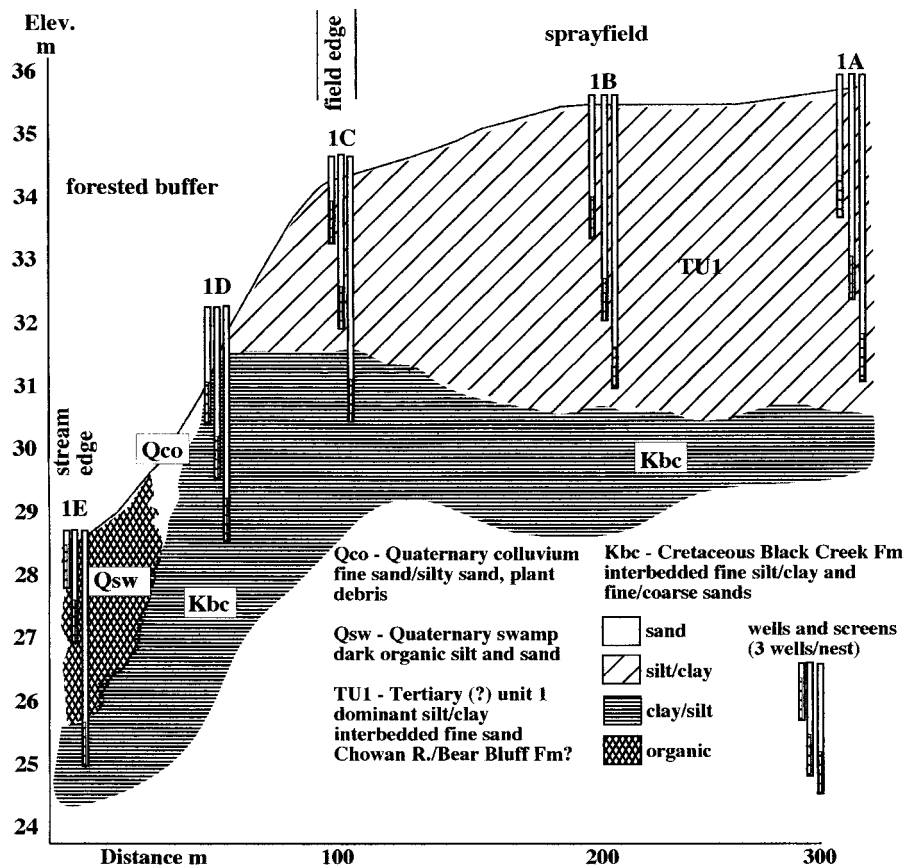


Fig. 2a. Geologic profiles of Well Transect 1. Nests consist of three individual wells each. Water table depth is generally 0 to 1 m at Nest D and E wells and 1 to 3 m at Nest B and C wells. Transport across confining clay layers within the Black Creek Fm (formation) is unknown, but upward flow of deep ground water may be significant near stream beds. The Black Creek Fm probably isolates Nests 1D and 1E from the sprayfields. The rest of Transect 1 probably receives some ground water flow from north of the sprayfields.

at the site ranging from several weeks to more than a decade, and much greater transport in the lowland portion of the site (Transects 3 and 6) than in the upland portion (Transects 1 and 4). Researchers from the USGS in Reston and in Raleigh have dated site ground water in the surficial unconfined aquifer as early 1980s to 1990s using chlorofluorocarbon (CFC) dating (L. Puckett and T. Spruill, personal communication, 1998).

Agricultural Use

Each farm is a confined, 1000 sow farrow-to-feeder operation using its own anaerobic waste lagoon. Lagoons are approximately 120 m long, 50 m wide, and 3 to 5 m deep, giving a maximum capacity of ~30 000 m³. Wastes are flushed twice daily from beneath the slotted floors of the houses into the waste lagoons near the northern border of each farm, using water and recycled lagoon liquids. The lagoon liquids are applied to adjacent fields with a hard hose and cable tow traveler irrigation system. The study site has been receiving swine waste for at least 20 yr, and has not received any artificial fertilizers for at least 10 yr, if not longer (Gilliam, unpublished data, 1998). The approximately 190 ha of waste application fields on these two farms have reportedly received biweekly applications of swine lagoon effluent equivalent to 300 to 400 kg plant-available N/ha/yr during the May through September growing season. However, since lagoon levels require control during rainy winter months, spraying operations have often occurred on a year-round basis. Coastal bermuda grass overseeded with rye (*Lolium perenne* L.) grown in the fields is

grazed by small herds of beef cattle (*Bos taurus*) and is occasionally harvested. Approximately 20 to 40 cattle are periodically rotated between small (<5 ha) plots separated by removable fencing on each farm. Because most of the crop is grazed and cattle wastes fall back on the fields, there is a low potential for net removal of nitrogen from the site as harvested hay. The hay that is harvested has often been observed to sit in fields as bales for extended periods, which may allow leaching of nitrogen compounds by rainwater.

METHODS

Sampling

The anaerobic waste lagoon of each farm was sampled at approximately monthly intervals. Lagoon spray was collected in freshly wetted hand-augered soil cores in September 1997 and in soil cores and sprayfield puddles in January 1998. Spray was also collected in buckets in July and August of 1997.

Partial transects (Transects 1, 3, and 6) from both farms were sampled monthly in a cross-section from sprayfield through field edge and riparian buffer to stream edge. Sampling focused on intermediate and deep wells. Shallow wells roughly intersect the expected mean water table and were often dry or very slow to recover from bailing. The stream-edge well nests in Transects 3 and 6 were sampled at all depths during summer 1997 in an attempt to better vertically delineate zones of denitrification and nitrate export. Well samples were taken either by polyvinyl chloride (PVC) bailer or by a peristaltic pump after purging 1 to 3 well volumes by bailing. In

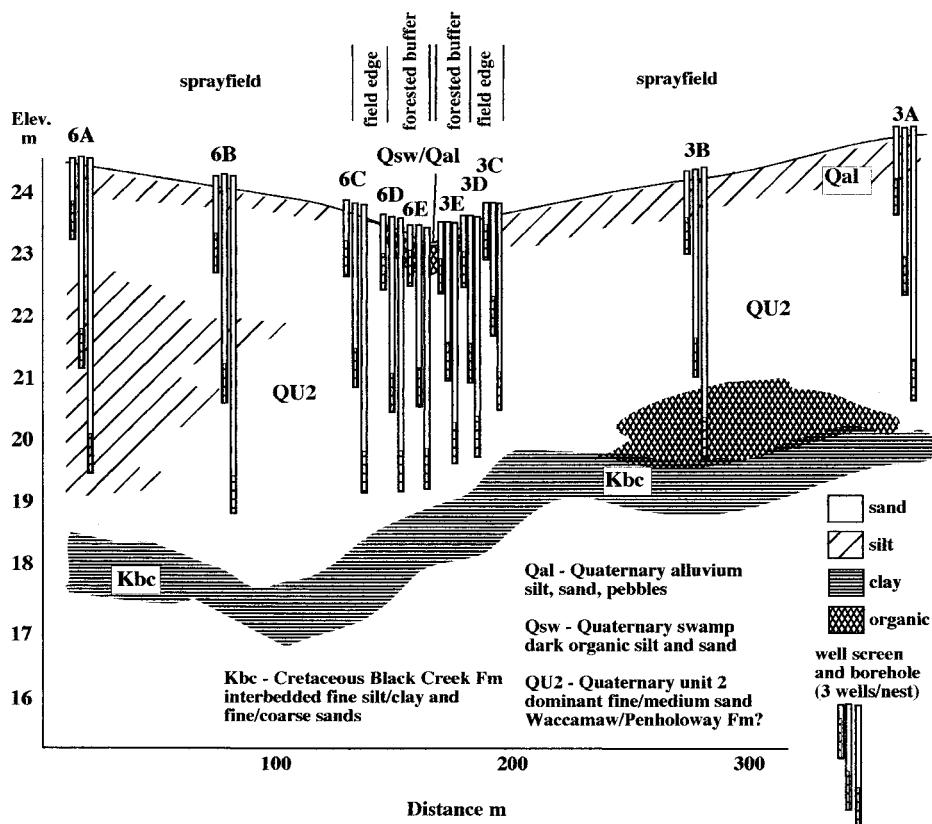


Fig. 2b. Geologic profiles of Well Transects 3 and 6. Nests consist of three individual wells each. Water table depth is generally 0 to 1 m at Nest D and E wells and 1 to 3 m at Nest B and C wells. Transport across confining clay layers within the Black Creek Fm (formation) is probably minor, as evidenced by nitrate-free water collected within the Black Creek, but upward flow of deep ground water may be significant near stream beds. The riparian zone between Transects 3 and 6 is very narrow (ca. 10 m max.).

situ pH, dissolved oxygen, and temperature were measured with field meters after well recovery. Samples were filtered with 0.45-micron filter capsules and stored in polyethylene bottles. Filtering was performed in the field when possible.

On-site streams and Stewarts Creek were sampled at the locations indicated in Fig. 1. Sampling and field measurements were performed in the same manner as for well samples, except that samples were taken in 4-L polyethylene cubitainers. All samples were kept cool until delivery to the lab, where they were stored at 4°C (well waters) or frozen at -20°C (surface waters, lagoon samples, and soil cores) until analysis.

Sample Preparation and Analysis

Lagoon samples were acidified to pH < 3 with concentrated HCl and vacuum-filtered in the laboratory with precombusted 0.7-micron glass fiber filters, then frozen until analysis. Sub-samples were taken for automated spectrophotometric analyses of nitrate + nitrite (USEPA Method 353.2; USEPA, 1979) and ammonium (USEPA Method 350.1; USEPA, 1979) on all samples. Allowable concentration error with these methods is $\pm 10\%$. No separate measurement of nitrite was made, and all nitrate N concentration and isotope analyses included any nitrite N present. Chloridimeter (Gilliam, 1971) and atomic absorption potassium (USEPA Method 258.1; USEPA, 1979) analyses were performed on a subset of lagoon and well samples. Kjeldahl digestions for total Kjeldahl nitrogen (TKN) (USEPA Method 351.3; USEPA, 1979) were performed on all stream samples and a subset of lagoon and well samples. Data from the North Carolina State University Soil Science Department biweekly sampling of all wells indicated only trace

ammonium N and TKN in wells. A small number of soil ammonium extractions were performed by shaking 10 g of soil recently wetted by waste-spraying operations in 40 mL of 1 M KCl for 1 h, then vacuum-filtering and diluting as needed with deionized water before concentration analyses and isotopic analyses.

Delta Nitrogen-15 Analysis

Analyses of water samples for $\delta^{15}\text{N}$ of nitrate (streams and wells) or total dissolved N (lagoons) used combinations of published methods with minor modifications. Enough sample liquid was processed to produce about 1 mg of N per sample. Dilute stream samples were concentrated by roto-evaporation at 55°C under moderate vacuum ($\sim 10^{-1}$ torr) to a volume of ~ 200 mL. Separation of nitrate in stream samples for isotopic analysis was performed by a 50-min steam distillation (Velinsky et al., 1989; Showers et al., 1990) with a Labconco (Kansas City, MO) Rapidstill II. This was preceded by a five-day predigestion at 65°C with 2 g MgO to remove labile organic N and ammonia (Sigman et al., 1997). After digestion, the sample was boiled down to ~ 50 mL to assure ammonia removal and was reconstituted to 200 mL with deionized water before distillation. The nitrate conversion to ammonia was accomplished at pH 10 by adding 1 g finely ground Devardas alloy and 1 g MgO before the distillation. Between samples, the still was flushed by distilling ethanol followed by deionized water for 15 min each to prevent cross-contamination. Distilled ammonia resulting from the reduction of sample nitrate was trapped and protonated in a collection flask containing 200 mL 0.0024 M HCl and 200 mg W-85 ion exchange zeolite

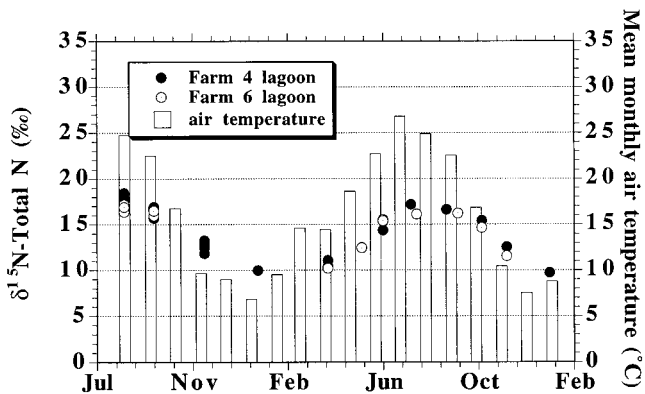


Fig. 3. Swine lagoon $\delta^{15}\text{N}$ -total N and monthly mean air temperature. Multiple samples from different points in lagoons were taken during three of the sampling events. Increased ammonia volatilization in warmer months should increase ^{15}N enrichment in residual lagoon ammonium.

(Union Carbide Corp., Danbury, CT). The collection flask was magnetically stirred during distillation and for 1 h afterward while sealed with parafilm. The ammonium-loaded W-85 was then collected on 0.7-micron glass fiber filters, rinsed with deionized water, and dried overnight at 65°C. The dried W-85 was loaded into silver foil boats for delivery into quartz combustion ampules. All reagents and filters were thoroughly pre-combusted before use to remove contaminants. Ammonium in soil extractions was loaded onto 200 mg W-85 by stirring 200 mL of diluted soil extraction solution adjusted to pH ~4 with 10% HCl for 90 min and filtering as above. Ground water samples containing only nitrate were freeze-dried (Böhlke and Denver, 1995) in 125-mL serum bottles. Lagoon samples were acidified to pH < 3 with HCl to prevent ammonia loss during freeze-drying. The final residues from freeze-drying were

transferred into combustion ampules via silver foil boats. A modified Dumas combustion method after Kendall and Grimm (1990) was used to convert all N species into purified nitrogen gas. Samples were analyzed on a Finnigan Mat 251 (Thermo-Finnigan, Bremen, Germany) dual-inlet dual-collector ratio mass spectrometer. Internal standards were calibrated to both purified atmospheric nitrogen and International Atomic Energy Agency (IAEA) N-1 ammonium sulfate. The median isotopic difference of 41 pairs of duplicated samples was 0.24‰. Duplicate or multiple analyses were averaged for reporting and calculations. Stream waters having organic N but no nitrate were spiked with 60 micromoles of nitrate isotopic standard and run through the complete predigestion, distillation, and combustion procedure, with a standard deviation of $\pm 0.1\%$. Freeze-dried ammonium standard solutions had a standard deviation of $\pm 0.1\%$, and freeze-dried nitrate standard solutions had a standard deviation of $\pm 0.05\%$.

RESULTS AND DISCUSSION

Swine Lagoon Samples

The median $\delta^{15}\text{N}$ -total N of swine lagoon samples was $+15.4 \pm 0.2\%$ vs. atmospheric nitrogen. Lagoons showed $\delta^{15}\text{N}$ -total N signals ranging from $+9.8 \pm 0.2\%$ to $+18.4 \pm 0.2\%$, with a smooth seasonal cycle of summertime isotopic enrichment and wintertime depletion. This variation closely tracked monthly mean air temperature (Fig. 3). The median ammonium N concentration in lagoons was 247 mg/L. Raw swine waste in houses was not sampled prior to flushing into lagoons. The lagoons were sources of concentrated chloride (54–153 mg/L) and potassium (175–371 mg/L). There are no other known significant sources of dissolved chloride or

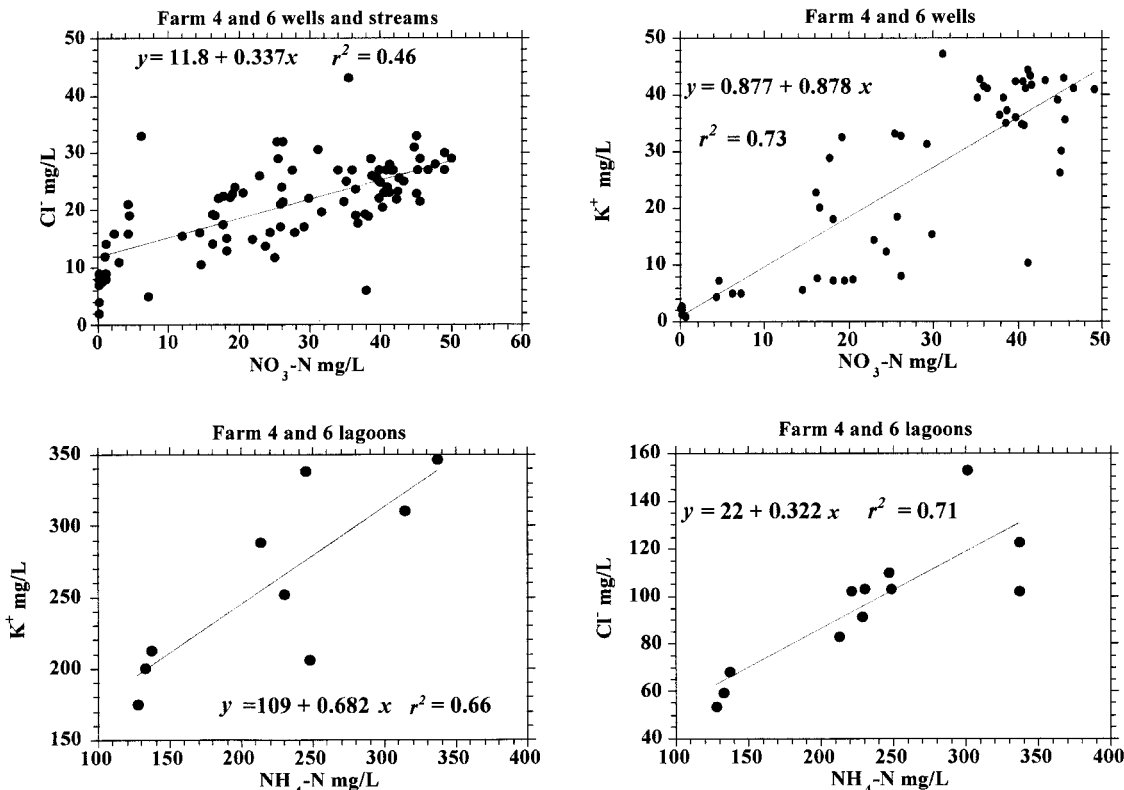


Fig. 4. Chloride and potassium vs. ammonium N in lagoons and nitrate N in wells. Swine waste lagoons were enriched in potassium and chloride.

Table 1. Summary of N concentration and isotope statistics for groups of samples.†

| Description | Number of samples | Mean $\text{NH}_4 \pm \text{SE}$ | Median NH_4 | mg N/L | | Mean $\delta^{15}\text{N} \pm \text{SE}$ | Median $\delta^{15}\text{N}$ | Concentration-weighted mean $\delta^{15}\text{N}$ |
|--|-------------------|----------------------------------|----------------------|----------------------------------|----------------------|--|------------------------------|---|
| | | | | Mean $\text{NO}_3 \pm \text{SE}$ | Median NO_3 | | | |
| Farm 4 lagoon | 12 | 248 \pm 17 | 247 | | | +14.4 \pm 0.7 | +14.9 | +14.8 |
| Farm 6 lagoon | 9 | 243 \pm 28 | 248 | | | +14.4 \pm 0.8 | +15.4 | +14.5 |
| Farm 4 and 6 lagoons | 21 | 248 \pm 16 | 248 | | | +14.4 \pm 0.5 | +15.4 | +14.6 |
| All wells | 100 | | | 28.6 \pm 1.4 | 30.0 | +16.7 \pm 0.5 | +15.4 | +15.9 |
| Sprayfield stream at 1E | 7 | | | 0.7 \pm 0.2 | 0.5 | +13.1 \pm 1.7 | +14.0 | +15.9 |
| Sprayfield stream at 3E/6E‡ | 11 | | | 8.6 \pm 1.4 | 6.7 | +15.2 \pm 0.3 | +15.4 | +15.7 |
| Stewarts Cr. Rt. 1927 | 7 | | | 0.4 \pm 0.1 | 0.3 | +13.2 \pm 1.2 | +13.8 | +13.8 |
| Stewarts Cr. below Farm 4 | 9 | | | 2.0 \pm 0.9 | 1.0 | +15.7 \pm 0.7 | +16.5 | +13.8 |
| Stewarts Cr. below Farm 6‡ | 7 | | | 1.7 \pm 0.6 | 1.1 | +15.2 \pm 0.3 | +15.3 | +15.3 |
| Stewarts Cr. Rt. 1943‡ | 5 | | | 0.9 \pm 0.1 | 0.9 | +14.8 \pm 0.9 | +15.4 | +14.9 |
| Total stream sites downstream from sprayfields | 23 | | | | | +15.2 | +15.4 | +15.7 |

† Data from duplicate analyses averaged. Duplicates not included in sample count.

‡ Data included in total stream sites downstream of sprayfields.

potassium at the site. Both lagoon ammonia and well water nitrate N concentrations were positively correlated to chloride and potassium concentrations with r^2 values ranging from 0.46 to 0.73 (Fig. 4). Table 1 lists means (\pm standard error [SE]) and medians for each group of samples. Concentration-weighted $\delta^{15}\text{N}$ means were also calculated as an estimate of “bulk” or total isotopic signal of the lagoon, ground water, and stream N reservoirs over the study period.

Well Samples

The median $\delta^{15}\text{N}\text{-NO}_3$ of well samples was also $+15.4 \pm 0.2\%$. Wells had a median nitrate N concentration of 30 mg/L. There was evidence of nitrate loss in some wells by processes other than dilution. Transect 1 had high nitrate N levels (> 30 mg/L) in middle-of-field and field-edge wells, which dropped off to zero or near zero at stream edge in the wide riparian buffer. Chloride and potassium also dropped by an order of magnitude from field edge to stream edge, but not to zero, indicating variable amounts of dilution as well as denitrification in producing low nitrate N levels in these wells. Transect 1 is probably receiving immediate ground water flow from both inside and outside of the application fields. Increasing chloride to nitrate N ratios have been considered an indicator of denitrification in previous studies (Jacobs and Gilliam, 1985; Lowrance, 1992; Gilliam et al., 1996; Sloan et al., 1999) because dilution is less likely to alter this ratio. Chloride is much less subject to adsorption on clay particles than potassium (Krauskopf, 1979), and is probably the more conservative tracer of dilution at this site. Chloride in Transect 1 dropped from sprayfield values of 16 to 44 mg/L by a variable factor of 5 to 10 toward the stream, while potassium consistently dropped from ~ 40 mg/L by a factor of 10. Chloride to nitrate N ratios increased from < 2 to 20–45 from field edge to stream edge in Transect 1. In contrast, Transects 3 and 6 showed high nitrate N concentrations in nearly all wells (generally more than 10 mg/L, and more than 40 mg/L in many cases). Little attenuation of nitrate was apparent in the narrow (~ 10 m) buffer zones of Transects 3 and 6, except in the shallowest wells. Chloride and potassium did not vary systematically over time along these transects, but chlo-

ride to nitrate N ratios in Transect 3 stream-edge wells did increase from ~ 1 to > 6 between deep and shallow wells during summer. Four deep wells were screened below the Black Creek confining unit in addition to the normal transect wells. These wells were generally nitrate-free.

Propagation of Swine Waste Isotopic Signal to Streams

The isotopic signal of nitrogen at the study site was propagated in approximately conservative fashion from swine waste lagoons through land application, nitrification, ground water transport, discharge to streams, and downstream transport up to 1.5 km. A Kruskal–Wallis χ^2 test (Helsel and Hirsch, 1992) comparing $\delta^{15}\text{N}$ of (i) lagoons, (ii) wells, and (iii) combined stream samples likely to be impacted (lower sprayfield stream and Stewarts Creek at Farm 6 and Rt. 1943 stations) found no significant differences between these three sample groups at the $\alpha = 0.05$ level ($K = 2.252$, $\chi^2 = 5.991$, $\text{df} = 2$). The interquartile and total ranges of $\delta^{15}\text{N}$ in the stream group were much smaller than the ranges in both lagoons and wells, while medians were identical (Fig. 5). This indicates that the nitrogen isotopic signal from lagoons was homogenized by mixing during ground water transport and discharge to streams. The outlying $\delta^{15}\text{N}\text{-NO}_3$ values within wells were predominantly at lower nitrate N concentrations, which would give them little weighting of the isotopic signal of the total nitrate load, as evidenced by concentration-weighted means of $\delta^{15}\text{N}$ (Table 1). The interquartile ranges of $\delta^{15}\text{N}\text{-NO}_3$ for wells in Nests D (mid-buffer) and E (stream edge) were less than those of Nests B (sprayfield) and C (field edge) for the combined transects. Median $\delta^{15}\text{N}\text{-NO}_3$ values remained very constant between depth-integrated nests in combined transects (Fig. 5). Outliers are indices of denitrification or spraying-induced fractionation.

Median concentrations of lagoon ammonium N were one and two orders of magnitude higher than those of well nitrate N and stream nitrate N, respectively. Dilution must be chiefly responsible for this difference, because median isotopic values were statistically identical. In describing stream stations individually, means are used here due to the small number of samples at each

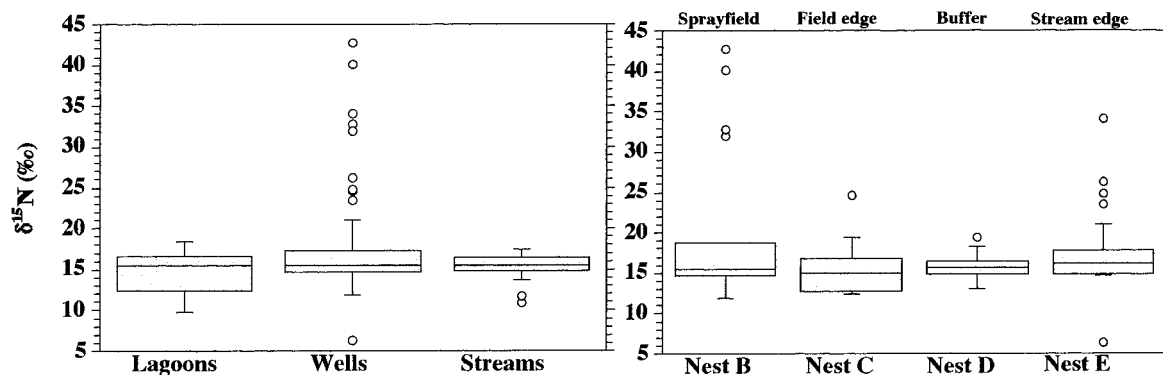


Fig. 5. Left panel: Boxplots of $\delta^{15}\text{N}$ in lagoon ammonium and in well and stream (onsite, adjacent, and downstream) nitrate. Right panel: Boxplots of $\delta^{15}\text{N}$ in depth-integrated nests for combined transects. Boxes enclose the upper and lower quartile (25%) of data about the median, which is represented by a horizontal line within each box. Whiskers above and below boxes represent the upper quartile plus 1.5 times the interquartile distance (IQD) and the lower quartile minus 1.5 times the IQD. Outliers are represented by circles. Since samples from Transect 1 Nest E contained insufficient nitrate for isotopic analysis, these were not included in the Nest E plot.

site, while medians are used for larger groupings (~ 20 data points or greater) due to non-normality of data distributions. The mean concentration of on-site stream nitrate N rose from 0.7 mg/L near Well Nest 1E (upstream, wide buffer) to 8.6 mg/L near Well Nests 3E and 6E (downstream, narrow buffer) indicating nitrate delivery from ground water as the stream passed between the sprayfields of the two farms. There were no visible surface runoff channels in the fields. Standard deviations at the two sites were different enough to preclude the *t*-test. A one-tailed unpaired Mann-Whitney test showed a very significant difference in nitrate N at these two sites ($P < 0.0001$, M-W $U = 3.0$, $U' = 95.00$). Same-day stream nitrate N levels at 3E and 6E were between 3 and 170 times higher than at 1E, with a maximum concentration of 16.9 mg/L on 9 Sept. 1997 (nitrate N at 1E measured 0.1 mg/L on the same day). These findings are in agreement with those of Sloan et al. (1999), who sampled the site intensively during the same period as this study. They found significant differences in mean nitrate N concentrations between the upstream tributaries above Wells 1E and 4E and the downstream site near 3E and 6E (Fisher Least Squared Difference, $\alpha = 0.05$). The $\delta^{15}\text{N}\text{-NO}_3$ at 1E ranged from $+7.3 \pm 0.2\text{‰}$ to $+19.8 \pm 0.2\text{‰}$, while $\delta^{15}\text{N}\text{-NO}_3$ at 3E and 6E stayed between $+14.0 \pm 0.2\text{‰}$ and $+16.6 \pm 0.2\text{‰}$. The Mann-Whitney test failed to detect significant differences ($P = 0.1496$), although the median rose between the two sites from $+14.0\text{‰}$ to $+15.4\text{‰}$. In February 1998, the nitrate N concentrations of the two streams entering the north end of the farm site at Rt. 1942 were both 0.2 mg/L, with $\delta^{15}\text{N}\text{-NO}_3$ of $+9.4 \pm 0.2\text{‰}$ and $+10.0 \pm 0.2\text{‰}$. These streams originate near a turkey operation. On the same day, the stream nitrate N concentration rose to 2.5 mg/L with a $\delta^{15}\text{N}\text{-NO}_3$ of $15.9 \pm 0.2\text{‰}$ below the confluence of the two streams in the lower sprayfields. The concentration of nitrate N in the stream between Well Nests 3E and 6E during the study was well-correlated with $\delta^{15}\text{N}$ in a power function ($\text{‰ } \delta^{15}\text{N} = 12.8 \times \text{mg/L NO}_3\text{-N}^{0.0878}$; $r^2 = 0.87$). The high $\delta^{15}\text{N}\text{-NO}_3$ end-member of the stream was consistent with the median value for stream-edge wells at the site ($+16.1\text{‰}$).

Along-Stream Trends in Stewarts Creek

Nitrate N concentrations in Stewarts Creek near the farms were much lower than concentrations in the lower sprayfield stream. Reconnaissance work by the USGS in Raleigh, NC and Reston, VA suggests that the bed of Stewarts Creek is receiving discharge of very-low-nitrate pre-1950 water from the deeper aquifer, based on chlorofluorocarbon (CFC) dating of streambed piezometer samples (L. Puckett and T. Spruill, personal communication, 1998). Streams often receive much older ground water through deeper flow paths beneath the channel bottom than along the banks (Modica et al., 1998). Any shallow ground water recharged in forested areas and discharging to the creek should also contain little nitrate in comparison with ground water beneath sprayfields, and would be a source of dilution without inducing isotopic shifts. The along-stream trends in mean nitrate N concentration and $\delta^{15}\text{N}\text{-NO}_3$ on Stewarts Creek and on the farm site are summarized in Fig. 6. Mean nitrate N concentrations rose from 0.4 mg/L at the Rt. 1927 bridge ~ 3 km upstream of the farm units to 2.0 mg/L adjacent to Farm 4 and 1.7 mg/L just downstream of Farm 6. This indicates nitrate export to Stewarts Creek via ground water beneath the farm sprayfields and the stream draining the sprayfields. A same-day $\sim 25\%$ rise in nitrate N concentration occurred consistently on Stewarts Creek from the sampling point adjacent to Farm 4 to that below Farm 6 (Farm 6 $\text{NO}_3\text{-N} = 0.0 + 1.26 \times \text{Farm 4 NO}_3\text{-N}$, $r^2 = 0.97$). Sloan et al. (1999) also found significant differences in mean nitrate N between these two sites over a similar time period (Fisher Least Squared Difference, $\alpha = 0.05$). The tributary stream that drains the sprayfields and divides the two farms joins Stewarts Creek between these two sampling points. Mean nitrate N was 0.9 mg/L at the Rt. 1943 bridge approximately 1.5 km downstream of Farm 6 on Stewarts Creek. Same-day nitrate N levels were always 1.5 to 10 times higher at points downstream of the farms vs. those upstream. The general rise in $\delta^{15}\text{N}\text{-NO}_3$ values along Stewarts Creek near the study farm units is consistent with delivery of nitrate generated from swine waste. The lower $\delta^{15}\text{N}\text{-NO}_3$ values up-

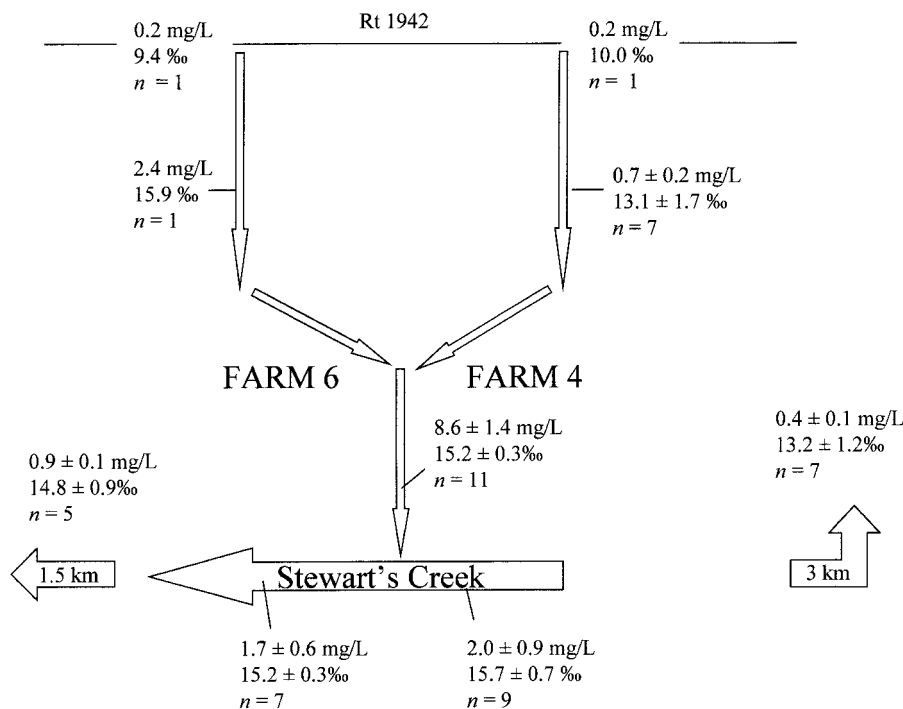


Fig. 6. Mean nitrate N concentrations and $\delta^{15}\text{N-NO}_3$ with standard error (no error shown for stations with only one sample) for on-site stream stations and Stewart's Creek stations upstream, adjacent to, and downstream of the farms.

stream at Rt. 1927 (Fig. 6) suggest a somewhat lower contribution of nitrate from animal waste sources, although numerous swine and poultry farms are located upstream within the watershed. On one occasion, three small tributaries within the headwaters of Stewart's Creek watershed upstream of the study site were sampled. The $\delta^{15}\text{N-NO}_3$ values of those samples ranged from $8.5 \pm 0.2\text{‰}$ to $22.1 \pm 0.2\text{‰}$. Same-day $\delta^{15}\text{N-NO}_3$ values near Farm 6 were higher than at Rt. 1927 on all but two occasions.

A Kruskal–Wallis test showed significant differences in median nitrate concentrations between the four Stewart's Creek stations ($K = 13.263$, $\chi^2 = 7.815$, $df = 3$). Dunn's Multiple Comparison test showed significant differences between Rt. 1927 and Farm 4 ($P < 0.05$) and Rt. 1927 and Farm 6 ($P < 0.01$). The same tests for $\delta^{15}\text{N-NO}_3$ values at the four Stewart's Creek stations failed to show significant differences ($K = 5.142$, $\chi^2 = 7.815$, $df = 3$), despite the higher medians at the downstream sites. The $\delta^{15}\text{N-NO}_3$ values at Rt. 1943 correlated well to those of the sprayfield stream near Well Nests 3E and 6E ($\delta^{15}\text{N-NO}_3$ at Rt. 1943 = $-2.3 + 1.15 \times \delta^{15}\text{N-NO}_3$ at stream between Nest 3E and 6E, $r^2 = 0.99$).

Non-Conservative Processes

The close agreement of both median and weighted-mean $\delta^{15}\text{N}$ values between lagoons, wells, and impacted streams indicates that the rates of nitrogen loading to the system are sufficient to largely mask the isotopic effects of non-conservative processes on the total N load from waste application. As long as the nitrogen lost to these processes represents a modest fraction of the total nitrogen loading at the site, the effect on the spatially and temporally integrated isotopic signal in ground wa-

ter and its expression in receiving surface waters should be minimal. To investigate the question of isotopic shifts during waste application, wetted soil cores were taken from sprayfields immediately following spraying operations in September 1997 and January 1998. Ammonium extracted from soils showed $\delta^{15}\text{N}$ essentially identical with that of the source lagoon (approximately $+16\text{‰}$ in September, approximately $+10\text{‰}$ in January, which was also identical to surface puddles). Spray collected in buckets during summer months showed up to approximately 50% ammonia loss relative to the lagoon, and isotopic values from $+20\text{‰}$ to greater than $+40\text{‰}$. However, these fractionations do not appear to alter the total ground water isotopic signal, and no effects of ammonia losses during spraying can be uniquely identified within site wells. This may be partly explained by the fact that the most efficient ground water recharge and nitrate delivery to the water table should occur during colder and/or wetter periods, particularly when the water table is high (Burt and Trudgill, 1993; Heathwaite, 1993; Johnes and Burt, 1993; Creed and Band, 1998). In winter, evapotranspiration and plant N uptake are minimal, net precipitation and ground water recharge are maximal, and stream-edge ground water nitrate concentrations tend to be highest at the site (Sloan et al., 1999). Any spraying at lower temperatures is less likely to induce large ammonia losses or isotopic shifts through excess volatilization. It has been the observation of the authors and associates that year-round spraying can occur on commercial swine farms in eastern North Carolina for purposes of lagoon level control. Spraying can occur during saturated soil conditions and during the winter. These factors would favor conservation of the total nitrogen isotopic signal of the wastes.

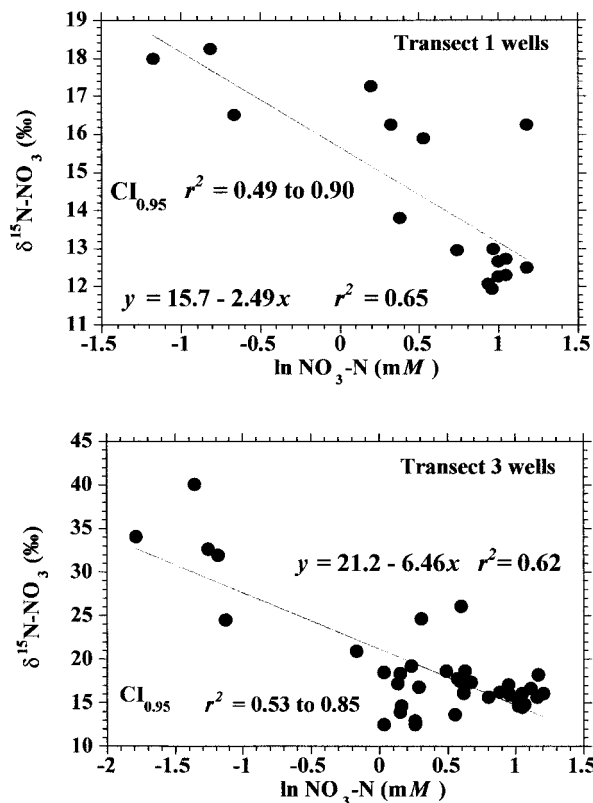


Fig. 7. Transects 1 and 3 log-linear relationships of nitrate N concentration vs. $\delta^{15}\text{N-NO}_3$. Slopes are indicative of denitrification enrichment of $\delta^{15}\text{N}$ of residual nitrate in some samples.

Once land-applied waste N has been nitrified, there is always potential for preferential loss of ^{14}N during any subsequent denitrification within reducing zones, producing more positive $\delta^{15}\text{N-NO}_3$ values in residual nitrate. When the natural logarithm of nitrate N (or nitrate N + nitrite N) concentration is plotted against $\delta^{15}\text{N}$ of nitrate (or $\delta^{15}\text{N}$ of nitrate + nitrite) in a denitrifying closed system with a single dominant nitrate source, the slope of the resulting line is the isotopic enrichment factor ϵ . Published values of ϵ for nitrate + nitrite (in units of ‰ vs. mM) in ground water wells and microcosms in temperate regions range from -15.9 to -3.8 (Mariotti et al., 1988; Böttcher et al., 1990; Bates and Spalding, 1998; Bates et al., 1998), while ϵ values for nitrate alone were measured up to -2.5 by Bates and Spalding (1998). Within this total range, it would require about a 50 to $>80\%$ reduction of the original nitrate N concentration by denitrification to produce a 10‰ isotopic enrichment above the original signal, for example. In the current study, large isotopic enrichments were observed in a small number of sprayfield and buffer wells. Negative logarithmic relationships were expressed in wells of Transects 1 and 3, with slopes between -2.5 and -6.5 , within the range of those described above (Fig. 7). The r^2 values for these transects were 0.62 and 0.65, which is near the low end of those of the above-mentioned studies ($r^2 = 0.71$ to 0.99). Stream-edge wells in Transect 1 generally had no measurable nitrate N, and are isolated from the Tertiary unit under the sprayfield by the intervening Black Creek unit. The

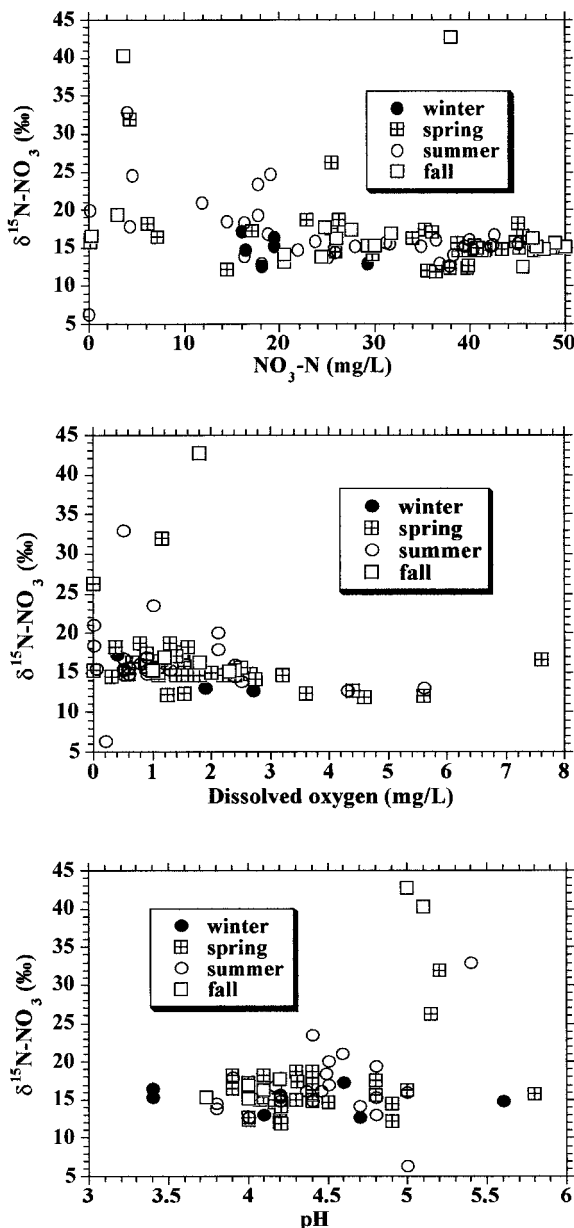


Fig. 8. $\delta^{15}\text{N-NO}_3$ vs. nitrate N concentrations, dissolved oxygen (DO) levels, and pH. The $\delta^{15}\text{N}$ well above the median is exhibited only in samples with $\text{DO} < 2 \text{ mg/L}$ and $\text{pH} > 5$, supporting the general trend of denitrification enrichment of $\delta^{15}\text{N}$ in a small number of samples.

more enriched values shown for Transect 1 were taken from mid-buffer wells. A sprayfield receives highly variable loading of waste N that creates pulses of incoming nitrate with variable concentration. This may complicate the relationship between nitrate N concentration and $\delta^{15}\text{N}$ and lead to less significant correlation than in some of the systems in the previous studies. Ammonia losses during spraying and dilution with low-nitrate water in the wider buffers could also complicate such a relationship. These factors would lead to lower r^2 values. Comparative plots of $\delta^{15}\text{N-NO}_3$ vs. nitrate N, dissolved oxygen, and pH are shown in Fig. 8. Highly elevated $\delta^{15}\text{N-NO}_3$ values in the current study occurred only in wells with $< 2 \text{ mg/L}$ dissolved oxygen and at pH of 5 or greater.

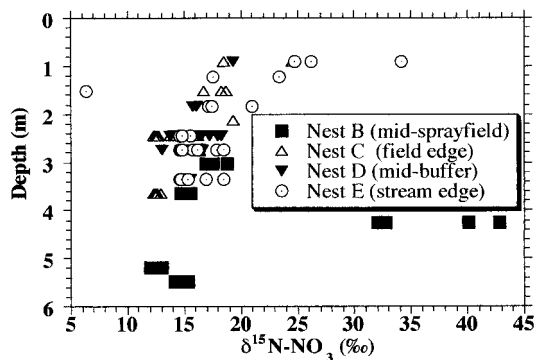


Fig. 9. $\delta^{15}\text{N-NO}_3$ values vs. depth (m). Well 3E-S had the most positive shallow well $\delta^{15}\text{N}$ value (in August, 1996). Well 1E-I had the least positive $\delta^{15}\text{N}$ value (in April, 1997). Well 3B-D showed several very positive $\delta^{15}\text{N}$ values, with dissolved oxygen < 2 mg/L and $\text{pH} > 5$. This well is within an organic silt layer (see Fig. 2b).

These factors point toward denitrification in some samples. Denitrification is favored energetically only in the absence of molecular oxygen, although it may occur in ground water with low, but measurable dissolved oxygen due to “patchiness” in soil or aquifer reduction sites (Lloyd et al., 1987; Gold et al., 1998). Nitrification lowers ground water pH by producing hydrogen ions while denitrification consumes hydrogen ions, raising pH (Stumm and Morgan, 1981), although highly organic soils are well buffered and may not exhibit this effect. Isotopic enrichment trends with decreasing well depth also support denitrification as the source of enrichment (Fig. 9). When the outlying deeper points are removed, $\delta^{15}\text{N}$ is negatively correlated with depth in a logarithmic function with $r^2 = 0.48$. The supply of labile organic carbon substrate for reduction is generally highest in organic soils and in the shallowest parts of aquifers (Starr and Gillham, 1993), and spraying of swine waste would increase this supply. Previous studies of denitrification in aquifers have found most denitrification occurring near shallow water tables (Gormly and Spalding, 1979; Postma and Boesen, 1991; Smith et al., 1991; Starr and Gillham, 1993; Desimone and Howes, 1998; Sloan et al., 1999) or in the organic soil horizon (Lowrance, 1992; Simmons et al., 1992). It is also possible for fractionation of ammonia during or following spraying to create isotopic enrichments of resulting nitrate. However, this process would not lead to a relationship between isotopic enrichment and dissolved oxygen or pH. It also would not provide a mechanism for consistently concentrating enriched $\delta^{15}\text{N-NO}_3$ values near the surface, especially in riparian buffers. Figure 10 compares nitrate N and $\delta^{15}\text{N-NO}_3$ trends of stream-edge wells of Transects 3 and 6 with depth. The shallow wells showed significantly higher $\delta^{15}\text{N-NO}_3$ than intermediate or deep wells in nest 3E (single factor ANOVA, $P < 0.01$) and in Nest 6E ($P = 0.02$). This indicated that denitrification was occurring in the upper meter or two, while little or no nitrate attenuation was occurring in the deep wells. Nitrate N concentration was generally depleted with decreasing depth in these nests, though not at the $P < 0.05$ value (Nest 3E $P = 0.07$, Nest 6E $P = 0.38$). These trends are also consistent with increasing chloride to

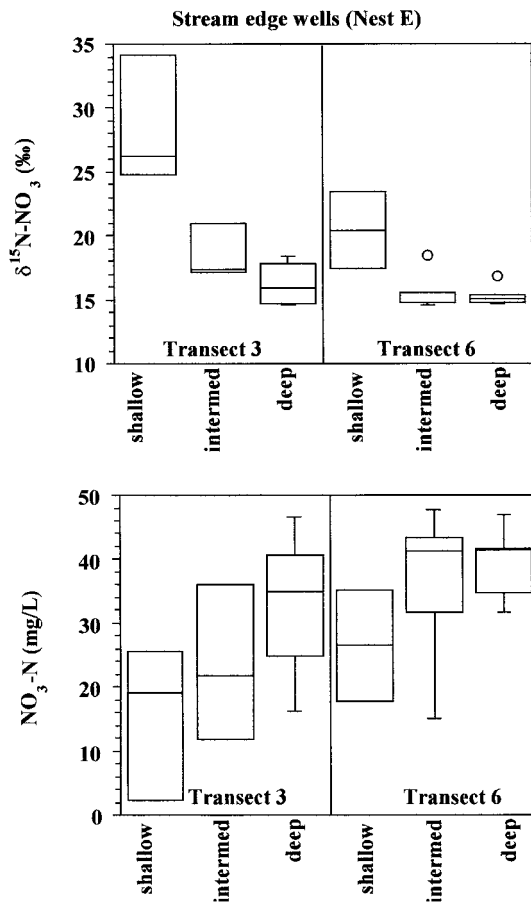


Fig. 10. Boxplots of $\delta^{15}\text{N-NO}_3$ and nitrate N concentrations in stream-edge (Nest E) wells of Transects 3 and 6, showing trends with depth. The $\delta^{15}\text{N}$ enrichment is pronounced only in shallow wells, indicating little denitrification in deeper stream-edge wells. This limited nitrate attenuation allows the off-site export of sprayfield nitrate via discharge of high-nitrate ground water to the stream that drains the sprayfields and then enters Stewarts Creek. Boxes enclose the upper and lower quartile (25%) of data about the median, which is represented by a horizontal line within each box. Whiskers above and below boxes represent the upper quartile plus 1.5 times the interquartile distance (IQD) and the lower quartile minus 1.5 times the IQD. Outliers are represented by circles.

nitrate N ratios in shallow buffer wells relative to deeper buffer wells. In summary, the only wells exhibiting $\delta^{15}\text{N-NO}_3$ values above +20 per mil were surface wells (primarily riparian buffer wells) and the deep well in Nest 3B. This deep well is situated within a layer of silt rich in organic matter (Fig. 2b), which would supply organic carbon to drive denitrification.

Additional wells (Wells 9A–C) were installed in a line between the southern boundary of Farm 4 and Stewarts Creek toward the end of the study. Well 9C (closest to Stewarts Creek) showed nearly complete loss of nitrate when sampled, with attendant drop in dissolved oxygen and rise in pH compared with Wells 9A (closest to field edge) and 9B. However, the $\delta^{15}\text{N-NO}_3$ in this well was $+5.0 \pm 0.1\text{‰}$, indicating that the small quantity of measured nitrate was generated from natural organic N and was not residual denitrified sprayfield nitrate. Wells 9A and 9B showed $\delta^{15}\text{N-NO}_3$ of $+14.5 \pm 0.1\text{‰}$ to $+14.9 \pm 0.1\text{‰}$ with nitrate N levels of 19.2 to

25.9 mg/L, consistent with typical sprayfield values. A wetland area within the wide riparian buffer exists ephemerally between the farm fields and Stewarts Creek, and showed near-zero nitrate N when sampled. Denitrification appears to attenuate nitrate within wide (>>10 m) buffers where the flow is confined to a few meters in depth, but it does not have a significant influence on the integrated isotopic signal of nitrate exported from the study site as expressed in the on-site stream. This study agrees with the finding of Sloan et al. (1999) that denitrification and significant nitrate losses within the narrow (~10 m) buffers at this site are apparent mainly in the shallowest wells. Deeper flow paths appear to export nitrate with little attenuation where only a narrow buffer exists. It is possible for deeper ground water flow paths to export nitrate beneath even very wide (100 m or wider) buffers in scenarios where no shallow aquitard is present (e.g., Böhlke and Denver, 1995).

CONCLUSIONS

The median $\delta^{15}\text{N}$ values of the three major classes of samples from the study site (lagoons, wells, impacted streams) were identical. The median and mean nitrate N concentration and $\delta^{15}\text{N}$ on Stewarts Creek were higher adjacent to and downstream from the farm site than at the upstream site, although statistically significant differences in $\delta^{15}\text{N}$ could not be shown at the $\alpha = 0.05$ level. Same-day nitrate N levels on Stewarts Creek were 1.5 to 10 times higher adjacent and downstream of the farms than upstream. Lagoons showed a smooth seasonal cycle of summertime isotopic enrichment and wintertime depletion, tracking the monthly mean air temperatures. This seasonal isotopic trend probably resulted from enhanced summertime ammonia volatilization. These variations point to the need for repeated sampling at multiple points at a site to properly characterize isotopic signals. Seasonal and spatial isotopic variations in lagoons and well waters were homogenized during ground water transport and discharge to streams. As long as denitrification in natural waters or ammonia loss during land application of wastes does not remove most of the nitrogen being applied, the isotopic shifts induced by these processes will not greatly alter the propagated median or weighted mean $\delta^{15}\text{N}\text{-NO}_3$ signal in affected ground water and nearby surface waters. The total $\delta^{15}\text{N}$ signal of the waste nitrogen was conserved during transformation and transport in ground water and streams at the study site. This net conservative behavior allows positive identification of the animal waste nitrate source in receiving waters and demonstrates nitrate export from the site, despite the presence of riparian buffers that meet current regulatory requirements.

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