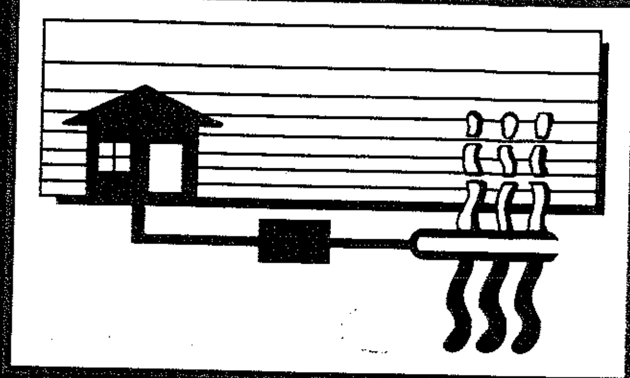

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Transformations and Transport of ^{15}N-Based Fixed Nitrogen from Septic Tanks in Soil Absorption Systems and Underlying Aquifers

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ABSTRACT

Evaluation of groundwater contamination by nitrate-nitrogen from domestic wastewater is limited by difficulties in determining the transformations of fixed nitrogen in the wastewater disposal system and uncertainties in differentiating origins of the nitrate present in groundwater. Three septic tank soil absorption systems in south-central Wisconsin were dosed with ^{15}N-enriched ammonium chloride and sodium bromide as taggants to track rates and forms of nitrogen movement from the systems into the vadose zone, as well as to describe transport and attenuation of the septic tank effluent-derived nitrate in aquifers underlying these systems. Results show that, on average, 44.5% of fixed nitrogen from household sewage was eliminated during the treatment in septic systems. ^{15}N-enriched nitrate-nitrogen plumes traveled in shallow aquifers with a mean velocity of 1.79×10^{-4} cm/sec and dissipated at a rate of 29.9% over a distance of 3 m. Denitrification was found to occur in an aquifer with depleted dissolved oxygen underlying a dosing system and eliminated 29.4% of the ^{15}N initially applied. ^{15}N abundance in the tracer was reduced to 74.7% of the original level as a result of joint treatment in the system and monitored groundwater, suggesting that septic systems are not necessarily a dominant source of the nitrate-nitrogen in groundwater underlying sewage disposal systems for treating household wastewater.

Keywords. Stable isotope, Nitrate, Groundwater contamination, Denitrification, Dispersion.

INTRODUCTION

Septic tank/soil absorption systems have been indicted as the most frequently reported source of groundwater contamination (USEPA, 1997). Among the potential contaminants in the septic tank effluent (STE), fixed nitrogen (N) forms pose the greatest threat to groundwater because of the formation and mobility of nitrate anion in aerated unsaturated soil. The distribution of nitrate-nitrogen (NO_3^--N) in groundwater from septic systems is of great concern since contamination of drinking water—frequently supplied by groundwater from unconfined aquifers in rural areas—with nitrate increases the risk of methemoglobinemia in infants and formation of carcinogenic nitrosamines (Williams and Weisburger, 1986). In Wisconsin, a two-tier system of regulation comprising an enforcement standard (ES) of 10 mg/L and a preventive action limit (PAL) of 2 mg/L was promulgated for NO_3^--N in groundwater (WDNR, 1995) regardless of the source of contamination. As the availability of land suitable for construction of conventional septic systems continues to decrease, the disposal of domestic wastewater has received more attention, and various efforts have been directed toward examining the performance of septic systems in terms of N removal and monitoring the influx and distribution of STE-derived NO_3^--N in groundwater (Alhajjar et al., 1990; Murphy, 1992; Cherry and Rapaport, 1994). One deficiency commonly observed in these studies, however, is the lack of direct information on N transformations in septic systems, and differentiation of the sewage-derived NO_3^--N from NO_3^--N originating from other sources. Komor and Anderson (1993) found that, among four different land settings, the group categorized as residential areas with septic systems had the lowest mean NO_3^--N concentration in the underlying aquifer. Thus whether the nitrate observed in groundwater in the vicinity of septic systems comes predominantly from treated STE remains unclear, and an evaluation to differentiate the impact of

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STE-derived NO_3^--N on groundwater quality from that of contributions from other sources associated with agricultural and domestic practices, e.g., feedlots, barnyards, and fertilized lawns, gardens and fields, is critically needed.

^{15}N, a stable isotope with a natural abundance of 0.3663 percent in atmospheric N_2, has been used qualitatively as an indicator to discriminate sources of NO_3^--N in the aquifer (Komor and Anderson, 1993) based on the fact that NO_3^--N of different origins in the environment can be characterized by its distinct isotopic composition. As techniques have become available for synthesizing ^{15}N-enriched and depleted chemicals, ^{15}N has also been used extensively as tracers in biological and agricultural studies (Barrie et al., 1989). However, use of the ^{15}N-labeled chemicals as tracers to quantitatively study the fate and transport of N originating from anthropogenic sources in the environment has not been frequently reported.

The work presented in this paper examined the long-term transformations of N from domestic wastewater in three septic systems and the underlying unsaturated zone, and evaluated the transport and attenuation of STE-derived NO_3^--N in the groundwater in the immediate vicinity of septic systems. ^{15}N-enriched ammonium chloride and sodium bromide were applied as separate markers into septic tanks. The ^{15}N label was used to quantitate the rates of fixed N conversions and elimination in the septic systems/underlying vadose zones, and to distinguish between NO_3^--N generated from the septic systems and that of other origins in groundwater. As a nonreactive tracer with chemical properties similar to nitrate but immune to denitrification, bromide was used to serve as a control in quantifying the rates of nitrification and subsequent denitrification of ^{15}N in the soil absorption system and unsaturated zone, and to provide information on the efficiency of the local groundwater to dilute the plume of contaminants physically by diffusion and dispersion. Potential for denitrification, the biological degradation of nitrate, was also examined to identify the influence of mechanisms other than advection and dispersion of groundwater flow to attenuate STE-derived NO_3^--N flux in the aquifer.

METHODS AND MATERIALS

Site Selection and Monitoring Wells Description

Three septic tank/soil absorption systems (2 pressurized-dosing systems, numbered S-9 and S-12; and 1 Wisconsin mound system, numbered S-15) in south-central Wisconsin (2 sites in Columbia County: S-9 and 12; 1 in Sauk Co.: S-15) previously studied in detail (Alhajjar, 1990) were selected for this study. Geological descriptions of these sites were summarized by Harkin and Chen (1996). These systems were constructed between 1970 and 1980 and have operated uninterruptedly since then. All systems were installed with networks of groundwater monitoring wells including one background (control) well hydrologically up-gradient from the septic system and three interceptor wells in the STE plume down-gradient from the drainfield of the system at each site. Interceptor wells labeled as number 1 were 30 cm from the edge of the drainfields and those labeled 2 and 3 were further down-gradient at intervals of 3 m. Background wells were 10 m or more up-gradient from the edges of the drainfields. The wells consisted of casings made of Schedule 40, 1.5-inch inner-diameter polyvinyl chloride (PVC) pipes and well screens of 30 cm length fitted with PVC well points at the lower ends. Shallow wells were installed by hand-augering using a 76-mm diameter Soil Conservation Service stainless steel bucket auger and driven to 1 m below the water table using a post driver. All wells were cased with bentonite and secured with screw-on caps of the same materials as the well casings to prevent intrusion of water from the land surface.

Application and Sampling of Tracers

A solution consisting of 200 g of ^{15}N-labeled ammonium chloride ($^{15}NH_4Cl$) with an isotopic enrichment of 10.5 atom-% (Isotec Chemical Co., Miamisburg, OH) and 1000 g of 99+% sodium bromide (NaBr; Aldrich Chemical Co., Milwaukee, WI) was prepared for the application of tracers into septic systems by dissolving the chemicals in 4 L of deionized distilled water (DDW). The 4-L solutions were applied into the septic tanks (S-9 and 12) or pumping chamber (S-15) of the systems on the following dates: S-9, June 27, 1996; S-12, June 18; S-15, June 27. Prior to the tracer application, STE and groundwater from the control and plume-interceptor wells were sampled and analyzed to provide background information on the levels of tracers in the natural as well as STE-contaminated groundwater. The tracer solution was released into septic tanks or pumping chamber using a peroxide-cured Masterflex 96400 silicone tubing (Cole-Parmer Instrument Co., Vernon Hills, IL) through a Masterflex L/S 12-VDC Powered-Drive peristaltic pump (Cole-Parmer Instrument Co.) at a rate of 20 mL/min. The tubing was extended into different layers of the tank/chamber during the delivery of tracer solution to ensure that the tracers were spread uniformly in the tank contents. Within 4 h of tracer application the STE was sampled again to obtain the concentrations of tracers and ^{15}N abundance of ammonium-N (NH_4^+-N) in the STE for use as the initial concentrations and ^{15}N ratio in the quantification of dilution factors and elimination rates for ^{15}N in the unsaturated and saturated zone. STE and groundwater from the background and plume-intercepting wells were continuously sampled at 2-week (14-d) intervals for 26 weeks (182 d) and analyzed for the concentrations of bromide, NH_4^+-N, and NO_3^--N as well as the isotopic ratios of ^{15}N in the form of NH_4^+-N ($^{15}NH_4^+$-N) and NO_3^--N ($^{15}NO_3^-$-N).

Determination of Ammonium-N, Nitrate-N, Bromide, and Dissolved Oxygen Concentrations

NH_4^+-N and NO_3^--N in STE and groundwater samples were determined by the direct steam-distillation procedure (Bremner and Keeney, 1965). An aliquot of the sample to be analyzed containing up to 2 mg of inorganic-N in the form under analysis, i.e., NH_4^+-N or NO_3^--N (5 mL effluent or 20 mL groundwater), was first steam-distilled with 1.1 g of reagent-grade heavy magnesium oxide (MgO) powder (Mallinckrodt Chemical Co., St. Louis, MO) to release NH_3 for the determination of NH_4^+-N concentration, then distilled with an addition of 0.2 g Devarda's alloy (Aldrich Co.) to reduce the NO_3^--N to NH_3 for determining the NO_3^--N concentration. The Devarda's alloy was previously ball-milled to pass a 100-mesh screen and for at least 75% to pass a 300-mesh screen. The NH_3 liberated via distillation was condensed and collected as NH_4^+-N in 5 mL boric acid-indicator solution prepared by dissolving 20 g reagent-grade boric acid (Mallinckrodt Co.) in a mixture including 700 mL hot DDW, 200 mL 95% ethanol, and 20 mL a mixed indicator that consisted of 330 mg reagent-grade bromocresol green (Matheson Coleman & Bell Manufacturing Chemists Co., Norwood, OH) and 165 mg methyl red (Mallinckrodt Co.) in 95% ethanol. The NH_4^+-N-containing boric acid-indicator solution was titrated with standardized 0.005 *N* H_2SO_4 solution (Fisher Scientific Co., Itasca, IL) using a Brinkmann digital buret (Brinkmann Instruments, Westbury, NY) with a reading accurate to 0.01 mL. Color change at the end point is from green to a permanent, faint pink. The reading expressed as the volume of titrant consumed in titration was converted into the quantity of N in distillate; 1 mL of 0.005 *N* H_2SO_4 used in the titration equals 70 µg NH_4^+-N in the distillate.

Concentrations of bromide were measured using a Fisher bromide ion-selective electrode and a Fisher silver-chloride double-junction reference electrode (Fisher Co.). Prior to measurement samples (100 mL per sample) were each mixed with 2 mL bromide ionic-strength adjustor buffer, a 5 M $NaNO_3$ solution (Orion Research, Beverly, MA). To evaluate the anaerobic status of septic tanks and the denitrification potential in groundwater, the solubility of oxygen in STE and groundwater (expressed as the concentration of dissolved oxygen; DO) was measured on-site before tracer application, using a YSI Model 58 digital dissolved oxygen meter (Yellow Springs Instrument Co., Yellow Springs, OH).

Preparation of ^{15}N Samples for Isotopic Abundance Analysis

To facilitate instrumental determination of the relative isotopic abundance of ^{15}N to ^{14}N for different forms of inorganic N in STE and groundwater, NH_4^+-N and NO_3^--N in the sample were first separated and concentrated. To meet the requirement for instrumental analysis, viz., a minimum concentration of 1000 µg/mL N as NH_4^+-N in 1 mL of sample ready for the isotope-ratio analysis.

each STE or groundwater sample was multiple-distilled (5 mL STE or 20 mL groundwater per distillation) based on the concentrations of NH_4^+-N and NO_3^--N pre-determined following the steam-distillation determinations described above. The NH_3 liberated for the separate determinations of $^{15}NH_4^+$-N and $^{15}NO_3^-$-N was collected in 10 mL boric acid-indicator solution and titrated to verify the recovery of N in the distillate after the multiple distillations. The distillation procedure was modified by adding a distillation of 15 mL 95% ethanol at the end of each distillation to remove traces of NH_4^+-N held up in the distillation apparatus. Between samples 1 mL 1 *N* acetic acid (Columbus Chemical Industries, Columbus, WI) was mixed with 15 mL DDW and distilled for 10 minutes followed by an additional 10-min distillation of 30 mL 95% ethanol to avoid cross-sample contamination.

After the separation of NH_4^+-N and NO_3^--N in the sample, each distillate solution was fortified with 2 mL 0.08 *N* H_2SO_4 and transferred to a 250- or 500-mL round-bottom flask for concentration using Büchi R-110 and RE-121 rotary evaporation systems (Brinkmann Instruments). The rotary evaporators were connected with ammonia-washing bottles filled with 50% H_2SO_4 solution at the valved air inlet to avoid any contact of atmospheric ammonia with samples when the vacuum was released. Samples evaporated to a volume less than 5 mL were transferred to 5-mL graduated v-shaped vials and placed in a Supelco 12-port solid-phase-extraction vacuum manifold (Supelco, Bellefonte, PA) connected with an ammonia-washing bottle. The manifold was modified to include a 350 Watt HP 3108 sun/heat lamp as a heat source to assist the evaporation and a remotely-probed thermometer (Cole-Parmer Instrument Co.) to control the temperature in the manifold during evaporation. Samples were evaporated until a final concentration of approximately 1000 µg/mL for NH_4^+-N was reached and then transferred to 1.8-mL amber borosilicate vials capped with PTFE-linered crimp-on aluminum seals (National Scientific, Lawrenceville, GA) for instrumental analysis.

Analysis of ^{15}N:^{14}N Isotopic Ratio by GC-IRMS

Measurement of ^{15}N:^{14}N isotopic ratios in each sample was performed by an automated $^{15}N/^{13}C$ analyzer-mass spectroscopy (ANCA-MS) instrument consisting of a gas-chromatography-(GC)-based NA 1500 Series 2 automatic nitrogen/carbon Analyzer interfaced with a combustion reactor for sample pretreatment and a TracerMass continuous-flow isotope-ratio mass spectrometer (IRMS; Europa Scientific, Crewe, UK). A 20-µL aliquot of each sample was pipetted onto an inert substrate (Chromosorb, Supelco) pre-loaded in tin capsules and oven-dried at 80°C. The capsules were sealed and loaded into the combustion chamber enriched with 99.998% pure oxygen for oxidation at 1700-1800°C to remove carbon-based impurities. The combustion products were delivered into a reduction tube to reduce the oxides of N to N_2 and remove excess O_2. The reduced N_2 was separated from trace impurities and determined by the IRMS for ^{15}N abundance. The isotopic composition of N in the sample was reported in both the atomic ratio of ^{15}N to ^{14}N (atom-%) and the $\delta^{15}N$ parameter (‰). The $\delta^{15}N$ parameter is defined as:

$$\delta^{15}N = \left[\frac{(^{15}N/^{14}N)_{Sample} - (^{15}N/^{14}N)_{Standard}}{(^{15}N/^{14}N)_{Standard}}\right] \times 10^3 \quad (1)$$

where the ^{15}N ratio in the standard, atmospheric N_2, equals 0.3663 atom-% (Barrie et al., 1989).

Rate of Elimination of Fixed N from Septic Systems

To assess the performance of septic systems in removing fixed N from STE and the potential for denitrification of NO_3^--N originating from STE in the aquifers underlying septic systems, a rate of elimination for the spiked $^{15}NH_4^+$-N in the septic system and natural soils, or when denitrification was found to be significant in an aquifer, in the system, unsaturated, and monitored saturated zone was evaluated as follows:

$$R_{Elimination} = 1 - ([NO_3^- - N]_{GW} \times Atom\text{-}\%_{GW}) \left(\frac{[NH_4^+ - N]_{Initial} \times Atom\text{-}\%_{Initial}}{[Br^-]_{Initial} / [Br^-]_{GW}} \right)^{-1} \quad (2)$$

where $[NH_4^+\text{-}N]_{Initial}$, Atom-$\%_{Initial}$, and $[Br^-]_{Initial}$ are the values obtained from STE samples at each site within 4 h after the application of tracers for NH_4^+-N concentration, ^{15}N atom-%, and bromide concentration respectively, and $[NO_3^-\text{-}N]_{GW}$, Atom-$\%_{GW}$, and $[Br^-]_{GW}$ are the values from GW sampled through the STE-plume interceptor wells during the period of investigation for NO_3^--N concentration, ^{15}N atom-%, and bromide concentration. The values generated from the quantities in the first parentheses indicate the genuine concentrations of $^{15}NO_3^-$-N found in the monitored aquifer, whereas the ratios in the second parentheses show the theoretical concentrations of the spiked ^{15}N in the groundwater samples, assuming dilution is the only mechanism responsible for the variation in concentration observed for the spiked ^{15}N moving with STE from the septic system to groundwater. Thus, assuming that the amount of ^{15}N from the applied tracer existing as $^{15}NH_4^+$-N in groundwater is negligible, $R_{elimination}$ represents the percentage of the N originally applied into the septic tank or pumping chamber which is removed from STE through treatment in the system, or in the system and underlying aquifer when the local groundwater is microbially active and relatively anaerobic. Displayed as the ratio of $[Br^-]_{Initial}$ to $[Br^-]_{GW}$, the dilution factor in the denominator of the second parentheses demonstrates the effects of soil and groundwater in diluting the tracers that traveled through the vadose and monitored saturated zone before being sampled. The rate of elimination was determined only for samples with atom-% higher than 0.4000%, since interference of naturally occurring N in groundwater with evaluation of N removal based on $R_{elimination}$ intensifies when the concentration and atom-% of the applied ^{15}N in groundwater become less distinct from background values.

RESULTS AND DISCUSSION

Elimination of Applied ^{15}N in Septic Systems

Tables 1 to 3 summarize the results of monitoring for the concentrations of NH_4^+-N, NO_3^--N, and applied tracers in STE and groundwater, and the correspondingly derived parameters for evaluating efficiencies of septic systems in removing the applied ^{15}N at systems S-9, S-12, and S-15, respectively. NH_4^+-N in groundwater in the vicinity of the examined systems throughout the sampling period was close to background levels, indicating that the domestic-wastewater-bound NH_4^+-N was predominantly nitrified in the purification process. To various extents depending on the operational conditions of the systems, the NO_3^--N generated was partially denitrified before intrusion into groundwater. As a result, the elimination of ^{15}N observed, when the groundwater underneath the septic systems was highly oxygenated, can be attributed to denitrification of NO_3^--N in the vadose zone below the systems under intermittent anaerobic or micro-aerobic conditions (i.e., periods of zero or extremely low DO concentrations). The N elimination rates at S-9 (LPD system) and S-15 (mound system), 46.7 and 54.8% respectively, are close to representative rates of denitrification reported for different types of septic systems during their early stage of operation: 0-35% for conventional systems, 46% LPD systems, and 44-86% mound systems (Degen et al., 1991), indicating that the current abilities of the systems serving S-9 and S-15 to eliminate fixed nitrogen in STE are just as effective as those during their initial operation.

Whereas the N elimination rates for different samples from the same site were consistent at S-9 and S-15, a significant deviation was found among the rates determined at S-12. At S-12 the $^{15}NO_3^-$-N in the STE percolating through soil was further transformed in the groundwater, at least for the distance monitored. Consequently, the mean N elimination rate for S-12 is a composite of the N removal by the septic system and in the aquifer, and is inappropriate for use in interpreting the efficiency of N removal accomplished by the septic system alone. The calculated elimination rate of 32.1% was based on the monitored results for the groundwater in Well 1 when sampled on Aug.

Table 1. Results of monitoring and N-removal evaluation for STE and groundwater at Site S-9.

	NH_4^+-N (μg/mL)	NO_3^--N (μg/mL)	Atom-%‡ (%)	Bromide (μg/mL)	^{15}N§ (ng/mL)	Dilution (Fold)	Elim Rate# (%)	Diss O_2# (mg/L)
Jun. 27, 1996								
Well BG	0.88	2.94	0.3676	0.10	10.81			
Well 1	1.19	22.30	0.3710	0.32	82.70			6.83
Well 2	0.98	14.35	0.3689	0.36	52.94			6.92
Well 3	0.98	5.88	0.3675	0.07	21.61			7.04
STE	47.32	3.52	0.3765	5.11	13.24			5.24
STE (Spiked)†	61.23	3.49	2.6767‡	210.28	1638.94§			0.37
Aug. 22, 1996								
Well BG	0.91	1.93	0.3666	0.12	7.08			
Well 1	1.19	12.56	1.1098	32.75	139.41	6.42	45.4	
Well 2	1.12	12.05	0.3993	0.84	48.10			
Well 3	1.26	6.76	0.3661	0.18	24.73			
STE	58.24	5.81	0.3748	2.38	21.77			
Sep. 05, 1996								
Well BG	1.13	2.41	0.3672	0.09	8.86			
Well 1	1.22	14.46	0.6832	23.64	98.77	8.90	46.4	
Well 2	1.15	11.99	0.9476	26.06	113.61	8.07	44.1	
Well 3	1.08	7.65	0.3687	1.19	28.20			
STE	52.19	4.75	0.3762	4.75	17.87			
Sep. 19, 1996								
Well BG	1.05	2.61	0.3675	0.07	9.58			
Well 1	1.16	21.23	0.4073	20.83	86.44	10.10	46.8	
Well 2	1.03	13.06	0.9628	20.15	125.75	7.21	44.7	
Well 3	1.08	8.14	0.6151	12.46	50.07	16.88	48.5	
STE	48.63	5.09	0.3758	3.19	19.14			
Oct. 03, 1996								
Well BG	1.21	2.17	0.3668	0.08	7.96			
Well 1	1.27	14.74	0.3713	2.53	54.74			
Well 2	1.28	10.55	0.7019	18.32	74.02	11.48	48.2	
Well 3	1.18	10.80	0.8625	22.75	93.15	9.24	47.5	
STE	55.42	3.64	0.3753	3.20	13.68			
Oct. 17, 1996								
Well BG	1.05	2.31	0.3674	0.10	8.48			
Well 1	1.36	9.52	0.3720	0.58	35.41			
Well 2	1.21	10.45	0.4165	10.86	43.52	19.37	48.8	
Well 3	1.23	9.22	0.8841	19.29	81.51	10.90	45.8	
STE	51.17	4.18	0.3767	2.73	15.75			
Oct. 31, 1996								
Well BG	0.94	1.88	0.3671	0.14	6.90			
Well 1	1.17	17.15	0.3694	0.32	63.34			
Well 2	1.11	7.81	0.3682	2.84	28.76			
Well 3	0.95	9.54	0.4217	9.85	40.23	21.35	47.6	
STE	53.60	4.45	0.3763	4.77	16.75			
Nov. 14, 1996								
Well BG	0.76	2.52	0.3673	0.10	9.27			
Well 1	1.01	27.31	0.3694	0.33	100.90			
Well 2	0.88	16.17	0.3682	0.39	59.53			
Well 3	0.82	6.59	0.3687	0.41	24.31			
STE	61.29	6.10	0.3770	5.47	23.01			
							Mean	Std. dev.
							46.7	1.5

† STE (Spiked) was sampled within 4 h after the application of tracers.

‡ Atom-% shows the isotopic abundance of ^{15}N (^{15}N:^{14}N) for NO_3^--N in the monitored STE or groundwater, and the abundance for NH_4^+-N in the STE (Spiked) sample.

§ Values reported are concentrations of $^{15}NO_3^-$-N, product of NO_3^--N concentration and Atom-%, in the monitored STE and groundwater; for STE (Spiked), the entry indicates $^{15}NH_4^+$-N concentration.

¶ Dilution Factor, defined as: Dilution F = $[Br^-]_{STE(Spiked)}/[Br^-]_{Sample}$, was determined only for samples with Atom-% higher than 4.0000.

Elim Rate = N elimination rate; Diss O_2 = Concentration of dissolved oxygen in the sample.

Table 2. Results of monitoring and N-removal evaluation for STE and groundwater at Site S-12.

	NH_4^+-N (μg/mL)	NO_3^--N (μg/mL)	Atom-%[‡] (%)	Bromide (μg/mL)	^{15}N[§] (ng/mL)	Dilution (Fold)	Elim Rate[#] (%)	Diss O_2[#] (mg/L)
Jun. 18, 1996								
Well BG	1.12	2.59	0.3675	0.11	9.52			6.64
Well 1	2.03	6.90	0.3646	0.13	25.14			1.42
Well 2	1.96	8.16	0.3671	0.17	29.94			2.21
Well 3	1.16	15.06	0.3666	0.12	55.19			2.90
STE	75.32	4.92	0.3699	0.81	18.20			0.57
STE (Spiked)[†]	93.87	4.81	2.3716[‡]	274.35	2226.22[§]			
Aug. 13, 1996								
Well BG	1.37	1.87	0.3673	0.07	6.88			
Well 1	1.74	20.62	1.1376	42.57	234.53	6.45	32.1	
Well 2	1.65	7.84	0.3715	0.37	29.13			
Well 3	1.36	10.26	0.3684	0.15	37.79			
STE	62.44	2.59	0.3708	0.87	9.60			
Aug. 27, 1996								
Well BG	1.28	2.25	0.3675	0.08	8.27			
Well 1	1.87	21.45	0.9924	42.18	212.90	6.50	37.8	
Well 2	1.60	12.41	0.4553	14.77	56.48	18.58	52.9	
Well 3	1.43	5.31	0.3678	0.46	19.53			
STE	70.68	3.08	0.3705	0.67	11.40			
Sep. 10, 1996								
Well BG	1.34	1.75	0.3669	0.07	6.42			
Well 1	1.66	14.48	0.3679	16.17	53.28	16.96	59.4	
Well 2	1.74	18.57	1.0744	43.24	199.48	6.35	43.1	
Well 3	1.53	8.21	0.3815	3.04	31.31			
STE	66.82	3.34	0.3712	0.80	12.40			
Sep. 24, 1996								
Well BG	1.34	2.17	0.3671	0.09	7.95			
Well 1	1.32	11.60	0.3675	4.15	42.62			
Well 2	1.14	16.13	1.0522	41.57	169.72	6.60	49.7	
Well 3	1.03	9.31	0.5912	15.84	55.04	17.32	57.2	
STE	58.40	4.14	0.3698	0.55	15.32			
Oct. 08, 1996								
Well BG	1.21	2.42	0.3670	0.07	8.88			
Well 1	1.70	8.82	0.3671	2.60	32.38			
Well 2	1.43	8.79	0.5292	22.38	46.51	12.26	74.4	
Well 3	1.51	15.38	0.9586	39.54	147.40	6.94	54.1	
STE	61.73	4.71	0.3701	0.48	17.42			
Oct. 22, 1996								
Well BG	1.00	1.93	0.3677	0.13	7.10			
Well 1	1.22	24.04	0.3680	2.37	88.48			
Well 2	1.19	11.28	0.3796	3.04	42.81			
Well 3	1.03	12.99	0.9748	40.49	126.58	6.78	61.5	
STE	69.25	2.64	0.3693	0.61	9.75			
Nov. 05, 1996								
Well BG	1.02	1.58	0.3673	0.12	5.79			
Well 1	1.26	12.66	0.3731	2.18	47.22			
Well 2	1.19	17.03	0.3789	2.05	64.53			
Well 3	1.16	7.19	0.3766	2.36	27.08			
STE	68.18	1.88	0.3699	0.73	6.95			
							Mean	Std. dev.
							52.2	11.7

[†] STE (Spiked) was sampled within 4 h after the application of tracers.

[‡] Atom-% shows the isotopic abundance of ^{15}N (^{15}N:^{14}N) for NO_3^--N in the monitored STE or groundwater, and the abundance for NH_4^+-N in the STE (Spiked) sample.

[§] Values reported are concentrations of $^{15}NO_3^-$-N, product of NO_3^--N concentration and Atom-%, in the monitored STE and groundwater; for STE (Spiked), the entry indicates $^{15}NH_4^+$-N concentration.

[¶] Dilution Factor, defined as: Dilution F = $[Br^-]_{STE(Spiked)}/[Br^-]_{Sample}$, was determined only for samples with Atom-% higher than 4.0000.

[#] Elim Rate = N elimination rate; Diss O_2 = Concentration of dissolved oxygen in the sample.

Table 3. Results of monitoring and N-removal evaluation for STE and groundwater at Site S-15.

	NH_4^+-N (μg/mL)	NO_3^--N (μg/mL)	Atom-%‡ (%)	Bromide (μg/mL)	^{15}N§ (ng/mL)	Dilution¶ (Fold)	Elim Rate° (%)	Diss O_2° (mg/L)
Jun. 27, 1996								
Well BG	1.34	1.65	0.3685	0.47	6.06			7.84
Well 1	1.23	27.25	0.3696	0.49	100.72			7.74
Well 2	1.23	20.30	0.3704	0.38	75.20			7.14
Well 3	1.44	11.26	0.3711	0.22	41.79			5.36
STE	56.70	5.32	0.3731	0.42	19.85			0.62
STE (Spiked)*	84.53	5.24	3.7068‡	410.76	3133.36§			
Jul. 25, 1996								
Well BG	1.23	1.52	0.3687	0.43	5.62			
Well 1	1.29	26.22	0.6424	48.32	168.43	8.50	54.3	
Well 2	1.25	20.02	0.3734	2.96	74.75			
Well 3	1.58	9.64	0.3698	0.23	35.65			
STE	51.86	7.90	0.3746	0.67	29.60			
Aug. 08, 1996								
Well BG	1.07	2.08	0.3679	0.29	7.67			
Well 1	1.13	23.90	0.9391	63.76	224.44	6.44	53.9	
Well 2	1.11	17.14	1.5275	73.62	261.74	5.58	53.4	
Well 3	1.08	17.27	0.4912	26.42	84.82	15.55	57.9	
STE	49.07	9.72	0.3732	0.40	36.28			
Aug. 22, 1996								
Well BG	0.95	2.22	0.3683	0.37	8.18			
Well 1	1.00	29.04	0.3927	4.52	114.05			
Well 2	1.06	19.57	0.7705	42.70	150.82	9.62	53.7	
Well 3	1.23	14.37	1.1359	47.34	163.20	8.68	54.8	
STE	43.65	6.60	0.3729	0.47	24.62			
Sep. 05, 1996								
Well BG	1.03	2.48	0.3685	0.48	9.15			
Well 1	1.06	32.54	0.3667	1.13	119.33			
Well 2	1.24	25.04	0.3726	3.80	93.31			
Well 3	1.23	13.98	0.5317	21.83	74.33	18.81	55.4	
STE	51.38	10.44	0.3736	0.72	39.00			
Sep. 19, 1996								
Well BG	1.12	2.58	0.3687	0.41	9.51			
Well 1	1.30	17.63	0.3659	0.55	64.51			
Well 2	1.19	12.08	0.3693	0.90	44.59			
Well 3	1.30	25.38	0.3867	2.03	98.13			
STE	53.06	9.66	0.3742	0.42	36.15			
							Mean	Std. dev.
							54.8	1.4

* STE (Spiked) was sampled within 4 h after the application of tracers.

‡ Atom-% shows the isotopic abundance of ^{15}N (^{15}N:^{14}N) for NO_3^--N in the monitored STE or groundwater, and the abundance for NH_4^+-N in the STE (Spiked) sample.

§ Values reported are concentrations of $^{15}NO_3^-$-N, product of NO_3^--N concentration and Atom-%, in the monitored STE and groundwater; for STE (Spiked), the entry indicates $^{15}NH_4^+$-N concentration.

¶ Dilution Factor, defined as: Dilution $F = [Br^-]_{STE(Spiked)}/[Br^-]_{Sample}$, was determined only for samples with Atom-% higher than 4.0000.

° Elim Rate = N elimination rate; Diss O_2 = Concentration of dissolved oxygen in the sample.

13, when the spiked ^{15}N plume in groundwater was first identified by a significantly elevated bromide concentration and ^{15}N signature; this value was used to represent the N elimination rate achieved by the septic system and the underlying vadose zone at S-12. In comparison with the denitrification rate for a representative LPD system, the system serving S-12 appeared to be less efficient in denitrifying the NO_3^--N formed from NH_4^+-N in STE. In an LPD system, the effluent dosing mechanism generates a fluctuating aerobic/anaerobic environment which promotes nitrifying and subsequent denitrifying reactions, because of simultaneous intermittent injection of biodegradable organic matters to fuel the denitrification process (Harkin et al., 1979). The less efficient denitrification observed at S-12 suggests a reduction of the intermittent anaerobic conditions generated at the interface between soil absorption bed and natural soils, due to a less efficient dosing regime or the variation in local soil biota.

Transport and Attenuation of Applied ^{15}N in Groundwater

Figures 1 to 3 show the temporal and spatial changes for the ^{15}N concentration and $\delta^{15}N$ value of the STE-derived $^{15}NO_3^-$-N in groundwater underlying septic systems to illustrate the transport and dissipation of contaminant plumes in shallow aquifers. Values for the first sampling date presented in each figure represent the background values for groundwater under the influence of septic systems, i.e., the $^{15}NO_3^-$-N observed in the aquifer originated completely from unamended household wastewater, not from a combination of the wastewater and applied

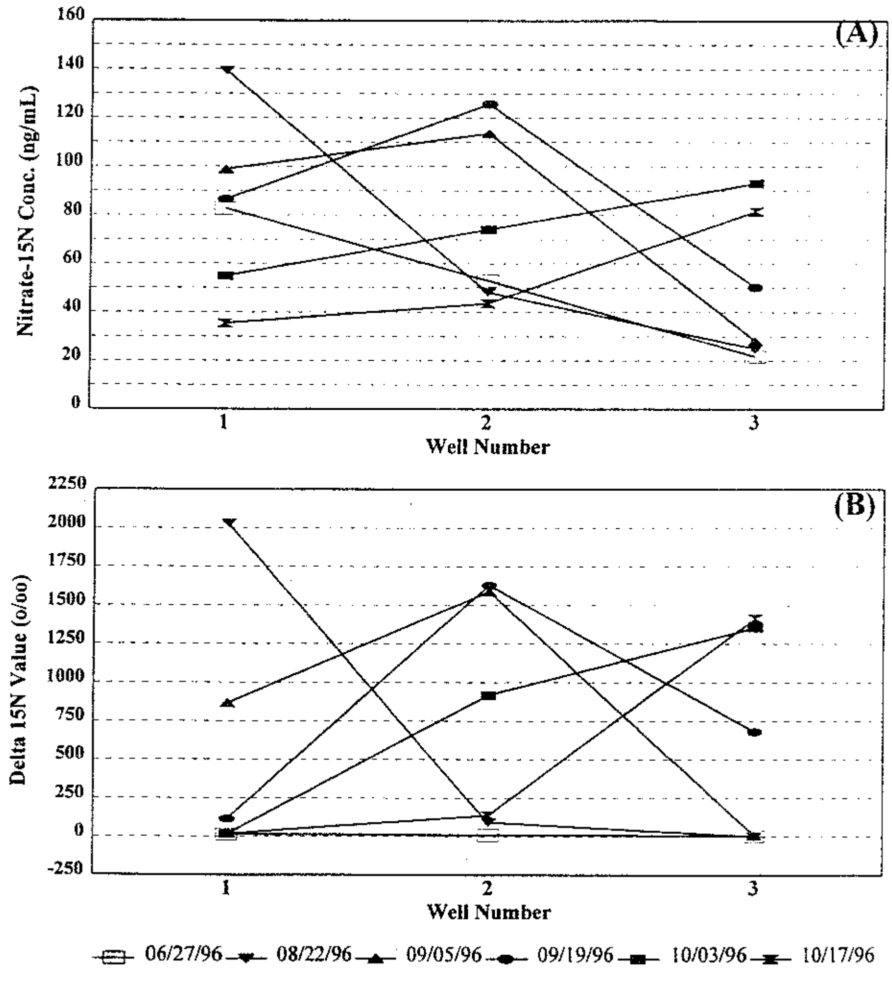

Figure 1. Temporal and spatial changes of (A) ^{15}N concentration and (B) $\delta^{15}N$ parameter for $^{15}NO_3^-$-N in aquifer underlying the pressurized dosing system at Site S-9. Groundwater monitoring wells 1, 2, and 3 were 0.3, 3.3, and 6.3 m down-gradient from the soil absorption bed of the septic system.

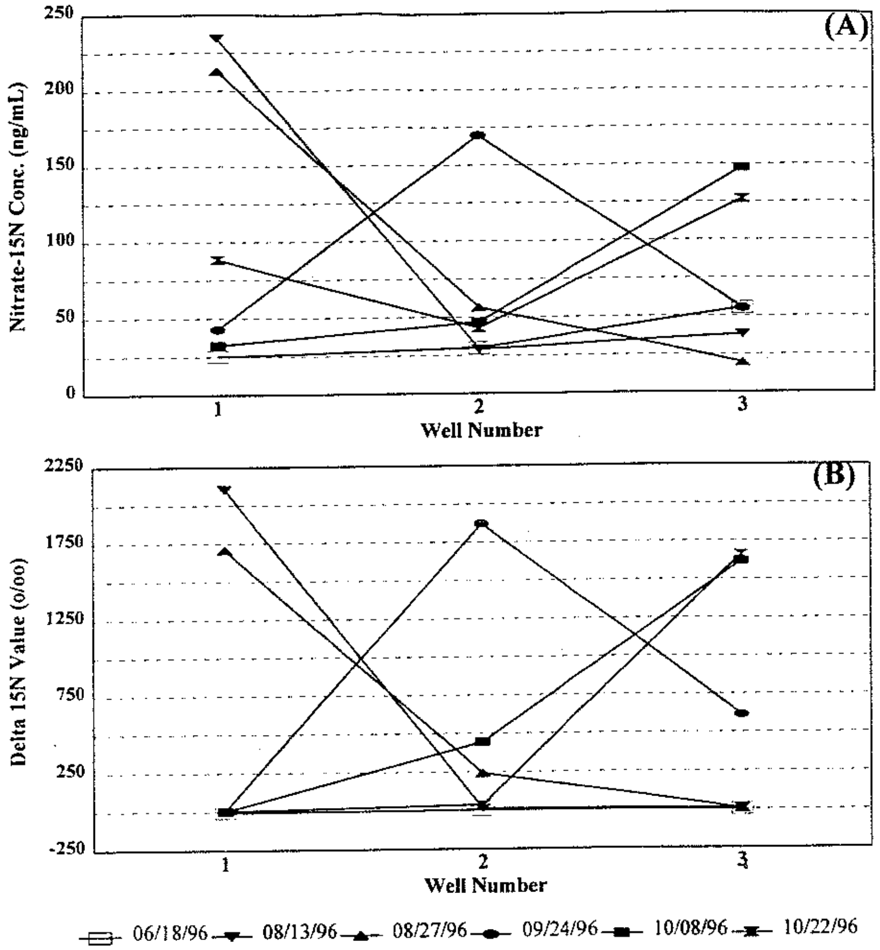

Figure 2. Temporal and spatial changes of (A) ^{15}N concentration and (B) $\delta^{15}N$ parameter for $^{15}NO_3^-$-N in aquifer underlying the pressurized dosing system at Site S-12. Groundwater monitoring wells 1, 2, and 3 were 0.3, 3.3, and 6.3 m down-gradient from the soil absorption bed of the septic system.

tracer. Data for the second sampling date shown in the figures indicate the initial appearance of the spiked ^{15}N plumes in the monitored groundwater. Assuming that the dates on which the highest $^{15}NO_3^-$-N concentrations were observed in groundwater from Wells 1 and 3 represent the initial and final appearance of the $^{15}NO_3^-$-N plume center in the monitoring zone, the velocity of advective transport for each plume in the aquifer was estimated and found to be 1.65×10^{-4} cm/sec for S-9, 1.24×10^{-4} for S-12, and 2.48×10^{-4} for S-15. All 3 values are typical velocities for a clean sandy aquifer according to Darcy's Law. The $^{15}NO_3^-$-N plume at S-15 traveled in groundwater 1.5- and 2.0-fold faster than those for the S-9 and 12 plumes, possibly due to the formation of a groundwater mound underneath the S-15 absorption bed, a phenomenon reported to occur in shallow aquifers with a high water table underlying septic-system drainfields in response to STE influx from the system (Finnemore, 1993). For one-dimensional transport of a contaminant

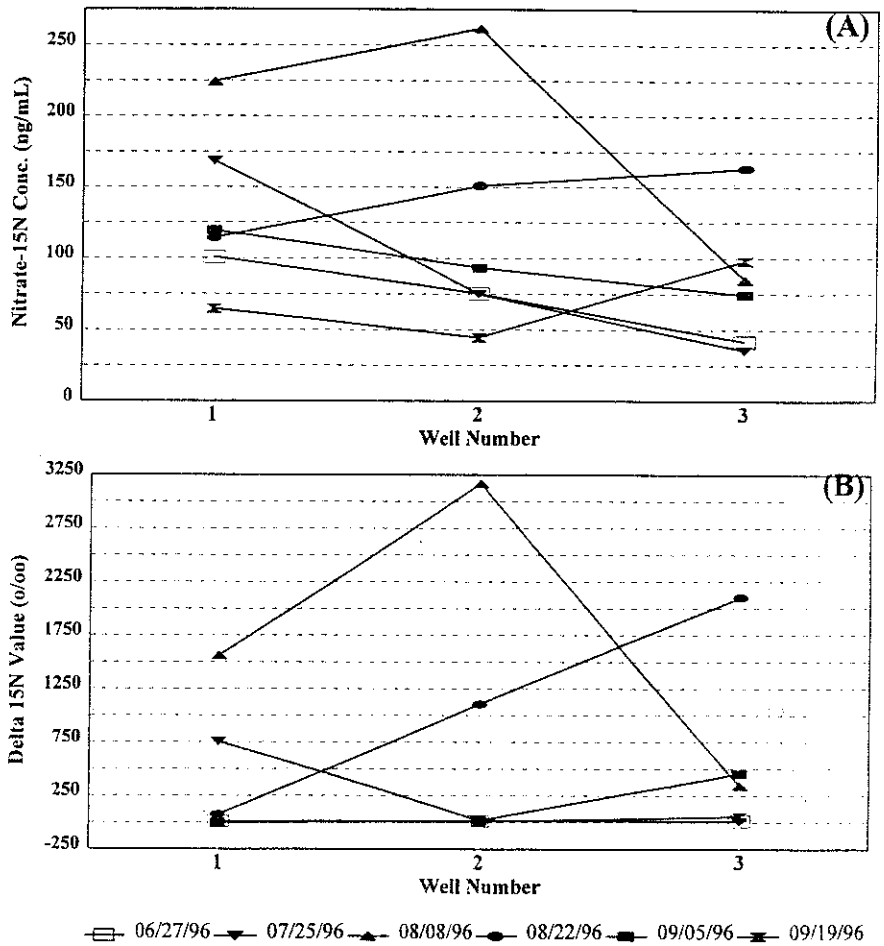

Figure 3. Temporal and spatial changes of (A) ^{15}N concentration and (B) $\delta^{15}N$ parameter for $^{15}NO_3^-$-N in aquifer underlying the mound-type system at Site S-15. Groundwater monitoring wells 1, 2, and 3 were 0.3, 3.3, and 6.3 m down-gradient from the soil absorption bed of the septic system.

plume, the hydrodynamic dispersion of the plume is proportional to the change of advective velocity (Fetter, 1992) and subsequently alters the rate of dispersion of the contaminants. The aquifer at S-15 had the greatest advective velocity for $^{15}NO_3^-$-N transport among the studied sites, and consequently should have the greatest dispersivity, contributing to a more rapid disappearance of the $^{15}NO_3^-$-N plume. A ratio of the greatest $^{15}NO_3^-$-N concentration observed in Well 3 to that in Well 2 (concentrations selected to represent the peak $^{15}NO_3^-$-N levels in the center of the plume breaking through at these locations; data from Well 1 were not used since breakthrough of the $^{15}NO_3^-$-N plume center there was not adequately captured during the sampling period) was determined for each plume and compared among the 3 sites to establish the rate of $^{15}NO_3^-$-N dissipation in groundwater. Over a distance of 3 m (from Well 2 to Well 3), $^{15}NO_3^-$-N in the aquifer at S-15 was reduced by 37.6% from the level initially found in groundwater to 62.4% while reduced by only 25.9% and 26.1% to 74.1% and 73.9% at S-9 and S-12. The loss of $^{15}NO_3^-$-N at S-12 was attributed to denitrification as well as dispersion in groundwater (see later). Since denitrification in groundwater does not appear to be a plausible mechanism for the reduction of $^{15}NO_3^-$-N at S-15, as evidenced by the high DO content indicative of aerobic conditions in groundwater down-gradient from the system, this result supports the earlier inference of enhanced hydrodynamic dispersion of the $^{15}NO_3^-$-N plume in the S-15 aquifer. As a result, although the concentration of NO_3^--N entering groundwater with STE percolate at S-15 was the highest among the 3 sites during the sampling period (Table 3), the plume was effectively reduced in groundwater to a level close to Wisconsin's ES value, 10 mg/L, within a distance of 6.3 m from the edge of the soil absorption bed, the highest efficacy of NO_3^--N attenuation in groundwater beneath these 3 septic systems.

In Table 2, the N elimination rates determined for S-12 increase from 32.1% (calculated from data for the groundwater sampled on Aug. 13 in Well 1-the rate of N removal for the tracer plume merely en route to groundwater) to 61.5% (sampled on Oct. 22 in Well 3-the rate for the plume center leaving the monitoring zone), showing that STE-derived NO_3^--N was substantially transformed further in the aquifer at this site, possibly as a result of denitrification, considering the depleted groundwater DO content in this area. Denitrification, the microbial reduction of nitrate to gaseous nitrogen (N_2) and nitrous oxide (N_2O) under anaerobic conditions or conditions of reduced oxygen availability, provides an ultimate sink to remove NO_3^--N built up in groundwater from N recycling. Starr and Gillham (1993) observed denitrification in shallow aquifers with an increased flux of labile organic carbon from the vadose zone. With sufficient nitrate supplied from STE as electron acceptor, occurrence of denitrification appears to be strongly encouraged in shallow aquifers near septic systems if the oxygen diffusing in from soils can be effectively depleted, e.g. by organic loadings from septage leachate. As a result of denitrification in both the septic system and aquifer, 61.5% of the ^{15}N originally applied in the septic tank of S-12 was removed, a rate of N elimination better than the rates for S-9 (46.7%) and S-15 (54.8%).

Presence of Nitrate-N from Septic Systems in Groundwater

Leachate from septic systems is undoubtedly a major source for the NO_3^--N found in groundwater beneath the drainfield of any system. However, the extent to which NO_3^--N in the aquifer underlying a septic system can be attributed to STE influx is uncertain and remains unanswered from most monitoring studies. Figures 1b, 2b, and 3b show that the $\delta^{15}N$ value for the $^{15}NO_3^-$-N plume in groundwater monitored at each site in this study generally decreases over time and distance, indicating that a merging between $^{15}NO_3^-$-N from the applied tracer and a significant amount of NO_3^--N of low $\delta^{15}N$ level from origins other than STE occurred in the contaminated groundwater. To examine the attenuation of $^{15}NO_3^-$-N during its passage through septic systems and natural soils, a dilution factor, expressed as the quotient of the concentration of bromide initially applied in STE divided by the concentration of bromide detected in the Well-1 groundwater as soon as breakthrough of tracer plume was identifiable (Tables 1 to 3), was determined for each site and found to range from 6.4 (S-9) to 8.5 (S-15). This nitrogen dilution effect indicates that a large influx of soil solution mixes with the STE after the STE percolated through the vadose zone. In addition to providing a substantial dilution to STE-derived NO_3^--N, the soil solution also introduced a new flux of low-level ^{15}N to the percolate. Calculating the ratio of the $\delta^{15}N$ value from the sample revealing the first appearance of the $^{15}NO_3^-$-N plume center in groundwater to the value from the STE sampled immediately after ^{15}N application shows that the $\delta^{15}N$ value for STE loaded with tracer was reduced to 32.2, 38.5, and 34.8% of the original levels at S-9, S-12, and S-15, respectively. These findings provide strong evidence for the considerable dilution of the ^{15}N from soil percolate to the STE percolate. When the rate of dissipation for the reduction in $^{15}NO_3^-$-N concentration over a distance of 3 m in groundwater from Well 2 to 3 was re-determined with the $^{15}NO_3^-$-N concentration replaced by $\delta^{15}N$ value, a reduction of $\delta^{15}N$ value in groundwater over and above the decrease caused by soil solution was 13.2, 14.1, and 33.7% for S-9, S-12 and S-15. Thus, as leachate from the septic systems progressed through the unsaturated and saturated zone, NO_3^--N was continuously mixed and diluted with NO_3^--N of origins other than septic systems. As the plume center approached the end of the monitoring zone (6.3 m from the soil absorption bed of the system), the overall reduction of $\delta^{15}N$ value for the ^{15}N-labeled tracer through elimination and dilution in the septic system, vadose zone, and monitored aquifer increased to 77.6% (S-9), 69.7% (S-12), and 77.0% (S-15), strengthening the contention that septic systems are not necessarily a dominant source for the NO_3^--N present in groundwater down-gradient from the systems.

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