2009

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Published in *Environmental Forensics* 10 (2009), pp. 19–26; doi: 10.1080/15275920802502075

Submitted July 11, 2007; accepted December 13, 2007.

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Abstract

High ammonium-N concentrations derived from animal wastes stored and partially treated in earthen anaerobic lagoons at confined feeding facilities can seep to groundwater. δ^{15}N-NH_4^+ values from +2.0 to +59.1‰ in 13 lagoons complicate identification of lagoon seepage as well as land-applied lagoon effluent in ground and surface waters. The spectrum of δ^{15}N values requires site-specific isotope characterization of the potential source. Feed and fresh manure and urine δ^{15}N values indicate that most N isotopic fractionation occurs after excretion. Lagoon management clearly affects enrichment. δ^{15}N-total Kjeldahl N (TKN) and δ^{15}N-NH_4^+ within each lagoon were not statistically different. δ^{15}N-NH_4^+ within the top 1.5 m of the lagoons was spatially uniform (CV [coefficient of variation] <5%).

Keywords: δ^{15}N, stable N isotopes, N contamination, animal waste lagoon, source characterization

Nitrate concentrations in excess of those deemed safe in drinking water are all too common in groundwater beneath agricultural lands (Nolan and Stoner, 1999). Infants are most at risk as consumption of high-nitrate water can lower the oxygen-carrying capacity of their blood, a potentially fatal condition (Fan and Steinberg, 1996). Not only is nitrate in groundwater a potential health hazard, but it also is an ecological concern. Nitrate in river base flow and in runoff contributes to the nitrate load in estuaries. The latter is an especially alarming concern in some of the world's large deltaic regions, where excess nitrate in rivers such as the Mississippi is associated with hypoxia (Puckett et al., 1999).

N isotope ratios are a popular source identification tool in groundwater investigations assessing potential N loading from lagoon seepage at animal feeding operations (AFOs). In the United States more than 454 million metric tons of manure are generated annually by 238,000 AFOs (Federal Register, 2003). Potential leakage of animal wastes stored and treated in anaerobic lagoons, as well as land application of the wastes, have heightened concern for potential ground and surface water contamination.

The pioneering work of Kreitler (1975) and Kreitler and Jones (1975) showed that δ^{15}N values greater than +10 per mil (‰) in groundwater are characteristic of N derived from animal waste applied to soils or leached from manure accumulations. δ^{15}N is defined as:

$$\delta^{15}\mathrm{N}(‰) = \left[\frac{(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{sample}} - (^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{std}}}{(^{15}\mathrm{N}/^{14}\mathrm{N})_{\mathrm{std}}}\right] \times 1000 \qquad (1)$$

Volatilization is the primary isotope fractionation mechanism for N isotope enrichment of waste N. It is an equilibrium isotope fractionation with a fractionation factor of 1.034 (Kirshenbaum et al., 1947):

$$^{15}NH_{3(gas)} + {}^{14}NH_{4(aq)} \Leftrightarrow {}^{14}NH_{3(gas)} + {}^{15}NH_{4(aq)}$$

$$\frac{(^{15}N/^{14}N)_{NH4(aq)}}{(^{15}N/^{14}N)_{NH3(gas)}} = 1.034 \qquad (2)$$

Since the mid 1970s, anomalously heavy δ^{15}Nvalues (> +10‰) have been used to identify groundwater impacted by leachates from animal waste (Kreitler, 1975; 1979) including the application of lagoon wastewater to agricultural land (Spalding et al., 1982; Exner and Spalding, 1994; Karr et al., 2001; 2002; 2003; Israel et al., 2005).

N isotope identification of waste sources in groundwater is dependent on the degree of N isotopic enrichment in the waste and the uniformity of the N isotope ratio in the source. Early in this investigation very light δ^{15}N values in two anaerobic waste lagoons prompted several follow-up studies. These studies included determinations of: 1) isotopic enrichment that occurs as N in feed is converted to urine and feces N; 2) the isotopic enrichment during the maturation of the waste in the lagoons; 3) spatial, vertical, and temporal variability of N isotope values within lagoons; and 4) the impact of lagoon management practices on isotopic enrichment.

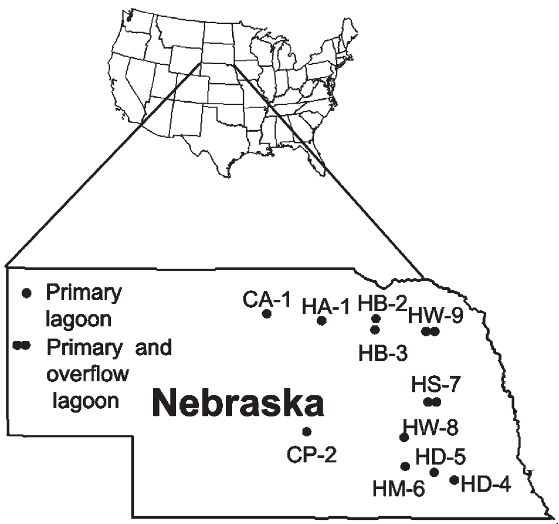

Figure 1. Locations of animal waste lagoons monitored in this study.

Materials and Methods

Lagoon Descriptions

Ten producers voluntarily participated in a Nebraska Department of Environmental Quality program to monitor water quality in 13 anaerobic lagoons at 11 AFOs in eastern and central Nebraska (Figure 1) during 1999 and 2000. The lagoons were constructed between 1973 and 1999. Their volumes ranged from 378 to ~30,000 m^3 (Table 1).

With the exception of lagoons CA-1 and CP-2,which received beef and dairy cattle wastes, respectively, the lagoons received waste from swine feeding operations. Two sites have primary and overflow lagoons. At HW-9 an overflow pipe diverts wastewater from the primary to the overflow lagoon. At HS-7 wastewater is cycled from the primary to the overflow lagoon, back to the swine barns where it is used to clean the pens, and subsequently returned to the primary lagoon. Table 1 lists manure collection and lagoon management procedures.

Sampling Procedures

The lagoons were sampled in 1999, 2000, and 2001. Only surface grab samples from the lagoons' perimeter were collected for the initial sampling in February 1999. Subsequent sampling events were conducted from a rowboat. Samples were collected from the surface, 1.5 m below the surface, and centimeters above the bottom (~3.3 m). Surface samples continued to be grab samples while deeper samples were collected using a peristaltic pump with a weighted 1-cm diameter sampling tube set at the desired sampling depth. The peristaltic pump was set a few inches above the lagoon bottom and slowly pumped to reduce additional turbidity from disturbed bottom sediments. Regardless of depth lagoon samples are characteristically very turbid. Field duplicates and field blanks were collected at a frequency of 5%. pH was measured in summer 2000.

Lagoon samples for the analysis of total Kjeldahl N (TKN), ammonium-N (NH_4^+-N), nitrate-N (NO_3^--N) and $\delta^{15}N$ were collected in acid-washed polyethylene bottles, transported to the laboratory on ice and frozen until the time of analysis. Fresh urine and feces were collected in polyethylene bottles and bags, respectively. Feed samples were collected in polyethylene bags. All samples were iced in a cooler for transport to the laboratory where they were frozen until the time of analysis. Swine feeds were corn and soybean meal mixtures fortified with molasses, amino acids and antibiotics. Cattle feeds were mixtures of corn, soybean meal, and alfalfa hay.

Analytical Procedures

TKN was measured in lagoon samples and source materials using the semimicro-Kjeldahl method (American Public Health Association [APHA], 1998). Briefly, an aliquot of sample was digested for 8–12 hrs to obtain a crystal-clear solution. The highly acidic solution was transferred to a side-arm distillation flask attached to a distillation system; neutralized using 40% NaOH; steam distilled and prepared for $\delta^{15}N$ analysis as described later in text. The process was designed to prevent significant loss of ammonia and thereby minimize isotopic effects.

Table 1. Lagoon Descriptions and Management.

Lagoon	Installation Date	Volume (m^3)	Herd Inventory/Use	Source	Pumping Schedule (times/yr)
CA-1	1994	17,000	1000 feedlot cattle	Feedlot runoff	0
CP-2	1973	378	75 dairy cows	Barn runoff	2
HA-1	1974	5,670	880 hogs	Barn flushing	1
HB-2	1997	3,780	500–800 finishing hogs	Barn flushing	2
HB-3	1985	9,450	600 finishing hogs, 400 sows	Barn flushing	5–6
HD-4	1988	24,570	1300 finishing hogs, 600 sows	Barn flushing	1
HD-5	1995	11,340	1000 hogs	Barn pull plug	0
HM-6	1994	6,048	600 hogs	Barn pull plug	0
HS-7-P	1984	25,751	2500 sows, 2500 piglets	Barn flushing	1
HS-7-O	1996	17,010	Overflow lagoon	HS-7-P	Frequent
HW-8	1999	30,240	1900 hogs	Barn pull plug	0
HW-9-P	1987	12,285	1000 piglets	Barn pull plug	1
HW-9-O	1987	5,670	Overflow lagoon	HW-9-P	0

Organic compounds with known δ^{15}N values were routinely analyzed and significant isotopic effects were not detected.

NH_4^+-N and NO_3^--N concentrations in lagoon samples were measured using the modified (Gormly and Spalding, 1979) steam distillation method (Bremner and Keeney, 1965) and titration. NO_3^--N was not detected in any of the lagoon samples. For N isotope analysis of ammonium, the ammonium sulfate distillate was oxidized to N gas; purified in a vacuum system whose design is similar to that of Kreitler (1975) and δ^{15}N measured using a stable isotope mass spectrometer and the procedures of Bremner and Edwards (1965) and Miyaka and Wada (1967). Atmospheric N_2, the primary standard, was prepared according to the procedure of Cline (1973). Ultrapure (99.999%) carrier-grade tank N_2 was the working standard. The calculated standard deviation for 10 preparations of the tank working standard was ± 0.1‰. The mean for 10 determinations of an $(NH_4)_2SO_4$ isotope standard analyzed daily was −1.2 ± 0.2‰. In a United States Geological Survey-sponsored accuracy crosscheck program, the laboratory's δ^{15}N results were well within acceptable limits (Bohlke and Coplen 1995).

δ^{15}N-NH_4^+ was measured in both filtered and unfiltered sample aliquots to assess the necessity of filtration. Filtered aliquots were prepared by centrifuging 40-mL sample volumes for 15 minutes, decanting the supernatant into an Acrodisc syringe (Gelman Laboratories, East Hills, NY, USA) fitted with a 0.45- μm filter and applying about 5 × 10^5 Pa. δ^{15}N-NH_4^+ values for eight filtered and unfiltered sample pairs from six lagoons were compared. The δ^{15}N values ranged from +4.2 to +24.2‰ in the unfiltered samples and from +4.1 to +20.2‰ in the filtered samples. The two-tailed paired t test showed no significant difference (P = 0.791, t = 0.275, df = 7, α = 0.05, t_{crit} = 2.36) between the filtered and unfiltered δ^{15}N values. The δ^{15}N-NH_4^+ values reported in this paper were measured on unfiltered samples.

Results and Discussion

delta^{15}N in Source Materials

δ^{15}N-TKN values in fresh cattle feces and fresh swine feces and urine were measured in samples collected from nine operations (Table 2). The δ^{15}N values are slightly lighter than the previously reported values of +2.6‰ for cattle feces (Motzel, 2001) and +4.8 ± 1.4‰, +2.9 ± 0.9‰, and +4.0‰ for cattle feces, swine urine, and swine feces, respectively (Gormly and Spalding 1979). As evidenced by the δ^{15}N-TKN values for the feeds and fresh manure (Table 2), there appears to be minimal fractionation during metabolism. The δ^{15}N-TKN values reported here are the most complete δ^{15}N-TKN values available for fresh urine and fecal input to lagoons and are the initial end members that are subjected to enrichment via ammonia volatilization on barn floors and in lagoons.

The δ^{15}N-TKN of the input to nine lagoons was determined from the δ^{15}N-TKN values for the feed and fresh manure for each operation (Table 3). It is not uncommon for as much as 5% of the feed to be wasted and ultimately transported to the lagoons (United States Department of Agriculture [USDA] 1992). Nonruminants are more efficient in metabolizing N in their feed than are ruminants. Swine excrete approximately 50% of their N intake as urine and15% as feces (Ferket et al., 2002). Feedlot beef cattle excrete approximately 65% of the N intake as urine and approximately 25% as feces (Bierman et al., 1999). Dairy cattle excrete approximately 40% of their N intake in feces and 34% in urine (Dou et al., 1996). These percentages are estimations and do not reflect the types of feed, diet, growth stage, or any of the other factors that impact the distribution of urine and feces in the manure. This extensive database of isotopically light N inputs emphasizes that isotopic N discrimination of animal waste sources in groundwater are solely dependent upon the isotopic enrichment that occurs after excretion. These results differ from those of Kreitler (1975) who suggested that the δ^{15}N of the excreted urea is 8‰ lighter than the N content of the feed which was assumed to be +5‰ (Gaebler et al., 1963).

Waste Lagoon delta^{15}N-TKN and delta^{15}N-NH_4^+

N enters waste lagoons as organic N compounds in urine and feces and as ammonia that has been rapidly released by the dissolution of urea. Waste lagoons receive both ammonia and organic N compounds on a relatively continuous basis (loading) and additional ammonium is released by ammonification of organic N as the wastes maturate. δ^{15}N-total N (Karr et al., 2001; 2002; 2003) and TKN, which comprises inorganic and organic N in the –3 oxidation state, have routinely been measured in anaerobic waste lagoon isotope stud-

Table 2. delta^{15}N of Fresh Hog and Cattle N inputs.

N inputs	# of Sites	TKN (mg/L)	δ^{15}N-TKN (‰)
Cattle feed	2	73550 ± 88318	−0.2 ± 2.3
Cattle urine	—	—	+1.7 ± 0.5*
Cattle feces	2	5460 ± 2546	+3.4 ± 0.8
Hog feed	7	23306 ± 2621	+1.7 ± 1.0
Hog urine	7	6063 ± 3778	−0.1 ± 1.1
Hog feces	7	10119 ± 1734	+ 2.4 ± 0.9

* Data from Gormly and Spalding, 1974.

Table 3. delta^{15}N in Feed, Urine, and Feces and Weighted Average Input for Nine Lagoons.

Lagoon	n	δ^{15}N Feed (‰)	n	δ^{15}N Urine (‰)	n	δ^{15}N Feces (‰)	δ^{15}N Input (‰)
CA-1	1	+1.4	—	—	1	+4.0	+2.4
CP-2	1	−1.9	—	—	1	+2.9	+2.3
HA-1	1	+1.2	1	+0.2	1	+1.8	+ 0.6
HB-3	2	+0.8 ± 0.1	2	0 ±0	2	+2.0 ± 0.1	+0.5
HD-4	2	+3.7 ± 0.4	2	+2.0 ± 0.1	2	+3.2 ± 0	+2.4
HM-6	1	+2.6	1	−0.4	1	+3.7	+0.7
HS-7	1	+1.2	1	−1.7	1	+1.0	−1.0
HW-8	1	+1.4	1	−0.9	1	+2.7	0
HW-9	1	+1.2 ± 0.1	2	+0.2 ± 0.5	2	+2.2 ± 0.4	+0.7

ies. Because the TKN digestion significantly increases isotope analysis preparation time, differences in the $\delta^{15}N$ of TKN and NH_4^+-N were evaluated.

Seven lagoons with a wide range of $\delta^{15}N$ values were chosen to evaluate the relationship of $\delta^{15}N$ in TKN to that in NH_4^+-N. Samples were collected throughout the water column. The $\delta^{15}N$-TKNranged from +2.3‰ to +52.1‰ and the $\delta^{15}N$-NH_4^+ ranged from +3.1‰ to +59.1‰ for 45 samples. The Mann-Whitney test showed that the $\delta^{15}N$-TKN and $\delta^{15}N$-NH_4^+ values were not statistically different ($P = 0.335$). Although a change in the distribution of the dominant N species occurred with depth, the statistical associations between the $\delta^{15}N$-NH_4^+ and $\delta^{15}N$-TKN in upper (≤1.5 m) and near bottom (≥3.3 m) samples were strong with r^2 values of 0.997 (n = 27) and 0.982 (n = 18), respectively. NH_4^+-N was the predominant N species in the upper water while organic N was the predominant species in samples collected near the bottom of the lagoons. NH_4^+-N concentrations averaged 80% of the TKN in the upper water. Organic N averaged 62% of the TKN in the near bottom water. Thus, isotopic dilution of the $\delta^{15}N$-TKN is more pronounced in the deep samples than in the shallower samples where the very high proportion of NH_4^+-N overwhelms the isotope dilution impact of the residual organic-N. While ammonification of organic N compounds in the waste is accompanied by only minimal (±1‰) isotopic fractionation (Heaton, 1986), it may account for slightly larger $\delta^{15}N$-TKN and $\delta^{15}N$-NH_4^+ differences in the deeper samples, which contain more particulate. The combination of the excellent statistical association between the $\delta^{15}N$ values from the two major N species in the lagoons and the knowledge that N is transported from lagoons to groundwater primarily as the ammonium species supports using $\delta^{15}N$-NH_4^+ in these N isotope studies.

delta^{15}N Ranges in Waste Lagoons

$\delta^{15}N$-NH_4^+ was measured in the surface water of as many as 13 anaerobic waste lagoons in February and early November 1999 and mid-March 2000. $\delta^{15}N$-NH_4^+ values in February 1999 ranged from +2.0 to +28.0‰ with a median of +14.5‰ (Table 4). Values in four lagoons (CP-2, HB-2, HB-3, HD-4) were below the +10‰ to > +20‰ range that has been used to characterize groundwater contaminated by animal waste applied to cropland (Kreitler and Jones, 1975; Spalding et al., 1982; Exner and Spalding, 1994; Karr et al., 2001; 2002; 2003). In November 1999 the $\delta^{15}N$-NH_4^+ range showed increased enrichment (+8.2 to +35.1‰) and a median of +22.6‰. $\delta^{15}N$ NH_4^+ was less than +10‰ in one lagoon. Data from three lagoons (CA-1, HA-1, and HW-8) added to the study after February 1999 further expanded the November 1999 $\delta^{15}N$-NH_4^+ range (+6.4 to +37.6‰) and slightly raised the median (+23.4‰). Lagoons HW-8, which began receiving wastes in October 1999, and HB-3 had values less than +10‰. In March 2000 the $\delta^{15}N$-NH_4^+ values in the 13 lagoons ranged from +4.1 to +36.7‰. Three lagoons (CP-2, HB-3, and HW-8) had $\delta^{15}N$ signatures less than +10‰. During this monitoring period $\delta^{15}N$-NH_4^+ for lagoons HB-3 and HW-8 remained below the $\delta^{15}N$ signature used to discriminate animal waste from other N sources in groundwater. Average $\delta^{15}N$-NH_4^+ values were +4.8‰ and +6.6‰ for HB-3 and HW-8, respectively, with median values of +4.1‰ and +6.6‰, respectively. Lagoon CP-2 averaged +8.3‰ and had a median of +7.8‰.

The low-end $\delta^{15}N$-NH_4^+ values reported in this study are below the range of values (+11.2 to +81‰) for 10 anaerobic waste lagoons analyzed in Colorado, Oklahoma, and Wisconsin (unpublished data). Karr et al. (2001) reported a $\delta^{15}N$-total N range of+9.8 to +18.4‰ and a median of +15.4‰ for monthly samples taken from two swine waste lagoons and +15.7‰ for a single sample from a third swine waste lagoon (Karr et al., 2002) in the North Carolina coastal plain. A similar isotopic range (+10.2 to +20.9‰) and mean (+15.6‰) characterized the primary lagoon at a dairy operation with a somewhat higher range and mean value in the secondary lagoon (+10 to +31‰ and +20.7‰, respectively) (Karr et al., 2003). The range of $\delta^{15}N$-NH_4^+ for anaerobic waste lagoons in other states suggests that low $\delta^{15}N$ outlier values (<10‰) are not frequently encountered.

$\delta^{15}N$-NH_4^+ increased in each of the lagoons between February and November 1999 and declined in eleven of the 13 lagoons during the colder months from November to March. These seasonal changes are indicative of increased fractionation during the warmer months when temperatures promote ammonia volatilization. Using monthly $\delta^{15}N$ values Karr et al. (2001) reported a smooth seasonal $\delta^{15}N$ cycle that corresponded with monthly mean air temperatures. The data suggest that there may be regional differences in enrichment but they appear to be slight.

Spatial delta^{15}N Variability within Lagoons

Surface and near bottom samples were collected in the center and in two diagonally opposite quadrants of five lagoons (HB-2, HB-3, HD-5, HW-9-P and HW-9-O) in summer 1999

Table 4. delta^{15}N in Surface Samples.

Date	Number of lagoons	‰ Range $\delta^{15}N$	Average	Median	Number < +10‰
February 1999	10	+2.0 to +28.0	+13.7 ± 7.7	14.5	4
November 1999	10	+8.2 to +35.1	+21.6 ± 9.4	22.6	1
March 2000	10	+4.1 to +36.7	+16.9 ± 9.1	18.2	2
November 1999	13	+6.4 to +37.6	+21.8 ± 10.3	23.4	2
March 2000	13	+4.1 to +36.7	+16.4 ± 8.7	17.8	3

to determine the effect of spatial location on δ^{15}N values. The coefficient of variation for the surface samples in each lagoon was less than 5%. Because surface δ^{15}N values are uniform during summer, representative surface samples can be obtained at the most accessible location. δ^{15}N values near the bottom of the water column, however, varied significantly with location in the lagoon. Coefficients of variation ranged from 7 to 17%. This variability may be associated with difficulties in sampling near the bottom without disturbing the sediments and with distance from the input pipe. Wastes entered most of the lagoons approximately 1.5 m below the surface.

Vertical delta^{15}N Changes

Vertical profiles were obtained at three depths in the center of four lagoons (HB-2, HB-3, HD-5 and HW-9-P) and at two depths in one lagoon (HW-9-O) in late July and late October 1999 (summer and fall, respectively, in Figure 2). δ^{15}N-NH_4^+ values were fairly homogeneous (CV < 4%) in the top 1.5 m of three lagoons (HB-2, HD-5, and HW-9-P) during summer and fall. Near bottom samples (~3.3 m) from four lagoons (HB-2, HD-5, HW-9-P, and HW-9-O) had lighter δ^{15}N values, which appear as especially sharp decreases in the summer profiles (Figure 2). Coefficients of variation between the surface and bottom samples in these lagoons were larger (18, 32, 37, and 45%) in late July than in late October (7, 11, 17, and 9%).Warm temperatures during summer promote ammonia volatilization with its associated enrichment in residual δ^{15}N of the ammonium-N. Ammonia generated in the deeper parts of the lagoon is transported upward and new equilibria ammonia-ammonium concentrations are continually established as partitioning into the atmosphere occurs. The increased rate of atmospheric partitioning in summer accentuates vertical differences in δ^{15}N. The cooler fall temperatures slow volatilization, which results in less isotopic fractionation and thus less atmospheric partitioning of ammonia from the upper water of the lagoons into the atmosphere and the isotopic values become lighter. Seasonal turnover induced by the sinking of the denser cold top water also mixes lagoon waters during the cold season and could explain the slightly more enriched δ^{15}N values in the bottom samples in late October.

Ham and DeSutter (1999) reported that earthen lagoons are designed to limit seepage to a target level controlled by the hydraulic properties of the soil and the lagoon design. They reported that bottom permeabilities are further reduced by the addition of organic sludge and the natural maturation of the lagoon. More vulnerable sites for N transport via seepage may occur in the upper sidewalls of lagoons where wetting and drying and freezing and thawing combined with biologically induced macropore formation can threaten the integrity of earthen-lined lagoons (Kim and Daniel 1992; McCurdy and McSweeney 1993). The δ^{15}N data indicate that samples collected from the top 1.5m have uniform isotopic content and would be good indicators of seepage from the potentially vulnerable upper sidewalls of the lagoons.

Lagoon HB-3 showed less variation with depth than the other lagoons. The lagoon is pumped frequently during the growing season and it appears that frequent pumping keeps the lagoon well-mixed. The more depleted δ^{15}N-NH_4^+ values (<10‰) that characterize this lagoon are directly related to the frequent removal of wastes. This phenomenon is discussed more thoroughly in the temporal variations section.

The Mann-Whitney test further supported that δ^{15}N-NH_4^+ in surface and near bottom samples from the centers of 13 lagoons during the colder months of November 1999 and March 2000 were not significantly different (P = 0.148 and 0.608, respectively).

Temporal delta^{15}N Responses to Lagoon Management

Local producers scheduled the waste inputs and pump out of the anaerobic waste lagoons monitored in this study. A

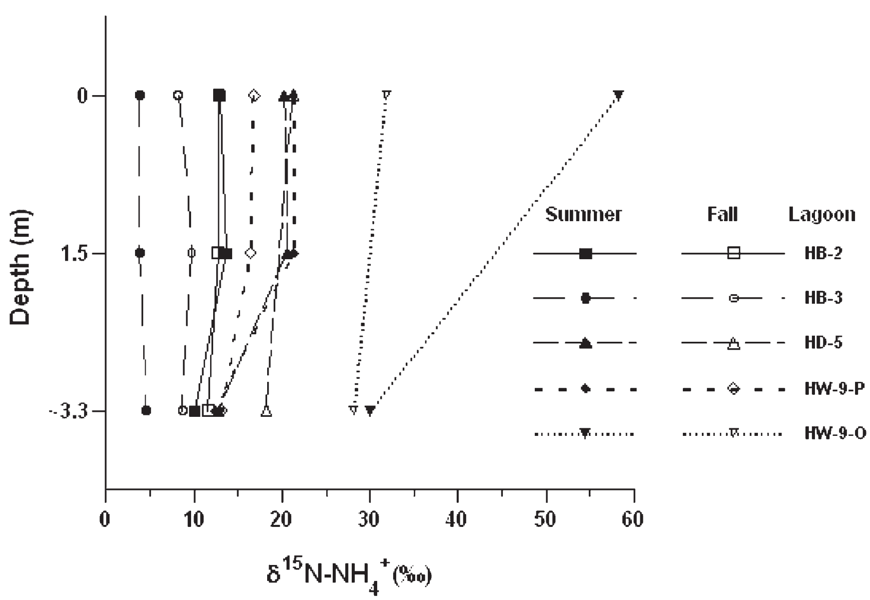

Figure 2. Vertical variations in delta^{15}N-NH_4^+ in selected lagoons.

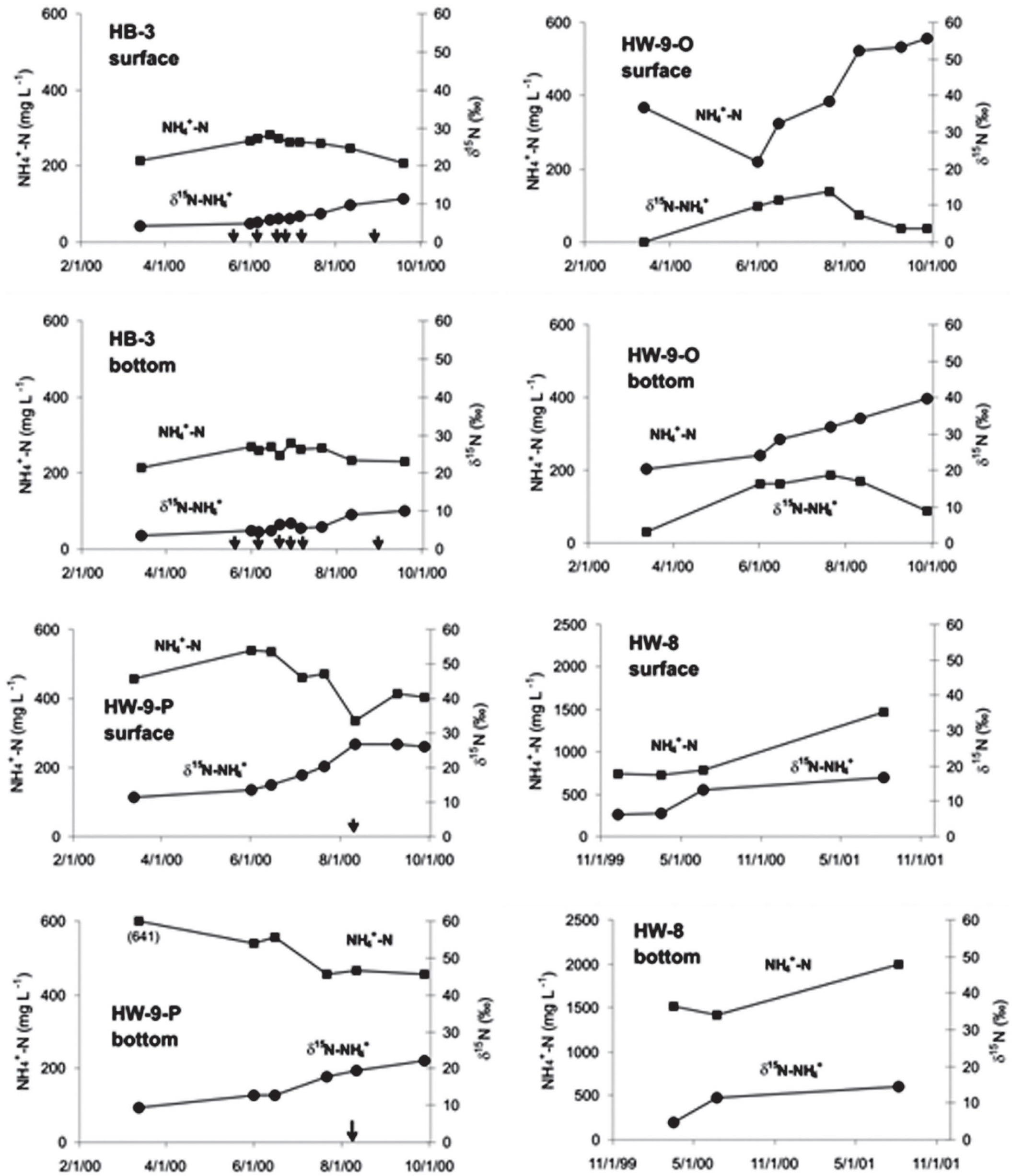

Figure 3. Temporal variations in delta^{15}N-NH_4^+ in surface and near bottom waters of intensively monitored lagoons. Arrows indicate dates wastes were removed from the lagoons.

spectrum of waste removal frequencies ranging from none to as many as six times during a four-month period directly affected the δ^{15}N-NH_4^+ values. The anomalous δ^{15}N-NH_4^+ values in some lagoons are associated with management outliers.

During the approximately 18 months of monitoring, HB-3 was characterized by lowδ^{15}N-NH_4^+ values. This lagoon was the most frequently pumped of the 13 lagoons. Between March and mid-September 2000, δ^{15}N-NH_4^+ ranged from +4.1 to +11.2‰ and averaged +6.7 ± 2.20‰ (Figure 3). This operation and four others in the study use the flush cleaning method of collecting and handling manure (Table 1). Because the method uses relatively large quantities of water, an irrigation system usually is a necessary part of the waste management system in Nebraska. While other producers using the flush cleaning method pumped their lagoon one to two times annually (Table 1), the slurry at HB-3 was pumped from the lagoon six times during the 2000 growing season. The slurry was removed five times between May and July and the δ^{15}N-NH_4^+ values were not appreciably enriched above the March values of ~4‰. The slurry was used to spoon feed N (injection of appropriate amounts of lagoon waste-N into irrigation water) to irrigated corn during critical growth stages. Thus application of the N to the crop when ammonia concentrations were relatively high maximized the beneficial use of the lagoon N and limited ammonia losses to the atmosphere. Frequent removal of the slightly ^{15}N-enriched slurry and the flushing of fresh wastes into the lagoon quenched the isotopic enrichment necessary for source identification of HB-3 leachate. Clearly, the homogeneous δ^{15}N-NH_4^+ values with depth (Figure 3) are footprints of the impact of isotope dilution. The δ^{15}N values increased approximately 3‰ in the 7-week interval between mid-July and late August before the slurry was removed once again.

δ^{15}N-NH_4^+ values were more enriched at HW-9-P, the primary lagoon at this swine operation. δ^{15}N-NH_4^+ values ranged from +11.4 to +26.8‰ and averaged 19.8 ± 6.3‰ (Figure 3). This lagoon and three others in the study received wastes via the pull plug waste handling method. The pull plug management system is commonly used in swine buildings with raised floors. After wastes accumulate in gutters for as long as several days, a drain plug is pulled and the highly concentrated wastes flow by gravity into the lagoon. This method uses considerably less water than the flushing method. The increased holding time of the waste in the barns likely results in N-isotope enrichment of the ammonium prior to its entry into the lagoon. Typically waste is removed from HW-9-P during the first half of August. Removal of waste in August 2000 lowered the lagoon's surface only about 0.6 m. During most of the warm season δ^{15}N values were slightly more enriched in the surface water samples than in the near bottom samples. Nebraska's warm season corresponds to the May 1 to September 15 growing season.

Excess water in HW-9-P flows through an overflow pipe into the secondary lagoon HW-9-O. δ^{15}N-NH_4^+ in HW-9-O was the most intensely enriched of all the monitored Nebraska lagoons (Figure 3). Only approximately 2 m deep, HW-9-O had high pH (8.4 ± 0.4) and relatively low NH_4^+-N concentrations. The concentrations ranged from 1.3 to 138 mg/L in the surface samples and from 31 to 188 mg/L in the near bottom samples. Between late July and mid-August δ^{15}N-NH_4^+ in the surface samples increased from +38.4 to +52.3‰ and further increased to a high of +55.5‰ by late September. Anomalously high δ^{15}N-NH_4^+ values of +78‰ and +81‰ also were measured in two overflow lagoons in another state (unpublished data). The lagoons also had very low ammonium-N concentrations (<10 mg/L) and trace concentrations of nitrate-N. These high enrichment values and trace nitrate levels suggest an additional enrichment process is involved. Nitrification of the residual ammonium-N produces a kinetic isotope effect that would allow significantly more enrichment. Bottom samples also became more enriched although not to the extent seen in the surface samples. Enrichment generally was accompanied by losses in NH_4-N concentrations. It certainly is possible that the organic material in HW-9-O was consumed and the lagoon had become partially oxygenated allowing denitrification and the high level of observed isotopic enrichment.

Constructed in fall 1999 lagoon HW-8 initially was filled with water to allow the clays to expand and improve the bottom seal. Wastes were added in November. The lagoon was monitored from December 1999 through August 2001 (Figure 3). δ^{15}N-NH_4^+ values were only slightly enriched in December (+6.4‰) and March (~ +5–7‰). Ammonia volatilization and enrichment commenced in the warmer weather. δ^{15}N-NH_4^+ values in June 2000 and August 2001 were > +10‰.

Conclusions

Isotope analysis of feeds and fresh urine and excrement from cattle and swine indicated that little, if any, isotopic fractionation occurred in the digestion process. Wastes must mature in lagoons in order to develop high levels (> +10‰) of δ^{15}N-NH_4^+ enrichment. Surface δ^{15}N-NH_4^+ values were spatially homogeneous in each lagoon. The vertical distribution of δ^{15}N-NH_4^+ values showed the lagoons were well mixed in all but summer when surficial enrichment was noted in several lagoons. Enrichment increased when ammonia volatilization increased in months with higher temperatures. Anomalously high isotope enrichment in an overflow lagoon appeared linked to kinetic isotope effects from nitrification. Lagoons that were frequently pumped and refilled with fresh wastes were not characterized by the enriched δ^{15}N values normally associated with animal wastes. Minimal δ^{15}N-NH_4^+ values for isotope source identification always occurred in the colder months and occasionally were below +10‰. In two of 13 lagoons enrichment was not sufficient to allow discrimination of waste N from soil N and commercial N fertilizer. Samples from ten lagoons in nearby states, however, had signatures sufficiently enriched to conclusively identify them as animal waste. The data from this study indicate that anomalously low δ^{15}N values may occur in <5% of earthen anaerobic waste lagoons.

These results strongly emphasize the necessity of measuring δ^{15}N-NH_4^+ in lagoon surface samples during groundwater nitrate source identification investigations. Previous research as well as assessments by regulators and consultants of groundwater contamination have relied on δ^{15}N values > +10‰ as signatures of animal waste from leaky lagoons. While this protocol may be acceptable in the majority of cases, it needs to be reevaluated in light of these findings.

Acknowledgements — This research was supported by the Nebraska Department of Environmental Quality. This manuscript has been assigned Journal Series no. 15235, Agricultural Research Division, University of Nebraska. The authors thank B. Genna and T. McDade of the North Carolina State University Stable Isotope Laboratory for their review comments.

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