PROJECT COMPLETION REPORT

Use of Stable Nitrogen Isotopes Determining Nitrogen Sources Entering Louisiana Surface Waters

Ву

R. D. DeLaune
C. W. Lindau
and
W. H. Patrick, Jr.

Laboratory for Wetland Soils and Sediments Center of Wetland Resources Louisiana State University Baton Rouge, LA 70803-7511

October, 1988

The activities on which this report was based were financed in part by the Department of the Interior, U.S. Geological Survey, through the Louisiana Water Resources Research Institute.

The contents of this publication do not necessarily reflect the views and policies of the Department of the Interior, nor does mention of trade names or commercial products constitute their endorsement by the United States Government.

ACKNOWLEDGEMENTS

I would like to acknowledge the Louisiana Water Resources Research Institute and the US Department of Interior, Geological Survey, who provided the funds for this investigation. Additional thanks are extended to Dr. Marty Tittlebaum, Director, and Ms. Brenda Kelly, Assistant Director of Louisiana Water Resources Research Institute.

ABSTRACT

Means for identifying sources of inorganic nitrogen entering Louisiana surface waters were developed. The isotopic signature of NH_4 +-N in water samples taken from selected streams was used to assess the contribution of NH_4 +-N from point source discharge. Ammonium nitrogen from sewage and industrial sources were found to have distinct signatures which was different from down stream inorganic nitrogen sources. We measured $\delta^{15}N\%_0$ values for NH_4 +-N ranging from +30 at point sources to as great as +200 with distance from the source. The hydrology of the stream was important in dilution of the NH_4 +-N source. In a slow flowing stream the signature was apparent for approximately 10 miles. In a stream with larger flow the signature was not identifiable for as great a distance, indicating dilution.

The large positive increase in $\delta^{15}N$ values over distance from a point source may also be showing that the original NH₄+ is undergoing transformations over time, but this effect is probably not as significant as the dilution effect. The changes in $\delta^{15}N$ values could also be due to kinetic isotope fractionation associated with bacteria. Also, if surface water pH is high some of the original NH₄+ can be lost through volatilization which could result in an isotopically heavier residual NH₄+ pool. Volatilization is probably not a major loss mechanism, however, because the pH of these surface waters is usually not high enough to support ammonia volatilization. The oxidation of NH₄+ to NO₃- (nitrification) in the oxygenated surface waters is also taking place. Nitrification of NH₄+ would result in a remaining residual NH₄+ pool which would be highly enriched in N-15 compared to the NO₃- N formed. As the residual NH₄+ is reworked and transformed further down stream the remaining inorganic NH₄+ pool would decrease in concentration and increase in N-15 content. The ammonium pool involved in equilibrium and kinetic isotopic fractionation reactions could be reduced in contaminated surface waters. Part of the ammonium pool could be lost as gaseous end products (NH₃, N₂O, N₂) through

volatilization and denitrification reactions. As the NH_4+ or NO_3- moves away from the point source dilution and bacterial effects alter the nitrogen isotopic values of the original nitrogen. This is reflected in the heavier $\delta^{15}N$ ammonia values over time and distance, which we feel is mainly due to dilution of the original NH_4+ with an isotopically heavier source down stream. Bacterial fractionation and subsequent enrichment of point source NH_4+ is probably only of minor significance in this case.

The fractionation of nitrogen isotopes by dilution and bacterially-mediated reactions is complex and not completely understood. For this reason the use of $\delta^{15}N$ values in identifying inorganic nitrogen surface water sources should only be used for semi-quantitative interpretations. However, the large range of $\delta^{15}N$ -NH₄+ values observed in this study suggest that nitrogen isotope ratios can be effectively used as tracers in the nitrogen cycle in surface contaminated waters.

BACKGROUND INFORMATION

In many areas of the Gulf Coast, including coastal Louisiana, water quality is deteriorating rapidly (Figure 1). This is one of the most pressing environmental problems today along the Gulf Coast. Many of the water bodies in northern portions of coastal estuaries are rapidly becoming eutrophic. This is the cumulative result of numerous interacting factors, many of which have a cultural origin. Domestic wastes are becoming an increasing problem because of inadequate sewage treatment and increasing population growth. Additionally, urban runoff is a significant source of pollution to the coastal margins. Agricultural runoff also results in large quantities of nutrients entering lakes via drainage canals. Wastes from industrial sites are also sources of high nutrient input.

Information is needed on inputs of nitrogen into these freshwater systems, their reactions and transformations, and the rate and form of their discharge from the system. In order to provide this information it is apparent that numerous facets of nitrogen cycling in Louisiana's wind-dominated shallow coastal lakes, swamp forest, and freshwater marshes need to be elucidated. In the past, internal nutrient cycling has not been considered in determining loading rate for Louisiana's freshwater wetlands. Emphasis must be placed on understanding the various nutrient cycles and related processes occurring within the water column and at the sediment-water interfaces of coastal bays, lakes, and channels. These processes have important effects on both present and future productivity and water quality in these systems. Reasonable estimates of critical loading rates of nitrogen need to be developed. Previous estimates have been based on population density and factors worked out for systems in other parts of the country (Craig and Day, 1977).

Nutrient exchange between sediment and overlying water, which indirectly controls the trophic state of waterbodies, is an ecologically significant process occurring in the

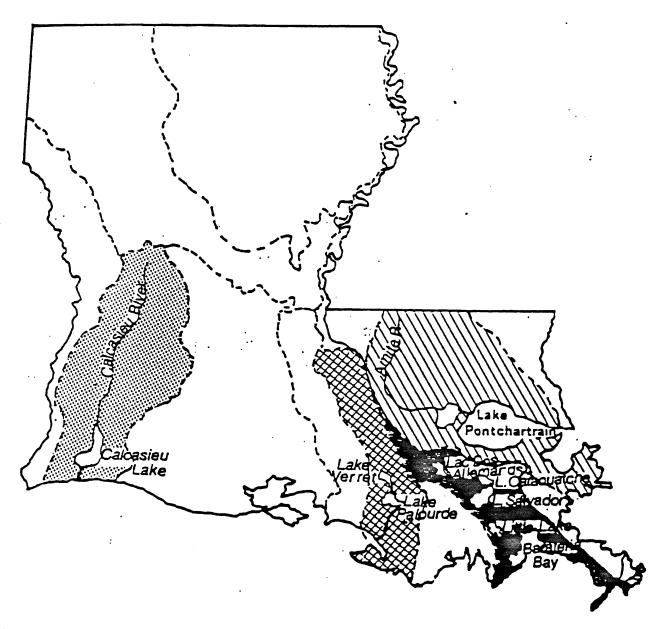


Figure 1. Coastal drainage basins whose water bodies are currently experiencing water quality problems as a result of either agricultural runoff or industrial and municipal discharge.

shallow bays and lakes of coastal states. Sediments can often absorb nutrients, thus lowering the degree of eutrophication in the overlying water. In such ecosystems an increase or decrease in the major inorganic nutrients, particularly nitrogen and phosphorus, can cause changes in the complex series of biological, chemical, and physical interactions in the system.

Natural and cultural enrichment with nutrients frequently result in excessive phytoplankton or algae growth (eutrophication), thereby reducing the use and quality of water. Inadequate treatment of domestic waste is an increasing problem in the upper drainage basins of coastal areas. In many areas at peak water levels, raw sewage is discharged directly into waterways. A recent report prepared for Louisiana's Department of Natural Resources reports that streams in the northern portion of the Pontchartrain basin are severely affected by domestic water discharge and runoff from urban areas. Even if secondary treatment (removal of BOD) were completely implemented, effluent from the secondary treatment plants could still lead to eutrophication because of high nitrogen and phosphorus levels. Determining what levels of nutrients these water bodies can assimilate without adversely affecting water quality is important for determining the loading rate Louisiana's coastal drainage basins and freshwater wetland can adequately handle.

The sediment load being deposited in these regions is also a source of nutrients and must be studied. Not all of the nutrients that enter Louisiana's freshwater wetlands are in a dissolved form as has been suggested (Craig and Day, 1977). Suspended and deposited sediment can contribute sufficient nutrients to the water to cause extensive algal growth without additional nutrient sources. In most waters nitrogen is considered as the growth-limiting nutrient. Under some conditions, the sediment also becomes a sink for nutrients. Effective control of cultural eutrophication in coastal Louisiana must involve a comprehensive understanding of nutrient cycling in waters and the sensitivity of the ecosystem to adjustments in nutrient loading. It should be emphasized that there is

insufficient information on the internal nitrogen cycling in Louisiana's coastal drainage basins. This information is needed by state officials to use in management decisions including allocating proper nutrient loading rates. The cost of exclusion of specific nutrients varies and from an economic standpoint it becomes important to identify which nutrients limit growth for a given situation and the capacity of the system to assimilate increased nutrient loading without any adverse effects. We cannot continue to extrapolate to studies done in other parts of the U.S. or overseas.

Agricultural runoff and municipal discharges are major contributors to nitrogen enrichment to Louisiana coastal wetlands. One primary agricultural nutrient source is from crops which are grown on the natural levees of the Mississippi River deltaic plain. The elevated natural levees of interdistributary channels bordering coastal drainage basins slope with distance into extensive cypress, tupelo gum swamps, and freshwater marshes. The swamps grade into freshwater marshes and lakes. The northern portion of these coastal drainage basins receiving agricultural runoff and nutrients from municipal discharge are rapidly becoming eutrophic. Any enroachment of eutrophication from the upper basin into brackish nursery ground could alter water quality and the fishing industry in the lower basin near the coast. Effective control of cultural eutrophication in coastal Louisiana must involve a comprehensive understanding of the role swamp forest and freshwater marsh play in improving water quality through nitrogen removal.

Nitrogen entering wetland systems can undergo a series of transformations.

Nitrification-denitrification reactions are of great importance in forested swamp soils and freshwater marsh. Appreciable nitrogen can be removed by this process. These reactions involving agricultural runoff filtering through swamps and marsh can protect surface water and streams from receiving excess nitrogen forms.

Ammonium nitrogen being discharged into these wetlands can be (1) nitrified,

(2) assimilated, or (3) adsorbed by bottom sediment. Nitrification can occur in the water column and in the surface oxidized layer in bottom sediment (Jenkins and Kemp, 1984).

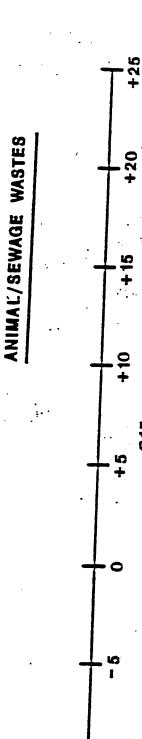
Ammonium adsorbed by bottom sediment can go through a series of reactions, including immobilization, nitrification and denitrification. Ammonium entering the sediment organic pool can be mineralized and again go through the inorganic nitrogen cycle. Nitrate diffusion from the water column can be either denitrified and released to the atmosphere or immobilized into the organic pool.

Stable Nitrogen Isotopes

Stable isotope ratios of nitrogen (15N/14N) have been used successfully to identify the sources of ground and surface water NO₃-N contamination (Kreitler, 1975; 1979; Kreitler and Browning, 1983; Lindau and Spalding, 1984). The three main sources of nitrogen pollution to the hydrosphere are nitrogeneous fertilizers, animal or sewage wastes, and mineralization of soil organic matter (Heaton, 1986). These sources can produce NO_3 -N with distinguishable $^{15}N/^{14}N$ ratios which can be used in a semiquantitative matter to interpret the source of the NO₃-N contamination (Hauck, 1973; Heaton, 1986). Nitrate formed by mineralization of soil organic nitrogen has a typical $\delta^{15}N$ range of +4 to +9% (Karamanos et al., 1981; Mariotti et al., 1984). Ammonium and NO₃-N in fertilizers are commonly derived by industrial fixation of atmospheric nitrogen and have $\delta^{15}N$ values close to zero (Figure 1) and usually range from -4 to +4% (Shearer et al., 1974; Kreitler, 1979). Nitrogen in animal and sewage waste is mainly in the form of urea which is hydrolyzed to ammonia and eventually converted to nitrate. The ammonia lost by volatilization from the system will be strongly depleted in ¹⁵N and the remaining ammonium in solution will be correspondingly enriched in ¹⁵N. Most of this NH₄+ can be converted to ¹⁵N enriched nitrate. Hydrolysis of urea from animal wastes ($\delta^{15}N = +5\%$) is converted to nitrate with δ^{15} N-values in the range of +10 to +20% (Kreitler, 1975, 1979). The data summarized in Figure 2 clearly indicates that the different potential

SOIL ORGANIC NITROGEN

> FERTILIZERS NH4 NO3



6 ¹⁵N-No₃ ranges for major sources of nitrogen in ground and surface water (after Heaton, 1986). Figure 2.

sources of NO_3^- in surface water can often be distinguished on the basis of their $^{15}N/^{14}N$ ratios.

A large number of nitrogen contamination studies have been conducted on groundwater because it is somewhat easier to study than surface water owing to greater temporal stability and chemical simplicity of nitrogen compounds. Surface water nitrogen pollution is much more complex but can be sorted out if a potential N source or sources (fertilizer runoff, industrial and animal wastes) have distinctive δ^{15} N signatures and input rates, dilution factors and mixing rates to surface waters are known (Heaton, 1986).

Sewage discharge into rivers and coastal water provides a source of inorganic nitrogen which could disturb the delicate balance between coastal and estuarine ecosystems. In addition, to using $^{15}\text{N}/^{14}\text{N}$ ratios to trace NO₃-N pollution from potential sources, organic nitrogen of continental origin has a different $\delta^{15}\text{N}$ value compared to organic N of marine origin. Nitrogen isotopic analysis in coastal environments could possibly be used in some cases to distinguish between organic matter of continental or marine origin (Sweeney et al., 1978; Mariotti et al., 1984). Organic nitrogen found in rivers has a $\delta^{15}\text{N}$ range of 0 to +3‰ and suspended authigenic organic matter in oceans have $\delta^{15}\text{N}$ values of +5 to +10‰ (Wada and Hattori, 1976; Mariotti et al., 1984). Bayou Fountain and Amite River (domestic wastes), Calcasieu Lake (industrial) were be sampled for stable nitrogen isotope source identification.

Preliminary studies by the PI show elevated levels of nitrogen from several sources are entering Louisiana Gulf Coast surface water. The specific objective of this project using stable isotope techniques was to fingerprint nitrogen sources entering surface waters of selected water bodies along the Louisiana Gulf Coast.

METHODOLOGY

Surface water from numerous sources were analyzed for determining the range in δ 15N signature of ammonium and nitrate nitrogen respectively, including several streams and point sources. These included runoff of a sugar cane field, sewage discharge into the Mississippi River, etc. The data generated from the initial sampling was used to select more detailed drainage basin studies.

Sites were also established along selected drainage Basins including 1) the Calcasieu River (Figure 3) which receives industrial point sources of nitrogen and 2) Bayou Fountain, Bayou Manchac, Amite River (Figure4) which receives nitrogen from sewage. Surface water samples were collected seasonally from streams in the drainage basins. Ammonium in waters representing point sources from a sewage treatment plant and industrial NH_4 +-N discharge were analyzed for 15N/14N ratios. The nitrogen isotopic signature in water samples with distance from the source was determined. Steam distillation and Kjeldahl procedures were used to prepare N samples for natural abundance 15N/14N analysis (Bremner and Mulvaney, 1982). In these procedures the inorganic N fractions were converted to NH_4 +-salts and conversion of NH_4 +-N to N_2 for mass spectrometer analysis was done by reacting with NaOBr. The purified N_2 gas sample was analyzed on a Finnigan Mat Delta E isotope ratio mass spectrometer and the 15N/14N ratio determined. The nitrogen isotopic composition in the samples was expressed in terms of its $\delta 15N$ -value, where:

$$\delta^{15}N$$
 (‰) = (R sample/R standard -1) x 1000

Nitrogen stable isotope notation defines R as the atomic $^{15}N/^{14}N$ ratio. The standard is atmospheric N_2 , with a ^{15}N abundance of 0.3663% (Junk and Svec, 1958). Surface water nitrogen pollution sources were determined from the distinctive $\delta^{15}N$ signatures, input.

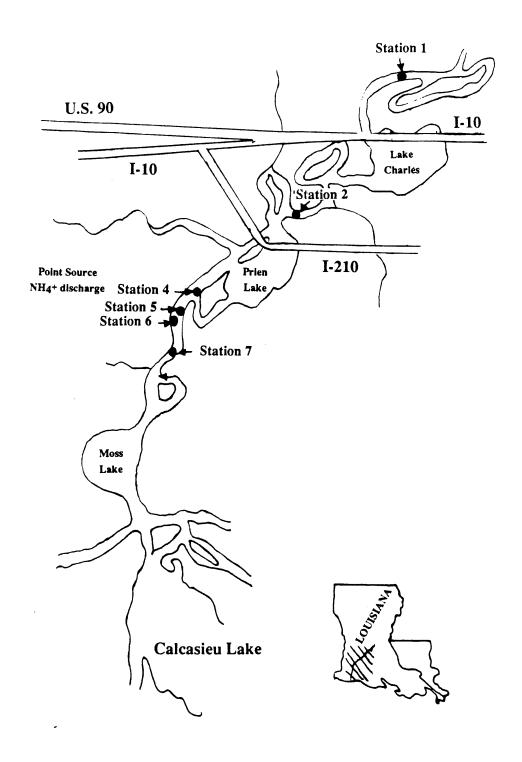


Figure 3. Locations in which surface water samples were collected in the Calcasieu River.

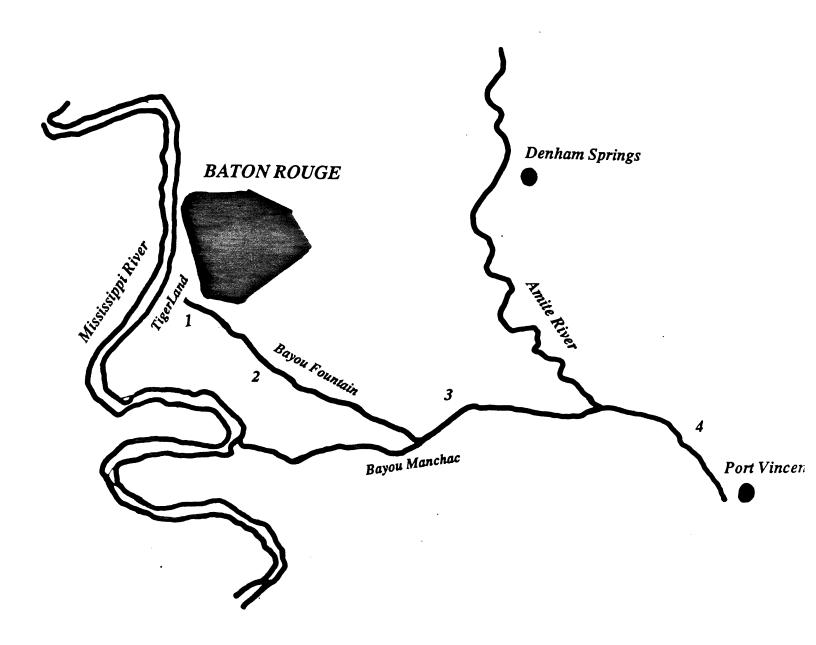


Figure 4. Locations in which surface water samples were taken in the Bayou Fountain, Bayou Manchac and Amite River drainage basin.

Table 1. $\delta^{15}N\%$ of NH₄+ and NO₃- in selected surface waters (Number in parenthesis indicate number of sampling dates).

		$+\delta^{13}$	5N ‰
		<u>NH4+</u>	<u>NO3-</u>
1.	East Baton Rouge Sewage Discharge into Mississippi River (Gardere Plant)	21(2)	22(2)
2.	Sewage discharge from Tigerland Apartments	43(3)	30(-3)
3.	Industrial Ammonia discharge into Calcasieu River	22(3)	16(3)
4.	Amite River (Port Vincent)	161(3)	44(3)
5.	Calcasieu River (upstream from Lake Charles)	124(3)	21(1)
6.	Calcasieu River (downstream from Lake Charles near Calcasieu Lake)	56(3)	24(2)
7.	Bayou Fountain (East Baton Rouge Parish)	48(3)	20(3)
8.	Runoff from Sugar Cane Field (Iberville Parish)	92(1)	20(1)
9.	Bayou Manchac	144(3)	99(3)
10.	Bayou Piere (discharging into Lake Verret)	71(1)	11(1)

RESULT

Variation in δ15N ‰ values

The $\delta^{15}N$ ‰ values for NH₄+-N varied considerably for the water sampled. The water ranged from 21 and 22 at a East Baton Rouge Sewage Treatment outfall and industrial ammonium discharge site on the Calcasieu River to 161 on the Amite River at Port Vincent (Table 1). In general NH₄+-N in surface water impacted with input from sources such as those from sewage contained lower $\delta^{15}N$ ‰ values than NH₄+-N in water at distance from such location. For instance $\delta^{15}N$ ‰ of NH₄+-N of surface water in the Calcasieu River were higher north of Lake Charles. Sites below Lake Charles reflected lower $\delta^{15}N$ ‰ values which we attribute to industrial and municipal input of ammonia and nitrate to the Calcasieu River.

The $\delta^{15}N$ % values for NO_3^--N also varied depending on source. The range in values were not as great as that for NH_4^+-N . The values ranged between 11 and 99 with the majority of the values between 20 and 30. The narrower range observed in $\delta^{15}N$ % of NO_3^--N would limit its usefulness fingerprinting nitrogen source entering Louisiana surface water.

Basin level studies

Discharge of nitrogen from Tigerland Apartments into Bayou Fountain, which drains into Bayou Manchac, which in turn empties into the Amite River showed a large range in δ15N ‰ values of NH₄+-N depending on distance from the source.

Concentration of inorganic nitrogen forms (NH₄+ and NO₃-) also varied (Table 2). In general, NH₄+ concentrations were greater near the Tigerland Apartments discharge site and decreased with distance downstream. Nitrate concentration did not vary as great with distance from the discharge site. Apparently some of the ammonia -N was being nitrified to nitrate which tended to mask dilution of nitrate in streams south of the discharge site.

Table 2. Nitrate and NH₄+ content of water samples (East Baton Rouge Parish).

	2/25/88 mg N 1 ⁻¹ NH ₄ + NO ₃ -		5/1/88 mg N 1 ⁻¹ NH ₄ + NO ₃ -		6/23/88 mg N 1 ⁻¹ NH ₄ + NO ₃ -		Average mg N 1 ⁻¹ NH ₄ + NO ₃ -	
Tigerland (Point Source)	7.91	0.27	0.50	2.95	1.27	0.38	3.20	1.20
Bayou Foutain	0.62	0.17	0.96	0.67	1.37	0.74	0.98	0.53
Bayou Manchac	0.25	0.06	0.29	0.18	0.38	0.76	0.31	0.33
Port Vincent	0.25	0.11	0.15	0.07	0.26	0.27	0.22	0.15

The $\delta^{15}N$ % values for NH₄+-N increased significantly with distance from the point source (Table 3). The increase was linear with the distance from the point source (Figure 4). There was no apparent trend in $\delta^{15}N$ % value of nitrate with distance from the Tigerland sewage outfall.

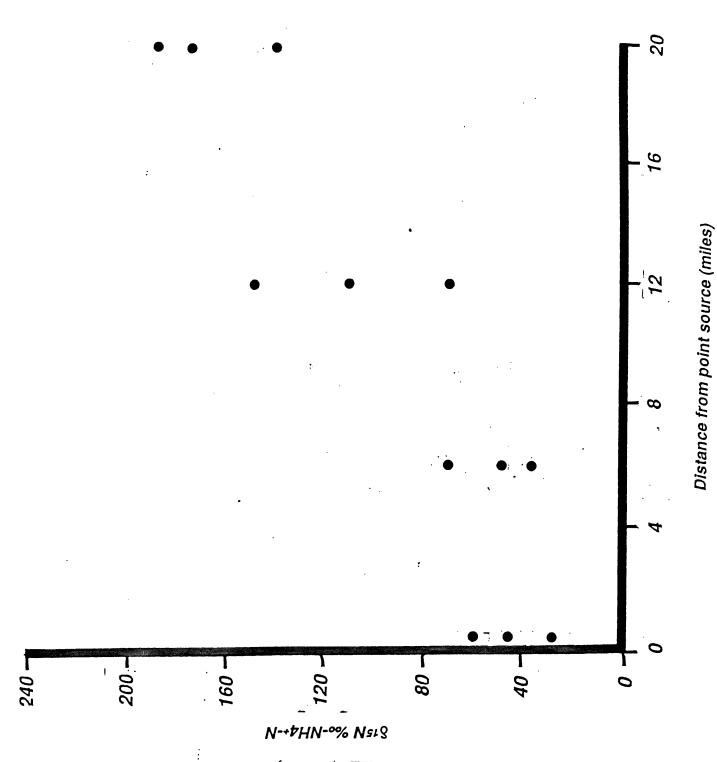
Sampling points established on the Calcasieu River showed that there was lower levels of NH₄⁺ and NO₃⁻ in its surface water than at the East Baton Rouge Parish drainage site (Table 4). The only exception was at Site 4, which is an industrial outfall which is permitted by the State to discharge ammonium nitrogen into the River. At Site 4 we measured NH₄⁺ and NO₃⁻ concentrations as great as 25 and 15 mg N 1⁻¹, respectively. The greater flow of the Calcasieu River and tidal flushing tend to dilute dissolved inorganic nitrogen levels in the surface waters.

The δ 15N ‰ of the NH₄+-N in water near the discharge was low ranging from 7 to 43 (Table 5). We did not observe a significant increase downstream as in the other basins studied. The sampling sites downstream were a lot closer from the point sources than the East Baton Rouge Parish site. In general δ 15N ‰ values for NH₄+-N was greater north of Lake Charles indicating there is some influence on isotopic signature of NH₄+-N in surface water from both municipal and industrial source. Even though there was an apparent dilution of nitrogen concentrations the isotopic signature (a reflection of municipal or industrial input) was apparent below the sources of inorganic nitrogen input.

The δ ¹⁵N ‰ values for nitrate were not as clear in identifying nitrogen source. These results on NO₃- signature were similar to those reported for the East Baton Rouge Parish drainage basin.

Table 3. $\delta^{15}N$ ‰ of NO_3^- and NH_4^+-N with distance from point source. (East Baton Rouge Parish)

	2/25/88 8 ¹⁵ N‰		5/1/88 δ ¹⁵ N‰		6/23/88 δ ¹⁵ N‰		Distance from Point Source	
Sites	NH ₄ +	NO ₃ -	NH ₄ +	NO ₃ -	NH ₄ +	NO ₃ -	(miles)	
Tigerland (point source)	23	2 4	61	10	46	5 5	0	
Bayou Fountain	63	28	4 5	1 3	3 7	18	6	
Bayou Manchac	153	99	221	170	60	30	1 2	
Port Vincent	132	29	183	74	170	30	20	



 $\$15_N$ signature of NH $_4^+$ -N with distance from point source discharge (Preliminary investigations of three sampling data). Figure 5.

Table 4. Nitrate and NH_4^+ content of Calcasieu River water.

Site	10/23/87 mg N 1 ⁻¹ NH ₄ + NO ₃ -	3/7/88 mg N 1 ⁻¹ NH ₄ + NO ₃ -	7/2/88 mg N 1 ⁻¹ NH ₄ + NO ₃ -		
1	0.10 0.11	0.27	0.18 0.13		
2	+		0.22 0.07		
4 (Point Source)	25.4* 14.6*	0.67 0.38	1.12 1.58		
5		0.40 0.27	1.00 1.40		
6			0.18 0.09		
7	0.09 0.20	0.17 0.16	0.14 0.11		

^{*}Direct discharge sample +Concentrations below detection limits

Table 5. δ ¹⁵N ‰ of NO₃ and NH₄+-N in surface water in Calcasieu River.

Site	10/23/87 δ ¹⁵ N ‰ NH ₄ + NO ₃ -		3/7/3 8 ¹⁵ 1 NH ₄ +	N ‰	7/2/88 δ ¹⁵ N ‰ NH ₄ + NO ₃ -		
1	164	145	134		75	21	
2	*				55	56	
4 (Point Source)	7	19	43	0.5	17	27	
5					18	28	
6			84	16	41	32	
7					47	28	

^{*}Insufficient nitrogen for mass spectrometer analysis

SUMMARY

Our research has provided a means for identifying sources of inorganic nitrogen entering Louisiana surface water. The isotopic signature of NH_4^+ -N in water samples taken from selected streams was used to assess the contribution of NH_4^+ -N from point source discharges. Ammonium nitrogen from sewage and industrial sources were found to have distinct signatures which was different from down stream inorganic nitrogen sources. We measured $\delta^{15}N$ % $_0$ values for NH_4^+ -N ranging from $^+30$ at point sources to as great as $^+200$ with distance from the source. The hydrology of the stream was important in dilution of the NH_4^+ -N source. In a slow flowing stream (Bayou Fountain) the signature was apparent for approximately 10 miles. In streams with larger flow (Calcasieu River) the signature was not identifiable for as great a distance indicating dilution.

The large positive increase in $\delta^{15}N$ values over distance from a point source may also be showing that the original NH₄+ is undergoing transformations over time but is not as significant as the dilution effect. The changes in $\delta^{15}N$ values could also be due to kinetic isotope fractionation associated with bacteria. If the surface water pH is high some of the original NH₄+ theoretically could be lost through volatilization which would result in isotopically heavier residual NH₄+ pool. Volatilization is probably not a major loss mechanism because the pH of these surface waters is not high enough to support ammonia volatilization. The oxidation of NH₄+ to NO₃- (nitrification) in the oxygenated surface waters is also taking place. Nitrification of NH₄+ would result in a remaining residual NH₄+ pool which would be highly enriched in N-15 compared to the NO₃- N formed. As the residual NH₄+ is reworked and transformed further down stream the remaining inorganic NH₄+ pool would decrease in concentration and increase in N-15 content. The ammonium pool involved in equilibrium and kinetic isotopic fractionation reactions could be reduced in contaminated surface waters. Part of the ammonium pool could be lost as gaseous end products (NH₃, N₂O, N₂) through volatilization and denitrification reactions. As the NH₄+ or NO₃- moves away from the point source dilution and bacterial effects alter

the nitrogen isotopic values of the original nitrogen. This is reflected in the heavier $\delta^{15}N$ ammonia values over time and distance, which we feel is mainly due to dilution of the original NH₄+ with an isotopically heavier source down stream. Bacterial fractionation and subsequent enrichment of point source NH₄+ is probably only of minor significance in this case.

The fractionation of nitrogen isotopes by dilution and bacterially-mediated reactions is complex and not completely understood. For this reason the use of $\delta^{15}N$ values in identifying inorganic nitrogen surface water sources should only be used for semi-quantitative interpretations. The large range of $\delta^{15}N$ -NH₄+ values in this study suggest that nitrogen isotope ratios have the potential to be used as tracers in the nitrogen cycle in surface contaminated waters.

LITERATURE CITED

- Bremner, J. M., and C. S. Mulvaney. 1982. Nitrogen total. In A. L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. 9:595--624.
- Craig, N. J. and J. W. Day. 1977. Cumulative impact studies in the Louisiana coastal zone: Eutrophication and land loss. Report to Louisiana's Department of Transportation and Development, Coastal Resources Program.
- Hauck, R. D., S. W. Melsted, and P. E. Yankwick. 1958. Use of N-isotope distribution in nitrogen gas in the study of denitrification. Soil Sci. 86:287-291.
- Heaton, T. H. E. 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere. A review. Chemical Geol. (Isotope Geoscience Sec.), 59, pp. 87-102.
- Hauch, R. D. 1973. Nitrogen tracers in nitrogen cycle studies; past use and future needs. J. Envir. Qual., 2:317-327.
- Jenkins, M. C. and W. M. Kemp. 1984. The coupling of nitrification and denitrification in two estuarine sediments. Limnol. Oceanogr. 29(3):609-619.
- Junk, G., and H. J. Svec. 1958. The absolate abundance of the nitrogen isotopes in the atmosphere and compressed gas from various sources. Geochim. Cosmochim. Acta. 14:234-243.
- Karamanos, R. E., R. P. Voroney, and D. A. Rennie. 1981. Variation in natural ¹⁵N abundance of central saskatchewan soils. Soil Sci. Soc. Am. J. 45:826-828.
- Keeney, D. R., and D. W. Nelson. 1982. Nitrogen: Inorganic forms. In A. L. Page et al. (ed). Methods of soil analysis. Part 2. 2nd ed. 9 643-598.
- Kreitler, C. W. 1975. Determining the source of nitrate in goundwater by nitrogen isotope studies. Univ. of Texas, Austin, Texas, Bun. Econ. Geol., Rep. Invest. No. 83. 57 pp.
- Kreitler, C. W. 1979. Nitrogen isotope ratio studies of soils and groundwater nitrate from alluvial fan aquifers in Texas. J. Hydrol. 42:147-170.
- Kreitler, C. W. and L. A. Browning. 1983. Nitrogen isotope ratio studies of soils and groundwater nitrate in carbonate aquifes: natural sources versus human pollution. J. Hydrol. 61:285-301.
- Lindau, C. W., and R. F. Spalding. 1984. Major procedural discrepancies in soil extracted nitrate levels and nitrogen isopotic values. Groundwater. 22:273-278.
- Mariotti, A., C. Lancelot and G. Billen. 1984. Natural isotopic composition of nitrogen as a tracen of origin for suspended organic matter in the scheldt estuary. Geochim. (osmochim. Acta.) 48:549-555.

- Shearer, G. B., D. H. Kohl, and B. Commoner. 1974. The precision of determinations of the natural abundance of nitrogen-15 in soils, fertilizers and shelf chemicals. Soil Sci. 118:308-316
- Sweeney, R. E., K. K. Liu and I. R. Kaplan. 1978. Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In: stable isotopes in the earth sciences. DSIR, Wellington, Bull. 220:9-26.
- Wada, E. and A. Hattori. 1976. Natural abundance of ¹⁵N in particulate organic matter in the North Pacific Ocean. Geochim. Cocomochim. Acta. 40:249-251.