Nutrient Cycling in Agroecosystems **71:** 131–137, 2005.
DOI 10.1007/s10705-004-1925-0

A study of tile drain nitrate – $\delta^{15}N$ values as a tool for assessing nitrate sources in an agricultural region

L.M. Kellman
Environmental Earth Sciences Laboratory, St. Francis Xavier University, Antigonish, Nova Scotia, Canada B2G 2W5; (E-mail: lkellman@stfx.ca; Tel.: (902)867-5086; Fax: (902) 867-2457)

Received 24 October 2003; accepted in revised form 21 July 2004

Key words: Agricultural pollution, Drainage tiles, Fertilizer N, Nitrate contamination, Nitrogen isotopes

Abstract

It is important to evaluate tools which provide insight into nitrate (NO_3^-) contamination source identification in watersheds where multiple nitrogen (N) sources are applied. As nitrate-N stable isotopes have been previously used to identify contaminant sources in groundwater environments, the application of the technique to tile drainage outflow was investigated. Nitrate-N isotopic and concentration analyses of tile drain discharges from six different fields with a range of mineral fertilizer N and hog manure applications were conducted to examine general isotopic patterns and their relation to N fertilizer sources. δ-^{15}N of NO_3^- draining fields were compared to $\delta^{15}N$ source signatures through a single growing season. The objective was to determine: (a) whether tile drainage water exiting fields receiving different N sources (inorganic mineral N, organic hog manure N, or a combination of the two) had distinct $\delta^{15}N$ values, and (b) whether $\delta^{15}N$ signatures of sampled tile drain water fell within expected source ranges. Results suggest that isotopic data differed between fields in a manner consistent with differences in NO_3^- sources, as fields only fertilized with mineral N had $\delta^{15}N$ values consistently lower than fields with hog manure applications. However, all fields showed isotopic values that were enriched in ^{15}N relative to their sources during the study period. Therefore, although these fields are discharging tile drainage water with distinctive isotopic signatures, the data suggests that a quantitative evaluation of individual NO_3^- source contributions is not possible within this watershed. Utilization of this tool in source discrimination in other tile drainage waters should only proceed if it can be demonstrated that isotopic fractionations are not altering source signatures.

Introduction

The excessively high levels of nitrogen (N) sources in intensively cultivated agricultural watersheds leads to elevated levels of nitrate (NO_3^-) in streams, rivers and groundwaters draining these areas (Cooper 1993; Spalding and Exner 1993), a problem that has been linked to infant methemoglobinemia (Rajagopal and Tobin 1989), identified as a contributor to eutrophication of downstream and coastal areas (Cooper 1993), and to the increased release of the greenhouse gas nitrous oxide (Paul and Clark 1996).

The flat nature and soil properties of many areas suited to agriculture, in particular lowlands, often results in engineered tile drainage systems that rapidly discharge water from field surfaces (Southwick et al. 1995; Randall and Iragavarapu 1995). This can in turn result in an increased loading of mobile agrichemicals such as NO_3^- into draining streams and ditches. Rapid export of NO_3^- from fields in the Corn Belt states of the USA via tile drains is thought to account for relatively low groundwater contamination (Spalding and Exner 1993). A rapid export pathway also reduces the residence time of NO_3^- in soils and groundwater

Table 1. Nitrate source isotopic signatures.

Nitrogen source	$\delta^{15}N$‰
Mineral fertilizer N	~1.5‰ (this site; Kellman 1997)
Hog manure organic N	~12.5‰ (this site; Kellman 1997)
Precipitation NO_3^--N	~0.5‰ (this site; Kellman 1997)
Soil organic matter N	~4 to 9‰ (Heaton 1986)

where natural soil removal via denitrification can occur.

Sources of N contamination in surface waters in agricultural regions are generally attributed to the use of mineral N (inorganic N fertilizers), animal waste and other organic residues. Increased atmospheric deposition of nitrogen has also disrupted N-cycles (Murdoch and Stoddard 1992), as has alteration of the natural N-cycle in soils as a result of changing land use and vegetation cover (Olof-Tamm 1991). Investigations of NO_3^- contaminant sources can be complicated in areas where multiple sources of N are applied to agricultural fields; the result is often a patchwork of fields with alternating application sources, and/or fields where more than one source is used.

It would be desirable to be able to distinguish between inorganic and organic N contributions in order to better evaluate contamination from various sources in the field setting and to provide guidelines to control such contamination. Use of a standard mass balance approach in areas with multiple N sources does not allow discrimination between NO_3^- originating from each source. However, stable isotopes of N in NO_3^- ($^{15}N/^{14}N$) have been used in groundwater studies to evaluate NO_3^- sources (Wells et al. 1989; Aravena 1993; Komor and Anderson 1993) as NO_3^- originating from inorganic fertilizers has an isotopic composition that is distinct from that of NO_3^- originating from animal wastes (Table 1). In the mineralization of soil organic matter N, the net δ^{15} of the resulting NO_3^- will be the same as that of the original organic N, with N-fixing plants having values at the lower end of this range (Table 1). Nitrate in precipitation typically has low $\delta^{15}N$ values (Heaton 1986). The $\delta^{15}N$ values of NO_3^- are retained during transport unless it undergoes a removal via microbial denitrification, resulting in an upward shift (enrichment) in $\delta^{15}N$ values (Mariotti et al. 1982; Mariotti 1986; Kellman and Hillaire-Marcel 1998; Kendall 1998; Kellman and Hillaire-Marcel 2003).

An investigation of NO_3^- N stable isotopes in surface water sources of an agricultural watershed in Eastern Canada (Kellman and Hillaire-Marcel 1998; Kellman and Hillaire-Marcel 2003) pointed to complications as a result of fractionations that altered original source signatures during N cycling processes. Transport via tile drains, however, provide a mechanism for rapidly moving water and leached NO_3^- from field surfaces and therefore may avoid this complication. Here NO_3^- concentrations and N-isotropic signatures of tile drain water exiting agricultural fields in the St. Lawrence Lowlands of Eastern Canada with various N-fertilizer applications were measured over a six month period encompassing the growing season. δ-^{15}N of NO_3^- draining fields was compared to $\delta^{15}N$ source signatures in order to determine: (a) whether tile drainage water exiting fields receiving N from different sources (inorganic fertilizer N, organic hog manure N, or a combination of the two) had distinct $\delta^{15}N$ values, and (b) whether δ^{15} N signatures of sampled tile drain waters fell within expected source ranges.

Study site and methods

This study was situated at an agricultural watershed draining into the St. Lawrence River of southern Quebec, Canada where applications of both mineral N and liquid hog manure of fields has generated interest in determining the extent to which each source is responsible for the loading of nitrate in major rivers (Simoneau and Grimard 1989). This area of study is typical of large agricultural areas in Canada and the St. Lawrence Lowlands in particular, where these types of fertilization practices are common.

The drainage stream where this investigation was carried out is located in the l'Assomption River Basin, about 70 km NE of Montreal. The site is typical of the temperate maritime agro-ecological zone within the St. Lawrence Lowlands, a low lying area with a Paleozoic carbonate bedrock that is overlain by glacial sediment and post-glacial marine clays. Fertile poorly drained soils are characteristic of this area and use of tile drainage is common. The drains at this site lie 70–100 cm below field surfaces, and are located above a clay lens. Soil texture is classified as sandy clay loam (Ste. Rosalie), and fields are conventionally tilled. The 30-year normal precipitation during the May-November period averaged 503 mm in the region.

A regular spraying with liquid hog manure takes place in early May (prior to planting) and in late September (following harvesting) on a subset of the fields at a rate of approximately 33,200 l ha^{-1}. Applications of inorganic nitrogen fertilizers (NPK of varying proportions) are also widespread, with application rates in the study year and previous year ranging from 116 kg ha^{-1} (27-0-0) to 380 kg ha^{-1} (17-17-20). Although crops grown on individual field vary from year to year, the types of fertilizers applied to individual fields tend to be consistent from year to year. Therefore fields with no hog manure application during the period of this study have no history of such applications in previous years. Similarly, fields were fertilized with mineral N fertilizer consistently from year to year. For the purposes of this study, all inorganic fertilizer N was treated as having a similar isotopic composition as isotopic differences between types of inorganic fertilizer N would be minor (Heaton 1986). Detailed monitoring of stream responses to individual rain events were shown to produce elevated concentrations of nitrate in stream waters at the site (Kellman 1997).

Figure 1 shows a schematic map of the field and tile drain locations. Seven tile drains (identified as D1, D2, D4, D5, D6, D7 and D8) draining six different fields were sampled regularly during the 1996 growing season from May to September when flowing. Only D4 was sampled the previous year (Kellman 1997). Specific type, placement and ages of the tile drains resulted in much more restricted flow from some drains than others. Drains D1, D2, D7 and D8 were relatively new plastic drains, while D4, D5 and D6 were older drains with metal outlets. As most tile drains only flowed following precipitation events, most samples were obtained within several days of a precipitation event at the site. Tile drains D5 and D4 in particular flowed for longer periods than the rest and were therefore sampled more frequently. Water in D6 tended to pool inside the drain outlet rather than exit it during low flow periods; during these times, water was sampled from this pool. The outlet of tile drain D8 was often submerged in the stream, limiting sampling.

Table 2 lists the crops and fertilizers applied to these fields during the 1995 and 1996 growing seasons. Specific types and applications of mineral inorganic N are identified below for the 1996 growing season. Applications were similar in the previous year (1995). Tile drains D1 and D2 draining fields F2D and F2C respectively, were both cropped with a N-fixing plant, and treated with an inorganic fertilizer N (46-0-0). Tile drain D6, draining field F2A, was cropped with a non-N-fixing plant and fertilized only

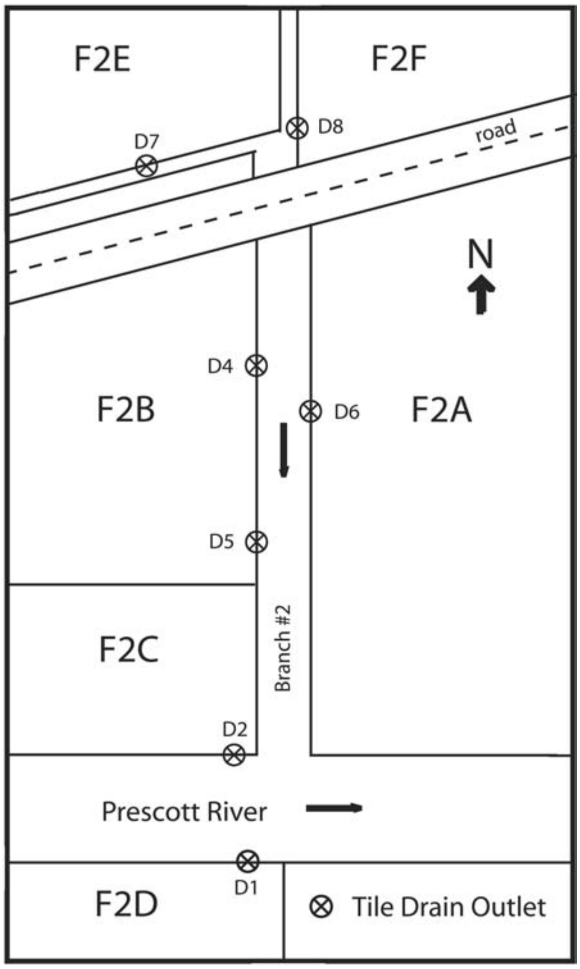

Figure 1. The relative positions of fields described in Table 1 and locations of tile drain outlets along streams and drainage ditches at the study site.

with mineral N (240 kg ha^{-1} 23-0-30; 200 kg ha^{-1} 10-31-10). Tile drains D4 and D5 drained the same field, F2B, which was fertilized with hog manure in the spring and previous fall and cropped with several strips of differing plants, one of which had inorganic fertilizer N applied (260 kg ha^{-1} 17-17-20). Tile drain D7, draining field F2E, was fertilized with hog manure the previous fall only, and had several strips of crops with some mineral N applied (380 kg ha^{-1} 17-17-20 and 116 kg ha^{-1} 27-0-0). Tile drain D8, drained field F2F which was fallow, and only fertilized with hog manure the previous fall.

To ensure sufficient nitrate-N recovery for isotopic analysis, 1 litre samples were collected from all tile drains for NO_3^- concentration and isotopic analysis. Samples were stored on ice immediately after collec-

Table 2. Field N application information for 1995 and 1996 (see text for more detailed application rates).

Field	Tile drain	1996 Crop	Hog manure applied	Fertilizer N applied
F2A	D6	Corn	No	Yes
F2B	D4 and D5	Barley	1995	No
		Beets	1995	Yes
		Carrots	1995	Yes
		Cabbage	1996/1995	No
F2C	D2	Soya (N-fixing)	No	Yes
F2D	D1	Soya (N-fixing)	No	Yes
F2E	D7	Barley	1995	No
		Carrots	1995	Yes
		Beets	1995	Yes
F2F	D8	Fallow	1995	No

tion, filtered in the lab within hours of sampling, and NO_3^- concentrations analyzed on an Autoanalyzer using the cadmium reduction method.

The isotopic signature of nitrogen is expressed as,

$$\delta^{15}N(0/00) = \left[\frac{^{15}N/^{14}N_{\text{sample}}}{^{15}N/^{14}N_{\text{standard}}} - 1 \right] \cdot 1000 \qquad (1)$$

where ^{14}N and ^{15}N are the two stable isotopes of N (abundance of $^{14}N \ggg {}^{15}N$) and the standard is atmospheric N_2. The method used for extraction of NO_3^--N for isotopic analysis from water samples was that of Silva et al. (2000). Nitrate was collected on anion exchange resins and further concentrated by freeze-drying before combustion of solid N to N_2 (Mariotti et al. 1982). In order to minimize measurement errors, attempts were made to ensure each sample contained at least 2 mg of N. Depending upon the mass of NO_3^- collected, duplicate and single samples were analyzed on a VG PRISM dual inlet, triple collector mass spectrometer. Instrumental precision is 0.02‰, with an overall analytical uncertainty as determined using KNO_3^- amended spring water with similar specific ion concentrations as sample waters of 0.2‰. Further details are provided in Kellman (1997). Nitrate concentrations and $\delta^{15}N$ values from each drain were plotted as time series for the period of observation, and averaged individual tile drain $\delta^{15}N$ values for the entire sampling period compared.

Results

The time series for all NO_3^--$\delta^{15}N$ values and NO_3^- concentrations, sampled from May to October during the 1996 growing season are shown in Figure 2a. Nitrate concentration trends were variable, although individual drains tended to be consistently high or low. Tile drain D8 had the lowest concentrations, while D7 was slightly more elevated. Drains D1 and D2 fell in the mid-range of the samples, with D4, D5 and D6

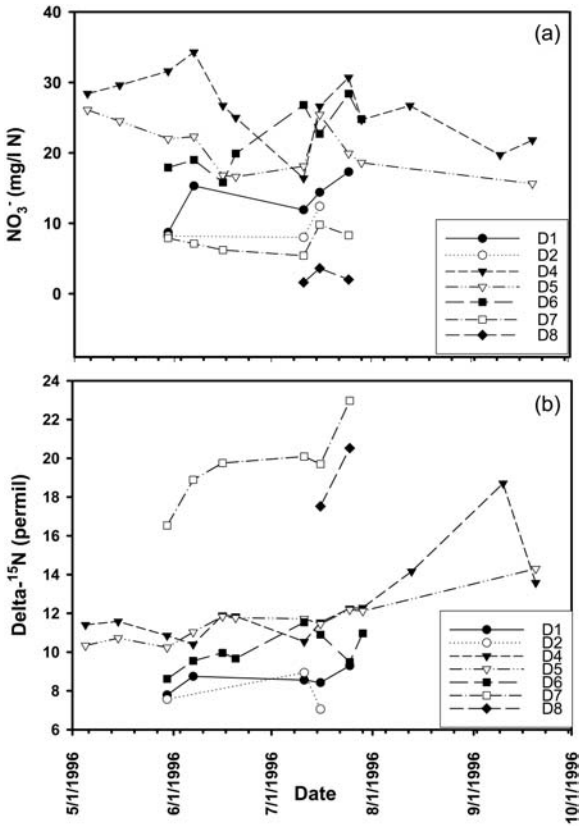

Figure 2. The 1996, May to October temporal series of tile drain discharge. (a) NO_3^- concentration and (b) NO_3^--$\delta^{15}N$ values for tile drains D1, D2, and D4 to D8. Dates are marked as month/day/year.

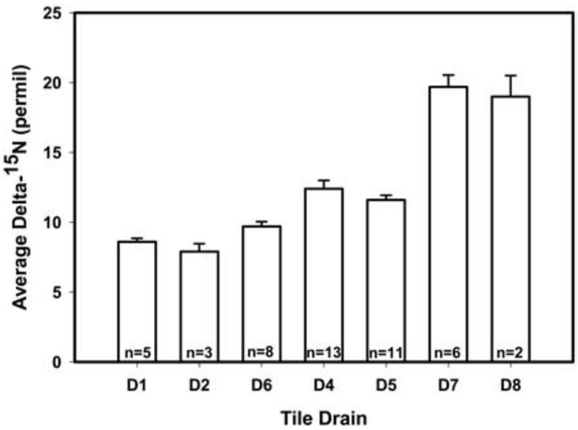

Figure 3. Average 1996 $\delta^{15}N$ values of NO_3^- from tile drains D1, D2, D6, D4, D5, D7 and D8. Note that the sequence of tile drain data in this figure follows the general order of expected $\delta^{15}N$ sources from low to high.

consistently the most elevated. On individual sampling dates a difference of up to or exceeding 10 mg/l N was observed between the tile drains below field F2B, D4 and D5.

The $\delta^{15}N$ results are also clearly different for individual fields (Figures 2b and 3). Generally, tile drains below fields to which only fertilizer mineral N was applied (D1, D2 and D6) had lower $\delta^{15}N$ values at any given time than those below fields to which hog manure was applied (D4, D5, D7 and D8). Tile drains D7 and D8 always exceeded the hog manure $\delta^{15}N$ value by at least 4‰. Tile drains D4 and D5 were generally close to the maximum $\delta^{15}N$ source value, exceeding it in August and September. Both of these tiles draining the same field had similar $\delta^{15}N$ values, generally falling within a 1‰ range when samples for both were obtained. The tile drain D4 series, which was the most comprehensive series, also showed the greatest range of $\delta^{15}N$ values. The maximum $\delta^{15}N$ measured at this site was collected on a day when no other drains were flowing; on all other sampling dates, the $\delta^{15}N$ values never exceeded 14.3‰. The sample series of fields with no hog manure applications, D1, D2 and D6, were shorter than for other fields due to insufficient flow later in the season.

Discussion

The data show that the sequence of $\delta^{15}N$ values from tile drains exiting different fields is consistent with what would be expected in terms of source signatures; the fields where NO_3^- source $\delta^{15}N$ values are low have the lowest $\delta^{15}N$ tile drain values and vice versa. As well, fields with similar crops and applications, such as D1 and D2 and tile drains exiting the same field (D4 and D5) have similar $\delta^{15}N$ values. However, the $\delta^{15}N$ values are not consistently within the expected source ranges, but generally exceed them. This suggests that fractionating processes such as denitrification have altered the source signatures.

Tile drains D1 and D2 drain fields with similar crop applications, N-fixing soya, and mineral N. It would be expected that $\delta^{15}N$ values of nitrate should fall in the lower end of the organic N values (Table 2). The observed $\delta^{15}N$ values (from 7–9‰), on the other hand, suggest that either another dominant N-source such as residual organic matter from non-N fixing plants is present, or that NO_3^--$\delta^{15}N$ enrichment has occurred.

The $\delta^{15}N$ values for tile drain D6 are greater than for D1 and D2, which is consistent with non-N fixing crops and mineral N. Again, the $\delta^{15}N$ values are elevated relative to potential sources (organic matter N and mineral N; Table 2), ranging from 8.6–11.5‰ (expected maximum $\delta^{15}N$ close to 9‰). The $\delta^{15}N$ values are most elevated later in the sampling period when samples were taken from the pooling of water inside the drain. Although this may have contributed to an enhanced $\delta^{15}N$ value if water was denitrified while pooled, it is also consistent with increased δ^{15} N values observed in other drains where this problem did not occur.

Tile drains D4 and D5 which drained different parts of the same field (F2B), fertilized with hog manure and mineral N, had $\delta^{15}N$ values below the maximum δ^{15} N source of hog manure (Table 2) for most of the growing season, but higher $\delta^{15}N$ values were observed later in August and September. The overall range was 10.2–18.7‰ (expected maximum δ^{15} N close to 12.5‰) for the two drains, with the maximum value of 18.7‰ measured from D4 at a time when no other tile drains had flow. Other samples never exceeded 14.3‰. During the periods when the $\delta^{15}N$ values were below 12.5‰ in D4 and D5, it is difficult to evaluate whether enrichment of NO_3^--$\delta^{15}N$ was occurring as $\delta^{15}N$ values still fell within the expected source range for this field. Later in the growing season $\delta^{15}N$ of NO_3^- exceeded the maximum $\delta^{15}N$ source in this field, suggesting NO_3^- has been enriched prior to sampling. δ-^{15}N samples from both D4 and D5 sampled on the same dates were generally within 1‰ of each other even during periods when NO_3^- concentrations differed substantially, implying that saturated zone sample $\delta^{15}N$ values were representative of the entire field saturated zone.

Tile drains D7 which drained a field with mineral N and a hog manure application the previous fall only, and D8, which drained a field with a hog manure application the previous fall, had the most elevated $\delta^{15}N$ values observed. In all of these samples, $\delta^{15}N$ values were well in excess of the maximum $\delta^{15}N$ source of 12.5‰, pointing to an enrichment of the NO_3^- pool prior to tile drain sampling. The elevated D8 $\delta^{15}N$ samples which could only have a hog manure or organic matter N source (expected maximum $\delta^{15}N$ close to 12.5‰) suggest that enrichment of residual hog manure provides an elevated background signal. Although NO_3^- concentrations are low relative to all other tile drains at 1.6–3.6 mg/l N, they remain well above natural levels expected for a non-fertilized field, indicating that previous applications did still play a role in contributing NO_3^- to the drainage waters. The elevated δ^{15} N values from both drains D7 and D8 with only residual hog manure and no new hog manure applications in 1996, suggest that isotopic enrichment of hog manure N may be an important contributor to the $\delta^{15}N$ values of NO_3^- in subsequent years. This may provide some insight into $\delta^{15}N$ values observed at field F2B drained by D4 and D5, as it suggests that any fields with regular hog manure applications probably have a residual elevated $\delta^{15}N$ signature raising $\delta^{15}N$ values above those expected for current year hog manure and mineral N values.

Conclusions

The $\delta^{15}N$ values of NO_3^- in tile drainage waters showed a pattern of distinct differences in drainage waters of fields with different N source contributions. Fields cropped with N-fixing crops and fields with only mineral N fertilizers applied had $\delta^{15}N$ values well below fields subjected to regular hog manure applications. This points to distinct N-isotopic signatures in tile drainage waters of fields with different N-sources. However, in order to allow relative contributions of N contamination sources to be quantified, $\delta^{15}N$ values must fall within expected source ranges. Since the $\delta^{15}N$ values of tile drain water existing fields in this study were consistently elevated above source signatures, it appears that evaluation of NO_3^- source contributions is not possible at this site. Although this suggests that N isotopes should not be used as a tool in nitrate contaminant source identification in tile drainage outflow of agricultural watersheds unless it can be clearly demonstrated that fractionation of the nitrate pool is not occurring, it also points to the potential utility of this technique in investigations of fractionation processes in drainage waters.

Acknowledgements

This research was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). Comments of MCK, HB and several anonymous reviewers are gratefully acknowledged.

References

Aravena R., Evans M.L. and Cherry J.A. 1993. Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems. Ground Water 31: 180–186.

Cooper C.M. 1993. Biological effects of agriculturally derved surface water pollutants on aquatic systems – A review. J. Environ. Qual. 22: 402–408.

Heaton T.H.E. 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review. Chem. Geol. (Isotope Geosciences Section) 59: 87–102.

Kellman L.M. and Hillaire-Marcel C. 2003. Evaluation of nitrogen isotopes as indicators of contamination sources in an agricultural watershed. Agric. Ecosyst. Environ. 95: 87–102.

Kellman L. and Hillaire-Marcel C. 1998. Nitrate cycling in streams: Using natural abundances of NO_3^--$\delta^{15}N$ to measure in-situ denitrification. Biogeochemistry 43: 273–292.

Kellman L.M. 1997. Surface water nitrate contamination: Monitoring sources and biogeochemical transformations using $^{15}N/^{14}N$. Ph.D. Dissertation, University of Quebec in Montreal, Canada.

Kendall C. 1998. Tracing nitrogen sources and cycling in catchments. In: Kendall C. and McDonnell J.J. (eds), Isotope Tracers in Catchment Hydrology. Elsevier Science, Amsterdam, The Netherlands, pp. 519–576.

Komor S.C. and Anderson H.W. Jr. 1993. Nitrogen isotopes as indicators of nitrate sources in Minnesota sand-plain aquifers. Ground Water 31: 260–270.

Mariotti A. 1986. La denitrification dans les eaux souterraines, principes et methodes de son identification: Une revue. J. Hydrol. 88: 1–23.

Mariotti A., Germon J.C. and Leclerc A. 1982. Nitrogen isotope fractionation associated with the NO_2^--N_2O step of denitrification in soils. Can. J. Soil. Sci. 62: 227–241.

Murdoch P.S. and Stoddard J.L. 1992. The role of nitrate in the acidification of streams in the Catskill Mountains of New York. Water Resour. Res. 28: 2707–2720.

Olof-Tamm C. 1991. Nitrogen in Terrestrial Ecosystem. Springer-Verlag, Heidelberg, Germany.

Paul E.A. and Clark F.E. (eds) 1996. Soil Microbiology and Biochemistry. Academic Press Inc., New York.
Rajagopal R. and Tobin G. 1989. Expert opinion and ground-water quality protection: the case of nitrate in drinking water. Ground Water 27: 835–847.
Randall G.W. and Iragavarapu T.K. 1995. Impact of long-term tillage systems for continuous corn on nitrate leaching to tile drainage. J. Environ. Qual. 24: 360–366.
Silva S.R., Kendall C., Wilkinson D.H., Ziegler A.C., Chang C.C.Y. and Avanzino R.J. 2000. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. J. Hydrol. 228: 22–36.
Simoneau M. and Grimard Y. 1989. Qualité des eaux du bassin de la Rivière L'Assomption 1976-1987. Direction de Qualité du Milieu Aquatique. Ministère de L'Environnement du Québec. EMA88-31, 234 pp.
Southwick L.M., Willis G.H., Johnson D.C. and Selim H.M. 1995. Leaching of nitrate, atrazine, and metribuzin from sugarcane in southern Louisiana. J. Environ. Qual. 24: 684–690.
Spalding R.F. and Exner M.E. 1993. Occurrence of nitrate in groundwater: A review. J. Environ. Qual. 22: 392–402.
Wells E.R. and Krothe N.C. 1989. Seasonal fluctuation in $\delta^{15}N$ of groundwater nitrate in a mantled karst aquifer due to macropore transport of fertilizer-derived nitrate. J. Hydrol. 112: 191–201.