Evaluation of contamination sources of groundwater NO_3^- using nitrogen isotope data: A review

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ABSTRACT: It has been accepted that variations in stable N isotope ratios ($^{15}N/^{14}N$) can potentially provide useful, sometimes unique, information on the sources of nitrate in groundwater, because N isotope compositions are generally different among various N pools such as atmospheric N_2, soil, chemical fertilizer, and manure. However, this review strongly suggests that interpretation of the nitrate source based on a single measurement of $\delta^{15}N$ may not be accurate because the isotopic composition of groundwater nitrate is a function of its source and any isotope fractionation that may occur during its generation or transport to groundwater. This review, therefore, shows that to evaluate the nitrate contamination source using $\delta^{15}N$ technique, it is more reasonable to use correlation between the concentrations and $\delta^{15}N$ of NO_3^-. For example, a positive correlation indicates ^{15}N-enriched source such as manure, while ^{15}N-depleted source results in a negative correlation. The correlation analysis can also be used in evaluation of denitrification and nitrification. Denitrification is a key process affecting $\delta^{15}N$ of NO_3^-, i.e. if significant amount of nitrate is removed through denitrification, it is not easy to discriminate fertilizer-derived nitrate from manure- or compost-derived one because denitrification increase the $\delta^{15}N$ of the remaining NO_3^-. Therefore, it is important to assess whether denitrification may be occurring or not when evaluating isotope data on nitrate. By using dual ($\delta^{15}N_{AIR}$ and $\delta^{18}O_{VSMOW}$) isotopic indicators, denitrification can be evaluated more accurately.

Key words: contamination source, groundwater, isotopic fractionation, nitrate, nitrogen isotope composition

1. INTRODUCTION

Natural level of groundwater nitrate originating from soil nitrogen is very low (Yoo et al., 1999a). Now, however, nitrate contamination in water system is a serious environmental problem world wide caused by anthropogenic activities, such as intensive land usage and the employment of N fertilizer in agriculture. Nitrate in drinking water can pose a health hazard causing methemoglobinemia (Ridder and Oehme, 1974), and the ingestion of water containing high concentrations of nitrate may cause chronic toxicity and possible developments of cancer from nitrosamines (Low, 1974). Groundwater survey showed that nitrate is a common contaminant with its concentration exceeding the national drinking water standards of 10 mg NO_3–N L^{-1} at numerous locations in Korea (Choi, 1994; Choi et al., 2000). Unlike

the confined aquifer, the water quality of unconfined aquifer is affected easily by the activities above aquifer because unconfined groundwater is recharged directly by precipitation from surface (Boulding, 1995). To prevent groundwater quality from nitrate contamination, the origin of nitrate in groundwater should be understood and corrective measures must be taken to prevent or minimize further contamination.

It has been accepted that variations in stable N isotope ratios ($^{15}N/^{14}N$) can potentially provide useful, sometimes unique, information on the sources of N used by plants and fluxes of N in agro-ecosystems since N isotope compositions are different among various N pools such as atmospheric N_2, soil, chemical fertilizer, and manure (Selles and Karamanos, 1986; Choi, 2002). Since the application of fertilizers and/or the influence of animal or sewage wastes contribute to the concentration of nitrate in rural groundwater, the natural abundances of the stable N isotope of NO_3^- are also commonly used in estimating the origins of nitrate in groundwater (Flipse and Bonner, 1985; Wells and Krothe, 1989; Feast et al., 1998). In Korea, several researches have been conducted to elucidate sources of nitrate contamination of groundwater in Cheju (Oh and Hyun, 1997), Kyonggi (Yoo et al., 1999a, 1999b), Kyoungnam (Min et al., 2002), and Kangwon province (Choi et al., 2002a) by analysis of nitrogen isotope ratio.

A major difficulty associated with the use of N isotope ratio to assess the origins of N is that the ^{15}N is not a conservative tracer of N source since the ^{15}N content of N-compounds in soil-plant system usually varied during N transformation accompanied by isotope fractionation (Delwiche and Steyn, 1970; Mariotti et al., 1981; Choi et al., 2002b). For instance, since ^{14}N is preferentially incorporated into nitrate during nitrification, the product (NO_3^-) is depleted in ^{15}N compared with the substrate (Mariotti et al., 1981). In contrast, denitrification results in a marked enrichment in the ^{15}N content of the remaining NO_3^- (Choi et al., 2001). However, variations in ^{15}N content of specific N-compounds, such as NH_4^+, NO_3^-, and organic N resulting from isotope fractionation can be used as indicators of the kind and magnitude of reaction occurred in a system. This is possible since N concentration and natural ^{15}N content of the N-compounds vary

depending on the extent and magnitude of specific reactions such as mineralization, nitrification, and denitrification (Högberg, 1997). Thus it is now concluded that the natural ^{15}N abundances of N ($\delta^{15}N$) in specific sinks, such as soil, plant, and groundwater, are the integrated results of interactions between N sources and N isotope fractionations (Robinson, 2001). This conclusion strongly suggests that since the isotopic composition of groundwater nitrate is a function of its source and any isotope fractionation that may have occurred during its generation or transport to groundwater, the origin of nitrate must be estimated in the context of the entire N cycle. In this paper, we attempt to review various application methods of $\delta^{15}N$ technique in estimating NO_3^- contamination source based on the both $\delta^{15}N$ of source and N isotopic fractionations.

2. $\delta^{15}N$ OF NITRATE SOURCES

Ammonia-based fertilizers are synthesized from NH_3 industrially produced through the so-called Harber–Bosch process. Since the reactant for the NH_3 is atmospheric N_2, the $\delta^{15}N$ values of fertilizers are close to 0‰. Generally, it is known that $\delta^{15}N$ values of chemical fertilizers are between −8 and +6.2‰ (Wassenaar, 1995) with 90% of the samples ranging from −3‰ to +2‰. Flipse and Bonner (1985) have suggested that difference in ^{15}N content among fertilizers are generally a result of fractionation during subsequent processing of the N fixed by the Haber-Bosch process.

Livestock manure and its compost have higher ^{15}N content than chemical fertilizers (Kreitler, 1975; Wassenaar, 1995) due to faster loss of ^{14}N than ^{15}N during ammonia volatilization (Kerley and Jarvis, 1996). Wassenaar (1995) has reported that the $\delta^{15}N$ values of turkey manure and poultry manure were +8.6 and +8.1‰, respectively. Gaebler et al. (1966) showed that proteins become enriched in ^{15}N relative to the isotope composition of the ingested amino acids. Myaka and Wada (1967) have also observed a gradual enrichment in ^{15}N with higher trophic levels of marine organisms. The average $\delta^{15}N$ of total N of phytoplankton and seaweed was +7‰, whereas the average $\delta^{15}N$ of zooplankton and fish was +10 and +15‰, respectively. As the organisms of higher trophic levels ingest the organisms of lower levels, the protein of higher levels of the food chain becomes enriched in ^{15}N. Therefore, excreted N would have to be isotopically lighter to maintain an isotope mass balance. Gormly and Spalding (1979) have shown that the isotopic composition of fresh animal excrement is not usually distinct from $\delta^{15}N$ values of the typical soil- or fertilizer-derived nitrate and that the average $\delta^{15}N$ values for cow and pig excrement ranged between +1.7 and +4.8‰. Because urea accounts for about 50% of the excreted manure N (70% excreted N is in urine, and 70% urine N is in urea), most of the ammonia from urea hydrolysis may be volatilized depending on various factors, such as temperature, air

speed, and moisture content (Kreitler, 1975). Since the isotopic fractionation factor associated with ammonia volatilization is greater than 1.02, the volatilization can result in high $\delta^{15}N$ of residual NH_4^+ under substrate-limited condition. Kreitler (1975) has collected and analyzed gaseous ammonia samples from urine-soaked soils in barnyards. The ammonia samples were consistently isotopically light (about −21‰), and the $\delta^{15}N$ of residual N was approximately +14‰. Using the values, −21 and +14‰, with some simple assumptions, Kreitler (1975) has calculated the $\delta^{15}N$ of the original urea in the excreted N as −3.5‰. Although the $\delta^{15}N$ data on composted manure are rare, the composts are also expected to be enriched in ^{15}N. Recently, Choi (2002) reported that $\delta^{15}N$ of composted manure ranged from +10.0 to +20.9‰ (Table 1).

However, the difference in $\delta^{15}N$ of source-N may become either smaller or greater because of the isotopic fractionation during transport to the aquifer. Once incorporated into soils, N participates in various transformation reactions such as immobilization, nitrificaiton, and denitrification. As seen in Table 2, each step in the N cycle results in isotope

Table 1. Nitrogen isotope composition of chemical fertilizers, composted manures, and manure slurry.

Sample	$\delta^{15}N$ (‰)
Chemical fertilizer (Total-N)	
Number of samples	8
Mean	−1.6±1.5
Range	−3.9 ~ +0.5
Composted manure (Total-N)	
Number of samples	27
Mean	+17.4±1.2
Range	+10.0 ~ +20.9
Manure slurry (Inorganic N)	
Human manure	+11.8
Pig manure	+10.3
Cow manure	+7.2

Data from Choi (2002).

Table 2. Nitrogen isotopic fractionation factors, $\alpha_{s/p}$, for various processes in the N cycle. Data largely from compilations by Hübner (1986) and Handley and Raven (1992).

Process	α[a]
N mineralization (org N→ NH_4^+)	≈ 1.000
Diffusion of NH_4^+, NH_3, NO_3^- in solution	≈ 1.000
Nitrification	1.015~1.035
Denitrification	1.000~1.033
NH_3 volatilization	1.025~1.027
N assimilation	1.000~1.020
	(mainly below 1.002)
N_2 fixation	0.998~1.002
Metabolic steps in plants	0.980~1.020

[a]The values give an overview and omit some exceptional values.

fractionation and the isotopic differences between substrate and product are thought to be 10–30‰ or more, with the reactant enriched in ^{15}N (Hübner, 1986; Handley and Raven, 1992). Therefore, alteration of the $\delta^{15}N$ of NO_3^- by isotopic fractionation should be taken into consideration for more reasonable usage of $\delta^{15}N$ signature in source identification of groundwater nitrate.

3. APPLIATION OF $\delta^{15}N$ TECHNIQUE

3.1. Source Identification Based on the Concentration and $\delta^{15}N$ of Nitrate

Despite the potential for significant alteration of isotopic signatures during transformation of nitrogenous compounds, many hydrogeological investigations report that distinctions between groundwater nitrate derived from animal or human waste and that derived from agricultural sources, such as inorganic fertilizers or mineralized soil organic N, can be made on the basis of $\delta^{15}N$ values. The widely accepted $\delta^{15}N$ ranges are between -3 and $+5‰$ for chemical fertilizers, between $+5$ and $+8‰$ for natural soil nitrate, and between $+8$ and $+20‰$ for human or animal manure nitrate (Iqbal et al., 1997; Choi et al., 2002a). Therefore, a rough classification of NO_3^- contamination source is possible by single measurement of the $\delta^{15}N$ of nitrate.

Figure 1 shows a typical distribution of the concentration and $\delta^{15}N$ of groundwater nitrate derived from each contamination source. When the N concentration is consistently lower than 3 mg L^{-1} and the corresponding $\delta^{15}N$ range from $+5$ to $+8‰$, the nitrate source can be assumed to natural soil-N, indicating the groundwater is not contaminated. For groundwater affected by manure-derived nitrate, the higher NO_3^-–N concentrations over 3 mg L^{-1} and the $\delta^{15}N$ value above $+8‰$ should be observed. Kreitler (1975), Gormly and

Fig. 1. A typical distribution of the concentration and $\delta^{15}N$ of groundwater nitrate from each source. A and B are denitrification zone and C is incomplete nitrification zone.

Spalding (1979), and Heaton (1984) reported that the $\delta^{15}N$ of nitrate in groundwater contaminated with animal waste as point sources in the vicinity of barnyards and cattle watering wells ranged from $+10$ to $+22‰$. Kreitler and Browning (1983) also reported that the high $\delta^{15}N$ values of nitrate were observed due to a non-point source associated with septic tank effluent. On the other hand, fertilizer-derived nitrate will decrease the $\delta^{15}N$ value to $<+5‰$, while increase the NO_3^-–N concentration over 3 mg L^{-1}. If the two contamination sources affected the groundwater quality concurrently, the $\delta^{15}N$ of nitrate may show intermediate value.

However, interpretation of the nitrate source based on the single measurement of $\delta^{15}N$ may not provide accurate information on the nitrate source because both the N isotopic fractionation and the mixing of nitrate from different sources cause deviation of the $\delta^{15}N$ value from the original value of the source. For example, fertilizer-derived nitrate may show higher $\delta^{15}N$ than the source through either denitrification or ammonia volatilization. In a survey of soils from Texas that were predominantly fertilizer influenced, Kreitler (1975) noted a difference of 2 to 3‰ between the fertilizers used and underlying groundwater nitrate caused by volatilization of ammonia following fertilization, leaving the residual ammonium enriched in ^{15}N. Townsend et al. (1996) have observed that groundwater in sandy soils area treated with fertilizer had NO_3^-–N above 10 mg L^{-1} with the $\delta^{15}N$ values of $+3$ to $+7‰$. Incomplete nitrification of manure-derived NH_4^+ may also result in lower $\delta^{15}N$ of NO_3^- than that of original source. In addition, the mixing of nitrate from several sources with different N isotopic composition may result in intermediate $\delta^{15}N$ value (Iqbal et al., 1997).

Therefore, it is difficult to expect that the $\delta^{15}N$ data fall into a critical range for each contamination source, because the consistent $\delta^{15}N$ of groundwater nitrate according to each contamination source as seen in Figure 1 is very rare case. Fluctuation of the $\delta^{15}N$ value is more usual case, especially for unconfined groundwater in rural area where complex contamination-sources exist and loading pattern of pollutants varies with season (Iqbal et al., 1997). For this case, a correlation between the concentration and $\delta^{15}N$ of NO_3^- in samples collected from various well in a study area can provide meaningful information on the contamination source (Choi et al., 2002a; Min et al., 2002). For example, it is more plausible to assume that a dominant contamination source is manure-N when $\delta^{15}N$ is positively correlated to the concentrations of nitrate (Fig. 2), i.e. the effect of manure-N on groundwater quality is greater than that of other sources, such as soil-N and fertilizer-N. Min et al. (2002) also observed a positive correlation between the two parameters and suggested that $\delta^{15}N$ of NO_3^- increased with increasing the effect of manure-N. In contrast, a negative correlation between the two parameters indicates that fertilizer-N affected the groundwater quality dominantly (Choi et al., 2002a). Kohl et al (1971) and Iqbal et al. (1997) also observed that decrease in
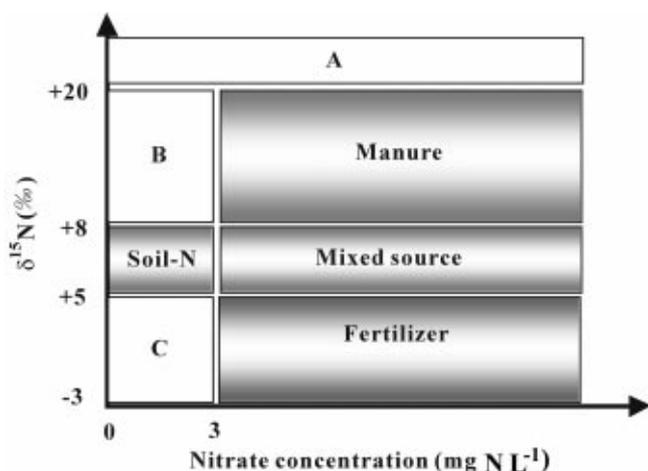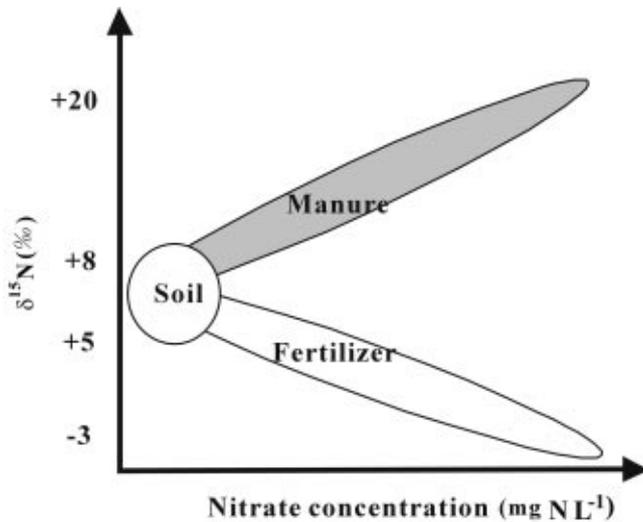
Fig. 2. General correlation patterns between the concentration and $\delta^{15}N$ of groundwater nitrate as affected by manure and fertilizer.

the $\delta^{15}N$ of NO_3^- correlated with the increase in nitrate concentration and they attributed the negative correlation to increased contributions of fertilizer to the background levels of soil-derived nitrate. These correlations would be more apparent when denitrification is negligible and groundwater quality is affected largely by a single contamination source.

3.2. Estimation of the Relative Contribution of the Dual Sources

Since land-use practices in Korea are very complex, groundwater quality is likely to be affected by the dual contamination sources (fertilizer and manure) concurrently. For that reason, several researches (Oh and Hyun, 1997; Yoo et al., 1999b; Min et al., 2002) have tried to estimate the relative contribution of the dual sources to groundwater NO_3^- using a linear interpolation between the poles representing the dual sources. For this approach, the contribution of soil-N is assumed to be negligible, and establishment of the poles ($\delta^{15}N$ of fertilizer and manure-derived NO_3^-) is critical. Oh and Hyun (1997) took median $\delta^{15}N$ values (0‰ for fertilizer and +14‰ for manure-derived nitrate) reported in other literatures as the poles. However, it is more plausible to take the lowest and the highest $\delta^{15}N$ values observed in a target groundwater or study area as the $\delta^{15}N$ of NO_3^- from fertilizer and manure, respectively, because the extent and magnitude of N isotopic fractionation are site specific depending on the characteristics of upper soil and vadose zone. For example, Yoo et al. (199b) took −1.5‰ for fertilizer-derived and +20.8‰ for manure-derived nitrate and observed that the contribution of manure-derived nitrate to the concentrations of groundwater nitrate decreased with increasing distance from a livestock feedlot from 79 to 44%. Min et al. (2002) assumed that most ^{15}N-depleted (+4.3‰) and enriched

(+19.9‰) values represented nitrate originated from two distinct sources. However, since the intrinsic $\delta^{15}N$ of NO_3^- from the dual sources would show spatial and temporal variations, the relative contribution of the dual sources calculated using a linear interpolation should be considered as a qualitative estimation.

3.3. Seasonal Variations in $\delta^{15}N$ of NO_3^-

Agricultural practices and precipitation pattern vary with season and thus the kind and amount of pollutant loading are likely to change seasonally. Therefore, long-term investigation on changes in the concentration and $\delta^{15}N$ of NO_3^- is necessary to evaluate the effect of contamination source on groundwater quality more precisely (Yoo et al., 1999b; Choi et al, 2002a). Wells and Krothe (1989) investigated the seasonal variations in $\delta^{15}N$ of groundwater nitrate during wet climatic periods and observed that fertilizer-derived nitrate was rapidly transported downward by macropore flow below the root zone into sediments with low denitrifying capacity, resulting in low $\delta^{15}N$ of groundwater nitrate. On the other hand, Iqbal et al. (1997) observed increased $\delta^{15}N$ of NO_3^- during a dry climate period due to an increased soil residence time that allowed for enhanced crop uptake of NO_3^- prior to leaching. However, Yoo et al. (1999a) observed that the $\delta^{15}N$ of NO_3^- (+8.9 to +11.7‰) in groundwater beneath paddy fields treated with chemical fertilizer did not show any significant variations with season due to consistent denitrification under water-saturated conditions. Similarly, they also reported that most samples collected from groundwater under the effect of livestock manure showed no consistent seasonal-variations in $\delta^{15}N$ of NO_3^-, with the values over +10.4‰.

However, in an area with complex contamination sources (fertilizer and manure), the $\delta^{15}N$ of groundwater NO_3^- would show a characteristic seasonal-pattern depending on fertilization, irrigation, and precipitation. Recently, Choi et al. (2002a) observed different pattern of nitrate contamination between wet (April to September) and dry (October to March) seasons through monitoring the concentration and $\delta^{15}N$ of NO_3^- in groundwater located in the North Han River basin, Korea. They observed higher $\delta^{15}N$ values over +10‰ and a positive correlation in dry season, suggesting greater effect of ^{15}N-enriched N such as compost and manure than that of ^{15}N-depleted fertilizer on groundwater nitrate. They attributed this result to the reduced loading of nitrate from fertilizer-applied filed as compared with wet season because dry season is a fallow season. Meanwhile, insignificant correlation and median $\delta^{15}N$ in wet season were attributed to accelerated mixing of nitrate originated from two sources showing different $\delta^{15}N$ value.

3.4. Estimation of Nitrification and Denitrification

Correlation between the concentration and $\delta^{15}N$ of nitrate

can also provide information on nitrification and denitrification of an area. Since ^{14}N reacts faster than ^{15}N during nitrification due to isotopic fractionation, incomplete nitrification results in ^{15}N-depleted nitrate (Mariotti et al., 1981). Therefore, preferential inflows of nitrate produced through incomplete nitrification into groundwater result in extremely low N concentrations and δ^{15}N of nitrate as seen in Figure 1 (C zone). With proceeding of nitrification to completion, the concentration and δ^{15}N of nitrate would increase gradually. The slope of regression line would be different depending on the initial δ^{15}N of original source-N, i.e. the final δ^{15}N of nitrate derived from manure-N would be greater than that from fertilizer-N (Fig. 3). Groundwater in an area with coarse-textured soil may not reveal any isotopic indicator of incomplete nitrification because nitrification of NH$_4^+$ under aerobic conditions proceeds quickly to completion with little N isotopic fractionation (Exner and Splading, 1994). However, it would be apparent in water-saturated area such as paddy fields, where nitrification is much slow and nitrate produced from nitrification is likely to diffuse into groundwater. In addition, storm event following fertilization in upland fields may result in considerably low δ^{15}N of NO$_3^-$.

Denitrification can be also inferred from the correlation analysis as shown in Figure 3. Since denitrification is a natural process removing nitrate, evaluation of denitrification in a study area is very important to manage groundwater quality (Wassenaar, 1995; Feast et al., 1998). In area with coarse-textured soil, denitrification may not play an important role in increasing the δ^{15}N of NO$_3^-$ because of aerobic conditions and low contents of electron donors such as organic matter. However, the continuous fine-textured layers can increase the δ^{15}N values to >+15‰ in accordance

with decreasing nitrate concentration as a result of denitrification (Fig. 3) because of low permeability and high contents of organic matter (Iqbal et al., 1997). For example, it has been estimated that as little as 20% of the total nitrate removal by denitrification will result in an increase of 8‰ in δ^{15}N of the remaining nitrate (Heaton, 1984). Therefore, it is plausible to classify the A and B zones of Figure 1 into denitrification zone. In Figure 3, although a negative correlation between the concentration and δ^{15}N of NO$_3^-$ for denitrification is very similar to that of fertilizer-derived N in Figure 2, the intercept of the regression line for denitrification would be considerably higher than that for fertilizer-derived N.

Denitrification can be also evaluated directly by using dual (δ^{15}N$_{AIR}$ and δ^{18}O$_{VSMOW}$) isotopic indicators as suggested by Aravena and Robertson (1998), who demonstrated that the heavy isotopes, ^{15}N and ^{18}O, become concurrently enriched in the residual NO$_3^-$ pool during microbial denitrification. In general, nitrate formed by nitrification in soils have δ^{18}O values between −2 and +6‰. If denitrification is the main process for NO$_3^-$ removal, ^{15}N and ^{18}O should become progressively more enriched as NO$_3^-$ depletion proceeds as shown in Figure 4. For example, Mengis et al. (1999) reported that δ^{18}O and δ^{15}N of NO$_3^-$ increased concurrently from 0 to +20‰ and +5 to +30‰, respectively, as a result of denitrification. Aravena and Robertson (1998), Cey et al. (1999), and Mengis et al. (1999) observed 1:2.1, 1:1.4, and 1:1.5 relationships between δ^{18}O and δ^{15}N of NO$_3^-$, respectively. These ratios demonstrate the enrichment factor of ^{15}N relative to ^{18}O. However, the δ^{18}O of NO$_3^-$ is also affected by oxygen isotope composition of soil H$_2$O (−15 to −5‰; Mayer et al., 2001), which is incorporated into NO$_3^-$ during nitrification. Enriched δ^{18}O and δ^{15}N values can also be generated by specific N sources, such as manure (Wassenaar,
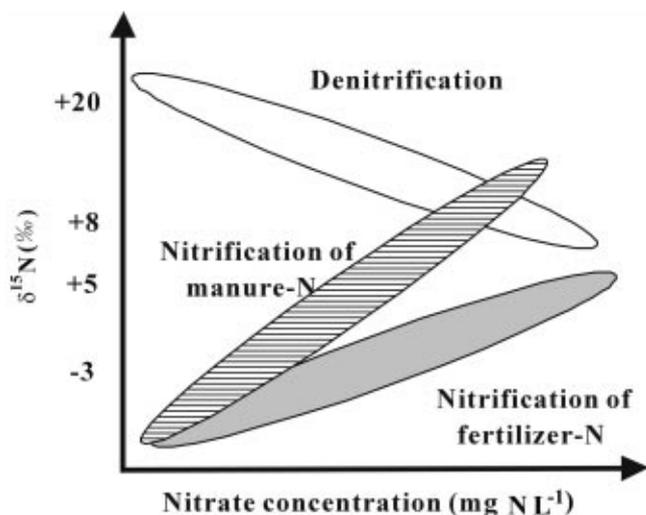
Fig. 3. General correlation patterns between the concentration and δ^{15}N of groundwater nitrate as affected by nitrification and denitrification.
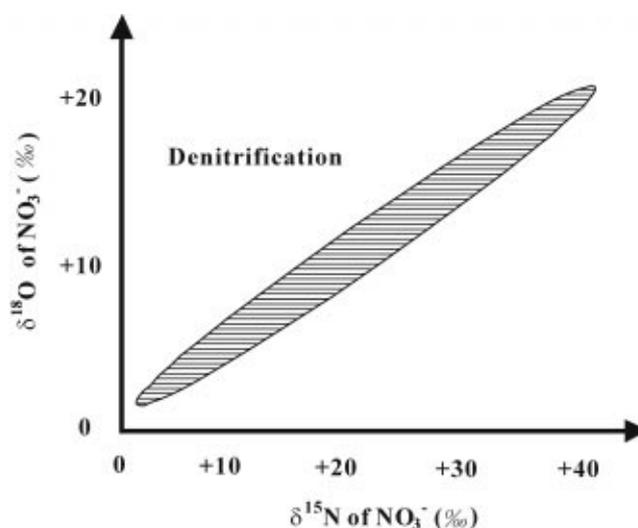
Fig. 4. Concurrent increase in the δ^{15}N and δ^{18}O of groundwater nitrate during denitrification.

1995). In addition, enriched $\delta^{18}O$ are found in inorganic NO_3^- fertilizer (+18 to +22‰) and in nitrate in atmospheric deposition (+30 to +70‰) as reported by Mengis et al. (1999). Therefore, much $\delta^{18}O$ data would be necessary to determine the occurrence of denitrification more precisely.

4. SUMMARY

The $\delta^{15}N$ of groundwater nitrate in rural area can provide information on the contamination source because dominant sources (chemical fertilizer and manure) have different N isotope compositions. However, interpretation of the nitrate source based on the single measurement of $\delta^{15}N$ may not provide accurate information on the nitrate source because the isotopic composition of groundwater nitrate is a function of its source and any isotope fractionation by nitrification and denitrification that may occur during its generation or transport to groundwater. Therefore, the origin of nitrate must be estimated in the context of the entire N cycle.

To evaluate the nitrate contamination source using $\delta^{15}N$ technique, it is more reasonable to use correlation between the concentrations and $\delta^{15}N$. A positive correlation indicates ^{15}N-enriched source such as manure, while ^{15}N-depleted source results in a negative correlation. These correlations would be more apparent when a single contamination source is predominant. Denitrification is a key process affecting $\delta^{15}N$ of NO_3^-, i.e. if significant amount of nitrate is removed through denitrification, it is not easy to discriminate fertilizer-derived nitrate from manure- or compost-derived one because denitrification increase the $\delta^{15}N$ of the remaining nitrate. Therefore, it is important to assess whether denitrification may be occurring or not when evaluating isotope data on nitrate. The correlation approach may also provide an indication of N transformations including nitrification and denitrification. Denitrification would result in a negative correlation with the high intercept $\delta^{15}N$ value over +15‰, while nitrification produce a positive correlation between the concentrations and $\delta^{15}N$ of nitrate. By using dual ($\delta^{15}N_{AIR}$ and $\delta^{18}O_{VSMOW}$) isotopic indicators, denitrification can be evaluated more accurately.

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