

Contamination Source Assessment of Groundwater Nitrate in a Complex Terrain

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Classification of land uses and analysis of nitrogen isotope fractionation in groundwater nitrate were carried out to examine its contamination sources in Jeju province. $\delta^{15}\text{N}$ values of urea (hydrolyzed with urease), ammonium sulfate, compost, water from septic tank were -1.7, -5.8, +14.1, and +24.0 ‰, respectively. Urea, when it was directly distilled, showed -16.5 ‰. Based on these $\delta^{15}\text{N}$ values, sources of nitrate could be classified as originated from chemical fertilizers with $\delta^{15}\text{N}$ values below +5 ‰ and as from animal manure or municipal waste with $\delta^{15}\text{N}$ values over +10 ‰. Results of $\delta^{15}\text{N}$ analysis of 33 wells showed that most wells had the chemical fertilizers as their dominant contamination source. However, some wells were contaminated by other sources: animal wastes or municipal wastes. Some wells were also contaminated by the combined sources of nitrate. It was also demonstrated that $\delta^{15}\text{N}$ analysis could be a useful tool even in the case where no apparent contamination source is found.

Key words: Nitrogen isotope, Chemical fertilizer, Animal manure, Land use, Kinetic isotope effect

Introduction

Groundwater contamination by human activity can be grouped into two classes; point-source and nonpoint-source pollution. Except for known large spills from a specified source, most contamination phenomena in groundwater are classed as nonpoint (Click, 1994). Nonpoint source pollutions are closely related to complex hydro-geologic processes such as precipitation, infiltration, drainage, percolation, seepage, etc. Therefore, an important aspect of nonpoint source is that planning and management practices based on a large area and long term are required to control the source and delivery of nonpoint pollutants, thereby limit them reaching groundwater (Armstrong and Burt, 1993). Most contamination-source assessments rely on apparent land use and land management such as application of fertilizers or irrigation (Evans et al., 1995; Richards et al., 1996; Zhang et al., 1996). However, this usual approach has limitation in Korea because of the complex and intensive land-use activities in complex terrain.

The sources of nitrate contamination in the groundwater include chemical fertilizers, soil organic matter, animal manure and municipal wastes (Madison and Brunett,

1985; Williams et al., 1998). It is known that ^{15}N analysis of nitrate in each groundwater is useful to investigate the sources of nitrate of that groundwater (Choi, 1998; Yoo et al., 1999). By studying the natural nitrogen isotope ratios of nitrate in groundwater and comparing them to the nitrogen isotope ratios of nitrate from different soil environment, the nitrate of certain groundwater can be traced to unique sources (Kreitler, 1975; Kreitler and Browning, 1983; Komor and Anderson, 1993; Wilson et al., 1994). These variations are commonly expressed as deviations from a standard:

$$\delta^{15}\text{N} (\text{‰ } ^{15}\text{N}) = (R_s - R_R) / R_R \times 1000 \quad (1),$$

where R_s and R_R represent the ^{15}N isotope ratio, $^{15}\text{N}/(^{15}\text{N}+^{14}\text{N})$, for sample and the reference (atmospheric N_2 , 0.3663 atom% ^{15}N), respectively. Physical fractionation, chemical equilibrium fractionation, and chemical kinetic fractionation are all important in the isotopic fractionation of nitrogen in natural biogeochemical systems (Kreitler, 1975; Shearer and Kohl, 1993).

Three nitrogen isotope ($\delta^{15}\text{N}$) ranges have been defined for nitrate from different sources. Kreitler (1975) and Kreitler and Jones (1975) found that the $\delta^{15}\text{N}$ values for nitrate from unfertilized cultivated fields (nitrate resulting from the oxidation of part of the organic nitrogen in the soil from crop plowing) range from +2 ‰ to +8 ‰, and

that nitrate from animal-waste nitrogen ranges from +10 ‰ to 20 ‰. $\delta^{15}\text{N}$ values of artificial fertilizer range from -8 ‰ to +6.2 ‰, with 90 percent of the samples ranging from -3 ‰ to +2 ‰ (Freyer and Aly, 1974; Kreitler, 1977; Mariotti and Letolle, 1977).

Kreitler et al. (1978) found that samples from urbanized environment had $\delta^{15}\text{N}$ values of +12.1 ‰ and 21.3 ‰, within the range representative of animal wastes. In general, $\delta^{15}\text{N}$ in groundwater for different contamination sources are known as: <+4 ‰ for chemical N-fertilizers, +4~+9 ‰ for natural soil nitrogen, +9~+18 ‰ for animal manures or municipal wastes.

The objective of the present study were (1) investigation of the probable nitrogen isotope ranges of common contamination sources in Korea, (2) assessment of contamination sources of groundwater nitrate based on the nitrogen isotope characteristics in a complex terrain of Jeju province, and (3) comparison of these results with those from the classical land use classification approach.

Materials and Methods

Groundwater Samples The water resource of Jeju Island depends predominantly on groundwater. Perennial surface water resources can hardly exist due to the highly water permeating nature of the soils (Song, 1989). Groundwater samples from 33 wells (Fig. 1) in Jeju province were collected from August to November in 1999 and analyzed for their ^{15}N isotope contents along with other properties: pH, electrical conductivity (EC), anions (F^- , Cl^- , H_2PO_4^- , SO_4^{2-} , NO_3^-), cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+), total phosphorus, total nitrogen, and organic nitrogen.

All the analyses were conducted by the standard methods (APHA, 1992). The pH and EC of samples were measured using a pH meter (DMS, DMP2000) and an EC meter (PHILIPS, PW9509), respectively. Anions

were determined using an ion exchange chromatograph (INSUNG, MIC2001) with anion exchange resin (Dionex, IonPac AS4 P/N 35311) after removing the suspended solids by filtering the water sample with 0.45 μm membrane filter. Bicarbonate was titrated with 0.01 N H_2SO_4 . Cations were measured with an atomic absorption spectrophotometer (Shimadzu, AA-6501F). For total phosphorus analysis, groundwater samples were digested with 4% $\text{K}_2\text{S}_2\text{O}_8$ at 121°C for 30 min. After digestion, the absorbance at 710 nm was measured by colorization through ammonium molybdate-ascorbate method.

Contamination source samples To confirm the categories for nitrogen sources, urea, water sample from septic tank, chemical ammonium sulfate, and compost made from animal manure were analyzed for their nitrogen isotope concentrations. Those samples were collected across Kyonggi province in 1998 and 1999. Two purified N_2 gases were prepared from 10 mg urea; one by direct distillation and the other by distillation after hydrolysis with 20 ml of 1% urease. For chemical ammonium sulfate (1000 mg/L), N_2 gas was produced directly by the Rittenberg reaction (see below). In case of compost, 0.1 g sample was finely ground and was distilled after digestion by the Kjeldahl method (ASI, 1988).

Isotope analysis The $\delta^{15}\text{N}$ analysis of groundwater samples were carried by the Kjeldahl-Rittenberg technique (Fig. 2). Water samples (350 ml) were transferred to distillation flasks and pHs were raised to 9.5 with MgO powder. Then, nitrate nitrogen was removed by distillation of the sample. Devarda's alloy (mixture of Al, Cu and Zn) was used for reduction of NO_3^- to NH_4^+ . Collected nitrate nitrogen solutions were then concentrated to about 0.5 to 1 mg as nitrogen using infrared lamps for 5-6 hrs. Nitrogen gas for ^{15}N isotope ratio analysis was generated utilizing the reaction between alkaline hypobromite and NH_4^+ under vacuum to exclude atmospheric N_2 . The produced N_2 gas was purified by sequentially passing through water trap (ethanol at -90°C) and CO_2 trap (molecular silica sieve with liquid nitrogen). Finally purified gas passing selective N_2 trap was analyzed by a mass spectrometer (VG Optima IRMS, VG ISOGAS, Manchester, UK) having 1.0 ‰ of reproducibility and 0.1 ‰ of precision.

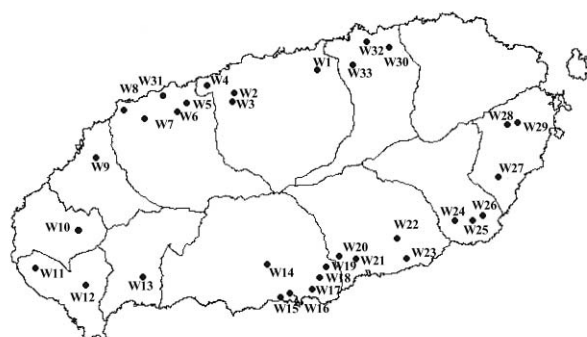


Fig. 1. Sampling wells for nitrogen isotope analysis of groundwater nitrate.

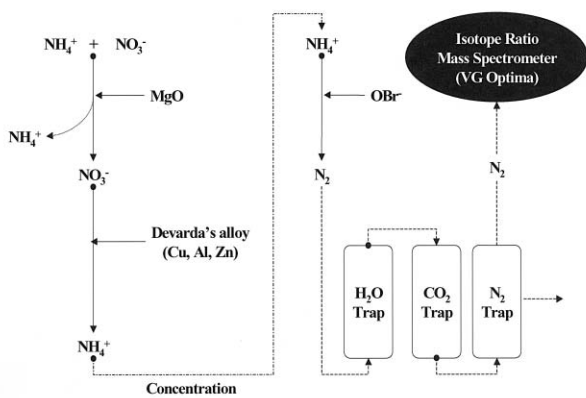


Fig. 2. Nitrogen analysis procedure (Kjeldahl-Rittenberg technique).

Land use analysis To address contamination sources of groundwater nitrate, land-use activities in Jeju Island were classified into 5 main types (forest, pasture, upland, orchard, and residential areas) based on the KRIHS (Korea Research Institute for Human Settlements) investigation in 1998. Along with this apparent land-use classification and the results of susceptibility assessments, highly vulnerable regions were selected and probable contamination sources were estimated.

Results and Discussion

^{15}N categories of contamination sources Before applying the $\delta^{15}\text{N}$ analysis to identifying contamination source of groundwater nitrate, it was necessary to confirm the categories for nitrogen sources. For this, urea, water sample from septic tank, chemical ammonium sulfate, compost made from animal manure were analyzed for their nitrogen isotope concentrations. Two purified N_2 gases were prepared from urea: one by direct distillation and the other by distillation after hydrolysis with urease. Figure 3 shows $\delta^{15}\text{N}$ values of those samples.

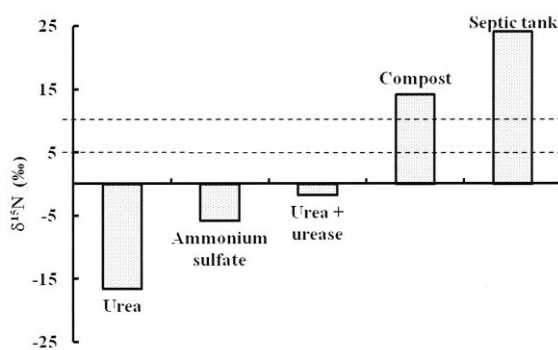


Fig. 3. $\delta^{15}\text{N}$ values of nitrogen in urea (treated with urease and not treated), ammonium sulfate, compost, and nitrate in water from septic tank.

Artificial nitrogen compounds (urea and ammonium sulfate) showed very low $\delta^{15}\text{N}$ values; -1.7 ‰ and -5.8 ‰ respectively. Generally, it is known that $\delta^{15}\text{N}$ values of artificial fertilizer range from -8 ‰ to +6.2 ‰ (Freyer and Aly, 1974; Kreitler, 1977; Mariotti and Letolle, 1977; Kreitler et al., 1978). $\delta^{15}\text{N}$ values of ammonium sulfate and urea were consistent with the range. However, they showed more fractionated compared to known values for urea 2.4 ‰ (Flipse and Bonner, 1985) and ammonium sulfate -2.4 ‰ (German fertilizer; Freyer and Aly, 1974). Flipse and Bonner (1985) have pointed that differences in ^{15}N content among fertilizers are generally a result of fractionation during subsequent processing of the nitrogen fixed by the Haber process.

In case of the directly distilled urea, -16.5 ‰, the most negative value was measured. Compared to the value -1.7 ‰ of urea with urease, this large fractionation was thought to be caused by the nonequilibrium kinetic fractionation. It was thought that some portion of urea was chemically hydrolyzed at the alkaline condition. About only 10% of the urea nitrogen was distilled and was collected in the form of ammonium sulfate. The nonequilibrium kinetic fractionation made the collected ammonium nitrogen depleted in ^{15}N . It is probable that the unreacted urea was highly enriched in the heavier nitrogen isotope. However, that was not checked. The nonequilibrium kinetic fractionation was often occurred within an organism and ecosystem. This implies that more negative $\delta^{15}\text{N}$ value than that of fully hydrolyzed urea can be measured in a real groundwater nitrate.

In contrast to the artificial nitrogen compounds, the compost and water sample from septic tank showed positively fractionated $\delta^{15}\text{N}$ values: 14.1 ‰ and 24.0 ‰ respectively. In composting process, large amounts of nitrogen are lost in the form of ammonia gas. This ammonia volatilization tends to enrich the condensed phase in the heavier isotope. The water sample from septic tank had also undergone the volatilization process. Only negligible nitrate was detected in the water sample. Most inorganic nitrogen in the form of ammonium was highly enriched in ^{15}N .

$\delta^{15}\text{N}$ values of groundwater samples Based on the measured $\delta^{15}\text{N}$ values and review of the previous studies (Kreitler, 1975; Kreitler and Browning, 1983; Komor and Anderson, 1993; Wilson et al., 1994), the sources of nitrate were classified as originated from chemical fertilizers with $\delta^{15}\text{N}$ values below 5 ‰ and as from animal

manure or municipal waste with $\delta^{15}\text{N}$ values over 10‰. Based on this classification, $\delta^{15}\text{N}$ values of groundwater samples from 33 wells were analyzed to differentiate contributions of various land uses to groundwater quality (Table 1). In case that $\delta^{15}\text{N}$ values were between 5 and 10 ‰, it was thought that two or more different sources affected groundwater. Although this range of $\delta^{15}\text{N}$ also reflects natural soil nitrogen, the source of nitrate was not classified as from that material except that the groundwater nitrate showed a lower concentration than 3.0 mg/L.

Most wells were had chemical fertilizers as their dominant contamination source. Among the 33 wells tested, 22 wells showed $\delta^{15}\text{N}$ values below than 5 ‰. And, additional 6 wells showed 5 to 7 ‰, which implies strong contribution of chemical fertilizers compared to

other probable sources. On the other hand, it was thought that the $\delta^{15}\text{N}$ values from 7 to 10 ‰ reflected more contributions of animal manure or municipal wastes to groundwater contamination. From the results of $\delta^{15}\text{N}$ analysis, it might be concluded that contribution of chemical fertilizers is much higher than those of other sources to groundwater contamination by nitrate in Jeju Island. It was found that several wells (W22, W31, W3, W9, and W25) were highly influenced by the municipal wastes or animal manure. In addition, there was a significant change in $\delta^{15}\text{N}$ in W15, suggesting a wide variation in contamination source between the sampling period.

Comparison with land use classification Land-use activities in Cheju Island were classified in to 5 main

Table 1. Concentrations and $\delta^{15}\text{N}$ values of NO_3^- in groundwater samples.

Well	Date	NO_3^- -N	$\delta^{15}\text{N}$	Date	NO_3^- -N	$\delta^{15}\text{N}$
		mg L ⁻¹	‰		mg L ⁻¹	‰
W 1	'99/11	5.5	3.72			
W 2	'99/11	2.6	3.53			
W 3	'99/10	3.3	8.34			
W 4	'99/11	4.6	4.24			
W 5	'99/10	9.3	2.58			
W 6	'99/11	11.2	2.89			
W 7	'99/11	9.3	2.53			
W 8	'99/11	8.7	3.71	'99/08	12.9	5.1
W 9	'99/08	14.3	8.39			
W10	'99/08	9.5	6.12			
W11	'99/11	6.0	2.65			
W12	'99/11	5.4	5.68			
W13	'99/10	21.6	2.32			
W14	'99/11	4.9	3.48			
W15	'99/11	8.6	5.15	'99/08	9.5	10.43
W16	'99/11	7.8	6.89	'99/10	8.0	5.36
W17	'97/08	19.2	5.11			
W18	'99/11	4.5	4.12			
W19	'99/10	16.6	2.87			
W20	'99/11	6.2	4.39	'99/10	8.1	2.18
W21	'99/11	3.0	3.72			
W22	'97/08	1.9	16.8			
W23	'99/08	5.9	6.71			
W24	'99/11	4.2	2.12			
W25	'99/11	9.2	7.89			
W26	'99/11	3.5	2.45			
W27	'99/11	4.0	1.60			
W28	'99/11	2.7	2.52			
W29	'99/11	5.0	1.82			
W30	'97/08	16.5	0.10	'99/11	14.4	3.67
W31	'99/08	13.4	21.77			
W32	'99/11	9.1	1.46	'99/11	6.0	2.65
W33	'99/11	7.5	2.92			

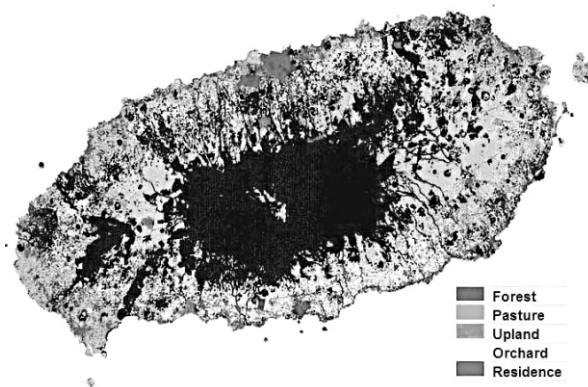


Fig. 4. Map of land use classification.

types: forest, pasture, upland, orchard, and residential areas (Fig. 4). Upland and orchard soils were widely distributed along the coastal line. The upland soils occupied about 340.1 km², about 18.6% of the total area of the island; orchard soils, 281.7 km², about 15.4%. Especially, the orchard soils were mainly found along the southern coast. The pasture soils were mainly located in the mid-mountainous areas and occupied 439.5 km², about 24.0% of the island. However, the residential areas were scattered widely along the coastal line. Residential areas occupied 69.1 km², 3.8% of the island. The forest lands (635.2 km², 34.8% of the island) were primarily located on the higher region around the main mountain Halla.

From the land-use map, a major contamination source for groundwater nitrate would be chemical fertilizer applied to upland and orchard soils, especially in the western, north-eastern, and southern areas. Municipal wastes and leaks of septic tanks at the scattered residential sites could be local contamination sources. And also the pasture soils, which are widely distributed in the mid-mountainous areas and somewhat extended to eastern region, could be a potential entrance of the contaminant that was affected by animal manure. Especially, the southern region along the coastal line was thought to be affected mainly by chemical fertilizer and partly by municipal wastes.

The above nitrogen isotope results were then geographically compared with the apparent land-use classification (Fig. 5). In accordance with the land-use classification, the major contamination source for groundwater nitrate was estimated to be the chemical fertilizers applied to upland and orchard soils, especially in the western, northeastern, and southern areas. Municipal wastes and leaks of septic tanks at the scattered residential sites could be local contamination

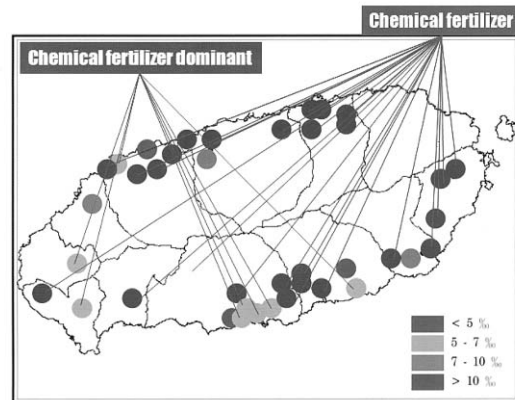


Fig. 5. Spatial distribution of $\delta^{15}\text{N}$ values of groundwater nitrate. Dominant contamination sources are indicated.

sources. And also the pasture soils could be a potential entrance of the contaminant that was affected by animal manure. It was shown that several wells were highly influenced by the municipal wastes or animal manure. However, only 5 wells were analyzed for their nitrogen isotope fractionation in the western region: Hanrim, Hankyeong, Daejeong, and Andeog. Therefore, it is thought that the contribution of livestock farming and residential land use on those areas is relatively ambiguous compared to other regions.

Conclusion

Based on the $\delta^{15}\text{N}$ values of possible groundwater nitrate sources (urea, ammonium sulfate, compost, water from septic tank) sources of nitrate could be classified as originated from chemical fertilizers with $\delta^{15}\text{N}$ values below 5 ‰ and as from animal manure or municipal waste with $\delta^{15}\text{N}$ values over 10 ‰. The $\delta^{15}\text{N}$ analysis of groundwater nitrate revealed that most wells had as their contamination source of nitrate, the chemical fertilizers. This coincided well with the apparent land-use classification. By using this technique, it was possible to find several wells where other non-apparent sources and combined sources contaminated groundwater. In many cases, especially in complex terrain with various land use activities, apparent land-use classification cannot distinguish the predominant contamination source. However, probable seasonal variation resulting from more than two contamination sources must be considered in applying $\delta^{15}\text{N}$ analysis.

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복잡한 지형에서 발생하는 지하수의 질산태 질소 오염원 평가

한광현

충북대학교 응용생명환경학부

토지이용에서 보았을 때 제주도는 해안을 따라 넓게 분포하는 밭과 과수원의 화학비료와, 중산간 지대 방목지의 가축분뇨 및 산발적으로 존재하는 주거지역의 생활하수에 의한 질산태 질소 오염이 추정되었다. 질소동위원소 분석이 이들 오염원들을 구분하기 위하여 사용되었으며, 주요 오염원인 요소, 유안, 축분정화조, 축분유기질 비료에 대해 측정된 $\delta^{15}\text{N}$ 값을 토대로 화학비료에 의한 오염은 5 % 이하, 생활하수 혹은 가축분뇨에 의한 오염은 10 % 이상으로 기준을 정하였다. 제주도 전역에 걸친 33개 관정의 질산태 질소 동위원소 분석결과는 대부분의 관정이 화학비료에 의해 오염되었으며, 일부 관정이 가축분뇨와 생활하수에 의해 영향받았음을 나타내었다. 이러한 결과는 질소동위원소분석이 토지이용분류로는 판별하기 어려운 오염원 추정에 매우 유용한 수단이 될 수 있음을 나타낸다. 특히 좁은 지역에서 토지이용이 다양하게 이루어 지고 있는 경우에 중요한 오염원 추정 수단이 될 수 있음을 경기, 강원 지역의 지하수 분석을 통해 확인할 수 있었으며, 또한 두 가지 이상의 오염원이 동시에 작용할 수 있고 그 기여도가 시기별로 달라질 수 있음을 확인하였다.
