Temporal Variations in Isotope Ratios and Concentrations of Nitrate-nitrogen in Groundwater as Affected by Chemical Fertilizer and Livestock Manure

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Isotope ratio ($^{15}N/^{14}N$) and nitrate-nitrogen concentration in groundwater were measured to investigate the effect of chemical fertilizer and livestock manure on temporal variations in nitrate-nitrogen concentration and to estimate the contribution of fertilizer and manure to groundwater contamination by nitrate. Four study wells from a rural area in Kyonggi province were selected. One well was located on an upper site from a livestock feedlot, and the others were situated at lower sites from the feedlot. The $\delta^{15}N$ values were analyzed by a stable isotope ratio mass spectrometer (Micromass, VG Optima IRMS). Reproducibility of the method and precision of the mass spectrometer were below 1.0 and 0.1‰, respectively. Even though study wells were located at the same area, nitrate-nitrogen concentrations and $\delta^{15}N$ values differed and fluctuated during the sampling period. The $\delta^{15}N$ values of well located at upper site from the feedlot were extremely variable (-1.48~20.80‰). The ranges of $\delta^{15}N$ value of three wells situated at lower sites from the feedlot were 11.83~20.73 (ave. 16.11), 8.90~11.73 (ave. 11.01), and 5.29~12.73‰ (ave. 8.21‰) with increasing distance from the feedlot. The average values of contribution proportion of nitrogen derived from livestock manure to nitrate-nitrogen in groundwater were 79% for the well closet to the feedlot, 44% for the well most distant from the feedlot, and 56% for the well in between the two wells.

Key words: *groundwater contamination, nitrogen-isotope ratio, nitrate, chemical fertilizer, livestock manure.*

Natural level of groundwater nitrate originating from soil nitrogen is very low.[1,2] However, nitrate is often enriched to hazardous levels by anthropogenic activities involving nitrogen from fertilizers or by-product of organic compounds such as livestock manure in rural area.[3] Nitrate in drinking water can pose a health hazard causing methemoglobinemia ("blue baby" disease),[4] and the ingestion of water containing high concentrations of nitrate may cause chronic toxicity and possible development of cancer from nitrosamines.[5,6] It is considered by regulatory standards as harmful at levels above the maximum contaminant level (MCL) of 10 mg l^{-1} as NO_3-N.

There is no centralized water supply system in most rural areas in Korea, therefore local groundwater is the major source of drinking water. At present, concerns on contamination of groundwater resources by nitrate are increasing. Nitrate contamination sources of the groundwater in rural areas include chemical fertilizers, soil organic matter, livestock manure, and municipal wastes.[7]

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Abbreviations: IRMS, isotope ratio mass spectrometer; MCL, maximum contaminant level; NDFM, nitrogen derived from manure; NDFF, nitrogen derived from fertilizer.

Identifying the major sources of nitrate in groundwater would help water managers and planners in developing measures to reduce groundwater contamination from nitrate. A nitrogen isotope ratio [$^{15}N/(^{15}N+^{14}N)$] analysis of groundwater is a useful method to identify the contamination source of nitrate in groundwater.[8,9]

Two stable isotopes of nitrogen occur naturally. Nitrogen 15 (^{15}N) has a natural abundance of 0.3663 atom percent. Although this value is essentially constant in atmospheric N_2,[10] it varies among other forms of nitrogen as a result of physical, chemical equilibrium, and chemical kinetic fractionations.[11]

These variations are commonly expressed as deviations from a standard (usually atmospheric N_2).

$$^{15}N \text{ (per mil } ^{15}N \text{ excess,‰ } ^{15}N) = \frac{R_s - R_R}{R_R} \times 1000^{12)} \qquad (1)$$

where, R_S is ^{15}N isotope ratio for sample, and R_R is ^{15}N isotope ratio for a reference (atmospheric N_2, 0.3663 atom % ^{15}N). A positive value of $\delta^{15}N$ indicates a higher proportion of ^{15}N in the sample than in the reference.

Three $\delta^{15}N$ ranges have been defined for nitrate in groundwater from different sources: (1) chemical fertilizers with values below 5, (2) livestock manure with values over

10, and (3) natural soil nitrogen with values between 5~10 ‰.[13] Thus, the $\delta^{15}N$ value of nitrate in groundwater is a direct indication of the nitrate source.

The objective of this study was to determine the contribution proportion of chemical fertilizer and livestock manure to nitrate-nitrogen concentration of groundwater in rural area by means of nitrogen isotope ratio analysis of nitrate.

Materials and Methods

Study wells and water sampling. Four study wells were selected in the rural area of Gunpo city, Kyonggi province. The soil of study area has been classified as Osan series (Coarse loamy, mesic family of Typic Dystrochrepts).[14] Locations and characteristics of study wells are shown in Fig. 1. The study area includes cropland and a livestock feedlot. All study wells were located within 50 m from the livestock feedlot. Well 1 was located at an upper site from the livestock feedlot, and Wells 2, 3, and 4 were situated at lower sites from the feedlot in the order of their numbers.

The major nitrogen fertilizer applied to the cropland was urea, and there was no septic tank for the treatment of livestock manure. The groundwater quality in this area seemed to be affected not only by urea applied to the field but also by the waste water from the feedlot.

Water samples were taken monthly from January 1997 to April 1998, and collected samples were kept in a freezer until analysis of concentration and isotope ratio of nitrate-nitrogen.

Anlaysis of nitrate-nitrogen. Nitrate-nitrogen concentrateions of water samples were determined using an ion exchange chromatograph (MIC2001, Insung, Korea) with anion exchange resin (IonPac AS4 P/N 35311, Dionex, USA) after removing the suspended solids by filtering the water sample with 0.45 μm membrane filter.

Analysis of nitrogen isotope ratio as $\delta^{15}N$. For the analysis of natural ^{15}N abundance of nitrate in groundwater samples, nitrate was collected as NH_4^+ in 0.01 N H_2SO_4 by Kjeldahl distillation.[15] After acidification of the NH_4^+ distillation solution with 0.08 N H_2SO_4, the distillation solution was concentrated with an infra-red lamp. The concentrated solution was reacted with LiOBr to generate N_2 gas using Rittenberg method, and the generated N_2 gas was injected into a mass spectrometer (VG Optima IRMS, Micromass, UK) for $\delta^{15}N$ analysis.[16] All values of $\delta^{15}N$ were reported with respect to atmospheric N_2 as the reference in this paper.

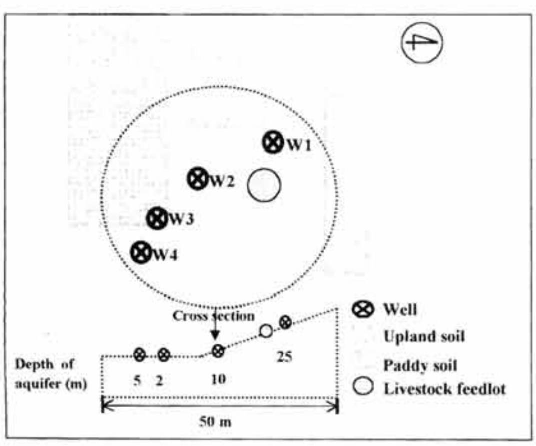

Fig. 1. Locations and characteristics of study wells.

Estimating the relative contribution of two contamination sources. A fractional contribution of chemical fertilizer and livestock manure to groundwater nitrate was calculated from a linear interpolation between the poles representing the two typical sources. The following equation were used for the estimation.

$$NDFF(\%) = \frac{(\delta^{15}N_M - \delta^{15}N_G)}{(\delta^{15}N_M - \delta^{15}N_F)} \times 100 \quad (2)$$

$$NDFM(\%) = 100\text{-}NDFF(\%) \quad (3)$$

where NDFF and NDFM are the nitrogen derived from chemical fertilizer and that from livestock manure, respectively. $\delta^{15}N_G$ is the $\delta^{15}N$ value of nitrate-nitrogen in groundwater. $\delta^{15}N_F$ and $\delta^{15}N_M$ are the $\delta^{15}N$ values of nitrogen derived from chemical fertilizer and that from livestock manure, respectively.[17]

Results and Discussion

Changes in concentrations and isotope ratios of nitrate-nitrogen. The changes in concentrations and isotope ratios of nitrate-nitrogen in groundwater of study wells are shown in Fig. 2. The NO_3^--N concentration in groundwater varied with season, and high concentration above 10 mg l^{-1} was observed during summer due to heavy rainfall. The variations in NO_3^--N concentration indicate the vulnerability of groundwater quality to contamination by land-use activities around the well.

The cause of elevated nitrate-nitrogen concentration could be deduced from $\delta^{15}N$ values of nitrate because the values varied with the contamination sources such as chemical fertilizers and livestock manure.[1,18,19]

Yoo *et al.* have reported that the $\delta^{15}N$ values of nitrogen originating from urea, ammonium sulfate, and animal manure were 1.4, -2.7, and 27.2‰, respectively.[1] Kreitler, and Kreitler and Jones found that the $\delta^{15}N$ values for nitrate from unfertilized cultivated fields (nitrate resulting from the oxidation of part of the organic nitrogen in the soil) ranged from +2 to +8‰ and those from livestock manure ranged from +10 to +20‰.[18,20] The $\delta^{15}N$ values of artificial fertilizer ranged from -8 to +6.2‰, with 90 percent of the samples ranging from -3 to +2‰.[20,21] Thus, a low $\delta^{15}N$ value of nitrate-nitrogen in groundwater indicates that the dominant source of nitrate is chemical fertilizer, whereas a high $\delta^{15}N$

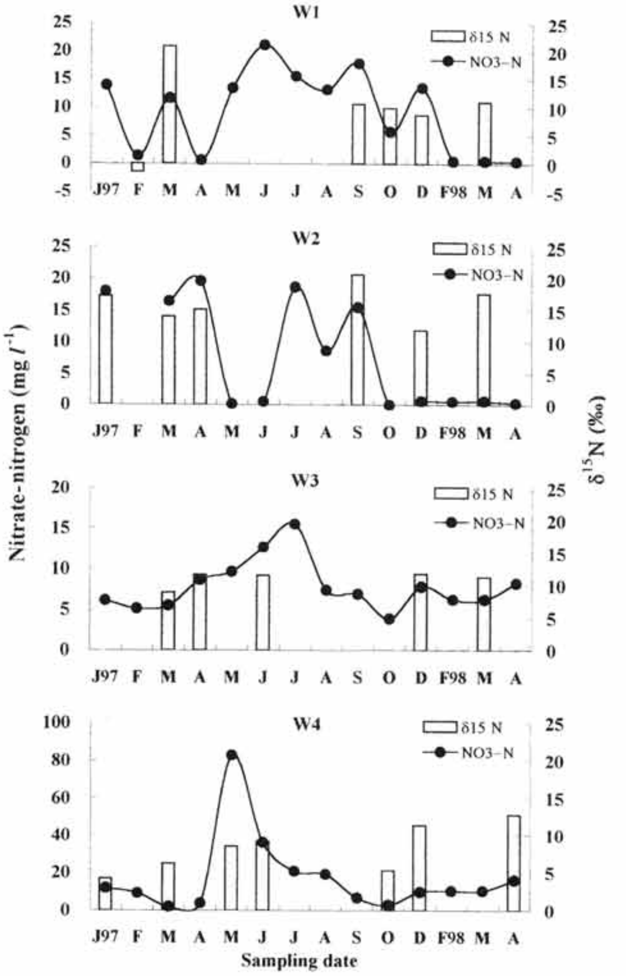

Fig. 2. Changes in concentrations and isotope ratios of nitrate-nitrogen in groundwater.

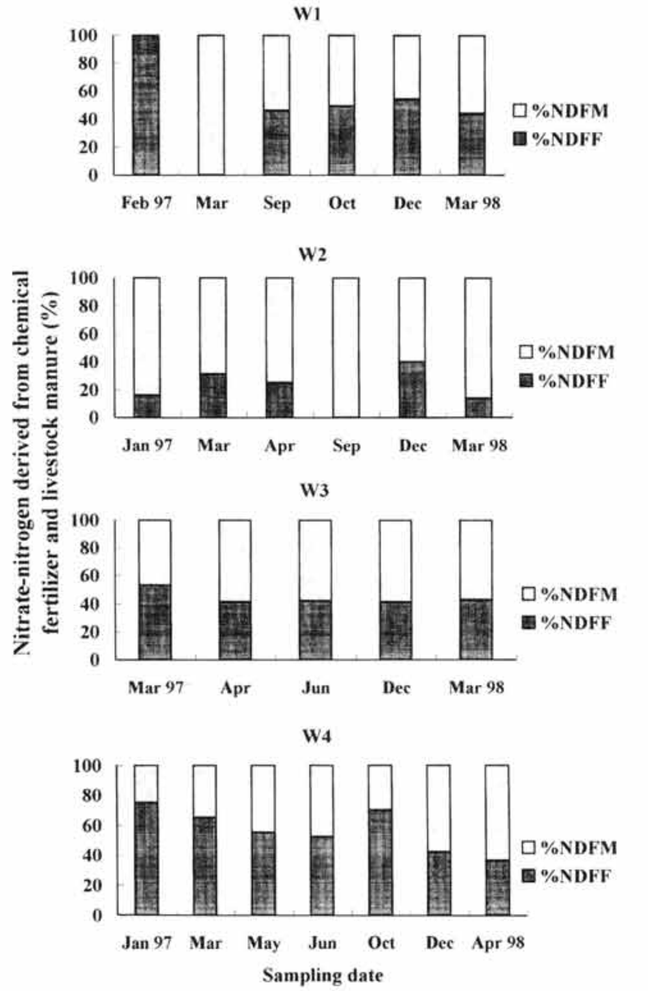

Fig. 3. Contribution of chemical fertilizer and livestock manure to nitrate-nitrogen concentration of study wells. NDFM indicates nitrogen derived from livestock manure and NDFF denotes nitrogen derived from fertilizer.

value represents that livestock manure is the major source of nitrate.

The NO_3^--N concentration of W1 ranged from <1 to 21.1 mg l^{-1}, and 60% of collected water samples exceeded the public drinking water MCL of 10 mg l^{-1}. The range of $\delta^{15}N$ value of W1 was -1.48~+20.8‰. The lowest $\delta^{15}N$ value is an indication that most nitrate was derived from fertilizer, and the highest value of 20.8‰ indicated that livestock manure was a major source of nitrate. Although the NO_3^--N concentrations fluctuated after September 1998, the $\delta^{15}N$ values of nitrate were consistent at about 10‰ during the sampling period. This result showed that effects of chemical fertilizer and livestock manure to groundwater were similar.

Fifty percent of samples collected from W2 showed higher NO_3^--N concentration than 10 mg l^{-1}. The values of $\delta^{15}N$ were between 11.83 and 20.73‰ indicating that the water quality of W2 was affected more by livestock manure than by chemical fertilizer.

Only two samples from W3 had higher NO_3^--N concentrations than 10 mg l^{-1} during summer. The $\delta^{15}N$ values were 8.90~11.73‰. The $\delta^{15}N$ value of about 10‰ during the study period seemed to be the result of consistent influences of chemical fertilizer and livestock manure on the water quality.

Though $\delta^{15}N$ values of samples taken from W4 on May and June 1997 were 8.53 and 9.15‰, respectively, these values can not be attributable to natural soil nitrogen but to the mixing of nitrate from livestock manure with high $\delta^{15}N$ value and from chemical fertilizer with low $\delta^{15}N$ value as it is not possible to have high nitrate concentrations on May (82.9 mg l^{-1}) and June (32.6 mg l^{-1}) without any other contamination source,

The average $\delta^{15}N$ values were 16.11, 11.01, and 8.21‰ for W2, W3, and W4, respectively. This result shows that the effect of livestock manure on ^{15}N values of groundwater seemed to decrease with increasing distance from the livestock feedlot.

Contribution of chemical fertilizer and livestock manure. The contribution of each contamination source to NO_3^--N in groundwater was estimated with equation 3. For the estimation, contamination by natural soil nitrogen and leaky sewers was assumed to be negligible.

Establishment of $\delta^{15}N_F$ and $\delta^{15}N_M$ values representing the two typical sources of chemical fertilizer and livestock manure are critical in the equation since the ratio of ^{15}N in the original source material is altered during transport process through soil due to the isotopic discrimination of nitrogen in soil. It is reasonable to take the $\delta^{15}N$ values after they have undergone isotopic discrimination as the $\delta^{15}N$ values representing the two typical nitrogen sources.[17] In our study, the $\delta^{15}N$ values of W1 were used as $\delta^{15}N_F$ (-1.48‰) and $\delta^{15}N_M$ (+20.80‰) because they were the lowest and the highest values throughout the study period. Yoo *et al.* also calculated the contribution of chemical fertilizer to nitrate concentration in groundwater for the samples with NO_3^--N concentration above 4 mg l^{-1} and $\delta^{15}N$ values between 5 and 10‰ by the same means.[1]

As shown in Fig. 3, the average values of concentration proportion of nitrogen derived from livestock manure to nitrate-nitrogen in groundwater decreased with increasing distance from the livestock feedlot, and their values were 79, 56, and 44% for W2, W3, and W4, respectively. The water quality of Wells 1 and 3 seemed to be affected by both chemical fertilizer and livestock manure equally because NDFM (%) and NDFF (%) of the Wells were about 50% except for the samples of W1 collected on February and March 1997. Contribution of livestock manure to water quality of W2 located at lowland and near livestock feedlot was even higher than that of chemical fertilizer. However, it was revealed that most of nitrate-nitrogen in groundwater of W4 had originated from chemical fertilizer rather than livestock manure.

In conclusion, even though study wells were located at the same area, and such factors including soil type, climate conditions, and land-use pattern which may affect water quality were thought not to be different from each other, nitrate-nitrogen concentration varied not only among wells but also in the same well during the sampling period. For the well located at upper site from the livestock feedlot, where the impact of livestock manure on water quality of the wells was thought to be less significant, the contribution of chemical fertilizer and livestock manure to the nitrate-nitrogen concentration of groundwater was similar. However, the well which was closer to the livestock feedlot seemed to be more largely influenced by livestock manure, and chemical fertilizer was thought to be the main contamination source of a well which was further away from the feedlot.

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