Dual isotopes of nitrate in Korean fertilizers and their application for identifying nitrate sources

Many studies have used typical ranges of $\delta^{15}N$ and $\delta^{18}O$ values to identify nitrate sources. However, it is questionable whether typical nitrate isotopes for various sources can be universally applied. Thus, for inorganic (IOF), organic (OF) and plant-based compound fertilizers (PCF) in South Korea, $\delta^{15}N$ and $\delta^{18}O$ were measured to evaluate their commonly used ranges. The $\delta^{15}N$ and $\delta^{18}O$ were 2.6 ± 2.5‰ and 19.3 ± 2.6‰ (n = 19) for IOFs, 14.7 ± 7.7‰ and 5.9 ± 4.9‰ (n = 30) for OFs, and 10.9 ± 6.7‰ and 16.0 ± 6.1‰ (n = 24) for PCFs, respectively. Some OFs showed relatively lower $\delta^{15}N$ than the previously reported values for NO$_3$ fertilizers but all PCFs had both $\delta^{15}N$ and $\delta^{18}O$ similar to them, indicating that $\delta^{15}N$ and $\delta^{18}O$ for the organic material-based fertilizers were likely affected by both the composition level of the main ingredients and various additives in them. Dual isotopic data for three types of fertilizer in this study can play a crucial role in-depth understanding the fate of natural and anthropogenic nitrate sources occurring in watershed.

Introduction

The rapid urbanization and development of riverine areas releases various contaminants into the environment, which can lead to serious environmental problems worldwide (Mayer et al., 2002; Xue et al., 2009). As one of the common contaminants in nature, nitrate (NO$_3$$^-$–N) pollution in drinking water poses a threat to human health, such as methemoglobinemia, cancer, and digestive problems, and can lead to eutrophication in surface waters (Ridder and Oechme, 1974; Krafte-Jacobs et al., 1997; Choi et al., 2003). Nitrate pollution is thus considered to be one of the most critical environmental issues, hence the World Health Organization (WHO) suggests a guideline value of 50 mg/L as nitrate ion (NO$_3$$^-$) or 11 mg/L as nitrate-nitrogen (NO$_3$$^-$–N) to protect a potential human health risk (WHO, 2008).

For these reasons, concentrations of n-containing compounds (e.g., ammonium, nitrate) and their isotopic compositions in many studies have been used to identify nitrogen sources and understand nitrogen transformation processes (e.g., mineralization, volatilization, nitrification, denitrification) during the nitrogen cycle. Especially, stable isotope techniques provide crucial information on potential sources and processes affecting isotopic compositions (e.g., Singleton et al., 2005; Diédhiou et al., 2012). For example, stable nitrogen isotope constraints sources of nitrate in agricultural areas to fertilizer and manure representing distinctive $\delta^{15}N$ values (Komor and Anderson, 1993; Iqbal et al., 1997; Curt et al., 2004).

However, only the use of nitrogen isotopes cannot differentiate other sources of nitrate, such as atmospheric deposition, synthetic fertilizers, and natural soil, due to their wide and similar ranges of $\delta^{15}N$ values (Silva et al., 2002; Fenech et al., 2012). Recent advances in analytical techniques have made it possible to analyze oxygen isotope of nitrate, which offers powerful opportunities for determining nitrate sources and understanding reactions in the environment (e.g., Casciotti et al., 2002; Mayer et al., 2002; Chmura et al., 2009). To investigate the origin of nitrate and understand various processes related to nitrogen transformation (e.g., Komor and Anderson, 1993; Vitória et al., 2004; Li et al., 2010), many studies have compared their nitrate dual isotopic compositions to the dual isotopic ranges for the main potential nitrate sources which was previously compiled (Kendall, 1998). It is questionable whether the dual isotopic ranges suggested in the previous studies could be representative of nitrate sources in all countries. For example, the degree of fermentation of raw materials in organic fertilizer and the type of main ingredients and additives used in inorganic fertilizer could impact on isotope ratios. Therefore, it is necessary to revisit compiled previous data to confirm the above approach, especially in South Korea.

To this end, we collected three different types of Korean fertilizers and investigated dual isotopic compositions of nitrate. Then, on plot of $\delta^{15}N$ and $\delta^{18}O$ values, our results were presented with typical ranges for main sources of nitrate to evaluate difference between them. In addition, in terms of identification of sources, nitrate isotopes from previous Korean case studies were reevaluated with the results in this study.

Materials and Methods

Samples

A total of 73 fertilizers commonly used in South Korea were purchased from many retailers in personal throughout South Korea during
the period of 2011−2012 (Fig. 1). The fertilizers were packed in various sizes from 1 kg to 20 kg. Based on the information attached in each container of the fertilizer, the Korean fertilizer samples used in this study were classified into three types, inorganic (synthetic; n = 19), organic (n = 30), and plant-based compound fertilizers (n = 24); hereafter, each fertilizer was abbreviated by IOF, OF, and PCF, respectively. The IOF samples were manufactured by three major companies (Punggong, Namhae Chemical, Dongbu Hannong) in South Korea, and the others were produced from small business companies located in each Province. Thus, the samples are regarded as representative Korean fertilizers, with excluding extensive mountainous areas (Fig. 1). The IOF with N, P, and K compounds includes N content from 11 to 30% (average 19.8 ± 6.51%). The OF mostly consists of chicken, pig, and cattle manure mixed with sawdust and bark, and includes a variety of additives such as slaughter byproducts, and enzyme. The PCF with a small N compound (4.0 ~ 6.0%, average 4.5 ± 0.8%) includes soybean, castor, rapeseed, and rice bran meals as main ingredients, and various additives such as fish meal, powdered bone, zeolite and dolomitic limestone.

**Sample Preparation**

Samples were crushed in a shatter box equipped with a tungsten carbide grinding container (Retsch MM400, Germany). About 2.0 g of the powdered fertilizers were soaked in 40 mL MQ water at room temperature for 24 h. The mixture was centrifuged at 4,000 rpm for 30 minutes (Combi 408, Hanil Science Co. Ltd., Korea), and the supernatant was passed through a 0.45-μm pore size polypropylene syringe filter (25 mm GD/X PVDF, Whatman, UK), adjusted to pH 10–11 using 1 N NaOH (Guaranteed reagent, Junsei) to inhibit microbial activity, and stored in a refrigerator at 4°C pending analysis.

Nitrate in the samples was converted to nitrous oxide (N₂O) using the denitrifier technique described in Sigman et al. (2001). In short, *Pseudomonas aureofaciens* (ATCC® 13985™) was cultivated at 27°C in media consisting of 30 g/L tryptic soy broth (TSB, BD; Ref #211825, USA), 0.5 g/L (NH₄)₂SO₄ (ACS grade, Fisher Scientific), 4.9 g/L KH₂PO₄ (Laboratory grade, Fisher Scientific), and 1 g/L KNO₃ (ACS grade, Acros Organics). After 6–10 days, working cultures were centrifuged, concentrated eightfold, and divided into 2-mL aliquots. Then, 0.1 mL of antifoaming emulsion (Antifoam B, Sigma Aldrich, USA) was added to prevent foam during the helium-purging process. After the purging, water sample reacting with fertilizers was added to the sample vials, and the amount of injected samples was determined based on N₂O concentration. The sample vials were placed up-side down at room temperature overnight to prevent leakage during the conversion of N₂O to N₂. The sample vials were crushed before analyzing isotopes to inhibit bacterial activity and scavenge the dissolved CO₂ (Casciotti et al., 2002).

**Isotope Analysis**

From gases formed by the denitrifier technique mentioned above, N₂O was stripped through chemical traps and GC column installed in a TraceGas Pre-Concentrator (IsoPrime, UK), and its isotopic composition was analyzed by online linked IsoPrime isotope ratio mass spectrometer (GV Instruments, UK) at the Korea Basic Science Institute (KBSI). All δ¹⁵N/¹⁸O and δ¹⁸O/¹⁶O ratios are reported in delta (δ) notation relative to Air and Vienna Standard Mean Ocean Water (VSMOW), respectively:

\[
\delta^{15}N = \left( \frac{\text{N}_{\text{sample}}}{\text{N}_{\text{Air}}} \right) \times 1000 - 1
\]

\[
\delta^{18}O = \left( \frac{\text{O}_{\text{sample}}}{\text{O}_{\text{VSMOW}}} \right) \times 1000 - 1
\]

The correction factor method was used to correct mass fractionation and instrumental mass bias during the measurement because it is suitable for raw δ¹⁵N and δ¹⁸O correction (Rock and Ellert, 2007; Xue et al., 2010). The correction factor (CF) is calculated as the ratio of the difference between the certified and the measured isotope (i.e., δ¹⁵N or δ¹⁸O) values of the samples:

\[
\text{CF}_{\text{iso}} = \left( \delta^{15}N_{\text{sample}} \right) / \left( \delta^{15}N_{\text{certified}} / \delta^{15}N_{\text{sample}} \right) - 1 \times 1000
\]

\[
\text{CF}_{\text{iso}} = \left( \delta^{18}O_{\text{sample}} \right) / \left( \delta^{18}O_{\text{certified}} / \delta^{18}O_{\text{sample}} \right) - 1 \times 1000
\]

where reference materials R1 and R2 are IAEA-NO3 and USGS-34, respectively. The measured δ¹⁵N and δ¹⁸O values of the samples were corrected using the following equations:

\[
\delta^{15}N_{\text{sample}} = \delta^{15}N_{\text{sample}} \times \text{CF}_{\text{iso}} / \text{CF}_{15N}
\]

\[
\delta^{18}O_{\text{sample}} = \delta^{18}O_{\text{sample}} \times \text{CF}_{\text{iso}} / \text{CF}_{18O}
\]
Replicate samples were analyzed (at least two samples), and uncertainties are reported as two standard deviations (2σ). The two reference materials, IAEA-NO3 and USGS-34 (4.7 ± 0.2‰ and -1.8 ± 0.2‰ for δ¹⁵N, and 25.6 ± 0.4‰ and -27.9 ± 0.6‰ for δ¹⁸O, respectively), were repeatedly measured during the period of analysis. IAEA-NO3 yielded 4.7 ± 0.2‰ for δ¹⁵N and 25.6 ± 0.6‰ for δ¹⁸O (2σ, n = 40), and USGS-34 yielded −1.8 ± 0.2‰ for δ¹⁵N and −27.9 ± 0.7‰ for δ¹⁸O (2σ, n = 40), all of which in a good agreement with the certified values.

Results and Discussion

Nitrate Isotopes for Korean Organic and Inorganic Fertilizers

Dual isotopic compositions of nitrate stripped from all inorganic, organic and plant-based compound fertilizer samples (IOF, OF and PCF) were given in Table 1. The nitrogen isotope composition of the IOF (δ¹⁵N) exhibited a relatively narrow range compared to those of the other fertilizers. The δ¹⁵N values of the OF and PCF (δ¹⁵N and δ¹⁸O, respectively) had the relatively wide ranges from -1.2 to 26.2‰ (average 14.7 ± 7.7‰, n = 30), and from -1.0 to 25.5‰ (average 10.9 ± 6.7‰, n = 24), respectively.

Most of the δ¹⁸O values in this study were within the ranges representative of chemical fertilizer and manure (Hübner, 1986; Aravena et al., 1993; Kendall, 1998, Vitòria et al., 2004; Fiorentino et al., 2015) (Fig. 2). The range of δ¹⁸O values was widest among all types of fertilizer, and much wider than the reported range of between ca. 10 and >20‰ for animal waste (Tihansky and Sacks, 1997 and references therein). This result would be triggered by various kinds of main ingredients and additives. By comparison, the PCFs have a wider range of δ¹⁸O values than the IOFs due to their diverse additives (including a small amount of N derived from inorganic compound, average 4.5 ± 0.8%).

Table 1. Dual isotope compositions of nitrate derived from three types of Korean fertilizers (unit in ‰)

| Sample | δ¹⁵N 2σ | δ¹⁸O 2σ | Sample | δ¹⁵N 2σ | δ¹⁸O 2σ | Sample | δ¹⁵N 2σ | δ¹⁸O 2σ |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| IOF-1  | 3.8    | 0.1    | 18.9   | 0.7    |        | OF-1   | 20.4   | 0.3    | 7.4    | 0.1 |
| IOF-2  | 5.3    | 0.2    | 16.5   | 0.8    |        | OF-2   | -0.6   | 0.1    | 8.0    | 1.0 |
| IOF-3  | 6.2    | 0.3    | 17.6   | 0.5    |        | OF-3   | 21.7   | 1.0    | 7.4    | 0.4 |
| IOF-4  | 3.9    | 0.0    | 17.3   | 0.7    |        | OF-4   | 18.8   | 0.4    | 8.8    | 0.1 |
| IOF-5  | 5.6    | 0.0    | 21.7   | 0.3    |        | OF-5   | 15.0   | 0.2    | 11.0   | 0.5 |
| IOF-6  | 4.7    | 0.1    | 19.0   | 0.7    |        | OF-6   | 15.7   | 0.5    | 7.1    | 0.6 |
| IOF-7  | 0.5    | 0.8    | 22.7   | 0.4    |        | OF-7   | 10.9   | 0.1    | 1.6    | 0.8 |
| IOF-8  | 0.9    | 0.6    | 21.8   | 1.1    |        | OF-8   | 17.2   | 0.3    | 1.0    | 0.1 |
| IOF-9  | 1.7    | 0.6    | 22.6   | 1.5    |        | OF-9   | 23.2   | 0.1    | 14.4   | 0.4 |
| IOF-10 | 0.4    | 0.1    | 21.9   | 1.2    |        | OF-10  | 21.7   | 0.2    | 3.5    | 0.2 |
| IOF-11 | 1.0    | 0.1    | 19.0   | 0.3    |        | OF-11  | 2.1    | 0.2    | 4.4    | 0.2 |
| IOF-12 | 3.0    | 0.0    | 20.9   | 0.6    |        | OF-12  | 7.5    | 0.3    | -4.0   | 0.8 |
| IOF-13 | 2.0    | 0.1    | 20.4   | 0.2    |        | OF-13  | 24.4   | 0.2    | 10.5   | 1.3 |
| IOF-14 | -0.9   | 0.6    | 15.1   | 0.2    |        | OF-14  | 11.5   | 0.3    | 14.1   | 0.2 |
| IOF-15 | 1.0    | 0.0    | 22.5   | 1.4    |        | OF-15  | 24.0   | 0.8    | 7.6    | 0.1 |
| IOF-16 | 3.8    | 0.4    | 16.5   | 0.0    |        | OF-16  | -1.2   | 0.1    | 4.4    | 0.6 |
| IOF-17 | -0.4   | 0.3    | 18.9   | 0.6    |        | OF-17  | 12.2   | 0.0    | 5.4    | 0.1 |
| IOF-18 | -1.1   | 0.3    | 14.1   | 0.3    |        | OF-18  | 22.6   | 0.2    | 12.5   | 0.2 |
| IOF-19 | 7.6    | 0.2    | 19.7   | 1.4    |        | OF-19  | 17.7   | 0.5    | 5.8    | 0.0 |
| PCF-1  | 8.0    | 1.1    | 19.4   | 1.2    |        | PCF-2  | 10.2   | 0.1    | 11.7   | 0.6 |
| PCF-3  | 2.0    | 0.3    | 19.4   | 0.6    |        | PCF-4  | 14.6   | 0.7    | 9.4    | 0.1 |
| PCF-5  | 17.8   | 0.3    | 17.7   | 0.1    |        | PCF-6  | 15.4   | 0.7    | 11.0   | 1.2 |
| PCF-7  | 13.2   | 0.2    | 18.3   | 0.5    |        | PCF-8  | 7.6    | 0.0    | 19.6   | 0.0 |
| PCF-9  | 0.7    | 0.1    | 10.6   | 0.8    |        | PCF-10 | 15.3   | 0.1    | 12.3   | 0.7 |
| PCF-11 | 8.7    | 0.2    | 12.7   | 0.6    |        | PCF-12 | 12.5   | 0.2    | 13.8   | 0.1 |
| PCF-13 | 21.6   | 0.5    | 12.4   | 1.2    |        | PCF-14 | 12.0   | 0.5    | 31.0   | 0.2 |
| PCF-15 | 15.4   | 0.1    | 1.8    | 0.8    |        | PCF-16 | 6.8    | 0.1    | 24.8   | 1.1 |
| PCF-17 | 1.8    | 0.3    | 21.1   | 0.2    |        | PCF-18 | 15.5   | 0.2    | 17.3   | 0.1 |
| PCF-19 | 15.8   | 0.1    | 15.0   | 0.4    |        | PCF-20 | 4.7    | 0.6    | 22.6   | 0.7 |
| PCF-21 | 6.0    | 0.1    | 18.6   | 0.2    |        | PCF-22 | -1.0   | 0.0    | 20.3   | 0.2 |
| PCF-23 | 12.2   | 0.3    | 10.2   | 0.9    |        | PCF-24 | 25.5   | 0.9    | 12.9   | 1.3 |
| PCF-25 | 17.1   | 1.0    | 2.6    | 0.6    |        | PCF-26 | 13.2   | 0.0    | 3.0    | 0.4 |
| PCF-27 | 15.4   | 0.2    | 1.0    | 0.2    |        | PCF-28 | 22.9   | 0.2    | 6.0    | 0.3 |
| PCF-29 | 14.8   | 0.1    | 7.0    | 0.1    |        | PCF-30 | 12.1   | 0.0    | 4.5    | 0.0 |

(a) Uncertainty: two standard deviations

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same decomposition level in subsurface environment. Nitrification processes compared to ABOF (or OF) if they are in the soil. On two samples, the δ 18O values ranged from 1.8 to 31.0‰ (average 16.0 ± 6.1‰, n = 24). With an exception of PBOF (or PCF) is characterized by the lower δ 18O values (<11‰). Meanwhile, it is important to note that PBOF contained more 15N-depleted organic N and total N than those of ABOF. According to the South Korea Rural Development Administration (Rural Development Administration, 2012), non-fermented raw materials are used to produce PBOF, and microbial biodegradation would not occur in the manufacturing process. In addition, composting process, degradation of organic waste by microbial communities, was typically performed for OF, but not for PCF, causing release of 15N-depleted NH3 gas (Ni et al., 2010; Shin et al., 2017). These imply that nitrate released from PBOF (or PCF) is characterized by the lower δ 15N values through nitrification processes compared to ABOF (or OF) if they are in the same decomposition level in subsurface environment.

The oxygen isotope compositions of IOFs and OFs (δ 18Oeff and δ 18Oex, respectively) differed from those of PCFs (Table 1, Fig. 2). The δ 18Oeff and δ 18Oex values ranged from 14.1 to 22.7‰ (average 19.3 ± 2.6‰, n = 19) and from -4.5 to 14.4‰ (average 5.9 ± 4.9‰, n = 30), respectively. In contrast, the PCFs exhibited δ 18O values ranging from 1.8 to 31.0‰ (average 16.0 ± 6.1‰, n = 24). With an exception on two samples, the δ 18Oex values were similar to but slightly wider than the indicative range (18 ~ 22‰) of NO3 fertilizer (Amberger and Schmidt, 1987) because all three oxygen atoms in the inorganic fertilizers are from atmospheric O2 with δ 18O value of 23‰, globally homogeneous (Kroopnick and Craig, 1972; Koch, 2007). The OFs had comparatively low δ 18O values, likely less than 15‰ (Wassenaar, 1995). The result indicates that δ 18O values of nitrate are determined by microbial nitrification. Typically, one-third of the oxygen atoms in nitrate are derived from air, and the rest from ambient water that nitrate is formed (Anderson and Hooper, 1983; Kumar et al., 1983; DiSpirito and Hooper, 1986).

According to previous study reporting δ 18O (approximately 6.8 ~ 22‰), regardless of their main ingredients (Fig. 2). These imply that nitrate released from manufacturing process. In addition, composting process, degradation of organic fertilizer and manure, and the range indicative of microbial biodegradation would not occur in the manufacturing process. As suggested in previous study (Shin et al., 2017), NH3 gas volatilization would occur during the laboratory extraction, subsequently resulting in 15N-enriched nitrate. The degree of fermentation of main organic materials would mainly affect isotopes of PCFs. For OFs, increase in dual isotope compositions would not be observed during the eluting nitrate in this study because main ingredients of OFs had been fermented during manufacturing processes (e.g., composting process); it is likely to result from mixing between manure (or OFs) and chemical fertilizer. Nonetheless, it is more reasonable that the behavior of isotopes of PCFs was due to nitrification occurring following manufacturing processes. As suggested in previous study (Shin et al., 2017), NH3 gas volatilization would occur during the laboratory extraction, subsequently resulting in 15N-enriched nitrate. The degree of fermentation of main organic materials would mainly affect isotopes of PCFs. For OFs, increase in dual isotope compositions would not be observed during the eluting nitrate in this study because main ingredients of OFs had been fermented during manufacturing processes (e.g., composting process); it is likely to result from mixing between manure (or OFs) and chemical fertilizer. Nonetheless, it is more reasonable that the behavior of isotopes of PCFs was due to nitrification occurring following manufacturing processes.
nitrification, i.e., -10% to 10% for δ15N values (Mayer et al., 2001; Michalski et al., 2004; Kendall et al., 2007). δ15N values of organic material-based fertilizers are closely related to the degree of fermentation of organic fertilizers. According to manure-hydrolysis experiment conducted by Lee et al. (2011), δ15N of manure rapidly increased due to NH3 volatilization during the hydrolysis. As mentioned earlier, OFs experienced composting process during manufacturing processes, implying that organic wastes were sufficiently degraded. Thus, for OFs, nitrogen isotope fractionation was negligible in this study even though NH3 would be released by volatilization process. Most OFs plotted in the cluster characterized by microbial nitrification processes. PCFs were produced by many small business manufacturers and the main ingredients used in PCFs would be at different decomposition level. In addition, the PCFs included the different kind of additives. For the reasons, dual isotopic ranges of PCFs can be away from manure cluster, with δ18O value higher than those in previous studies (approximately 10%). Nonetheless, we should consider possibility that dual isotopic compositions originating from PCFs is subsequently in the manure cluster due to microbial nitrification processes occurring in subsurface environment.

Application for Identifying Nitrate Sources

Many studies conducted in various countries have used a typical cluster of δ15N and δ18O values (Kendall, 1998) to determine nitrate sources and understand the reactions in the study area. In many previous studies in South Korea, both of the isotope values have been determined to trace nitrate sources in groundwater and surface water (Lee et al., 2008; Koh et al., 2010; Choi et al., 2011; Cheong et al., 2012; Shin et al., 2014; Kim et al., 2015; Kaown et al., 2018) in South Korea superimposed on the revised fields of nitrate from fertilizers determined in this study. Main factors determining the isotopic ranges were shown in italic.

Figure 4. Plot of δ15N and δ18O values of nitrate from previous studies (Lee et al., 2008; Koh et al., 2010; Choi et al., 2011; Cheong et al., 2012; Shin et al., 2014; Kim et al., 2015; Kaown et al., 2018) in South Korea superimposed on the revised fields of nitrate from fertilizers determined in this study. Main factors determining the isotopic ranges were shown in italic.

Dissolved nitrate in the Han River (HR) was explained by soil organic matter in the North Han River and by either manure/sewage in the South Han River (Lee et al., 2008). However, according to our results, the dissolved nitrate could be mainly derived from OFs with markedly low δ15N value and fermented PCFs, and OFs; the both organic material-based fertilizers would be evolved into nitrate with the higher isotopic compositions because of transformation processes (e.g., volatilization, nitrification, denitrification) occurring in agricultural field. Considering the transformation processes, the nitrate with relatively low isotopic values was closely related to soil organic matter as well. This possibility seems to be reasonable because the sampling sites in the HR Basin are dominated by agricultural land use. In similar, the water samples collected from areas with dominant agricultural land uses within the Geum River (GR) Basin and Odae stream (OS) watershed were characterized by nitrate derived from a mixture of manure-derived fertilizers (Choi et al., 2011; Shin et al., 2014). The suggestion in the previous studies is also supported by our results, with a consideration for transformation processes as mentioned above.

In addition, our results revealed that the nitrate sources in groundwater collected from eastern part of the study area were mainly derived from organic fertilizer including manure, while those in groundwater collected from the other parts was attenuated by denitrification processes (Kaown et al., 2018). A study conducted in mid-western South Korea investigated the sources of nitrate in the shallow groundwater of an agricultural area, and indicated that it is derived predominantly from several sources; i.e., septic waste, inorganic fertilizers, and atmospheric deposition (Koh et al., 2010). Nitrate of groundwater in areas where paddy fields are exclusively distributed was mainly derived from two main sources (i.e., soil organic matter and manure-based fertilizers; Kim et al., 2015).

Although Cheong et al. (2012) indicated that most samples were in the representative range of manure and sewage (Figs. 2 and 3), our results revealed that nitrate in their studies could be mainly derived from soil organic N, organic material-based fertilizers (i.e., PCFs and OFs). These results suggest that determination of the typical ranges of δ15N and δ18O for the dominant nitrate sources in the study area should be completed before attempting to identify nitrate sources and understand related processes using the δ15N and δ18O values of nitrate.

Conclusions

The dual isotopic compositions of nitrate (δ15N and δ18O) for three types of Korean fertilizer were determined and their usefulness for identifying nitrate sources was evaluated, with a suggestion for dual isotopic ranges of nitrate derived from fertilizer. The average δ15N and δ18O values were 2.6 ± 2.5‰ and 19.3 ± 2.6‰ for inorganic fertilizer (IOF, n = 19), 14.7 ± 7.7‰ and 5.9 ± 4.9‰ organic fertilizers (OF, n =30), and 10.9 ± 6.7‰ and 16.0 ± 6.1‰ for plant-based compound fertilizer (PCF, n = 24), respectively. The combined δ15N and δ18O values enabled identification of the inorganic fertilizers and organic material-based fertilizers. On the plot of δ15N and δ18O values, PCFs varied between NO3 fertilizer and manure clusters. A type of additives and amount of N compound in the PCFs would not be related to the behavior of isotopic values for PCFs. The δ15N and δ18O values of PCFs would...
be dependent on their decomposition levels of main ingredients used during manufacturing processes. In similar, manure-based organic fertilizers can lie on the representative soil cluster as depending on various additives. The results indicate that the typical ranges of $\delta^15N$ and $\delta^18O$ for the dominant nitrate sources should be carefully determined to identify the origin and understand the fate of nitrate in South Korea.

Acknowledgements

This work was supported by the National Research Council of Science & Technology (NST) grant by the Korea government (MSIP) (No. CAP-17-05-KIGAM).

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