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The use of δ^{15}N and δ^{18}O tracers with an understanding of groundwater flow dynamics for evaluating the origins and attenuation mechanisms of nitrate pollution

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ABSTRACT

During early 2000, a new analytical procedure for nitrate isotopic measurement, termed the "denitrifier method", was established. With the development of the nitrate isotope tracer method, much research has been reported detailing sources of groundwater nitrate and denitrification mechanisms. However, a shortcoming of these tracer studies has been indicated owing to some overlapping of isotope compositions among different source materials and denitrification trends. In order to reduce these uncertainties, we examined nitrate isotope ratios within a frame of "regional groundwater flow dynamics" to eliminate unnecessary uncertainties in elucidating nitrate sources and behaviors. A total of 361 samples were collected from the Kumamoto area: the circulated groundwater system with a scale of 10^3 km^2 in southern Japan. Subsequently, the nitrate pollution was examined within the above-mentioned framework. As a result, a reasonable identification of the sources and attenuation behaviors (both denitrification and dilution) of groundwater nitrate pollution was obtained over the study area. This study demonstrates that the use of nitrate isotope tracers efficiently improves with a comprehensive understanding of groundwater flow dynamics. The approach emphasized in this study is important and should be applicable in other areas.

1. Introduction

Groundwater nitrate pollution is one of the most prevalent and on-going global natural water environmental problems (Rivett et al., 2008). The comprehension of nitrate pollution sources and natural attenuation mechanisms is of prime importance for better management of groundwater resources. The stable isotope ratio of nitrogen in nitrate ($\delta^{15}N_{NO_3}$) has been used since the 1970s as a powerful tracer revealing concealed pollution sources and to understand the mechanisms of denitrification (i.e. Kreitler, 1979; Kaplan and Magaritz, 1986; Mariotti et al., 1988; Smith et al., 1991). By the early 1990s, the combined use of $\delta^{15}N_{NO_3}$ with the stable isotope of oxygen in nitrate ($\delta^{18}O_{NO_3}$) was proposed and applied for groundwater study (for example Böttcher et al., 1990; Wassenaar, 1995; Aravena and Robertson, 1998; Fukada et al., 2003). In addition, the newly established analytical procedure of nitrate isotopic measurement termed the "denitrifier method" (Sigman et al., 2001; Casciotti et al., 2002) enables the determination of dual $\delta^{15}N_{NO_3}$ and $\delta^{18}O_{NO_3}$ using a smaller volume of water (<8 ml) with lower NO_3^- concentration in quicker preparation time than previous methods. The

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nitrate isotope tracer method has become established as a better tracing tool and has increasingly been applied in many parts of the world (i.e. Umezawa et al., 2008; Otero et al., 2009; Hosono et al., 2011a).

Within a nitrate isotope tracing study, the pollution sources can be estimated by isotopic comparison between the water samples and possible source materials (Kendall, 1998). The isotopic comparison can also be used as a denitrification indicator by analyzing isotopic enrichment trends of water samples (Kendall, 1998). However, source distinguishment becomes difficult when different possible source materials, such as manure and sewage, have a similar isotope signature (Xue et al., 2009; Fenech et al., 2012; Minet et al., 2012). Moreover, if isotopic compositions overlap between the source characteristics and denitrification trends, this distinction becomes difficult (Xue et al., 2009). These difficulties complicate data interpretation. Therefore, it has recently been argued that a new approach and concept are needed to reduce the above mentioned shortcomings in nitrate isotope tracer studies (Xue et al., 2009; Fenech et al., 2012; Minet et al., 2012).

In a circulated groundwater system, dissolved nitrate is introduced to groundwater at the recharge zone and transported through the lateral flow zone to the discharge zone within a frame of "groundwater flow dynamics" (Böhlke and Denver, 1995; Böhlke et al., 2002; Hosono et al., 2011b). Therefore, having a good understanding of the three-dimensional groundwater flow pathway is very important when tracing complicated nitrate sources and behaviors using a nitrate isotope tracer. In addition, it is important to prepare detailed land-use information for the target area, especially for the assessment of potential impacts from manure and sewage (Xue et al., 2009; Fenech et al., 2012; Minet et al., 2012). The nitrate isotope tracer study method with a combined use of the above mentioned control information appears to be an efficient approach for reducing uncertainties in the past study. However, emphasis has not been clearly placed on its importance in previous articles.

Kumamoto City is located in the central part of the Kyushu Islands in southern Japan. The city is known as the largest groundwater utilization region in Japan where about one million people in and around the city depend entirely on groundwater for drinking purpose (Oshima, 2010; Shimada, 2012). However, the monitoring data for groundwater quality show that nitrate concentrations have been increasing since 1970s (Tomiie et al., 2009, 2011). For example, NO_3^- concentrations for some wells (Fig. 1a) increased by a factor of 2–7 during the last 40 years (Appendix 1). Although nitrate source controls have been implemented since the 1990s, such as control of fertilizer applications and the construction of barriers around manure storage sites, groundwater NO_3^- is still increasing and becoming an increasingly serious environmental issue (Kumamoto Prefecture and Kumamoto City, 2005; Kumamoto City Waterworks and Sewerage Bureau, 2008; Kumamoto City, 2009; Oshima, 2010). However, the principal causes of the pollution and natural attenuation mechanisms have not been fully understood.

This study presents a comprehensive amount of nitrate isotope data (total of 361 samples) for groundwater (confined and unconfined) and comparison water (spring and river water) during different seasons, and possible source materials (chemical fertilizers, manures, and sewage water) taken from the Kumamoto area. These data were used within a tracer study in the context of groundwater flow dynamics. We firstly tried to understand the general view of the origins of groundwater nitrate pollution, and then examined detailed attenuation mechanisms along the flow paths by denitrification as well as by mixing of the different source water. The results from these investigations were used to emphasis the usefulness of the above approach for reducing uncertainties encountered in previous studies, which is the prime objective of this study. The approach could be applicable in future studies for a better understanding of the sources and attenuation mechanisms of groundwater nitrate pollution.

2. Outline of the research area

2.1. Topography and climate

The Kumamoto groundwater area is defined as an area (945 km^2) surrounded by the divide of the Shira River watershed to the north, the Midori River to the south, the Aso Mountain (1592 m) to the east, and the Ariake Sea and Kinpo Mountain (665 m) to the west (Fig. 1a). The altitude of this area tends to decrease westward from land to ocean. Importantly, volcano-pyroclastic and lava flow deposits derived at the time of the Aso Caldera formation formed three major highlands with altitudes around 100 m: the Kikuchi and Takayubaru highlands extending westwards and the Ueki highlands to the north of the Kumamoto area (Fig. 1a). In addition, volcanic flow deposits of the Pre-Aso activity formed small hills in the central area such as Tatsuta Mountain (Fig. 1a). Kumamoto had an average annual temperature and precipitation of 16.9 °C and 1986 mm, respectively during 1980–2010. The rainy season occurs from June–July with around 40% of the total annual precipitation occurring during this period.

2.2. Geology

The study area is composed of four major geological constituents (Fig. 2): the Paleozoic basement of metamorphic and sedimentary rocks; the Pre-Aso volcanic rocks of Tertiary–Quaternary age; the Quaternary Aso volcanic rocks; and overlaying alluvium deposits. Paleozoic basement rocks do not outcrop at the surface within the study area. The Pre-Aso volcanic rocks generally consist of lavas and tuff breccia (Ono and Watanabe, 1985; Miyoshi et al., 2009), while the Aso volcanic rocks are composed of pyroclastic deposits and flow lavas (Ono and Watanabe, 1985). The former rocks are present at/around the Kinpo and Tatsuta Mountains (Fig. 1a), while latter rocks are distributed around the eastern side of the Kinpo Mountain and the western side of the Aso Caldera. Both rock types have a wide chemical range between basaltic–rhyolitic compositions (Ono and Watanabe, 1985; Miyoshi et al., 2009). The Aso volcanic rocks are subdivided into four units according to eruption stages: Aso-1 (270 ka); Aso-2 (140 ka); Aso-3 (120 ka); and Aso-4 (89 ka) (Ono and Watanabe, 1985). Of these, the Aso-2 unit is unique in its composition of andesitic lava with joints and porous structures. It is also important to note that clay impermeable layers of lacustrine