

Combined use of stable isotope ratios to understand groundwater quality changes in Kumamoto area, southern Japan

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Abstract Combined use of several stable isotope ratios is increasingly recognized as an important approach for comprehensive understanding of water deterioration mechanisms. However, such trials have not often been seen and the importance of the application of these tracers has not been fully demonstrated. This paper presents a case study in Kumamoto groundwater, southern Japan, applying multiple isotope ratios ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{15}\text{N}_{\text{NO}_3}$, and $\delta^{34}\text{S}_{\text{SO}_4}$) for better understanding the causes of groundwater deterioration. Our results showed that sulfate in the groundwater originates from multiple sources (pyrite oxidation, volcanic components and anthropogenic materials), but nitrate was mostly derived from anthropogenic sources. Anthropogenic impact to DIC was also assessed by using $\delta^{13}\text{C}_{\text{DIC}}$ data. This study showed that multiple-use of isotope tracers is advantageous for comprehensive understanding of the cause of water quality change. However, the utility of this approach should be developed as a better tool for elucidating the pollution attenuation mechanisms in future work.

Key words groundwater; quality change; multiple stable isotope ratios; Kumamoto area, Japan

INTRODUCTION

Deterioration of groundwater quality has become a serious environmental problem worldwide. The stable isotope ratios of dissolved ions have been applied for elucidating the groundwater deterioration mechanisms and pollution attenuation processes (Clark & Fritz, 1997). In terms of dissolved elements of environmental concern, groundwater nitrate pollution is the major problem reported in Japan. Therefore, nitrate isotope ratios ($\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$) have been given the greatest attention among several other stable isotope ratios in our country. However, other ions and elements will also contribute to water quality change in the areas where non-point source groundwater pollution occurs. Thus, their concentrations and isotope ratio data potentially supply important information for better understanding the water deterioration mechanism. Among the major dissolved ions in groundwater (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , HCO_3^- , NO_3^- , and SO_4^{2-}), HCO_3^- and SO_4^{2-} have stable isotope ratios of $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$. The $\delta^{13}\text{C}$ in HCO_3^- is generally measured as the carbon isotope ratio in dissolved inorganic carbon (DIC). These isotope ratios (expressed as $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{34}\text{S}_{\text{SO}_4}$, respectively) have been conventionally applied in hydrogeochemical studies as good markers for examining the origins of these ions and their biogeochemical processes (Clark & Fritz, 1997). Since 2000, the importance of multiple uses of all of these isotope ratios ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{15}\text{N}_{\text{NO}_3}$, and $\delta^{34}\text{S}_{\text{SO}_4}$) has increasingly been emphasized by many workers (Vengosh *et al.*, 2002; Widory *et al.*, 2004; Vitòria *et al.*, 2008; Otero *et al.*, 2009; Hosono *et al.*, 2009, 2010, 2011). However, multi-dimensional investigations of groundwater quality changes by such an approach have not been adequately discussed.

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. The Kumamoto groundwater area (945 km²) is surrounded by the divide of the Shira River watershed to the north, the Midori River to the south, Aso Mountain (1592 m) to the east, and the Ariake Sea and Kinpo Mountain (665 m) to the west (Fig. 1(a)). Because of the importance of groundwater here, the long-term records for groundwater potential and quality, flow dynamics and ages, and land-use character are well summarized and understood (Fig. 1). The aquifers are divided into two main types: unconfined and confined aquifers. Unconfined groundwater is situated generally at ~50 m under the surface and

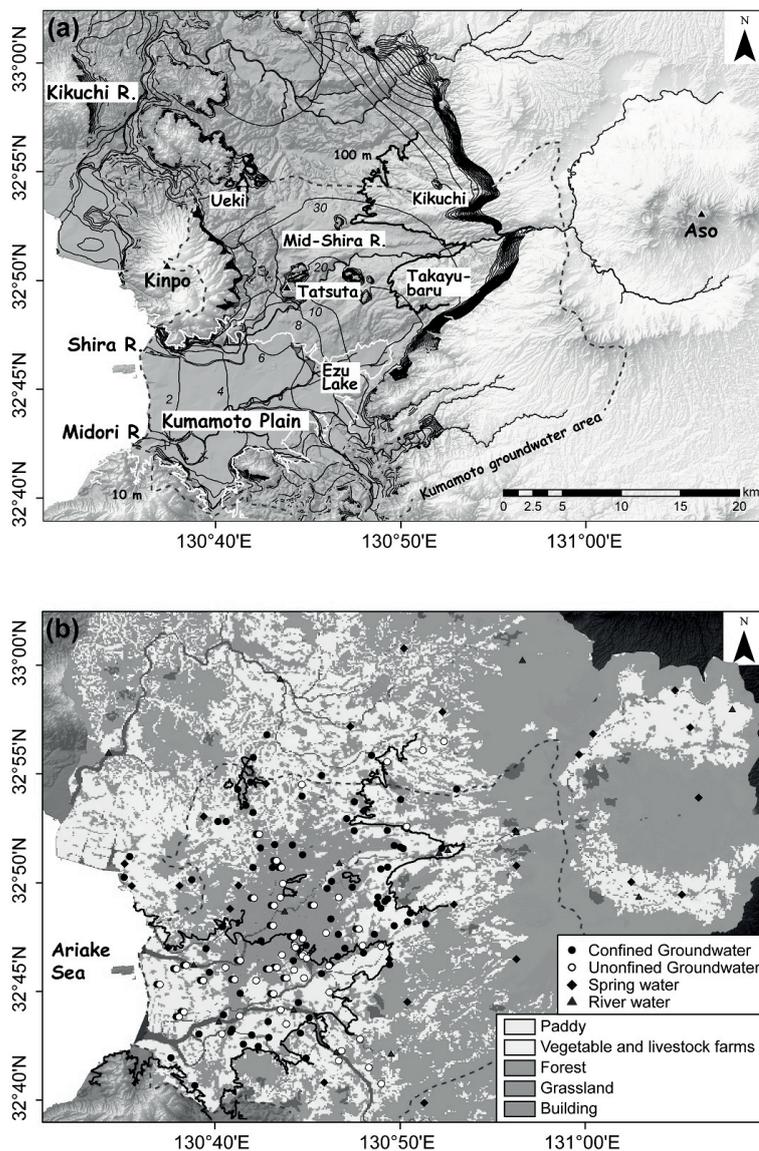


Fig. 1 Map showing: (a) topography and groundwater potential and (b) land-use and sampling locations in the Kumamoto area. Solid contour lines with numbers in Fig. 1(a) represent groundwater levels (m, above sea level) calculated with a groundwater flow model using a surface and subsurface coupling flow simulator, GETFLOWS (Tosaka *et al.*, 2000).

confined groundwater occurs at 60–200 m b.g.l. More detailed information regarding topography, climate, geology, hydrogeology, groundwater flow and age, and land-use and groundwater use in Kumamoto groundwater area is described in Hosono *et al.* (2013).

The groundwater quality monitoring showed an increasing trend of nitrate concentrations, with increases of 2 to 7 fold since the 1970s (Tomiie., 2011), which is recognized as a serious environmental concern in the Kumamoto. Recently, a nitrate isotope tracer study revealed that the application of chemical fertilizers is a prime cause of groundwater nitrate pollution in Kumamoto (Hosono *et al.*, 2013). It is clear that high nitrate concentrations are distributed in the recharge zone where agricultural farms widely occur (Fig. 2(a)). This zone is also characterized by high DO, $>6 \text{ mg L}^{-1}$ and a non-fractionated $\delta^{15}\text{N}_{\text{NO}_3}$ signature of generally $<8\text{‰}$ (Fig. 2(b)). However, $\delta^{15}\text{N}_{\text{NO}_3}$ drastically increased with decreasing of NO_3^- along the groundwater flow toward the coastal anaerobic zone (Fig. 2(a) and (b)), suggesting the occurrence of denitrification (Hosono *et al.*, 2013). Moreover, in a more reduced environment than the environment where denitrification

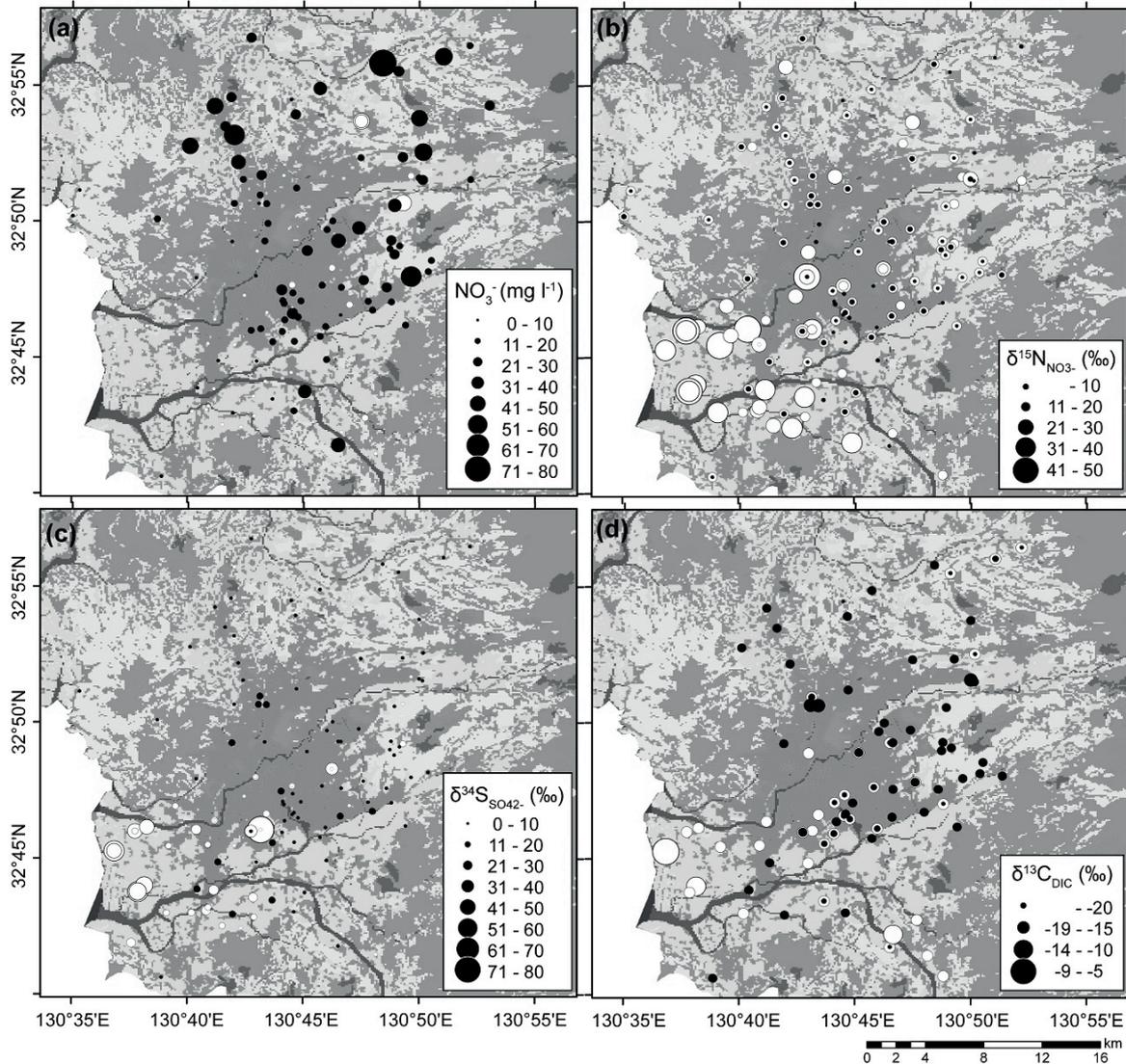


Fig. 2 Distribution map for: (a) NO_3^- , (b) $\delta^{15}\text{N}_{\text{NO}_3^-}$, (c) $\delta^{13}\text{C}_{\text{DIC}}$, and (d) $\delta^{34}\text{S}_{\text{SO}_4}$ in the study area. Black circle represents groundwater (confined + unconfined) samples with $\text{DO} > 6 \text{ mg L}^{-1}$ and $\delta^{15}\text{N}_{\text{NO}_3^-} < 8\text{‰}$, which are discussed in this paper. White circle indicates all samples collected over Kumamoto area (Hosono *et al.*, 2013).

would occur, similar isotopic fractionation might occur for $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ (Clark & Fritz, 1997) due to anaerobic bacterial reactions such as methanogens and bacterial sulfate reduction (Morris *et al.*, 2003). Therefore, when applying these isotope tracers as source determination tools and discussing source mixing, one should exclude $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{15}\text{N}_{\text{NO}_3^-}$, and $\delta^{34}\text{S}_{\text{SO}_4}$ data which have been affected by isotopic fractionation during the above-mentioned anaerobic bacterial activities.

In this paper, we used multiple isotope ratios ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{15}\text{N}_{\text{NO}_3^-}$, and $\delta^{34}\text{S}_{\text{SO}_4}$) as source determination tracers for groundwater samples with high DO ($> 6 \text{ mg L}^{-1}$) and non-fractionated $\delta^{15}\text{N}_{\text{NO}_3^-}$ signature (generally $< 8\text{‰}$) under the hypothesis that isotopic fractionation due to anaerobic bacterial activity does not take place within these samples (the effect of isotopic fractionation due to anaerobic bacterial activities could be neglected). Emphasis is placed on discussing detailed source characteristics of dissolved HCO_3^- , NO_3^- , and SO_4^{2-} based on previously published $\delta^{15}\text{N}_{\text{NO}_3^-}$ and newly added $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ data. We attempt to demonstrate the utility of the multiple-isotope ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{15}\text{N}_{\text{NO}_3^-}$, and $\delta^{34}\text{S}_{\text{SO}_4}$) approach for better understanding the groundwater quality deterioration mechanism. The multiple isotope approach for elucidating pollution attenuation mechanisms will be discussed in a separate paper.

SAMPLING AND ANALYTICAL METHOD

The sampling locations are shown in Fig. 1(b). A total of 239 groundwater samples (83 for unconfined and 156 for confined groundwater) were collected during November 2009–November 2011 for measurements of major ion concentrations and $\delta^{15}\text{N}_{\text{NO}_3}$ compositions (Hosono *et al.*, 2013). In this paper, we use only the samples with $\text{DO} > 6 \text{ mg L}^{-1}$ and $\delta^{15}\text{N}_{\text{NO}_3} < 8\text{‰}$ from these samples. Furthermore, representative samples were chosen for $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ analysis from these selected samples. Seasonal changes of chemical and isotopic compositions were checked using samples collected during October–November 2011 for the high water season, and January–March 2011 for the low water season, respectively. In addition, a total of 86 river and spring water samples were collected during April 2011 (low water season) and July 2011 (high water season). Detailed sampling procedures are described in Hosono *et al.* (2013).

The dissolved oxygen (DO), NO_3^- , and $\delta^{15}\text{N}_{\text{NO}_3}$ data discussed in this paper are from Hosono *et al.* (2013). Concentrations of HCO_3^- and SO_4^{2-} were measured manually by titration of sulfuric acid and determined by using ion chromatography (Compact IC 761, Metrohm, Switzerland), respectively. The $\delta^{34}\text{S}$ of BaSO_4 and $\delta^{13}\text{C}$ of BaCO_3 were analysed on SO_2 and CO_2 gases, respectively, in a continuous-flow gas-ratio mass spectrometer (Thermo Fisher Delta V Advantage) interfaced with elemental analysers (Thermo Fisher Flash2000). Standardization was based on international standards and several other sulfate and carbonate materials that have been compared between laboratories. The precisions for both $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ were estimated to be better than $\pm 0.2\text{‰}$ based on repeated internal standards.

RESULTS AND DISCUSSION

Chemical and isotopic comparison between the samples collected in the high and low water seasons showed no significant seasonal differentiation for all parameters assessed in this study (Fig. 3). This suggests that the observed chemical and isotopic variations were generally related to a factor of space rather than time (seasonal scale). Since we are assuming that isotopic fractionation effects due to anaerobic bacterial activities can be neglected within the framework of this study, observed isotopic variations against ion concentrations (Figs 4 and 5) should be explained by different source mixing. In Figs 4 and 5, clear compositional gaps between the confined and unconfined groundwater were not observed, except for the HCO_3^- vs $\delta^{13}\text{C}_{\text{DIC}}$ diagram, which tended to show more depleted $\delta^{13}\text{C}_{\text{DIC}}$ and concentrated HCO_3^- for confined groundwater compared to those of unconfined groundwater (Fig. 4(b)). Hosono *et al.* (2013) found similar spatial compositional distributions between confined and unconfined groundwater for nitrate concentrations and isotope ratios, and concluded that in each case, similar processes were taking place along groundwater flows. A similar scenario can be expected for sulfate behaviour.

More detailed source characteristics can be found by looking at the plots signature in each isotope ratio vs concentration diagram (Figs 4 and 5). At first, it is clear from Fig. 4(a) that most of NO_3^- concentration groundwater samples and spring water samples ($> 40 \text{ mg L}^{-1}$) fall within a narrow $\delta^{15}\text{N}_{\text{NO}_3}$ compositional range of 2–8‰. It has already been concluded by detailed isotopic comparison with possible source references that long-term application of chemical fertilizers in the farm fields is the prime cause of groundwater nitrate contamination in Kumamoto (Hosono *et al.*, 2013). Therefore, NO_3^- concentration can be regarded as a water pollution indicator of agricultural impact. The $\delta^{15}\text{N}_{\text{NO}_3}$ compositions of river water were clearly higher than those of groundwater and spring water (Fig. 4(a)). It was concluded that nitrate in river water was partly derived from wastewater of sewage origin (Hosono *et al.*, 2013).

Figure 4(b) shows systematic compositional changes of $\delta^{13}\text{C}_{\text{DIC}}$ and HCO_3^- as water evolved from the surface, through spring, shallow unconfined, to deeper confined groundwater toward depleted $\delta^{13}\text{C}_{\text{DIC}}$ and concentrated HCO_3^- . In an environment where anaerobic bacterial activities would not occur, $\delta^{13}\text{C}_{\text{DIC}}$ in freshwater systems is controlled by four major processes: (1) oxidation of organic matter, (2) dissolution of carbonate minerals (if present), (3) exchange with atmospheric carbon dioxide, and (4) photosynthetic activity (in the surface environment) (Hélie *et al.*, 2002).

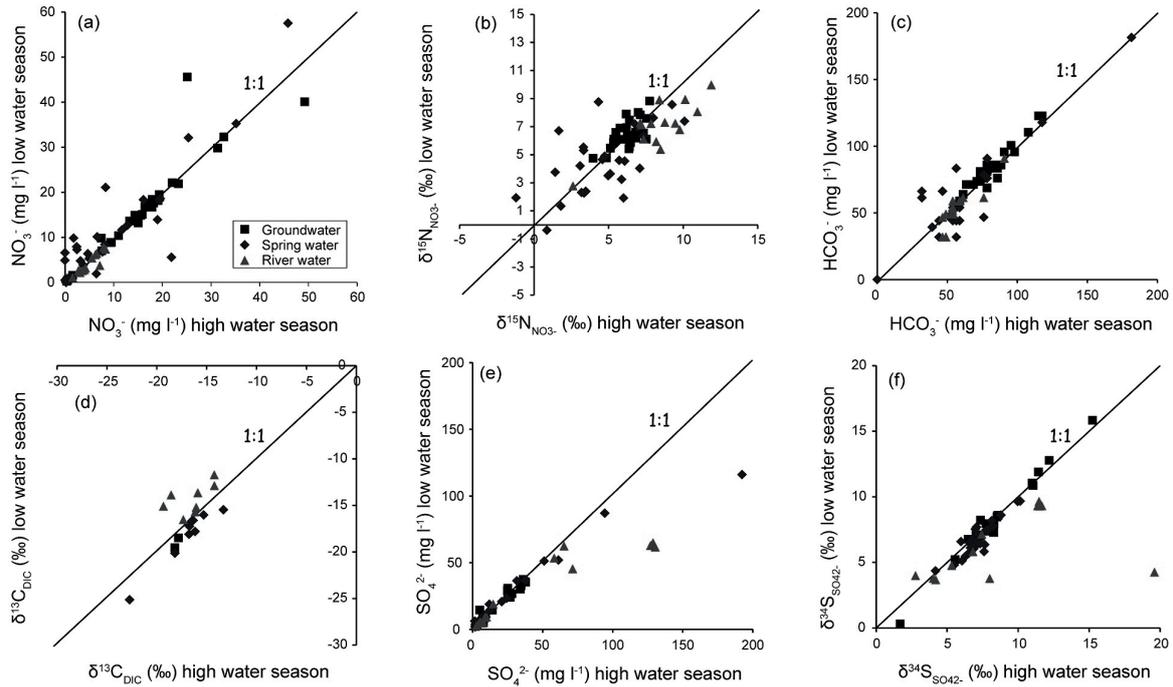


Fig. 3 Comparison between the high and low water seasons for: (a) NO_3^- , (b) $\delta^{15}\text{N}_{\text{NO}_3}$, (c) HCO_3^- , (d) $\delta^{13}\text{C}_{\text{DIC}}$, (e), SO_4^{2-} and (f) $\delta^{34}\text{S}_{\text{SO}_4}$. Groundwater samples plotted in the figures are selected only if $\text{DO} > 6 \text{ mg L}^{-1}$ and $\delta^{15}\text{N}_{\text{NO}_3} < 8\text{‰}$ for both confined and unconfined groundwater (see text for details).

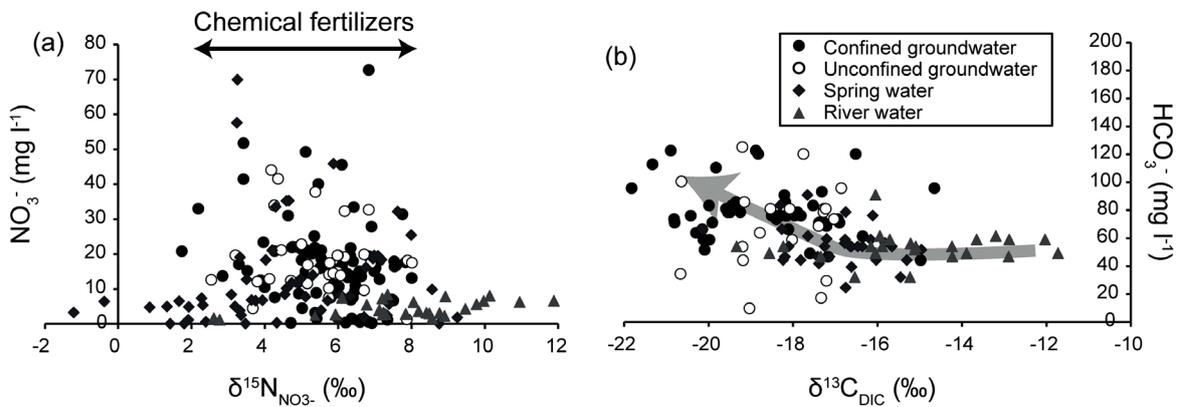


Fig. 4 (a) $\delta^{15}\text{N}_{\text{NO}_3}$ vs. NO_3^- and (b) $\delta^{13}\text{C}_{\text{DIC}}$ vs. HCO_3^- diagram for water samples (river water, spring water, and groundwater) collected from Kumamoto area. Groundwater samples plotted in the figures are selected only the water with $\text{DO} > 6 \text{ mg L}^{-1}$ and $\delta^{15}\text{N}_{\text{NO}_3} < 8\text{‰}$ for both confined and unconfined groundwater (see text for details).

Processes (2) and (3) play a major role in raising the $\delta^{13}\text{C}_{\text{DIC}}$ value to nearly 0‰, whereas, processes (1) and (4) act to decrease the $\delta^{13}\text{C}_{\text{DIC}}$ value to around -27‰ (Hélie *et al.*, 2002) with increasing HCO_3^- . Considering these basic facts, it is reasonable to interpret that river water with the least contribution of organic source C evolved as it moved to deeper zones which contain more. In addition, our results suggest that carbonate dissolution could not be a major cause of the compositional evolution found in Fig. 4(b). A decreasing tendency of $\delta^{13}\text{C}_{\text{DIC}}$ along the flow path was not confirmed (Fig. 6); rather, the lowest $\delta^{13}\text{C}_{\text{DIC}}$ groundwater was found at Ueki and Kikuchi highland (Fig. 1) where agricultural and livestock farms are widely distributed. It may be assumed that the impact of organic sources such as fertilizers and manures is related to the presence of the lowest $\delta^{13}\text{C}_{\text{DIC}}$ groundwater in these areas.

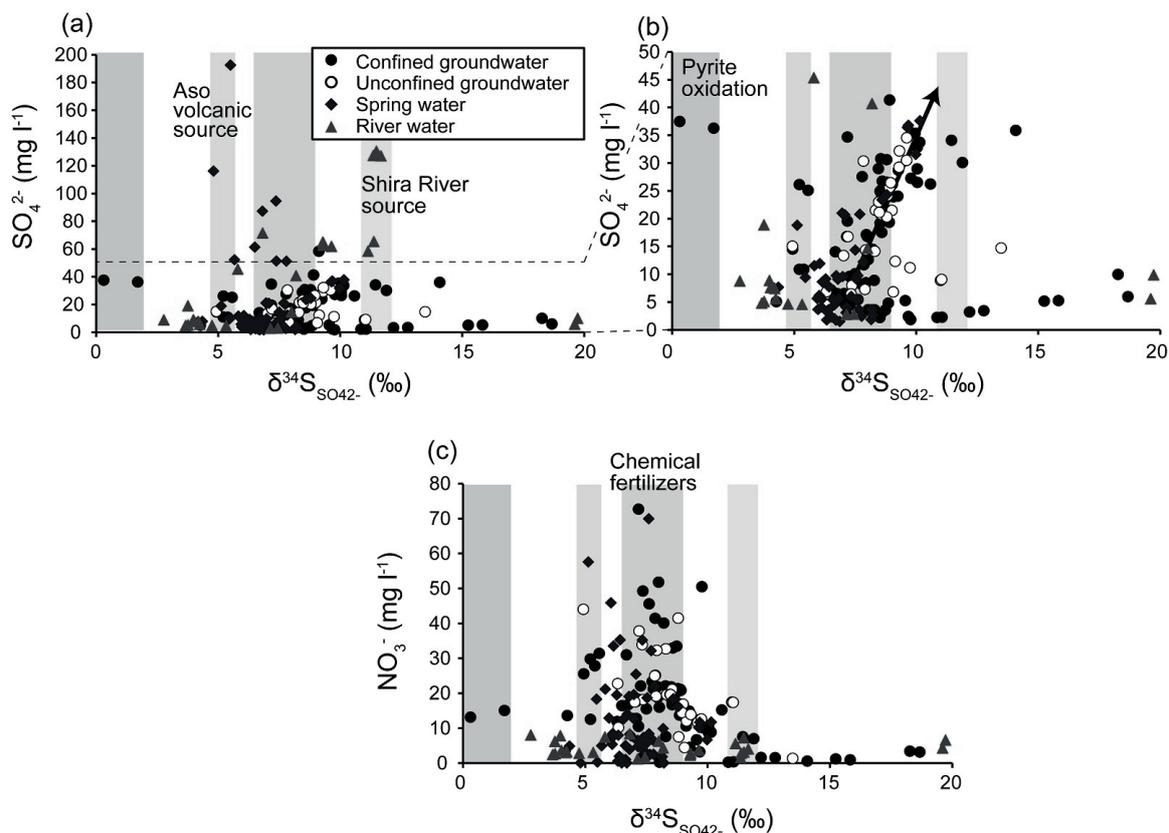


Fig. 5 (a) $\delta^{34}\text{S}_{\text{SO}_4}$ vs SO_4^{2-} with wide scale, (b) $\delta^{34}\text{S}_{\text{SO}_4}$ vs SO_4^{2-} with enlarged scale, and (c) $\delta^{34}\text{S}_{\text{SO}_4}$ - NO_3^- diagram for water samples (river water, spring water, and groundwater) collected from Kumamoto area. Groundwater samples plotted in the figures are only those with $\text{DO} > 6 \text{ mg L}^{-1}$ and $\delta^{15}\text{N}_{\text{NO}_3} < 8\text{‰}$ for both confined and unconfined groundwater (see text for details).

The $\delta^{34}\text{S}_{\text{SO}_4}$ compositions of the groundwater samples showed a wide range, between 0 to 20‰ (Fig. 5(a)). The $\delta^{34}\text{S}_{\text{SO}_4}$ vs SO_4^{2-} diagrams (Fig. 5(a) and (b)), show some high SO_4^{2-} peaks at certain $\delta^{34}\text{S}_{\text{SO}_4}$ compositional ranges. The first peak was found at the lowest $\delta^{34}\text{S}_{\text{SO}_4}$ compositions, 0–3‰. From its low $\delta^{34}\text{S}_{\text{SO}_4}$ signature, it can be assumed that this sulfate originates from oxidation of sulfide minerals such as pyrite in the aquifer geology (Krouse & Mayer, 2000). The second peak represents two spring water samples collected at the central Aso volcano with the highest SO_4^{2-} concentrations (120–200 mg L^{-1}) and shows $\delta^{34}\text{S}_{\text{SO}_4}$ compositions around 5‰ (Fig. 5(a) and (b)). This isotopic range represents volcanic source sulfate. Sulfate in some groundwater samples showing similar isotopic composition might be partly derived from such a volcanic sulfate source. These two sulfate sources are of natural origin.

It is important to note that most high NO_3^- water samples have $\delta^{34}\text{S}_{\text{SO}_4}$ compositions between 6 and 9‰ (Fig. 5(c)). There are some groundwater and spring water samples having elevated SO_4^{2-} concentrations within this $\delta^{34}\text{S}_{\text{SO}_4}$ compositional range (Fig. 5(a) and (b)), suggesting the presence of a partial contribution of fertilizers-bearing SO_4 to groundwater sulfate. However, the most significant trend found in Fig. 5 is the increasing trend of $\delta^{34}\text{S}_{\text{SO}_4}$ with increase of SO_4^{2-} concentrations shown by the black arrow in the figure. It is clear from this trend that the chemical and isotopic compositions of groundwater and spring water changed toward the compositional field of the Shira River water with the highest SO_4^{2-} concentrations (around 140 mg L^{-1}). It appears likely that sulfate in these groundwater samples was largely derived from recharged river water, as suggested by previous analysis based on the major ion chemical balance (Nagai *et al.*, 1983). River sulfate may be affected by the contribution of anthropogenic materials such as sewage (Hosono *et al.*, 2013) and also by sulfate of volcano-hydrothermal origin with a different isotopic signature to that we found at the Aso volcanic centre (the second peak sulfate source). More detailed isotopic

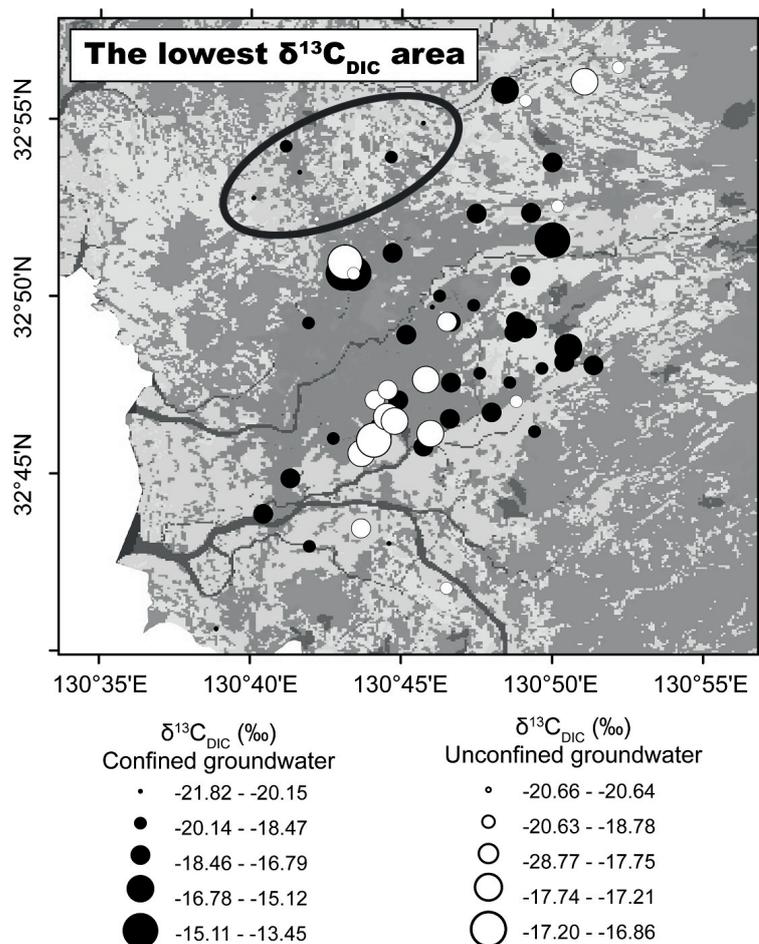


Fig. 6 Distribution map for groundwater $\delta^{13}\text{C}_{\text{DIC}}$ in the study area. Groundwater samples plotted in the figures are only those with $\text{DO} > 6 \text{ mg L}^{-1}$ and $\delta^{15}\text{N}_{\text{NO}_3} < 8\text{‰}$ for both confined and unconfined groundwater (see text for details).

characteristics of possible source materials should be clarified to differentiate these effects. Overall, these two sulfate sources include anthropogenic origins whereas the first two sulfate sources (oxidation of sulfide minerals and volcanic source) are of natural origin.

CONCLUSIONS

In order to understand the causes of groundwater deterioration in Kumamoto groundwater, detailed source characteristics of dissolved HCO_3^- , NO_3^- , and SO_4^{2-} were discussed using previously published $\delta^{15}\text{N}_{\text{NO}_3}$ and newly added $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ data. Our results show that these anions originate from multiple sources of both natural and anthropogenic materials. We demonstrated that multiple isotope ratios ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{15}\text{N}_{\text{NO}_3}$, and $\delta^{34}\text{S}_{\text{SO}_4}$) are useful to differentiate the different source effects for each ion, and therefore for better understanding of the causes of groundwater deterioration. However, this paper has only discussed source determination. The effects of biogeochemical reactions in anaerobic aquifer environments should be considered using multiple isotope ratios in a future work.

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