Using dual isotopic data to track the sources and behaviors of dissolved sulfate in the western North China Plain

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ABSTRACT

This paper investigated the sources and behaviors of sulfate in groundwater of the western North China Plain using sulfur and oxygen isotopic ratios. The groundwaters can be categorized into karst groundwater (KGW), coal mine drainage (CMD) and pore water (subsurface saturated water in interstices of unconsolidated sediment). Pore water in alluvial plain sediments could be further classified into unconfined groundwater (UGW) with depth of less than 30 m and confined groundwater (CGW) with depth of more than 60 m. The isotopic compositions of KGW varied from 9.3‰ to 11.3‰ for $\delta^{34}S_{SO4}$ with the median value of 10.3‰ ($n = 4$) and 7.9‰ to 15.6‰ for $\delta^{18}O_{SO4}$ with the median value of 14.3‰ ($n = 4$) respectively, indicating gypsum dissolution in karst aquifers. $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values of sulfate in CMD ranged from 10.8‰ to 12.4‰ and 4.8‰ to 8.7‰ respectively. On the basis of groundwater flow path and geomorphological setting, the pore water samples were divided as three groups: (1) alluvial–proluvial fan (II_1) group with high sulfate concentration (median values of 2.37 mM and 1.95 mM for UGW and CGW, respectively) and positive $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values (median values of 8.8‰ and 6.9‰ for UGW, 12.0‰ and 8.0‰ for CGW); (2) proluvial slope (II_2) group with low sulfate concentration (median values of 1.56 mM and 0.84 mM for UGW and CGW, respectively) and similar $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values (median values of 9.0‰ and 7.4‰ for UGW, 10.2‰ and 7.7‰ for CGW); and (3) low-lying zone (II_3) group with moderate sulfate concentration (median values of 2.13 mM and 1.17 mM for UGW and CGW, respectively) and more positive $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values (median values of 10.7‰ and 7.7‰ for UGW, 20.1‰ and 8.8‰ for CGW). In the present study, three major sources of sulfate could be differentiated as following: sulfate dissolved from Ordovician to Permian rocks ($\delta^{34}S_{SO4}$ = 10–35‰ and $\delta^{18}O_{SO4}$ = 7–20‰), soil sulfate ($\delta^{34}S_{SO4}$ = 5.9‰ and $\delta^{18}O_{SO4}$ = 5.8‰) and sewage water ($\delta^{34}S_{SO4}$ = 10.0‰ and $\delta^{18}O_{SO4}$ = 7.6‰). Kinetic fractionations of sulfur and oxygen isotopes as a result of bacterial sulfate reduction (BSR) were found to be evident in the confined aquifer in stagnant zone (II_3), and enrichment factors of sulfate–sulfur and sulfate–oxygen isotopes calculated by Rayleigh equation were −12.1‰ and −4.7‰ respectively along the flow direction of groundwater at depths of 60–100 m. The results obtained in this study confirm that detailed hydrogeological settings and identification of anthropogenic sources are critical for elucidating evolution of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values along with groundwater flow path, and this work also provides a useful framework for understanding sulfur cycling in alluvial plain aquifers.

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1. Introduction

Groundwater in alluvial aquifers has been widely used in many countries, especially in China (and particularly in the North China Plain (NCP)), for irrigation purposes and drinking water because of increasing population and food demand (Chen et al., 2003; Kendy et al., 2004; Chen et al., 2005; Li et al., 2011; Cao et al., 2013). However, for decades, the quality of alluvial groundwater has been degraded by the infiltration of agricultural and domestic contaminants (Ju et al., 2006; Choi et al., 2011; Li et al., 2011; Wang et al., 2013). The sulfate in alluvial groundwater is derived from both natural (pyrite oxidation, gypsum dissolution, soil sulfate, atmospheric precipitation) and anthropogenic (sewage, livestock, fertilizer and industrial wastes) sources (Krouse and Mayer, 2000; Einsiedl and Mayer 2005; Vitòria et al., 2008; Tuttle et al., 2009; Hosono et al., 2011a; Li et al., 2011; Szynkiewicz et al., 2012; Hosono et al., 2014). Excessive amounts of sulfate in groundwater may affect the quality for the hardness and taste (Trettin et al., 2002; Choi et al., 2011). Since the early 1990s, combined use of $\delta^{34}S_{SO4}$ with the stable oxygen isotope in sulfate ($\delta^{18}O_{SO4}$) had been proposed and applied in identification

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of sources and transformation of sulfate in groundwater (Strebel et al., 1990; Bottrell et al., 1995; Dogramaci et al., 2001; Rock and Mayer 2002; Massmann et al., 2003; Einsiedl and Mayer, 2005; Bottrell et al., 2008; Vitòria et al., 2008; Kaown et al., 2009; Samborska and Halas, 2010; Choi et al., 2011; Hosono et al., 2011a; Szynkiewicz et al., 2012; Gammons et al., 2013; Pu et al., 2013; Puig et al., 2013).

The major factors controlling $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values of dissolved sulfate in groundwater include mixing processes between potential sources with different isotopic compositions, kinetic isotope effects during biochemical transformations and isotope exchange reactions (Krouse and Mayer, 2000; Spence et al., 2001,2005; Hosono et al., 2011a; Puig et al., 2013). Dual sulfate isotope compositions of source materials have been used successfully to elucidate the mixing processes of sulfate and microbial reactions in aquifers (Krouse and Mayer, 2000; Dogramaci et al., 2001; Otero et al., 2009; Tuttle et al., 2009; Hosono et al., 2011a; Li et al., 2011; Puig et al., 2013).

Detailed knowledge of the isotope compositions of potential sulfate sources should be a prerequisite for examining local sulfur cycles (Bottrell et al., 2008; Tuttle et al., 2009; Hosono et al., 2011a, 2011b). Sulfate derived from dissolution of gypsum usually has positive $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values with ranges from 10‰ to 35‰ and from 7‰ to 20‰, respectively (Krouse and Mayer, 2000; Gunn et al., 2006; Samborska et al., 2013). Except in extreme cases (such as acid mine drainage and aquifer dewatering – Bottrell et al., 2008; Samborska and Halas, 2010; Gammons et al., 2013) mineralization of soil organic sulfur and oxidation of sulfide rarely significantly modify the sulfur isotopic composition of the original sulfate pool (<5‰) (Tuttle et al., 2009), but can substantially alter the oxygen isotopic composition of the new-produced sulfate due to incorporation of oxygen atoms from ambient water and molecular oxygen during the oxidation processes (Dogramaci et al., 2001; Tuttle et al., 2009; Miles et al., 2012). $\delta^{34}S_{SO4}$ value of sulfate in precipitation has become more negative (from 0‰ to 5‰) because of much sulfur dioxide depleted in ^{34}S released from coal burning since the industrial revolution (Einsiedl and Mayer, 2005), but $\delta^{18}O_{SO4}$ value tends to be high owing to the participation of molecular oxygen which having a $\delta^{18}O$ value of 23.5‰. Notably, sulfate in precipitation dominated by sea spray tends to have a marine-like signature of $\delta^{34}S$ as ∼21‰ (Dogramaci et al., 2001, references therein). Anthropogenic sources of sulfate have a range of isotopic compositions that are dependent on production processes. Fertilizer, widely used in rural area, could release nitrate and sulfate into soil and groundwater. It has been found that fertilizer has variable $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values with the range of −7‰ to 21‰ and 8–17‰ respectively, which attributed to the use of sulfuric acid and/or marine evaporites during production (Mizota and Sasaki, 1996; Robinson and Bottrell, 1997; Moncaster et al., 2000; Otero et al., 2004; Hosono et al., 2007, 2009, 2010, 2011a,b; Jiang 2012). Meanwhile detergent is another important source for groundwater sulfate with positive $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values ranging from 8.5‰ to 13.6‰ and from 14.7‰ to 16.9‰ respectively in Spain (Vitòria et al., 2004) and from −3.2‰ to 25.8‰ (mean value of 9.3‰) and from 11.2‰ to 20.6‰ (mean value of 14.7‰) respectively in Asian cities (Hosono et al., 2007, 2009, 2010, 2011a,b). Pig manure tended to be widely applied in rural area and had narrow $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values ranging from −0.9‰ to 5.8‰ and from 3.8‰ to 6.0‰ respectively in Spain (Otero et al., 2007; Puig et al., 2013) and had $\delta^{34}S_{SO4}$ value of 4.0‰ in England (Bartlett et al., 2010). The research of Otero et al. (2008) showed that sewage water as potential anthropogenic source had the mean $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values of 9.6‰ and 10‰ respectively. Bottrell et al. (2008) also reported that sewage water in Birmingham and Leeds (UK) had the mean $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values of 7.2‰ and 9.8‰, and of 7.2‰ and 14.9‰, respectively.

Biogeochemical processes in aquatic system may alter the isotopic composition of dissolved sulfate including adsorption/desorption, immobilization, mineralization, sulfide oxidation and bacterial sulfate reduction (BSR) (Einsiedl and Mayer, 2005). It is worth noting that BSR is the critical processes in earth's sulfur cycle causing obvious isotope fractionation, enriching $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ in the residual sulfate with the ratio of about 4:1 (Tuttle et al., 2009), and decreasing the sulfate concentration in closed system (Einsiedl and Mayer, 2005). Oxygen isotope composition of sulfate derived from oxidation of sulfide/organic sulfur should be determined by the oxygen isotope composition of ambient water and molecular oxygen, while little to no sulfur isotope fractionation occurs during those reaction (Tuttle et al., 2009).

Combination of hydrogeological settings and sulfate isotope composition of groundwater have been proved to be efficient tools for tracking sources and transformation of sulfate in volcanic/alluvial aquifer and karst groundwater system (Einsiedl and Mayer, 2005; Tuttle et al., 2009; Hosono et al., 2011a; Li et al., 2011). In the current study, groundwater in a piedmont alluvial plain in the NCP was selected, and dual sulfate isotope compositions together with hydrogeological settings were employed to: (1) identify the sulfate sources of local groundwater, (2) elucidate the BSR reaction in local groundwater flow system, and (3) establish a model for sulfur cycling in the piedmont-alluvium plain.

2. Description of the study area

2.1. Climate and geomorphology

The North China Plain (NCP), with an area of approximately 320,000 km^2 and population of more than 200 million, is one of the largest alluvial plains in Eastern Asia (Li et al., 2011). The NCP is mainly composed of (from west to east) the piedmont alluvial plain, central alluvial-lacustrine plain and littoral plain (Li et al., 2011). The study area is located in the west part of NCP between Taihang Mountain and the Yellow River (Fig. 1) and is classified as the piedmont plain, which has a temperate continental monsoon climate with an average annual mean temperature and precipitation of 14 °C and 600 mm, respectively between 1951 and 2010. The rainy season occurs from June to September when around 70% of the total annual precipitation falls. This strong seasonality, along with low annual precipitation, makes it a dry area for much of the year that relies heavily on groundwater resources to meet its agricultural and domestic water demand. The studied piedmont alluvial plain has an area of about 220 km^2, and the altitude tends to decrease eastward from 170 m to 90 m. The alluvial plain consists of three smaller geomorphic units (Fig. 1): the alluvial–proluvial fan (II$_1$); the proluvial slope (II$_2$); and the low-lying depression (II$_3$). Four types of land use are mainly distributed in study area including residential areas, industrial areas, arable farming (wheat and corn rotation) areas, and greenhouse vegetable cultivation area. Residential land is mainly concentrated in the II$_2$ geomorphic unit, and industrial land predominantly located in the west of II$_2$ geomorphic unit and northwest of II$_1$ geomorphic unit. The Sha River receives much waste water from chemical factories in the main industrial area (Fig. 1). Wheat and corn rotation land occupies the most ranges of II$_1$ and II$_3$ geomorphic units, and greenhouse vegetable land is only distributed in small part of II$_3$ geomorphic unit which is close to the residential zone, like sample site 104.

2.2. Geology

Sedimentary rocks are widely exposed at the surface in the mountain area, and the bedrock consists predominantly of carbon-