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Natural and anthropogenic sources and processes affecting water chemistry in two South Korean streams

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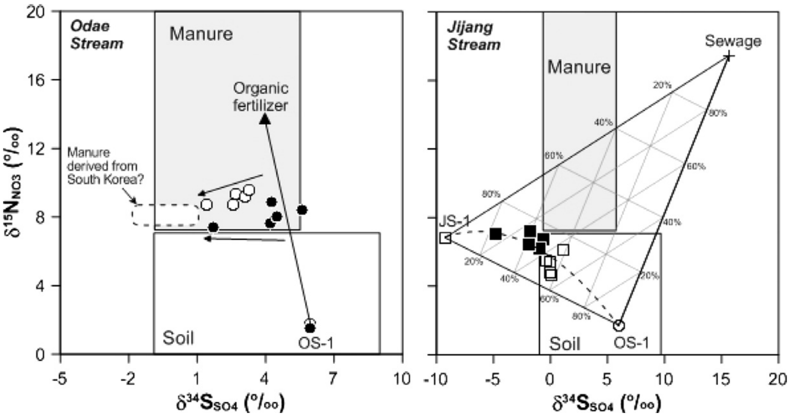
HIGHLIGHTS

- Isotopes were used to identify natural and anthropogenic sources in streams.
- Water chemistry is dependent upon land use patterns in watersheds.
- Manure is the main source supplying sulfate and nitrate to a stream.
- Sulfate and nitrate in stream are derived mostly from AMD and soil solution.

GRAPHICAL ABSTRACT

The distinct $\delta^{34}S$ and $\delta^{15}N$ values of the various source end-members enabled us to estimate the respective contributions of the various anthropogenic sources to stream water quality based on the sulfate and nitrate isotopic compositions of the analyzed water samples



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ABSTRACT

Acid mine drainage (AMD) in a watershed provides potential sources of pollutants for surface and subsurface waters that can deteriorate water quality. Between March and early August 2011, water samples were collected from two streams in South Korea, one dominantly draining a watershed with carbonate bedrock affected by coal mines and another draining a watershed with silicate bedrock and a relatively undisturbed catchment area. The objective of the study was to identify the sources and processes controlling water chemistry, which was dependent on bedrock and land use. In the Odae stream (OS), the stream in the silicate-dominated catchment, Ca, Na, and HCO_3 were the dominant ions and total dissolved solids (TDS) was low (26.1–165 mg/L). In the Jijang stream (JS), in the carbonate-dominated watershed, TDS (224–434 mg/L) and ion concentrations were typically higher, and Ca and SO_4 were the dominant ions due to carbonate weathering and oxidation of pyrite exposed at coal mines. Dual isotopic compositions of sulfate ($\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$) verified that the SO_4 in JS is derived mainly from sulfide mineral oxidation in coal mines. Cl in JS was highest upstream and decreased progressively downstream, which implies that pollutants from recreational facilities in the uppermost part of the catchment are the major source governing Cl concentrations within the discharge basin. Dual isotopic compositions of nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) indicated that NO_3 in JS is attributable to nitrification of soil organic matter but that NO_3 in OS is derived mostly from manure. Additionally, the contributions of potential anthropogenic

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sources to the two streams were estimated in more detail by using a plot of $\delta^{34}S_{SO4}$ and $\delta^{15}N_{NO3}$. This study suggests that the dual isotope approach for sulfate and nitrate is an excellent additional tool for elucidating the sources and processes controlling the water chemistry of streams draining watersheds having different lithologies and land-use patterns.

1. Introduction

Acid mine drainage (AMD) due to sulfuric acid produced by the oxidation of iron sulfide minerals such as pyrite in active and/or abandoned coal mining regions has generated severe environmental problems (Edraki et al., 2005). For example, pyrite exposed to the surface by the excavation of coal can produce sulfuric acid via oxidation in the presence of water and air, resulting in leachate that can enter groundwater and surface water and cause low pH and extremely high sulfate concentrations. This consequence is observed frequently in surface water in the vicinity of coal mine sites (Gammons et al., 2010; Davies et al., 2011) and can result in sulfate concentrations much greater than 250 mg/L, the maximum level recommended by the U.S. Environmental Protection Agency for drinking water (US EPA, 2009). Despite the negative effects of AMD on water quality, an enhanced sulfate concentration resulting from several different anthropogenic inputs could regionally obscure efforts to identify the sources of sulfate in surface water. Precisely estimating the sources of sulfur-bearing materials is important to effectively restrain the adverse effects of effluent from coal mine sites on the environment and human health. In terms of lithology, stream water overlying carbonate rocks in watersheds containing coal mines can precipitate gypsum through reactions between the abundant sulfates and carbonates in the stream (Davies et al., 2011), resulting in lower sulfate concentrations downstream. In addition, the abundant sulfide minerals in sedimentary rock, compared with igneous and metamorphic rocks (Krouse and Mayer, 2000), would be readily introduced into aquatic systems as a form of sulfate (e.g., soil sulfate), which could be masked by sulfate associated with coal mines. Thus, given that coal mines are distributed within the discharge area, sulfur in surface water should be identified more cautiously considering lithology.

Sulfur and oxygen isotopic compositions of dissolved sulfate ($\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$, respectively) can be used to clarify sources and transformation processes of sulfur in aquatic systems associated with coal mines (Gammons et al., 2010; Liuting et al., 2011) because they can provide meaningful information about various potential sources of sulfate (e.g., oxidation of sulfide minerals, atmospheric deposition, fertilizers, and soil) in the watershed (Krouse and Mayer, 2000; Rock and Mayer, 2009). For example, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ range from less than −30‰ to near 10‰ and about −10‰ to 5‰ for sulfate derived from the oxidation of sulfide minerals and from about −2‰ to 12‰ and about 8‰ to 15‰, respectively, for synthetic fertilizers (Krouse and Mayer, 2000; Vitòria et al., 2004). Along with isotopic data on sulfate, numerous studies on water chemistry have focused on the two isotopic compositions of nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) because these isotopic compositions have representative ranges for several sources of nitrate (e.g., atmospheric input, fertilizers, soil organic material, sewage, and manure) in a watershed. For example, $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ typically range from about −20‰ to less than 10‰ and about −8‰ to 15‰ for soil nitrification and from about 7‰ to more than 30‰ and about −8‰ to more than 10‰ for manure/sewage, respectively (Mayer et al., 2001; Mayer, 2005; Johannsen et al., 2008).

In addition to using the isotopic compositions of sulfate and nitrate in combination, concentrations of Cl, NO_3, and SO_4 and/or their correlations are frequently used to demonstrate the effects of anthropogenic and natural sources on watersheds because the ions are clearer source indicators and can be easily linked to isotopic data. For example, no evaporites exist in South Korea (Chough et al., 2000), so high Cl concentrations in a watershed can be readily regarded as having arisen from anthropogenic sources. $\delta^{34}S_{SO4}$ is closely related with either elevated or decreased sulfate concentrations due to the amount of precipitation and varying land-use patterns, such as forest, urban, and agricultural areas (Brenot et al., 2007), which helps identify potential contaminants within the discharge area. $\delta^{15}N_{NO3}$ is enhanced by NO_3 supply from manure/sewage and decreased by soil organic N flushed out due to intense runoff in summer (Shin et al., in review). Consequently, the use of particular major ions (Cl, NO_3, and SO_4), isotopic data on nitrate and sulfate, and isotopic values in combination with their concentrations allows hydrogeochemical processes to be assessed in more detail.

The objective of this study was to identify the natural and anthropogenic sources and processes controlling the water chemistry in streams in two watersheds in South Korea with different bedrock, land-use, and anthropogenic effects. We also intended to quantitatively estimate the contributions of anthropogenic and natural sources to the two streams using isotopic values.

2. Description of the study area

The Han River is the largest river on the Korean Peninsula and is subdivided into the North Han River (NHR) and South Han River (SHR). We studied two main tributaries of the SHR, the Odae and the Jijang streams, in Kangwon Province, which are characterized by different bedrock and exposed to different land-use and anthropogenic impacts (Fig. 1).

The Odae watershed has a discharge area of 452 km^2 and a length of 58 km. The bedrock consists predominantly of siliciclastic crystalline rocks, including Precambrian metamorphic rocks, Permian to Triassic sandstone and shale, and Jurassic to Cretaceous granite. The relative proportions of bedrock types exposed at surface are approximately 45% granite, 15% metamorphic rock, and 40% sandstone. In contrast, the Jijang watershed has a discharge area of 225 km^2 and a length of 46 km. The bedrock consists mainly of carbonate rocks of Cambro-Ordovician age in the middle to lower reaches and silicates composed of Permian to Triassic sandstones in the upper reaches (Kim et al., 2001; Fig. 1). The bedrock exposed at the surface is approximately 55% carbonate rock, 40% sandstone, and 5% metamorphic rock. Soils in the watersheds of both streams are mainly Entisols (about 2% in the Odae watershed and 22% in the Jijang watershed), with little profile development and low organic contents, Inceptisols (about 97% in the Odae watershed and 73% in the Jijang watershed), showing more profile development than the Entisols, and rarely Alfisols (about 0.1% in the Odae watershed and 3% in the Jijang watershed), with moderate to high cation exchange capacity for base cations (Ca, Mg, and K), or Mollisols (about 0.1% in the Odae watershed and 1.9% in the Jijang watershed), with accumulated organic material (Brady and Weil, 2002). The soil distributions were characterized by referring to statistical data available from the Korean Soil Information System (KSIS, 2012).

Both the Odae and Jijang drainage basins are mostly forested (88.2% and 87.7%, respectively) with small agricultural regions of rice cultivation and dry paddies (7.5% and 7.3%, respectively). The amount of livestock is an order of magnitude higher in the Odae watershed (1272 cows and 3260 pigs) than in the Jijang watershed (330 cows and 61 pigs). The populations of the Jijang and Odae watersheds are 15,921 and 11,692, respectively, according to the Ministry of Environment (MOE, 2006). Active coal mining in Kangwon Province occurred during the 1960s to 1970s, but most of the mines were closed before the end of the 20th century due to a government policy pertaining to the economic feasibility of the coal industry. However, two major coal