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Sulfur isotopic signatures in rainwater and moss *Haplocladium microphyllum* indicating atmospheric sulfur sources in Nanchang City (SE China)

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ABSTRACT

Sulfur source identification previously reported has been based on sulfur isotopic ratios in either rainwater or mosses. The $\delta^{34}S$ values of rainwater sulfate and the epilithic moss *Haplocladium microphyllum* in Nanchang region (China) were determined for comparisons and used to delineate atmospheric sulfur sources. At the urban and rural sites, similar mean $\delta^{34}S$ values were observed between rainwater sulfate (+1.6‰ and −0.2‰, respectively) and epilithic mosses (+1.7‰ and +0.6‰, respectively), suggesting that mosses acquire $\delta^{34}S$ values similar to those found for rainwater sulfate. This has further demonstrated that moss $\delta^{34}S$ signatures hold valuable source-specific information as rainwater $\delta^{34}S$ values do. The $\delta^{34}S$ values of both rainwater sulfate and epilithic mosses indicated that atmospheric sulfur in Nanchang region was mainly associated with coal combustion. The lower $\delta^{34}S$ values at the rural site can be explained by higher contribution of local coals (lower $\delta^{34}S$ values relative to those of north Chinese coals) and biogenic sulfur.

1. Introduction

Sulfur in the atmosphere occurs in a variety of gaseous, liquid and solid chemical forms. In remote regions, natural sources such as biogenic emissions in the form of dimethyl sulfide (DMS) and H_2S, volcanic SO_2, and sea salt sulfate are the dominant origins of atmospheric sulfur compounds (Nriagu et al., 1987; Yang et al., 1996; Shooter, 1999). Major inputs in heavily industrialized areas are anthropogenic SO_2 mainly due to the combustion of fossil fuels in the form of coals (Kellogg et al., 1972; Li et al., 1999; Mukai et al., 2001). SO_2 plays an important role in the development of acid rain. Deposition of acid compounds from the atmosphere has increased in some Chinese areas during recent decades (e.g. Lü and Tian, 2007). High sulfur deposition has resulted in sulfur accumulation in forest soils, which will further acidify surface waters (Duan et al., 2000).

Since numerous potential sources likely exist, it is vital to be able to distinguish them from each other in a given area in order to assess their relative impacts. The atmospheric sulfur isotope ratio ($\delta^{34}S$) may hold source-specific information that can serve as a fingerprint to identify sulfur sources. The $\delta^{34}S$ values of anthropogenic emissions in industrial and consumer processes generally show a wide range depending on the nature of the source (coal, oil, or natural gas): petroleum natural gas, −20 to +30‰; coal, −35 to +30‰ (Nielsen, 1978). The $\delta^{34}S$ values of Chinese coals at different localities also show wide variations, while specific individual coal deposits are relatively uniform in isotopic ratios (Hong et al., 1993). Flue gas desulfurization affects the isotopic composition of the emitted SO_2 and particulates. For instance, Derda et al. (2007) showed that during desulphurization process (wet limestone method), sulfur in the outlet gases has lower $\delta^{34}S$ values (−4.03 ± 0.03‰) and the by-product from this process (gypsum: ± 2.29 ± 0.03‰) has higher $\delta^{34}S$ values than the SO_2 at the inlet (± 1.56 ± 0.03‰).

The $\delta^{34}S$ average of sea spray sources is around +21‰ (Rees et al., 1978) while most of the biogenic emissions are isotopically lighter (−10 to −2‰; Liu et al., 1996; Panettierea et al., 2000; Zhang et al., 2010). Moreover, atmospheric isotopic signatures can tell us about mixing processes, oxidation processes, transport pathways and deposition of sulfur in the environment (Ohizumi et al., 1997; Leung et al., 2001; Xiao and Liu, 2002; Pruett et al., 2004; Sinha et al., 2008). Atmospheric oxidation of SO_2 occurs by both heterogeneous and homogeneous paths. Homogeneous oxidation of SO_2 results in isotopically lighter sulfate S (Tanaka et al., 1994), in contrast to heterogeneous oxidation which results in isotopically heavier sulfate S (Eriksen, 1972).

In acid rain regions where more intensive study has occurred, rainwater sulfate sources are better understood through sulfur isotopic signatures. Considerable previous studies on rainwater sulfur isotopes have suggested that coal burning makes a significant contribution to rainwater sulfate in most southern Chinese cities (Xiao and Liu, 2002; Zhang et al., 2010). In addition to the well-established coal source for rainwater sulfate, previous works have indicated an important contribution of biogenic sulfur (BS) in some urban regions (Zhang et al., 1995; Yao et al., 2003; Zhang et al., 2010; Liu, 2007). For instance, Zhang et al. (1995) reported that coal

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combustion and BS contributed about 43% and 46%, respectively, to rainwater sulfate in Guangzhou area based on isotopic mass balance. Yao et al. (2003) found that sulfur isotopic values of rainwater sulfate were higher in winter than in summer in Hengyang and attributed it to higher contribution of BS in summer.

In addition to those in atmospheric samples, measurements of sulfur isotopic ratios in mosses have been exploited in the study of atmospheric sulfur pollution (Nriagu and Glooschenko, 1992; Bottrell and Novak, 1997; Novák et al., 2001a,b; Xiao et al., 2009; Migaszewski et al., 2010). We also used moss sulfur isotopic ratios to indicate atmospheric sulfur sources in some southern Chinese mountainous areas (Xiao et al., 2008).

At present, almost all previous studies were focused on sulfur isotopic ratios in either rainwater (e.g. Panettierea et al., 2000; Xiao and Liu, 2002) or mosses (e.g. Xiao et al., 2008, 2009). To our knowledge, source identification based on sulfur isotopic ratios in both rainwater and mosses has not been reported previously. So, the aims of this work were firstly, to compare the δ^{34}S values of rainwater sulfate and epilithic mosses in Nanchang region and, secondly, to identify sulfur sources in the atmosphere using sulfur isotopes in rainwater and mosses.

2. Materials and methods

2.1. Study area description

In Nanchang region (S China) acid rain has been observed since the 1980s. The SO_2 emission rates slightly increased as a result of the expansion of coal consumptions from 2000 to 2006 (Fig. 1). Although ambient SO_2 concentration averaged only 56 μg/m^3 in the city, almost all of the rainwater was found at pH<5 in 2006 (Nanchang Environmental Protection Bureau, 2007). The major sulfur pollution source is Nanchang Power Plant (NPP) which is located in the north direction and about 2 km away from the north campus of Nanchang University (NNU). Due to shortage of local coals, coals from northern China are introduced for combustion in NPP. The predominant wind direction is southerly in summer and northerly in winter in the Nanchang region.

One site in the urban area (NNU) and one site in the rural area (QH) were chosen for rainwater collection, both of which lie in Nanchang University (Fig. 2). Besides the above two sites, one site in a clean area (ML) was also chosen for moss sampling for comparisons. Both local coals (δ^{34}S: -5.8 ± 1.7‰) and northern Chinese coals (δ^{34}S: $+9.7\pm5.2$‰) were combusted in the city (Xiao et al., 2009). The sampling site in the Meiling forest (ML) is >20 km away from the urban area.

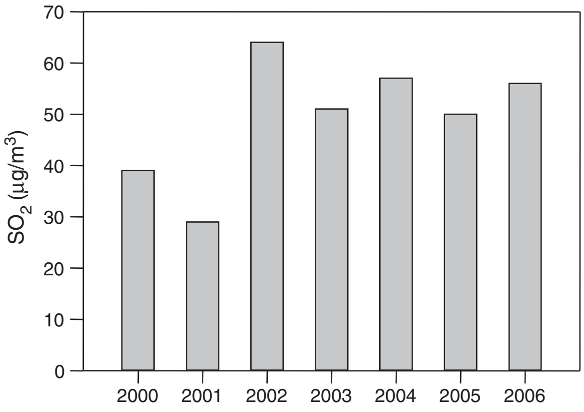

Fig. 1. Temporal changes of ambient SO_2 from 2000 to 2006 in Nanchang City.

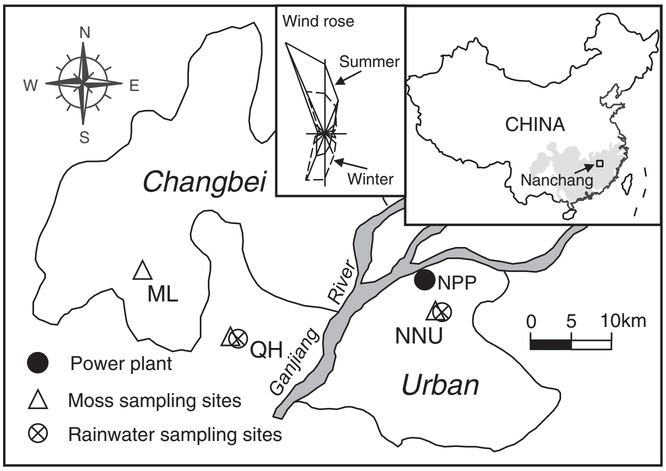

Fig. 2. Map of China showing the sampling sites of rainwater and mosses in Nanchang region. ML—Meiling forest; QH—Qianhu campus of Nanchang University; NNU—north campus of Nanchang University; NPP—Nanchang Power Plant. Wind rose of Nanchang region is also presented. The shaded regions represent areas where acid rain was measured (pH<5) in 2004 (revised from China Environmental Protection Bureau, 2005).

2.2. Sample collection methods

Rainwater samples were collected on building roofs of Nanchang University in the whole year of 2007. In order to collect enough water samples for isotope analysis, a sampler with a large polyethylene sheet (1.5 m × 2 m) served as the collection device. Prior to use, the polyethylene sheet was cleaned with 2 N HCl solution and rinsed with Milli-Q water, and dried. Then a hole of 2 cm in diameter was punched in the center of the sheet. The polyethylene sheet was fastened 1.5 m upon the floor by a stainless bracket beforehand. Between rains, the polyethylene sheet was closed to avoid dry deposition and other contaminations. After collection, the samples were immediately filtered to exclude material greater than 0.45 μm using Whatman acetate membrane filters. A small aliquot of these filtered samples was stored in brown clean plastic bottles for chemical determination, while other aliquots were stored at 4 °C for isotopic analysis after poisoned by $HgCl_2$(s).

The moss materials (*Haplocladium microphyllum*) at all studied sites were collected in the spring and summer of 2006–2007. Urban mosses were mainly collected around parks or hills. The sampling sites in the rural areas were selected to be located in open habitats like heaths or clearings and at least 500 m away from main roads and at least 100 m away from other roads or houses. All mosses were obtained from natural rocks without canopies or overhanging vegetation ensuring no influenced from throughfall sulfur compounds. Sampling was performed only at those sites above ground level to avoid surface water splashes. Sites possibly disturbed by domestic animals or other point sources were also avoided. We collected 5–10 subsamples at each site and combined them into one representative sample. Only green, healthy samples were taken, avoiding yellow or dark samples.

2.3. Sample analytical methods

All rainwater samples were acidified at pH<2 with 2 mol/L HCl solution, then sulfate was recovered from rainwater by precipitating as $BaSO_4$ with enough 2 mol/L $BaCl_2$ solution. After precipitating for 24 h, the mixture was filtered through 0.22 μm acetate membrane filters.

Using the treatment method by Liu et al. (2007), moss samples were gently rinsed with 1.5 mol L^{-1} HCl solution, then sonicated and washed with deionized water for several times. All samples were