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Monthly variations in nitrogen isotopes of ammonium and nitrate in wet deposition at Guangzhou, south China

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ABSTRACT

Monthly nitrogen isotopes of ammonium and nitrate in wet deposition in the city of Guangzhou, and the causes of their variability, are reported in this paper. Nitrate $\delta^{15}N$ showed nearly constant values around zero in the dry season (October to April), but oscillating values from negative to positive in the rainy season (May to September). By contrast, ammonium $\delta^{15}N$ displayed lower values during the rainy season than in the dry season. The rural area north of the city was considered as the prominent source of ammonium and nitrate in spring and early summer (May and June), as suggested by their concurrent negative isotopic trends and higher NH_4^+/NO_3^- ratios. From July to September, different dominating sources from the city, i.e., fossil fuel combustion for nitrate, and sewage and waste emission for ammonium, caused disparate $\delta^{15}N$ trends of the two species, showing positive nitrate $\delta^{15}N$, but still negative ammonium $\delta^{15}N$. During the cool dry season, the high values of ammonium $\delta^{15}N$ and concurrently low NH_4^+/NO_3^- ratios suggested the decrease in NH_3 volatilization and relatively important thermogenic origin of ammonium, but the intermediate nitrate $\delta^{15}N$ values around zero may be a result of a balanced emission of NO_x from the city and the rural areas. The isotopic effects of chemical conversion of NO_x to nitrate and washout of nitrate were ruled out as significant causes of nitrate $\delta^{15}N$ variability, but ammonium washout, during which ^{15}N is assumed to be preferentially removed, may partly contribute to the ammonium $\delta^{15}N$ variability.

1. Introduction

Atmospheric nitrogen deposition has sharply increased in recent decades due to extensive use of fossil fuels in industry and transportation, heavy application of fertilizers in agriculture, and expansion of animal husbandry (e.g. Galloway et al., 2004). This issue is especially prominent in south and east China due to rapid economic development, and has caused serious air pollution and acid rain (State Environmental Protection Administration of China, 2009). Public and social concerns about the issue have stimulated intensive research and control on pollutant emission in recent years in China.

Information on the origin of pollutants is important for pollution control. However, it is usually difficult to differentiate autochthonous from allochthonous origin of pollutants in the air because of the changeable air mass pathways. The climate of south China is characterized by monsoon conditions, with southerly moist wind from the South China Sea prevailing during summer and northerly dry wind from the continent predominant during winter. Therefore, in addition to local pollutant production at a site, the monsoon could carry particles and gases in the air from seasonally different directions to the site, and thereby makes pollutant source analysis by the conventional monitoring of pollutant concentrations difficult.

The stable nitrogen isotope ($\delta^{15}N$) has been recognized as a novel method to investigate the contributions from various sources to atmospheric nitrogen (e.g. Kendall et al., 2007). Atmospheric nitrate mainly originates from the transformation of gas-phase nitrogen oxides ($NO_x = NO + NO_2$) produced from natural sources such as lightning, biomass burning and soil emissions, and anthropogenic sources from the oxidation of nitrogen in fuel or of atmospheric N_2 at high temperatures. Lightning-produced NO_x is assumed to have $\delta^{15}N$ values around zero (Hoering, 1957). $\delta^{15}N$ of NO_x produced through biomass burning and soil emissions has been suggested to have extremely negative $\delta^{15}N$ values due to the preferential volatilization of ^{14}N (Freyer et al., 1993; Kendall et al., 2007; Li and Wang, 2008). On the contrary, anthropogenic NO_x generally exhibits positive $\delta^{15}N$ values, which are usually subdivided into stationary source and vehicle source (Elliott et al., 2007; Kendall et al., 2007). Stationary sources characterized by coal-combustion produce NO_x with higher $\delta^{15}N$ values (+6 to +13‰ reported by Heaton, 1990; +4.8 to +9.6‰ by Kiga et al., 2000), whereas vehicle sources

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produce NO_x with less positive (+3.7‰ reported by Moore, 1977; +5.7‰ by Ammann et al., 1999; +3.8‰ by Pearson et al., 2000) or even negative values (e.g., −13 to −2‰ by Heaton, 1990).

Atmospheric NH_4^+ is derived from heterogeneous reactions involving NH_3 that is mainly produced from animal or sewage waste, fertilizer application, soil emissions, biomass burning and industrial emissions (Dentener and Crutzen, 1994). In terms of its $\delta^{15}N$ value, two classes can be distinguished: volatilized NH_3 from waste, fertilizer and soil, and thermogenic NH_3 produced during combustion of biomass and fossil fuel. Volatilization is a unidirectional step accompanied by kinetic isotopic fractionations, resulting in strongly ^{15}N-depleted NH_3 lost into the atmosphere (Heaton, 1986). For example, Freyer (1978) analyzed NH_3 in sheep and poultry sheds and reported mean $\delta^{15}N$ values of −15.2‰ and −8.9‰ for these sources. However, a wide range of $\delta^{15}N$ of NH_3 from animal excreta has been reported, between approximately −15‰ and +28‰ (Moore, 1977; Freyer, 1978; Heaton, 1986, 1987; Yeatman et al., 2001). The reported highly positive values are enigmatic, considering that waste materials generally have $\delta^{15}N-NH_4^+$ values less than +30‰ (mostly in the range between +10‰ and +20‰), and that the kinetic fractionation during volatilization could be as large as −40‰ (Kendall, 1998; Occhipinti et al., 2008). The isotopic signature of thermogenic NH_3 has not been well characterized. The limited $\delta^{15}N$ data currently available for NH_3 from coal combustion range between approximately −7‰ and +2‰, with a mean value of approximately +4‰ (Freyer, 1978; Heaton, 1987). Aerosol samples collected next to a busy high street, with higher impacts expected from vehicle emissions, exhibit a mean $\delta^{15}N-NH_4^+$ value of $+9 \pm 4$‰ (Yeatman et al., 2001). Therefore, thermogenic NH_3 should be characterized by higher $\delta^{15}N$ values than volatilized NH_3.

However, source analysis for atmospheric nitrogen based on $\delta^{15}N$ measurement appears complicated due to the isotopic effect arising during washout of nitrogen itself or during the chemical conversion of NO_2 to nitrate. For example, the often observed seasonal $\delta^{15}N-NO_3^-$ pattern in polluted areas, showing high values during winter and low values during summer (see Kendall et al., 2007 and references therein), has been attributed to seasonal shifts in prevailing NO_x oxidation pathways (i.e., negative fractionation via OH radicals during daytime and positive fractionation via O_3 at nighttime) in the atmosphere (Freyer, 1991; Freyer et al., 1993). Furthermore, isotopic fractionation associated with the washout of nitrate by rain appears large, although it is not well characterized hitherto, and has been assumed to be a key process for the large $\delta^{15}N-NO_3^-$ variations observed in remote polar areas (Morin et al., 2008, 2009). As to the ammonium isotope, ^{15}N has been observed to be preferentially washed out, thus rendering successive precipitation progressively depleted in $^{15}N-NH_4^+$ (Moore, 1977; Heaton, 1987; Xiao and Liu, 2002).

The overall goal of this study is to characterize the seasonal variability of $\delta^{15}N$ of ammonium and nitrate in wet deposition in Guangzhou, a severely polluted city in south China. By analyzing the monthly mean $\delta^{15}N$ values and N species concentrations in rainfall, as well as some available information on nitrogen sources, conversion and washout, we aim to (1) assess the possible isotopic effects of nitrogen oxidation pathways and washout on the observed variation of $\delta^{15}N-NO_3^-$ and $\delta^{15}N-NH_4^+$, and (2) evaluate the importance of various nitrogen sources for the observed isotope variations.

2. Study site, samples and experiments

The city of Guangzhou (22.4°–23.9°N, 112.9°–114.2°E) is located in south China (Fig. 1). The climate of south China is of typical monsoon nature, with a hot wet season from April to September,

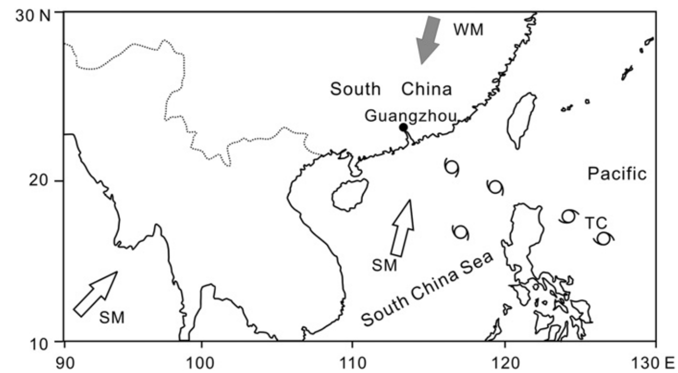

Fig. 1. The location of Guangzhou in China. WM: winter monsoon; SM: summer monsoon; TC: tropical cyclone.

and a cool dry season from December to February. The average annual temperature and rainfall in Guangzhou is 22 °C and 1840 mm, respectively (from 1971 to 2000). April is a transitional month from winter monsoon to summer monsoon, and precipitation usually increases greatly during that month (Fig. 2a). During May and June, the quasi-stationary front above south China, due to the convergence of the southerly moisture and the northerly cold air mass, generally causes strong and long-lasting rainfalls. From July to September, the frontal zone is pushed northward to central and north China, and rainfalls usually result from tropical convective activity and cyclones.

Guangzhou is the most rapidly developing city in China. During the past two decades, industry, population and agricultural productivity increased explosively in the city and the surrounding rural areas. For example, in 1991 there were about 0.36 million motor vehicles in the city; by 1997 and 2007, the numbers increased to 1.0 million and 1.83 million, respectively (Jin, 2009). Power production mainly by coal combustion increased from 2.1×10^{10} kW h in 1999–4.0×10^{10} kW h in 2008. Human population also rose from 6 million in 1990–10 million in 2007. To the north and northeast of Guangzhou there is an area of intensive agricultural activity. Taking the Qingyuan region to the north as an example, application of fertilizer increased from 1.2×10^5 tons in

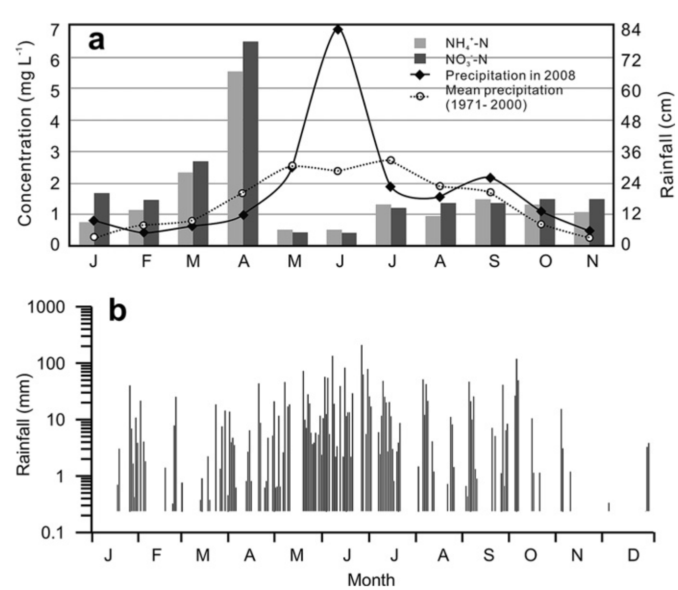

Fig. 2. Wet deposition in Guangzhou. (a) Monthly rainfall and mean concentrations of ammonium and nitrate. (b) Daily distribution of rainfall in 2008.