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Variations in atmospheric concentrations and isotopic compositions of gaseous and particulate boron in Shizuoka City, Japan

Masahiro Sakata^{a,*}, Hang Giang Phan^a, Satoshi Mitsunobu^b^a Graduate Program in Environmental Health Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan^b Graduate School of Agriculture, Ehime University, 3-5-7 Tarumi, Matsuyama 790-8566, Japan

HIGHLIGHTS

- The concentrations and $\delta^{11}\text{B}$ of gaseous and particulate B were measured concurrently.
- There was a strong temperature dependence on the phase partitioning of B.
- A positive correlation was observed between the $\delta^{11}\text{B}$ of gaseous and particulate B.
- Particulate B is enriched in ^{10}B relative to gaseous B due to isotopic fractionation.
- Gaseous B may be transformed to particulate B through the precipitation of borates.

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ABSTRACT

To clarify the partitioning and isotopic fractionation of boron (B) into the gas and particle phases in the atmosphere, the concentrations and isotopic compositions of gaseous and particulate B were measured concurrently for more than one year at a site in Shizuoka City, Japan. This area has few anthropogenic sources of B, such as coal combustion facilities. Gaseous B concentration showed clearly a seasonal variation, increasing during summer and decreasing during winter. Conversely, particulate B concentration tended to decrease during the warm season and increase during winter. The increase in gaseous B concentration during summer is attributable to the enhanced emissions of B from sea-salt degassing owing to higher temperatures and the predominance of winds from the Pacific Ocean. Moreover, the decrease in gaseous B concentration and the increase in particulate B concentration during winter is probably due to the enhanced condensation of gaseous B on atmospheric particles. The $\delta^{11}\text{B}$ values of gaseous and particulate B varied largely, and did not indicate a distinctive seasonal variation. A positive correlation was observed between the $\delta^{11}\text{B}$ values of gaseous and particulate B ($R^2 = 0.518$, $P < 0.001$). Moreover, the $\delta^{11}\text{B}$ values of particulate B were approximately 0–20‰ lower than those of gaseous B. There is an isotopic fractionation ($\Delta_{\text{B(OH)}_4^- - \text{B(OH)}_3}$) of about –20‰ between B(OH)_3 and B(OH)_4^- species in solution (Kakihana et al., 1977). This tends to support the hypotheses that gaseous B is transformed to particulate B through the reaction of condensed B(OH)_3 with chemical constituents on particles to precipitate borates, and that the condensed B(OH)_3 remaining on particles is unstable and evaporates.

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1. Introduction

Boron (B) is present in the atmosphere both in the gaseous [probably boric acid, B(OH)_3] and particulate forms, with total concentrations ranging from few ng B m^{-3} to more than 100 ng B m^{-3} (Fogg and Duce, 1985; Anderson et al., 1994; Miyata et al.,

2000). Although measurements of atmospheric concentrations of gaseous and particulate B are currently limited, Fogg and Duce (1985) reported that at several marine and continental sites, atmospheric B is primarily in the gaseous form (>95% of the total). Moreover, Anderson et al. (1994) found that atmospheric B concentrations are predominantly attributable to gaseous components at both continental and marine sites except during periods of extreme cold. Thus, it is likely that there is a strong temperature dependence on the phase partitioning of B. This may be due to the enhanced condensation of gaseous B on atmospheric particles at

* Corresponding author.

E-mail address: sakatam@u-shizuoka-ken.ac.jp (M. Sakata).

low temperatures. Rose et al. (2000) suggested that Henry's law constant would favor B volatilization from atmospheric sea salt at temperatures higher than 20 °C, whereas at temperatures lower than 20 °C, gaseous B would condense on particles. However, whether this is truly the case should be confirmed by field measurements.

It has been reported that sea-salt degassing over the ocean may be the most important source of gaseous B in the atmosphere (Fogg and Duce, 1985; Anderson et al., 1994; Park and Schlesinger, 2002). The estimates of the global B budget by Fogg and Duce (1985) suggest that volcanic emissions are also one of the major sources, but they are not significant on the basis of the estimate by Park and Schlesinger (2002). On the other hand, the principal anthropogenic sources of B are coal combustion and biomass burning (Fogg and Duce, 1985; Anderson et al., 1994; Park and Schlesinger, 2002; Zhao and Liu, 2010). On a regional scale, these anthropogenic inputs will be quite significant. For example, emissions from China have increased rapidly in recent years owing to the marked consumption of coal. Coal accounts for 64% of the total primary energy consumption in China in 2015, amounting to 50% of the total worldwide coal consumption in that year (BP Statistical Review of World Energy, 2016).

Boron is a major component of coal and has two stable isotopes, ^{10}B and ^{11}B , the relative abundance of which is approximately 1:4. Boron isotopes are fractionated easily in nature owing to the relatively large differences in their isotopic masses, reaching up to 10% of isotope abundance variations (Williams and Hervig, 2004). Coal is dominated by ^{10}B , representing a significantly lighter B isotopic composition ($\delta^{11}\text{B} = -1$ to -70‰) than most terrestrial materials (e.g., rocks, evaporates, crude oil, and water) ranging approximately from -30 to $+45\text{‰}$, with most of the values higher than 0‰ (Williams and Hervig, 2004). If coal combustion facilities are not sufficiently equipped with a flue gas control system, coal combustion is considered to contribute considerably to the emissions of common air pollutants (e.g., SO_2 , NO_x , and particles) and hazardous air pollutants (e.g., heavy metals and PAHs) to the atmosphere. From the above-mentioned characteristic of B isotopic composition, it is reasonable to expect that B isotopes are useful as a chemical tracer of the emissions of air pollutants from coal combustion (Sakata et al., 2010, 2013; Zhao and Liu, 2010). Such a tracer is crucial for clarifying the sources and transport routes of air pollutants not only on a local scale but also on a regional scale.

Sakata et al. (2013) measured the atmospheric concentration and isotopic composition of B in aerosol samples collected from April 2004 to March 2006 at two sites on the Japan Sea coast. By air trajectory analysis, they found that aerosols during winter, during which airflows from northern China are dominant, are characterized by negative $\delta^{11}\text{B}$ values, whereas aerosols during summer, during which airflows from Japan and the Pacific Ocean are dominant, are characterized by positive $\delta^{11}\text{B}$ values. This suggests that the $\delta^{11}\text{B}$ values of aerosols transported from northern China during winter satisfactorily reflect the characteristic of $\delta^{11}\text{B}$ of coals generated in this region. Boron is volatilized easily during coal-combustion processes. As a result, the B isotopic composition of aerosols from northern China may be dependent on the extent of isotopic fractionation during the condensation of gaseous B on a solid or water surface at low temperatures in the atmosphere (Chetelat et al., 2005; Rose-Koga et al., 2006). However, presently we have insufficient knowledge of the partitioning and isotopic fractionation of B into the gas and particle phases. This knowledge is important for the use of B isotopes as an effective tracer of emissions from coal combustion.

Hence, in this study, we investigated the variations in atmospheric concentrations and isotopic compositions of gaseous and particulate B at a site in Shizuoka City, Japan, which is on the Pacific

Ocean side (Fig. 1). In the area within approximately 100 km of the site, there are few anthropogenic sources of B, such as coal combustion facilities (e.g., coal-fired power stations and iron works). Moreover, it has not been significantly affected by the long-range transport of air pollutants from the Asian continent (Sakata et al., 2014).

2. Materials and methods

2.1. Sampling

The sampling site is on the rooftop of a building (22.5 m above ground) on the campus of the University of Shizuoka ($34^\circ 59' 45.7''\text{N}$ and $138^\circ 26' 43.5''\text{E}$). This site is located in the southern area of Shizuoka City with a population of about 700,000, which is the capital of Shizuoka Prefecture, as shown in Fig. 1. Gaseous B was collected using three impingers containing 50–70 mL of Milli-Q water at a flow rate of 2 L min^{-1} . The impingers made of polycarbonate plastic, not borosilicate glass, were used to avoid B contamination. Prior to sampling each time, the impingers were cleaned carefully with $1\text{ mol L}^{-1}\text{ HNO}_3$ solution and Milli-Q water. First, air was passed through a $0.2\text{ }\mu\text{m}$ -membrane filter (material: PTFE) to remove particles and was then introduced into the impingers. The sampling was performed 3–5 times a month from October 2014 to April 2016. The sampling durations were 24–96 h, depending on the atmospheric concentration of gaseous B. After the collection, the samples collected in the three impingers were combined. The combined sample was weighed and stored in a refrigerator until analysis.

For the determination of particulate B concentration, total suspended particulate (TSP) samples were collected on quartz fiber filters ($20 \times 25\text{ cm}^2$) at a flow rate of 1000 L min^{-1} using a high-volume air sampler (Shibata HV-1000R). Sampling was performed from April 2015 to April 2016, and the sampling durations synchronized those for gaseous B. After the collection of the samples, the filters were immediately weighed and stored with shading until analysis.

2.2. Chemical analyses

To determine the atmospheric concentration and $\delta^{11}\text{B}$ of gaseous B, the sample solution from the impingers was purified and concentrated by ion exchange using boron-specific resin Amberlite IRA 743 (Kiss, 1988; Leeman et al., 1991; Nakamura et al., 1992). The sample solution (pH > 10 adjusted by adding 25% ammonia) was loaded onto the resin bed (volume, $\sim 0.5\text{ mL}$; length, $\sim 20\text{ mm}$; diameter, $\sim 6\text{ mm}$). The resin, which was ground to a grain size between 75 and $212\text{ }\mu\text{m}$, was rinsed sequentially using H_2O (Milli-Q water), $2\text{ mol L}^{-1}\text{ HNO}_3$, H_2O , 3 mol L^{-1} ammonia, and H_2O . Boron was eluted by loading 5 mL of $2\text{ mol L}^{-1}\text{ HNO}_3$ twice. The B concentration in this solution was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES; Varian 730ES). The recovery rate of B during the ion exchange separation was always higher than 98%. Hence, there was no significant isotopic fractionation due to partial loss of B during the ion exchange separation, as determined on the basis of the single-stage separation factors for B isotopes between an ion exchange resin and an external solution (Kakihana et al., 1977). This was confirmed by the fact that the B isotope ratio of the feed solution of NIST SRM 951 (certified value: $^{11}\text{B}/^{10}\text{B} = 4.044 \pm 0.003$; <https://www.nist.gov/srm>) coincided with that ($^{11}\text{B}/^{10}\text{B} = 4.041 \pm 0.010$) of the eluted solution after the ion exchange separation.

On the other hand, B isotope analysis was conducted using the purified sample solution by inductively coupled plasma quadrupole mass spectrometry (ICP-QMS; Varian 820-MS). ICP-QMS has a

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