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Trends in hazardous trace metal concentrations in aerosols collected in Beijing, China from 2001 to 2006

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ABSTRACT

Daily observations of hazardous trace metal concentrations in aerosols in Beijing, China were made in the period from 2001 to 2006. We considered coal combustion as a major source of some anthropogenic metals by achieving a correlation analysis and by investigating enrichment factors and relative composition of metals. A possible extra source of some specific metals, such as Cu and Sb, was brake abrasion particles, however, we did not think the transport-related particle was a major source for the hazardous anthropogenic metals even though they could originate from vehicle exhaust and brake/tire abrasion particles. A time-trend model was used to describe temporal variations of chemical constituent concentrations during the five-year period. Several crustal elements, such as Al, Ti, V, Cr, Mn, Fe, and Co, did not show clear increases, with annual rates of change of −15.2% to 3.6%. On the other hand, serious increasing trends were noted from several hazardous trace metals. Cu, Zn, As, Cd, and Pb, which are derived mainly from anthropogenic sources, such as coal combustion, showed higher annual rate of change (4.9–19.8%, $p < 0.001$) according to the regression model. In particular, the Cd and Pb concentrations increased remarkably. We hypothesize that the trend towards increasing concentrations of metals in the air reflects a change that has occurred in the process of burning coal, whereby the use of higher temperatures for coal combustion has resulted in increased emissions of these metals. The increasing use of low-rank coal may also explain the observed trends. In addition, nonferrous metal smelters are considered as a potential, albeit minor, reason for the increasing atmospheric concentrations of anthropogenic hazardous metals in Beijing city.

1. Introduction

Many trace metals and metallic compounds are harmful to the human body. According to the International Agency for Research on Cancer (IARC), arsenic and arsenic compounds, cadmium and cadmium compounds, hexavalent chromium, and nickel compounds are classified into Group 1 (carcinogenic to humans), inorganic lead compounds are classified into Group 2A (probably carcinogenic to humans), and many other metals are classified into Group 2B (possibly carcinogenic to humans) (IARC, 2006). Atmospheric metal exposure represents a serious concern for human health.

Generally, trace metals exist in the particulate phase in the air. In many of the mega-cities, large amounts of aerosols are emitted from anthropogenic sources and natural sources (Gutiérrez-Castillo et al., 2005; Manalis et al., 2005; Valavanidis et al., 2006; da Silva et al., 2008). In particular, Beijing city, which has a population of approximately 15 million and annual coal consumption of 29 million tonnes in 2004 (NBSC, 2005a,b), has a serious air pollution problem. For example, the atmospheric particulate matter (PM_{10}) concentration in Beijing is 5-fold higher than that in the Tokyo metropolitan area, and atmospheric hazardous trace metal concentrations in Beijing are 2–22-fold higher than the corresponding levels in Tokyo (Okuda et al., 2004). Moreover, many East Asian cities have undergone rapid development in recent years, especially Beijing, which is being developed at a rapid pace in preparation for the Olympic Games in the summer of 2008. Therefore, dramatic changes in the atmospheric environment of Beijing are expected in the near future. It is very important to investigate the trend towards higher concentrations of air pollutants associated with the rapid development of this city. There are some previous studies investigated the characteristics of aerosols in Beijing (Duan et al., 2003; Sun et al., 2004; Feng et al., 2005; Wang et al., 2005, 2006), however these previous studies analyzed fewer than a few hundred samples, and the sampling frequency or period was limited. In contrast, in the present study, we analyzed more than 1500 samples over five years (2001–2006). No other studies

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involving such a large collection of samples in Beijing have been published previously. In the present study, daily observations of hazardous trace metal concentrations in aerosols from Beijing, China were made in the period from 2001 to 2006, and serious increasing trends were noted for several kinds of metals.

2. Experimental section

2.1. Site descriptions

Beijing city is geographically located at the northwestern border of the Great North China Plain. The closest coast from Beijing city is Bohai Sea, which is 160 km away from the city to the southeast. The wind system of this region is basically controlled by the westerly wind as well as the Asian monsoon which provides warm and humid southern wind in summer and cold and dry northern wind in winter.

The details of the experimental procedure used in the present study have been described elsewhere (Tanaka et al., 1998; Okuda et al., 2004, 2006a,b). The sampling site is on the rooftop of a building (5 m above the ground) at a center of the campus of Tsinghua University which is located 20 km in the northwesterly direction from the center of Beijing. This site is located in the Haidan district which is a residential area where many universities are located. The campus has a 4 km^2 area which is covered by many grasses, trees and lakes, and it is approximately 1 km away from the Fourth Ring Road highway. Most vehicles are restricted to enter the campus.

PM_{10} concentrations were monitored with a TEOM (tapered element oscillating microbalance, R&P 1400, Rupprecht and Patashnik, Inc.) for the purpose of comparison between the PM_{10} concentrations observed at Tsinghua University in the present study and those reported by another institution. The detailed study concerning this issue has been described by Okuda et al. (2004). In brief, we referred to the PM_{10} concentrations which were posted on the website of the Beijing Environmental Protection Bureau (BJEPB, 2005). We used the data for 12 observation sites which covered a 2500 km^2 area of Beijing city. As the results, the PM_{10} concentrations and variations observed at our sampling site were quite similar to those reported for the 12 sites which were posted by the BJEPB. Therefore, our data obtained at Tsinghua University in the present study can be considered a good representative of the current situation of the entire area of Beijing city.

2.2. Analytical procedures

Total suspended particles (TSP) were collected for the purpose of obtaining the chemical characteristics of the aerosols in Beijing. Daily TSP samples were collected on cellulose nitrate filters (0.8 μm of pore size) over a period of 24 h at an air flow rate of 10 l min^{-1} using a low-volume air sampler set inside a shelter. More than 1500 samples were collected from March 2001 to March 2006. Trace metal concentrations in TSP samples were determined using an inductively coupled plasma mass spectrometer that was equipped with a laser ablation sample introduction system (LA/ICP-MS). Details of the LA/ICP-MS system have been described by Tanaka et al. (1998). We measured 16 kinds of metals in every aerosol sample by monitoring the following ions: ^{27}Al, ^{42}Ca, ^{47}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{67}Zn, ^{75}As, ^{82}Se, ^{111}Cd, ^{121}Sb, and ^{208}Pb. The absolute detection limits ranged from 5 pg for Cd to 15 ng for Ca. The detection limits of the trace metals analyzed by LA/ICP-MS were almost the same, and were slightly better than those obtained by instrumental neutron activation analysis (INAA) or X-ray fluorescence spectrometry (XRF, for Ni, Cd, and Pb determinations). The precision of the replicated LA/ICP-MS measurements ($n = 8$) was within 10% as the relative standard deviation. The analytical results obtained by LA/ICP-MS were in good agreement with those determined by INAA or XRF. Four anions (F^-, Cl^-, NO_3^-, and SO_4^{2-}) and five cations (Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+}) were extracted by mechanical shaking (15 min) with deionized water (15 ml, 18.3 MΩ cm), and analyzed by ion chromatography (Okuda et al., 2004, 2006b).

2.3. Regression model

Time-trend models have been used to describe temporal variations of chemical constituent concentrations, including annual rate of change and seasonal variations (Buishand et al., 1988; Seto et al., 2002, 2004; Okuda et al., 2005). In the present study, we assume that temporal variations of chemical constituent concentrations can be described by the following regression model, which is based on the least squares method:

$$\log \mathrm{Ct} = \alpha + \beta t + \gamma \sin\{(2\pi/12)t + \phi\}, \quad t = 0, 1, 2, \ldots n, \tag{1}$$

where t denotes the elapsed month since the initial observation ($t = 0$ for March 2001 in the present study), and n is the number of months of interest. The term βt represents the linear trend of the annual rate of change in the concentration of the target constituent. The annual rate of change in the chemical constituent concentration R is defined by the following equation:

$$R = (10^{12\beta} - 1) \times 100\ (\%). \tag{2}$$

The sine term represents a systematic seasonal variation cycle with phase angle ϕ.

3. Results and discussion

3.1. Overall results

Table 1 shows the PM_{10}, metal, and ionic constituent concentrations in TSP collected in Beijing from March 2001 to March 2006. Average (arithmetic mean), median, and geometric mean were used to describe the concentration in this table. We used arithmetic mean as "average value" of the concentration for further comparison between our data and the other studies, because many previous studies had used arithmetic mean as average concentration. In addition, it is worth to note that there were no significant differences among the relative compositions of each analyte using arithmetic mean, median, and geometric mean. The average PM_{10} concentration in Beijing was greater than 150 μg m^{-3}, and it was similar to those reported in previous studies (Sun et al., 2004; Xu et al., 2005). The PM_{10} concentration in Beijing was almost the same level in comparison to that observed in Mexico City, which had also serious air pollution caused by aerosols (Vega et al., 2003). The PM_{10} concentration was approximately several times higher than those observed in some other cities in the world, such as London and Tokyo (Okuda et al., 2004; Charron et al., 2007). All the metal and ionic concentrations in the Beijing aerosols were at least 2-fold higher than those in the Tokyo aerosols (Matsuda et al., 1999; Furuta et al., 2005). In particular, the As and Ca^{2+} concentrations in the Beijing aerosols were 25-fold and 15-fold higher, respectively, than those in the Tokyo aerosols. It is clear that Ca^{2+} is a major neutralizing chemical in the Beijing aerosols. These findings corresponded well with the results obtained by some other previous studies (Duan et al., 2003; Sun et al., 2004; Wang et al., 2005, 2006).

Table 1 also shows the enrichment factors (EFs) of each metal concentration which were calculated relative to the average crustal rock composition (Mason and Moore, 1982) with Al as the reference element. The EFs of Al to Ni were approximately below 10.