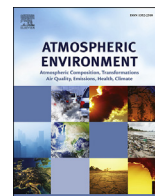




Contents lists available at ScienceDirect

## Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

# Characteristics of size-fractionated atmospheric metals and water-soluble metals in two typical episodes in Beijing



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## HIGHLIGHTS

- Metals and water-soluble metals were both at high level in Beijing.
- Water solubility of all metals was low in Aitken mode and coarse mode.
- Water-soluble metals had closer relationships with  $\text{SO}_4^{2-}$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ .

## ARTICLE INFO

### Article history:

Received 6 February 2015

Received in revised form

18 August 2015

Accepted 21 August 2015

Available online 24 August 2015

### Keywords:

Water-soluble metals

Size-fractionated

Aerosol

Haze

Beijing

## ABSTRACT

The abundance and behaviour of metals and water-soluble metals (V, Cr, Mn, Fe, Cu, Zn, As, Sr, Ag, Cd, Sn, Sb, Ba and Pb) in size-fractionated aerosols were investigated during two typical episodes in Beijing. Water-soluble inorganic ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) were also measured. Atmospheric metals and water-soluble metals were both found at high levels; for  $\text{PM}_{2.5}$ , average As, Cr, Cd, Cu, Mn and Pb concentrations were 14.8, 203.3, 2.5, 18.5, 42.6 and 135.3  $\text{ng}/\text{m}^3$ , respectively, and their water-soluble components were 11.1, 1.7, 2.4, 14.5, 19.8 and 97.8  $\text{ng}/\text{m}^3$ , respectively. Daily concentrations of atmospheric metals and water-soluble metals were generally in accordance with particle mass. The highest concentrations of metals and water-soluble metals were generally located in coarse mode and droplet mode, respectively. The lowest mass of metals and water-soluble metals was mostly in Aitken mode. The water solubility of all metals was low in Aitken and coarse modes, indicating that freshly emitted metals have low solubility. Metal water solubility generally increased with the decrease in particle size in the range of 0.26–10  $\mu\text{m}$ . The water solubility of metals for  $\text{PM}_{10}$  was: 50%  $\leq$  Cd, As, Sb, Pb; 26%  $<$  V, Mn, Cu, Zn and Sr  $\leq$  50%; others  $\leq$  20%. Most metals, water-soluble metals and their water solubility increased when polluted air mass came from the near west, near north-west, south-west and south-east of the mainland, and decreased when clean air mass came from the far north-west and far due south. The influence of dust-storms and clean days on water-soluble metals and size distribution was significant; however, the influence of rainfall was negligible. Aerosols with high concentrations of  $\text{SO}_4^{2-}$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  might indicate increased potential for human health effects because of their high correlation with water-soluble metals. Industrial emissions contribute substantially to water-soluble metal pollution as water-soluble metals show higher correlation with Cd, Sn, Sb and Pb that are mainly derived from industrial sources.

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## 1. Introduction

With rapid economic growth and urbanization in China, air pollutants are increasing rapidly and air pollution has become a

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serious issue in China in recent decades. Many studies have documented the adverse health effects of air pollution in China, including increases in respiratory symptoms, hospitalization and premature mortality (Chen et al., 2004). The World Health Organization (WHO) estimated that air pollution was associated with approximately 300,000 premature deaths per year in China (Cohen et al., 2005). Atmospheric heavy metals pose a great threat to human health. After entering the body through breathing, they can cause a variety of human dysfunctions or lead to various diseases: As, Cr, Ni, Pb and Cd have some carcinogenic capacity, As and Cd have potential teratogenic effects on the human body, and Pb and Hg are toxic to the fetus (Hu et al., 2012a, 2012b). Atmospheric heavy metals are continually being deposited onto the ground by dry and wet deposition, from where they can be absorbed by plant roots and stems or impact soil enzyme activity, biological activity and biodiversity (Morselli et al., 2003), resulting in persistent negative impacts on the ecosystem biogeochemical cycles (Kelly et al., 1996; Nriagu and Pacyna, 1988; Wong et al., 2003). Heavy metals are difficult to degrade because they are non-biodegradable and cannot be removed by chemical reactions in the atmosphere; however, they are easy to enrich, which makes heavy metal pollution an intractable issue. Air pollution from heavy metals such as Pb, Hg, Cr, Cd and As has become increasingly prominent, seriously endangering the health of local citizens (He et al., 2009).

Bioavailability is an important parameter in the evaluation of metal health risk (Moscoso et al., 2012) and water-soluble metals are a surrogate for bioavailability (Adamson et al., 2000; Birmili et al., 2006; Feng et al., 2008; Heal et al., 2005; Niu et al., 2010). Thus, water-soluble metals are attracting increasing research interest. Toxicological research has shown that heavy metals, especially water-soluble transition metals, can induce reactive oxygen species (ROS) production (Costa and Dreher, 1997; Heal et al., 2005). The level of water-soluble metals rather than the mass concentration of particulate matter led to acute inflammation in rats (Dreher, 2000), water-soluble Cu and Fe could stimulate lung epithelial cell nuclear transcription factor NF- $\kappa$ B (Jimenez et al., 2000) and water-soluble Zn was a toxicity factor for mice pulmonary disease (Adamson et al., 2000). Water-soluble metals might also promote the formation of OH radicals (Shi et al., 2003), which cause adverse effects on human health. The health effects of metals depend not only on their types, concentrations and chemical forms (Gao et al., 2005; Li et al., 2013a, 2013b), but also on the size of adherent particles (Birmili et al., 2006). Size distribution can affect the distribution of heavy metals and their bioavailability (Niu et al., 2010); for example, PM<sub>2.5</sub> usually contains more water-soluble metals than PM<sub>10</sub> (Karthikeyan et al., 2006; Mukhtar and Limbeck, 2013; Schneidmesser et al., 2010).

Many studies have been conducted on heavy metals to provide data for human health risk assessment in China. A review of atmospheric heavy metals of 44 cities in China suggested that there was serious pollution by Cr, As and Cd (Duan and Tan, 2013). Although a number of studies have been conducted on the properties of water-soluble metals, few have related the size distribution of water-soluble metals. Water-soluble metals in PM<sub>2.5</sub> from 15 samples in Xi'an (Duan et al., 2012), 10 samples in Guangzhou (Feng et al., 2008), 20 samples in Beijing (Wang et al., 2014), in PM<sub>10</sub> from 16 samples in Macao (Shao et al., 2013) and in TSP from 47 samples over the East China Sea (Hsu et al., 2010) were reported, suggesting that considerable attention is being paid to water-soluble metals. This might be particularly relevant for the Beijing area, which is characterized by complex meteorology that favours the ageing of pollutants and is influenced by the transportation of anthropogenic and natural pollutants from the neighbouring area as a consequence of its geographic location.

In this study, size-segregated aerosol samples were collected at

the University of Chinese Academy of Sciences (UCAS) in Beijing in April and May 2012 by a MOUDI sampler (7-stage cascade impactor). Metals, water-soluble metals and water-soluble ions for these samples were analysed. Chemical characteristics and size distribution of metals, water-soluble metals and metal water solubility were examined to detect the abundance and behaviour of metals and water-soluble metals. Meteorological factors and water-soluble inorganic ions were also considered to study their influence on water-soluble metals. These findings provide information on health effects and policy with regard to atmospheric metals.

## 2. Experimental

### 2.1. Sampling

The sampling site was located on the roof (fifth floor) of a research building on the UCAS campus (39.91 N, 116.24 E) in the Shijingshan District, Beijing, which is surrounded by roads, residential buildings and office buildings (Fig. 1). There are no obvious industrial sources in the vicinity. Sampling was conducted in the periods 6–26 April and 24–30 May, 2012, by a 7-stage cascade impactor sampler (Model 130 High-Flow Impactor, MSP Corp) at a flow rate of 100 L/min; the cut size and median diameter (MD) are shown in Table 1. The quartz membrane diameter was 75 mm for the zero stage to the 5th stage, and 90 mm for the 6th stage. The sampling duration was 24 h and filters were changed at 10:00 am. The zero stage is the inlet stage; samples from this stage will suffer the collision loss of particles and are not used for analysis. Samples were stored at  $-17^{\circ}\text{C}$ .

### 2.2. Chemical analysis

#### 2.2.1. Water-soluble inorganic ions

Half of the filter was ultrasonically extracted with 10 mL ultra-pure water for 15 min and then filtered. During ultrasonic extraction, ice was put in the water bath to prevent the temperature from increasing. This procedure was repeated and the extractions were divided into halves: one half was for the analysis of water-soluble inorganic ions; the other was for the analysis of water-soluble metals. Extractions were kept at  $-4^{\circ}\text{C}$  until analysis. A Dionex DX-600, which consists of a separation column (Dionex Ionpac AS11 for anion and CS12A for cation), a guard column (Dionex Ionpac AG 11 for anion and AG12A for cation), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50), and a gradient pump (Dionex Ionpac GP50), at the Analysis and Testing Centre of Beijing Normal University were used to analyse the water-soluble inorganic cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ) and anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ). The weak acid eluent (20 mM MSA) was used for the detection of cations, while the gradient weak base eluent (76.2 mM NaOH + H<sub>2</sub>O) was used for the detection of anions. The recovery of each ion was in the range 80–120%. The relative standard deviation (SD) of each ion was less than 5% for the reproducibility test. The limits of detection ( $S/N = 3$ ) were less than 0.04 mg/L for anions and 0.006 mg/L for cations. The concentrations of the water-soluble inorganic ions in the field blanks were 0.22, 0.11, not detected (nd), 0.21, nd, 0.32, nd, 0.35 and 0.21  $\mu\text{g m}^{-3}$  for  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , respectively.

#### 2.2.2. Water-soluble metals and metals

The pretreatment of samples for extraction of water-soluble metals was given in Section 2.2.1. The pretreatment of total metals was performed as follows. One quarter of each filter was cut using stainless steel scissors and placed in a Teflon tube with an 8 mL mixture of concentrated high-purity hydrofluoric acid and nitric acid with a volume ratio of 1:3, in preparation for microwave

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