Progress and prospects of atmospheric environmental sciences in China

Fahe Chai, Abdelwahid Mellouki, Yujing Mu, Jianmin Chen, Huiwang Gao, Hong Li
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Size distribution, characteristics and sources of heavy metals in haze episod in Beijing

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ABSTRACT

Size segregated samples were collected during high polluted winter haze days in 2006 in Beijing, China. Twenty nine elements and 9 water soluble ions were determined. Heavy metals of Zn, Pb, Mn, Cu, As, Cr, Ni, V and Cd were deeply studied considering their toxic effect on human being. Among these heavy metals, the levels of Mn, As and Cd exceeded the reference values of National Ambient Air Quality Standard (GB3095-2012) and guidelines of World Health Organization. By estimation, high percentage of atmospheric heavy metals in PM2.5 indicates it is an effective way to control atmospheric heavy metals by PM2.5 controlling. Pb, Cd, and Zn show mostly in accumulation mode, V, Mn and Cu exist mostly in both coarse and accumulation modes, and Ni and Cr exist in all of the three modes. Considering the health effect, the breakthrough rates of atmospheric heavy metals into pulmonary alveoli are: Pb (62.1%) > As (58.1%) > Cd (57.9%) > Zn (57.7%) > Cu (55.8%) > Ni (53.5%) > Cr (52.2%) > Mn (49.2%) > V (43.5%). Positive matrix factorization method was applied for source apportionment of studied heavy metals combined with some marker elements and ions such as K, As, SO42− etc., and four factors (dust, vehicle, aged and transportation, unknown) are identified and the size distribution contribution of them to atmospheric heavy metals are discussed.

INTRODUCTION

Urban air pollution is a worldwide problem causing a variety of risks to human health. Fast growing cities in developing countries such as China are strongest affected by urban air pollution showing highest burden of diseases (Cohen et al., 2004; Chen et al., 2011). The World Health Organization (WHO) estimated that annually about 300,000 people prematurely die due to urban air pollution in China. Atmospheric heavy metals can impose a long term burden on biogeochemical cycling in the ecosystem (Kelly et al., 1996; Nriagu, 1988; Nriagu and Pacyna, 1988). Among them, As, Cr, Ni, Pb, Zn, Cu, V and Cd are carcinogenic, As and Cd are potentially mutagenic, Pb and Hg are fetal toxic (Cheng, 2003; He et al., 2001). In recent years, the heavy metal pollution accidents have been reported frequently in China (Zhou, 2011). In February 2011, the State Council officially approved the “12th Five-Year Plan” for comprehensive prevention and control of heavy metals pollution. A new National Ambient Air Quality Standard (NAAQS) (GB3095-2012) was promulgated in China in 2012, and it will be formally implemented since January 1, 2016. In addition to tightening the Pb limit, for the first time, NAAQS (GB3095-2012) included in the limits of Cd, Hg, As, Cr(VI) in appendix as a reference for local governments to set up local ambient air quality standards in due time. Atmospheric emission is one of important ways of heavy metal pollution; however, insufficient attention...
has been paid to it in China.

Knowledge of the size distribution of particulate matter (PM) is not only vital in understanding its effects on human health, its sources and transformation processes during atmospheric transport, but also for estimation the dry deposition and light extinction of the aerosol (Trijonis, 1983; Pakkanen et al., 2001; Salma et al., 2005; Tang et al., 2006; Duan et al., 2005, 2007, 2012; Tan et al., 2009a; Tao et al., 2012a, 2012b). However, few research on size distribution of inorganic components in aerosol have been carried out in China, especially for heavy metals in Beijing (Ning et al., 1996), particularly for aerosol down to ultrafine fraction.

Beijing is the capital of China with a population of over 19.61 million. Serious air pollution has been reported in Beijing, and great efforts have been made to improve the air quality, especially since 1998. From then on, the air pollution in Beijing has changed from simple type of coal burning to mixed type of traffic exhaust and coal burning contributed by improvements of industrial and energy structure, usage of clean energy including nature gas and clean coal, reduction in pollution sources, and implementation of advanced environmental standards (Zhang et al., 2011). In this study, source apportionment of heavy metals was first employed in Beijing by positive matrix factorization (PMF) base on size segregated data, and both sources and their size distribution were obtained. The data is important for studies on both health effect and policy-making. As Fig. 1 shows, the sampling period was in the year of 2006 with high pollution of PM$_{10}$ in Beijing, so the result of this study will also help to evaluate the effect of environmental policies since then.

1 Materials and methods

1.1 Study area and sampling

A 13-stage low pressure impactor (Dekati, Tampere, Finland) was used to provide resolution of the size distribution of aerosol populations from coarse particles to ultrafine particles. PTFE filter substrates (Waters, USA) were used on all stages, and at a flow rate of 10 L/min the 50% cut off diameters (D50, µm) were 9.92, 6.68, 4.00, 2.39, 1.60, 0.948, 0.613, 0.382, 0.263, 0.157, 0.095, 0.056 and 0.028.

Sampling site of Tsinghua is an urban site on the rooftop of a building (5 m above the ground) within Tsinghua University, which is located 20 km in the northwest direction from the center of Beijing and 2 km from 4th Ring Road. Some boilers for heating and cooking may exist in the vicinity. More detail information can be found in previous publication (Duan et al., 2008).

Four sets of samples BJ1, BJ2, BJ3 and BJ4 with duration ranges from 48–72 hr were collected during 4th–7th, 10th–13th, 17th–20th and 25th–27th, Dec. 2006, respectively. Totally, 48 samples were collected. As Fig. 1 shows, the PM$_{10}$ levels were very high in 2006, and the samples collected in this study can represent the situation before Beijing Olympic Games in 2008 for which the government had taken great efforts to control the air pollution and the PM$_{10}$ levels had gradually decreased from 161 to 114 µg/m$^3$ since then.

1.2 Chemical analysis

The aerosol-loaded filters were cut into halves, and samples of one half were placed in Teflon tubes with a 4-mL mixture of concentrated hydrochloric acid and nitric acid at volume ratio of 3:1, and then microwaved for 58 min to ensure the complete digestion of particles collected on Teflon filters. The microwave process consisted of four steps under the operation power of 1200 W. The first step is to have temperature ramping to 120°C from room temperature in 5 min and holding for 5 min; the second is ramping to 155°C in 8 min and holding for 8 min; the third is ramping to 180°C in 5 min and holding for 5 min; and the last step is ramping to 195°C in 2 min and holding for 12 min. Then, the digested solution was diluted to 10 mL using ultrapure water (specific resistance 18 MΩ·cm) to perform the metal analysis by inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo, X serial) and ICP-AES (Thermo, IRIS Intrepid II XSP). The calibration was made using multi-element (metal) standards (certified reference materials; National Analysis Center for Iron and Steel, China) in a 3% (V/V) HNO$_3$ solution. Six blank filters were treated and analyzed in the same way as for the actual samples. In addition, the approximate detection limits (three times the standard deviation of blanks analyzed) were Si (216 µg/L), Al (33 µg/L), Na (55 µg/L), Mg (40 µg/L), S (92 µg/L), K (102 µg/L), Ca (221 µg/L), Sc (0.15 µg/L), Ti (5.14 µg/L), V(0.083 µg/L), Cr (0.93 µg/L), Mn (1.14 µg/L), Fe (40 µg/L), Co (0.71 µg/L), Ni (0.41 µg/L), Cu (0.74 µg/L), Zn (2.85 µg/L), Ga (0.16 µg/L), As (0.17 µg/L), Se (0.22 µg/L), Sr (0.77 µg/L), Zr (0.57 µg/L), Mo (0.09 µg/L), Ag (0.11 µg/L), Cd (0.027 µg/L), Sb (0.14 µg/L), Ba (1.43
Unc = \frac{5}{6} \times \text{MDL} \quad (1)

If the concentration is greater than the MDL provided, the calculation is

Unc = \sqrt{\text{(Error fraction} \times \text{Concentration})^2 + \text{MDL}^2} \quad (2)

2 Results and discussion

2.1 Levels of atmospheric PM and heavy metals

Some epidemiological evidences suggest mortality in urban areas may be linked to PM$_{10}$ (Lippmann, 1998). As shown in Table 1, the averaged PM$_{10}$ and PM$_{2.5}$ were 192.2 and 119.0 µg/m$^3$ respectively during the study period in winter in Beijing, much higher than the NAAQS of China for PM$_{10}$ (100 and 70 µg/m$^3$ annually for GB3095-1996 and GB3095-2012, respectively) and PM$_{2.5}$ (35 µg/m$^3$ annually GB3095-2012). The PM$_{10}$ and PM$_{2.5}$ also exceed WHO guidelines more than 8.61 and 10.90 times. It indicates the PM pollution in winter in Beijing is much serious.

Pb is a heavy metal nerve toxic. According to Table 1, the average concentration of atmospheric Pb is 281.6 ng/m$^3$ in Beijing comparable to reported average concentration of 261.0 ng/m$^3$ in China, which fall below the annual limits of current NAAQS of China (GB3095-1996) of 1000 ng/m$^3$, appendix of NAAQS (GB3095-2012, 500 ng/m$^3$) and the WHO guideline of 500 ng/m$^3$. This can be mainly attributed to the nationwide prohibition of leaded gasoline in China since July 1, 2000. Previous study (Li

### Table 1 Comparison of PM$_{10}$, PM$_{2.5}$ and atmospheric heavy metals with NAAQS and WHO guidelines

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>PM$_{10}$ (µg/m$^3$)</td>
<td>100</td>
<td>70</td>
<td>20</td>
<td>192.2</td>
<td>9.61</td>
</tr>
<tr>
<td>PM$_{2.5}$ (µg/m$^3$)</td>
<td>35</td>
<td>10</td>
<td>100</td>
<td>119.0</td>
<td>11.90</td>
</tr>
<tr>
<td>Hg (ng/m$^3$)</td>
<td>50</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb (ng/m$^3$)</td>
<td>1000</td>
<td>500</td>
<td>500</td>
<td>281.6</td>
<td>0.56</td>
</tr>
<tr>
<td>V (ng/m$^3$)</td>
<td></td>
<td>1000</td>
<td>1000</td>
<td>10.7</td>
<td>0.01</td>
</tr>
<tr>
<td>As (ng/m$^3$)</td>
<td>6</td>
<td>6.6</td>
<td>47.1</td>
<td>7.14</td>
<td>51.0</td>
</tr>
<tr>
<td>Mn (ng/m$^3$)</td>
<td>150</td>
<td>163.7</td>
<td>1.09</td>
<td></td>
<td>198.8</td>
</tr>
<tr>
<td>Ni (ng/m$^3$)</td>
<td>25</td>
<td>22.7</td>
<td>0.91</td>
<td></td>
<td>29.0</td>
</tr>
<tr>
<td>Cr(VI) (ng/m$^3$)</td>
<td>0.025</td>
<td>0.25</td>
<td>41.6</td>
<td></td>
<td>85.7</td>
</tr>
<tr>
<td>Cd (ng/m$^3$)</td>
<td>5</td>
<td>5</td>
<td>5.8</td>
<td>1.16</td>
<td>13.2</td>
</tr>
<tr>
<td>Zn (ng/m$^3$)</td>
<td>501.9</td>
<td></td>
<td></td>
<td></td>
<td>424.5</td>
</tr>
<tr>
<td>Cu (ng/m$^3$)</td>
<td>72.2</td>
<td></td>
<td></td>
<td></td>
<td>117.0</td>
</tr>
</tbody>
</table>

$^*$ Duan and Tan, 2013
et al., 2000) had shown that, since the phase out of the leaded gasoline, the average annual concentration of Pb decreased by 74% compared with before. However, except for vehicle emissions, coal combustion is also a major source for anthropogenic Pb (Duan et al., 2012).

V can be emitted into the atmosphere by three ways (Al-Momani, 2003; Lin et al., 2005): natural rock weathering; combustion of fossil fuels such as coal and oil; mining and smelting of vanadium containing minerals such as vanadium-titanium magnetite. The concentration of atmospheric V is 10.7 ng/m³ in Beijing which is much lower than the reported average concentration of 17.9 ng/m³ in China, and much lower than the limit of WHO's limit of 25 ng/m³. There is no limit of V in both current and new NAAQS (GB3095-1996, GB3095-2012).

As is one of the most dangerous carcinogenic elements to human. Although As is not a heavy metal, considering its health effect, it is discussed as a heavy metal(loid) in the context. Studies have shown that coal combustion is one of the important anthropogenic source (Nriagu and Pacyna, 1988). The concentration of atmospheric As is 47.1 ng/m³ in this study which is similar to the reported average concentration of 51.0 ng/m³ in China, and much higher than the limit of the new NAAQS (GB3095-2012) in China (6 ng/m³) and the limit of WHO (6.6 ng/m³³).

Excess Mn will do harm to the nervous, immune and reproductive systems of human beings. Atmospheric Mn comes mainly not only from anthropogenic sources such as coal combustion, metal smelting and gasoline antiknock additive, but also from natural sources of soil erosion. Atmospheric Mn is enriched in both coarse and fine particles (Duan et al., 2012). The concentration of atmospheric Mn is 163.7 ng/m³ in this study, which is close to WHO’s limit of 150 ng/m³. There is no limit of Mn in both current and new NAAQS (GB3095-1996, GB3095-2012).

Ni is defined as the first class of carcinogens by Cancer Research Center. Petroleum and coal combustion are the major sources of Ni, and some industry processes such as smelting of nickel ore and nickel-containing metal ores (especially iron or steel) can also emit Ni. The concentration of atmospheric Ni is 22.7 ng/m³ in this study, near to WHO’s limit of 25 ng/m³. There is no limit of Ni in both current and new NAAQS.

Most atmospheric Cr exists in two forms of inorganic Cr(III) and Cr(VI). Cr(VI) can do harm to the kidneys and heart, and have a carcinogenic effect. Both new NAAQS (GB3095-2012) of China and limit of WHO only list out the Cr(VI) concentration limit, however, generally the data reported in the literature is of total Cr and few data on Cr(VI). The total concentration of atmospheric Cr is 41.6 ng/m³ in this study. The studies on the forms of atmospheric Cr are limited, and atmospheric Cr(VI) needs to be further studied.

After breathing into the body, most Cd will get into the liver and kidneys. The concentration of atmospheric Cd is 5.8 ng/m³ in this study, similar to the new NAAQS (GB3095-2012) in China and the WHO limit of 5 ng/m³. Cu and Zn can become toxic when presenting in excessive amount. The concentration of atmospheric Cu and Zn are 72.2 ng/m³ and 501.9 ng/m³ respectively in this study.

As Table 1 shows, compared with concentrations, the atmospheric heavy metals in Beijing in winter rank as: Zn > Pb > Mn > Cu > As > Cr > Ni > V > Cd, and all these heavy metals are near the average levels in China which reviewed by Duan and Tan (2013). The concentration ratios of atmospheric heavy metals to WHO guidelines can reach as high as 7.14 (0.01–7.14), however, compared with the ratios of PM_{10} and PM_{2.5} (9.61 and 11.90), they are still much lower. It indicated that it is more important to control atmospheric heavy metals by control PM first.

2.2 Size distribution of atmospheric heavy metals

Generally, typical aerosol spectra have three peaks (modes). Coarse mode particles (> 2 μm) tend to be mechanically generated such as soil dust, sea spray aerosol, and road dust in urban areas. Nucleation (< 0.1 μm) and accumulation mode (0.1–2 μm) particles tend to be produced either directly from combustion sources, or by gas to particle conversion involving reaction products of sulphates, nitrates, ammonium and organics. Figure 2 shows the size distribution of the studied atmospheric heavy metals in Beijing.

All the studied heavy metals exist in all of the nucleation mode, accumulation mode and coarse mode particles. Among them, Pb, Cd, As and Zn show mostly in accumulation mode; V, Mn and Cu exist mostly in both coarse and accumulation modes; and Ni and Cr exist in all of the three mode. Considering the health effect and visibility degradation, a new NAAQS (GB3095-2012) was promulgated in China in 2012, and PM_{2.5} limits were added in to it for the first time. As Fig. 2 shows, by estimation, the ratios of atmospheric heavy metals in PM_{2.5} (PM_{2.5} in this study) to those in PM_{10} (PM_{10} in this study) ranked as Pb (88.5%) > Cd (81.8%) > Zn (81.5%) > As (77.1%) > Cu (75.9%) > Cr (71.7%) > Ni (67.9%) > Mn (63.3%) > V (46.8%). It indicates that it is an effective way to control atmospheric heavy metals by PM_{2.5} controlling.

Considering health effect, since smaller aerosol can easily get into the human respiratory system, the heavy metals associated with smaller aerosol will do more harm to human health. US EPA (1982) presented the deposition rates of particles in the respiratory tract for mouth breathing as a function of particle size. According to it, the breakthrough of atmospheric heavy metals into pulmonary alveoli are shown in Fig. 2. By calculation, the breakthrough rates of the studied heavy metals into pulmonary alveoli are: Pb (62.1%) > As (58.1%) > Cd (57.9%) > Zn (57.7%) > Cu (55.8%) > Ni (53.5%) > Cr (52.2%) > Mn (49.2%) > V (43.5%).
2.3 Source apportionment of atmospheric heavy metals

Four sets of 48 size segregated samples were input to EPA PMF 3.0. In order to simplify the model calculation, except for the nine heavy metals, only elements and ions as good source markers and with low uncertainties were included in the modeling: Al, Ca, Fe, K, Mg, V, Cr, Mn, Ni, Cu, Zn, As, Se, Cd, Sb, Ba, Pb, Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺, Cl⁻, SO₄²⁻, NO₃⁻ and mass concentration. Among them, Al and Ca are indicators of crust related dust (Duan et al., 2012); K is a marker of biomass burning (Duan et al., 2004); As and Se generally most come from coal burning (Duan et al., 2012); NH₄⁺, SO₄²⁻ and NO₃⁻ are indicator of secondary aerosol and long range transportation. Tan et al. (2009) reported these ions are significantly higher in haze days than normal days.

Four factors are identified by EPA PMF 3.0, and factor profiles (% of species total) are illustrated as Fig. 3. Factor 1 (dust) has high contribution of Al (91.2%), Ca (95.8%), Fe (81.4%), Mg (89.3%) and Ba (84.1%) indicating crust related dust (He et al., 2001). Factor 1 is the main source of V (58.2%) and Mn (35.1%), and contributes less than 20% to other heavy metals.

Factor 2 (vehicle) has high contribution of Mn (39.5%), Cu (35.6%), Zn (50.5%), As (40.7%), Cd (55.7%) and Pb (26.9%) indicating vehicle emission, and Factor 2 contributes less than 20% to other heavy metals. It is concluded that vehicle emissions may be the major source of Pb, Cu, Zn and Cd urban contamination (Johansson et al., 2009).

Factor 3 (aged transportation) contributes high to K (73.2%). It indicates it is a mixture of aged long range transportation source. The mixture may include biomass burning, coal burning and other industries such as iron and steel industry. Beijing was surrounded by Tianjin City and Hebei Province. Tianjin is one of the biggest industrial city with a population of 9.3 million. Hebei Province has the highest iron and steel productivity in China, and the coal consumption was much high. Biomass burning was often reported in Hebei Province. Rural biomass burning...
has also been identified as an important contributor to fine PM concentrations in Beijing (Duan et al., 2004). Factor 3 also contributes to other heavy metals of V (26.6%), Cr (5.3%), Cd (37.8%) and Mn (25.4%).

Factor 4 (unknown) contributes high to Cr (65.7%), Ni (56.3%), Na (50.1%) and Cl (33.55%). The source of Factor 4 is still need to be further studied. Factor 4 contributes much less to other heavy metals (< 10%).

As to mass concentration contributions, it can be ranked as Factor 3 (aged and transportation: 46.7%) > Factor 1 (dust: 40.7%) > Factor 2 (vehicle: 8.8%) > Factor 4 (unknown: 3.8%). This result is similar to those found by other researchers that about 34% of PM\textsubscript{2.5} on average can be attributed to sources outside Beijing, and during sustained wind flow from the south, Hebei Province can contribute 50%–70% of PM\textsubscript{2.5} concentrations in Beijing (Streets et al., 2007).

Although the total contribution of atmospheric heavy metals as discussed afore, the contribution strongly rely on the size distribution as Fig. 4 shows. Generally, Factor 1 contributes more to coarse mode and little in nucleation and accumulation mode concentrations; Factor 2 contributes more to accumulation mode and a little coarse mode concentrations; Factor 3 contributes most to accumulation mode concentrations; and Factor 4 contributes to all of the three mode.

### 3 Conclusions

A study on size distributions of atmospheric heavy metals was carried out during haze in winter in Beijing, China. The levels, size distributions and sources of heavy metals (Zn, Pb, Mn, Cu, As, Cr, Ni, V and Cd) were discussed. Among them, atmospheric Mn, Ni, As, Cd and Pb exceed the reference values of NAAQS (GB3095-2012) and guidelines of WHO. The concentration ratios of atmospheric heavy metals to WHO guidelines can reach as high as 7.14, however, compared with the ratios of PM\textsubscript{10} (9.61) and PM\textsubscript{2.5} (11.90), they are still much low. It indicated that it is more important to control atmospheric heavy metals by control PM first. Pb, Cd, and Zn show mostly in accumulation mode, V, Mn and Cu exist mostly in both coarse and accumulation modes, and Ni and Cr exist in all of the three mode. By estimation, high percentage of atmospheric heavy metals in PM\textsubscript{2.5} indicates it is an effective way to control atmospheric heavy metals by PM\textsubscript{2.5} controlling. Considering the health effect, the breakthrough rates of atmospheric heavy metals into pulmonary alveoli are: Pb (62.1%) > As (58.1%) > Cd (57.9%) > Zn (57.7%) > Cu (55.8%) > Ni (53.5%) > Cr (52.2%) > Mn (49.2%) > V (43.5%). PMF method was applied for...
source apportionment of studied heavy metals combined with some marker elements and ions such as K, As, SO$_4^{2-}$ etc. Four factors are identified: Factor 1 (dust) is the main source of V (58.2%) and Mn (35.1%), and contribute less than 20% to other heavy metals. Factor 2 (vehicle) has high contribution of Mn (39.5%), Cu (35.6%), Zn (50.5%), As (40.7%), Cd (55.7%) and Pb (26.9%), however contributes less than 20% to other heavy metals. Factor 3 (aged and transportation) contributes high to As (48.1%), Pb (62.8%), and also contribute to V (26.6%), Cr (5.3%), Cd (37.8%) and Mn (25.4%). Factor 4 (unknown) contributes high only to Cr (65.7%), Ni (56.3%), and contributes much less to other heavy metals (<10%).

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References


Tan J H, Duan J C, He K B, Ma Y L, Duan F K, Chen Y et al., 2009b. Chemical characteristics of PM$_{2.5}$ during a typical haze episode in Guangzhou. *Journal of Environmental Sciences*, 21(6): 774–781.


US EPA (Environmental Protection Agency), 1982. *Air quality criterion for Particulate Matter*.


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