Source apportionment and water solubility of metals in size segregated particles in urban environments

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HIGHLIGHTS

- PM$_{2.5}$ and coarse PM showed highly different metals distributions.
- PMF identified three key sources: road dust, vehicular exhaust and ship emission.
- Ship emission contribution to metals has increased since last decade.
- High metal solubility in PM$_{2.5}$ than coarse PM shows size dependent chemical state.
- Findings are useful for emission control to alleviate adverse metallic pollution.

GRAPHICAL ABSTRACT
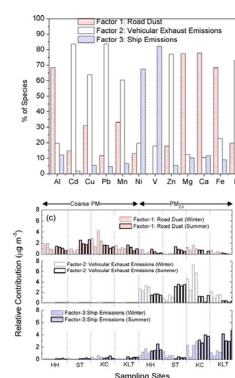
ABSTRACT

Metals in atmospheric particulate matter (PM) have been associated with various adverse health effects. Different factors contributing to the characterization and distribution of atmospheric metals in urban environments lead to uncertainty of the understanding of their impact on public health. However, few studies have provided a comprehensive picture of the spatial and seasonal variability of metal concentration, solubility and size distribution, all of which have important roles in their contribution to health effects. This study presents an experimental investigation on the characteristics of metals in PM$_{2.5}$ and coarse PM in two seasons from four urban sites in Hong Kong. The PM samples were extracted separately with aqua regia and water, and a total of sixteen elements were analyzed using ICP–MS and ICP–OES to determine the size segregated concentration and solubility of metals. The concentrations of major metals were distributed in similar patterns with the same order of magnitude among different urban sites. Source apportionment using Positive Matrix Factorization (PMF) indicated that three sources namely road dust, vehicular exhaust and ship emission are major contributors to the urban atmospheric metal concentrations in Hong Kong with distinctly different profiles between coarse PM and PM$_{2.5}$ fractions. The individual metals were assigned to different sources, consistent with literature documentation, except potassium emerging with substantial contribution from vehicle exhaust emission. Literature data from past studies on both local and other cities were compared to the results from the present study to investigate the impact of different emission sources and control policies on metal distribution in urban atmosphere. A large variation of solubility among the metals reflected that the majority of metals in PM$_{2.5}$ were more soluble than those in coarse PM indicating size dependent chemical states of metals. The data from this study provides a rich dataset of metals in urban atmosphere and can be useful for targeted emission control to mitigate the adverse impact of metallic pollution on public health.

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1. Introduction

Atmospheric particulate matters (PM) have been reported to cause a variety of adverse health effects depending on their physical and chemical characteristics. Due to their small size, $PM_{2.5}$ (particle aerodynamic diameter, $d_p < 2.5$ μm) particles have the capability to penetrate deeper into the airways of the respiratory system and reach the alveoli where they are retained in the lung parenchyma which consequently lead to adverse health effects such as asthma, cardiopulmonary diseases and lung cancer (Chen and Lippmann, 2009; Li et al., 2010; Valavanidis et al., 2008). In addition to fine PM, previous studies have also shown that coarse PM may play an important role in human health implication and causes severe human health problems (Pakbin et al., 2011).

In order to identify the causal relation of exposure to PM and health effect, many epidemiology studies have used area $PM_{2.5}$ concentration from ambient monitoring stations as a surrogate of exposure by population in a city. However, recent studies have shown that physical and chemical properties of PM are actually responsible for the observed health effects, in which particle bound metals, especially transition metals, emerged as an active player in reactive oxygen species (ROS) generation leading to cellular toxicity. The bioavailability of transition metals in PM together with their redox properties plays an important role in oxidative damage in a cardiopulmonary system (Costa and Dreher, 1997; Dominici et al., 2007; Roemer et al., 2000). Janssen et al. found that high fractions of soluble metals of manganese (Mn 91%), iron (Fe 68%), copper (Cu 80%), and zinc (Zn 83%) are present in PM (Janssen et al., 1997), and the water soluble fraction of PM elicits DNA damage due to the hydroxyl radicals (•OH) (Knaapen et al., 2002) that would react with biological molecules to activate cellular signals and consequently result in cellular damages (Chen and Lippmann, 2009). Transition metals, especially Fe, Cu, vanadium (V), cobalt (Co), and chromium (Cr) act as catalysts in the Fenton reaction (as shown in Eqs. (1) & (2)), generating hydroxyl radicals and inducing cellular oxidative stress (Donaldson and MacNee, 2001).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + •OH + OH^- \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + •OOH + H^+ \tag{2}$$

In urban atmosphere, different source emissions may contribute to the metallic content of atmospheric PM. For example, wear of brake lining and tire wear contribute to the high metal contents in traffic dominant environments (Bilos et al., 2001; Chan and Stachowiak, 2004; Iijima et al., 2007). Road dust is also one of the primary metal contributors enriched in mineral materials including Al, Ca, K, Ti, etc. and heavy metals (Gandhi et al., 2003).

Although many studies have investigated the metallic composition of ambient aerosols for source identification, little information is available in the literature on variability of metal interaction and seasonal variation of the PM metal concentrations in the urban atmosphere, limiting a refined understanding of their contribution to the population exposure. In addition, the water solubility of individual metals also played a vital role in their bioavailability and relation to the adverse health effects, but information on their relation with particle size, temporospatial variation has not yet been fully characterized. This study presents a comprehensive experimental investigation of $PM_{2.5}$ and coarse PM metal composition, concentration and solubility at four urban sites in Hong Kong with different characteristics and their seasonal variation. Source apportionment of the measured metals was also carried out to identify the major sources contribution, and their impact on the heterogeneity of the metals characteristics in urban atmosphere.

2. Materials and methods

2.1. Sampling site and protocol

The sampling campaign was carried out from 12 November 2012 to 10 December 2012 (Winter season) and 8 April 2013 to 13 May 2013 (Spring/Summer season). Personal Cascade Impactor Samplers (PCIS, SKC Inc., Eighty-Four, PA) were used to collect coarse PM ($PM_{2.5 - 10}$) and fine PM ($PM_{2.5}$) on 25 mm and 37 mm Teflon filter (PALL Life Sciences, Ann Arbor, MI), respectively. Four weekly samples were collected for each season with each sample lasting for 7 days. Each PCIS was run at flow rate of 9 liter per minute which was checked regularly with a Gillian air flow calibrator (Sensidyne Inc., Clearwater, FL) during the weekly sampling period. The sampling sites were situated at four areas of Hong Kong with different characteristics (sites descriptions and location shown in Table 1 and Fig. S1).

2.2. Chemicals and materials

Multi-element standard solutions were purchased from Fluka (Mo, USA). All stock solutions prepared using standard solutions were stored at 4 °C. Hydrochloric acid fuming (37%) and Nitric acid (65%) were purchased from Merck KGaA (Germany). All the calibration standards from 0.005 to 5 mg L^{-1} for daily use were prepared from the diluted stock solution with Milli-Q water, produced by a Milli-Q PURELAB Classic Water Purification System of Millipore (ELGA®, VWS Ltd., England & Wales). The San Joaquin Soil (NIST, USA), a reference material (SRM) 2709a of National Institute of Standards and Technology (NIST) was used to evaluate the performance of acid digestion procedures.

2.3. Inductively Coupled Plasma–Mass Spectrometry (ICP–MS)

The concentrations of trace metals Al, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, V, Zn were analyzed by Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) equipped with a 7500cx System (Agilent, USA). Parameters including carrier flow 0.93 L min^{-1}, RF power (W) 1600, makeup gas flow 0.24 L min^{-1}, nebulizer pump rate 0.2 rps, and sample pump rate 1.0 rps were set in operation. The analytical drifts were corrected using spiked standard solution in 100 μg L^{-1} at regular intervals for Al and 10 μg L^{-1} for all other analytes during analysis. Argon with purity ≥99.995% used in Inductively Coupled Plasma (ICP) was obtained from Hong Kong Linde Ltd.

2.4. Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP–OES)

ICP–OES was used to determine the five basic elements Ca, Fe, K, Mg, Na in extracts due to their relatively high concentrations in samples and the spectral interference of chloride in ICP–MS detection. The analysis was carried out using an Optima 2100 DV system (Perkin Elmer, USA) in scanning mode, with ion lenses to increase the maximum sensitivity. Parameters were set at plasma flow rate 15 L min^{-1}; auxiliary flow at 0.3 L min^{-1}; nebulizer flow at 0.8 L min^{-1}; RF power at 1300 W; Flow rate of pump at 1.00 mL min^{-1}. Analytical drifts were monitored using 1.0 mg L^{-1} spiked multi-elements standard solution.

2.5. Water and acid extraction

A total of 64 filter samples were collected during the campaign. The filters were cut into one fourth prior to analysis: one half was used for water extraction and one quarter of the other half was used for acid extraction. For water extraction, filters were soaked in 8 mL of Milli-Q water in 15 mL metal free centrifuge tubes, then extracted using a multi-tube vortex mixer (Model X-2500, VWR). After 12 h of vortexing, the extracts were filtered with 0.22 μm filter membranes and stored at −20 °C. Extracts were acidified with 2% HCl prior to storing in order