Water solubility of metals in coarse PM and PM2.5 in typical urban environment in Hong Kong

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Atmospheric Pollution Research

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ABSTRACT

An investigation of abundance and solubility of metals in size–segregated particulate matter (PM) was conducted at a typical urban site during the winter between late 2011 and early 2012 in Kowloon Tong, Hong Kong. The samples were extracted by both strong acid and water, and fourteen elements including Al, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, V, and Zn were analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP–OES) and Inductively Coupled Plasma Mass Spectrometry (ICP–MS). The metals in PM showed distinctly different profiles of their distribution between coarse particles (2.5 µm<d_p<10 µm) and PM₂.₅ (d_p<2.5 µm). The upper continental crustal enrichment factors (CEFs) of the measured metals for two particle size fractions showed that CEFs for nine of fourteen metals in PM₂.₅ were higher than 10 while Cd, Pb, Zn, Mn and Cu were far above 100; whereas for coarse particles, the CEFs of most elements were lower than 10, except for Cd being higher than 100. Water and acid extractable fractions of coarse PM and PM₂.₅ were analyzed and compared to investigate the transition metals solubility. The water extractable fraction was found to be present mainly in the fine particles, whereas more of the coarse fraction mass remained as insoluble fraction. The results from this study demonstrated large variation of water solubility of metals in urban aerosols in different size fractions and highlighted solubility as an important metric for considering the relation between metals and adverse health effects in epidemiological and toxicological studies.

Keywords: Metals, size fractionated PM, acid digestion, water solubility, crustal enrichment factor

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1. Introduction

Exposure to atmospheric particulate matter (PM) has been linked with increased human mortality and morbidity (Valavanidis et al., 2008; Chen and Lippmann, 2009; Brook et al., 2010). It has been reported in the literature that particulate air pollutants may elicit oxidative damage and inflammatory injury (Ghio and Devlin, 2001) and have numerous potential linkages to human diseases, such as asthma (Li et al., 2010), cardiopulmonary diseases and lung cancer (Valavanidis et al., 2008). However, the exact mechanisms that cause the adverse health effect still remain unclear to date. Different metrics of PM physical and chemical characteristics have been investigated in literature to understand the driving mechanisms, such as particle size, surface area, and their chemical compositions (Harrison and Yin, 2000).

Atmospheric particulate matter is a complex mixture of a variety of chemical constituents from different sources. Typically PM contains basic metals, transition metals, organic compounds, ions, carbonaceous materials, and materials of biological origin (Valavanidis et al., 2008; Ning and Sioutas, 2010). The identification of surrogates for PM toxicity has been the key in many recent studies, with emphasis on volatile or semi–volatile organic species (e.g. Polycyclic Aromatic Hydrocarbons (PAHs)), ions (e.g. sulfate, nitrate) and transition metals. Several epidemiological and toxicological studies have shown that metals in PM contribute to the carcinogenic effects (Lippmann et al., 2006; Kawata et al., 2007) and the toxic effects are also linked to the water solubility of metals in size–fractionated atmospheric particles (Ghio and Devlin, 2001; Birmili et al., 2006). For example, (Chen and Lippmann, 2009) found that nickel (Ni), vanadium (V), lead (Pb) and zinc (Zn) are

particularly influential components in terms of acute cardiac function changes and excess short–term mortality. (Jarup and Akesson, 2009) reported in details that cadmium (Cd) exposure is linked with kidney damage and bone effects, and long–term exposure to high Cd may cause skeletal damage.

PM bound metals come from a variety of origins, especially in urban areas with mixed sources and aging processes, and these also affect their distribution in different PM size fractions and form of existence, which consequently determine their respiratory deposition and bioavailability. (Canepari et al., 2008) reported coarse PM (2.5 µm<d_p<10 µm) and PM₂.₅ (d_p<2.5 µm) metals distribution in Rome, Italy and found that elements of natural origin, such as barium (Ba), calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn) are mostly in the coarse fraction, whereas elements of anthropogenic origin, i.e., vehicle emissions, non–tailpipe traffic sources, railway emissions are found in the fine fraction with more than 50% of the total mass of Cd, Pb and V being in the size range below 1.0 µm. Investigations of atmospheric PM₂.₅ and PM₁₀ in Hong Kong also reported similar observations (Ho et al., 2003; Louie et al., 2005). However, a number of toxicological studies have indicated that solubility of transition metals, a crucial factor in PM bioavailability, may play a more significant role in chronic and acute adverse health effects than the total metals. Costa and Dreher (1997) found that the lung dose of bioavailable transition metals, not the PM mass, was the primary determinant of the acute inflammatory response for both the combustion source and ambient PM samples. Knaapen et al. (2002) demonstrated that the water–soluble fraction of PM elicits DNA damage was due to soluble transition metal–dependent hydroxyl radical (·OH) formation. It has been well documented that Fe,

along with other transition metals such as copper (Cu) and V, has the redox active ability to exchange electrons in aqueous solution and catalyze free radical generation via the Fenton reaction (Donaldson and MacNee, 2001), thus associated with increased reactive oxygen species (ROS) production and cellular oxidative stress (Verma et al., 2009).

The solubility of transition metals has a wide range of reported values in literature due to the variation in their sources and processes. For example, Fe, a major component of atmospheric PM transition metals, has a solubility of 10–30% in urban aerosols (Espinosa et al., 2002) while only <5% in subway microenvironment (Kam et al., 2011). It is reported that the solubility of Fe is the key to the primary nutrient production in marine environment which controls the rate of photosynthesis in the ocean and the transformation and uptake of major nutrients such as nitrogen (Morel and Price, 2003). Other transition metals have much higher reported solubility of more than 60% for V (Espinosa et al., 2002) and Cd (Heal et al., 2005) in $PM_{2.5}$ indicating the significant difference in the form of existence of transition metals, and in their potency of linkage with health outcomes (Birmili et al., 2006). However, detailed information on the distribution and solubility of redox active transition metals in urban aerosols is still not well characterized. The present study focuses mainly on the characterization of transition metals $PM_{2.5}$ and coarse PM in typical urban environment in Hong Kong through the winter season. Fourteen metals were analyzed after both water extraction and strong acid digestion to determine their solubility profile and their distribution in the two size fractions. The possible sources of reported metals and the implications of solubility on health impact were also discussed in the study.

2. Materials and Methods

2.1. Sampling site and protocol

The sampling site is located in Kowloon Tong (22°20'0.00"N, 114°10'10.90"E), about 1.5 km north of Mongkok, one of the busiest districts in Hong Kong with very high traffic flow of an average volume ranging from 26 000 to 50 000 vehicles per day (Hong Kong Transport Department, 2012), making the site representative of the urban Hong Kong environment. The sampling took place on the rooftop of an eight story university building from December, 2011 to January, 2012 as northeasterly winds are typically prevailing in winter time facilitating the regional transport of pollutants. Figure 1a shows the location of sampling site in Hong Kong and its relative location in South China. Five weekly filter samples were collected using a Personal Cascade Impactor Sampler (SKC Inc., Eighty–Four, PA, also referred to as PCIS) running at standard flow rate of 9 liters per minute. The flow rates were checked and calibrated regularly during the sampling with a Gilian air flow calibrator (Sensidyne Inc, Clearwater, FL). The PCIS was installed with one impaction stage at a cut point of 2.5 μm and an after–filter stage, where coarse and fine PM were collected, respectively. A 25 mm Zefluor filter (PALL Life Sciences, Ann Arbor, MI) and a 37 mm PTFE filter (PALL Life Sciences, Ann Arbor, MI) were loaded in PCIS to collect coarse and $PM_{2.5}$, respectively. The samples filters were equilibrated for 24 hours in a temperature and relative humidity–controlled room (22–25 °C, 35–40% RH) before and after sampling prior to the gravimetric measurement by a Micro Balance (MSA6.6S–000–DM, accuracy 0.001 mg, Sartorius Cubis) in order to minimize the effects from changes in temperature or humidity. At least three measurements were made for each filter to ensure the uncertainty of filter weight is within ±3 μg. All the filters were stored in petri dishes, lined with aluminum foil baked for 24 hours at 550 °C. The filter samples were stored in a freezer at −20 °C prior to chemical analysis. The sampling and preservation of the PM samples are common practice and we followed standard procedures and protocols adopted from our previous investigations (Ning et al., 2007; Pakbin et al., 2011) and the methods used by Kleeman et al. (2000) and Rees et al. (2004).

2.2. Acid digestion and water extraction procedures

The collected filter samples were first cut in half prior to the treatment: one half was used for acid digestion and the other half for water extraction. In order to maximize the recovery of particle bound metals, a procedure was developed and optimized for acid digestion of metals in PM samples. The optimization is carried out by comparing the extraction performance using different concentrations of acids. All digestion Teflon vessels were first cleaned by soaking in 10% nitric acid bath for 24 hours, followed by rinsing for three times using Milli–Q water, produced by a Milli–Q PURELAB Classic Water Purification System of Millipore (ELGA®, VWS Ltd., England & Wales). An acid digestion matrix was prepared with 16 N HNO_3 and 12 N HCl in a volume ratio of 3:1, and each filter section was placed in a 100 mL Teflon vessel with 8 mL of the prepared digestion acid matrix. The extraction was carried out in Microwave digester (ETHOS EZ, Milestone, Sorisole, Italy) and digestion parameters were set at 12 minutes ramping up to 180 °C, held for 10 minutes, followed by cooling and ventilating within 2 hours. For water extraction, each filter section was soaked in 8 mL of Milli–Q water in pre–cleaned 15 mL metal–free centrifuge tubes and extracted by vortex–assisted shaking using a multi–tube vortex mixer (Model X–2500, VWR) for 12 hours. Immediately after extraction, the extracts were filtered with 0.22 μm filter membranes and stored in a freezer at −20 °C. Prior to analysis, the water extracts were acidified to 2% HNO_3 to prevent losses of metal ions from storage.
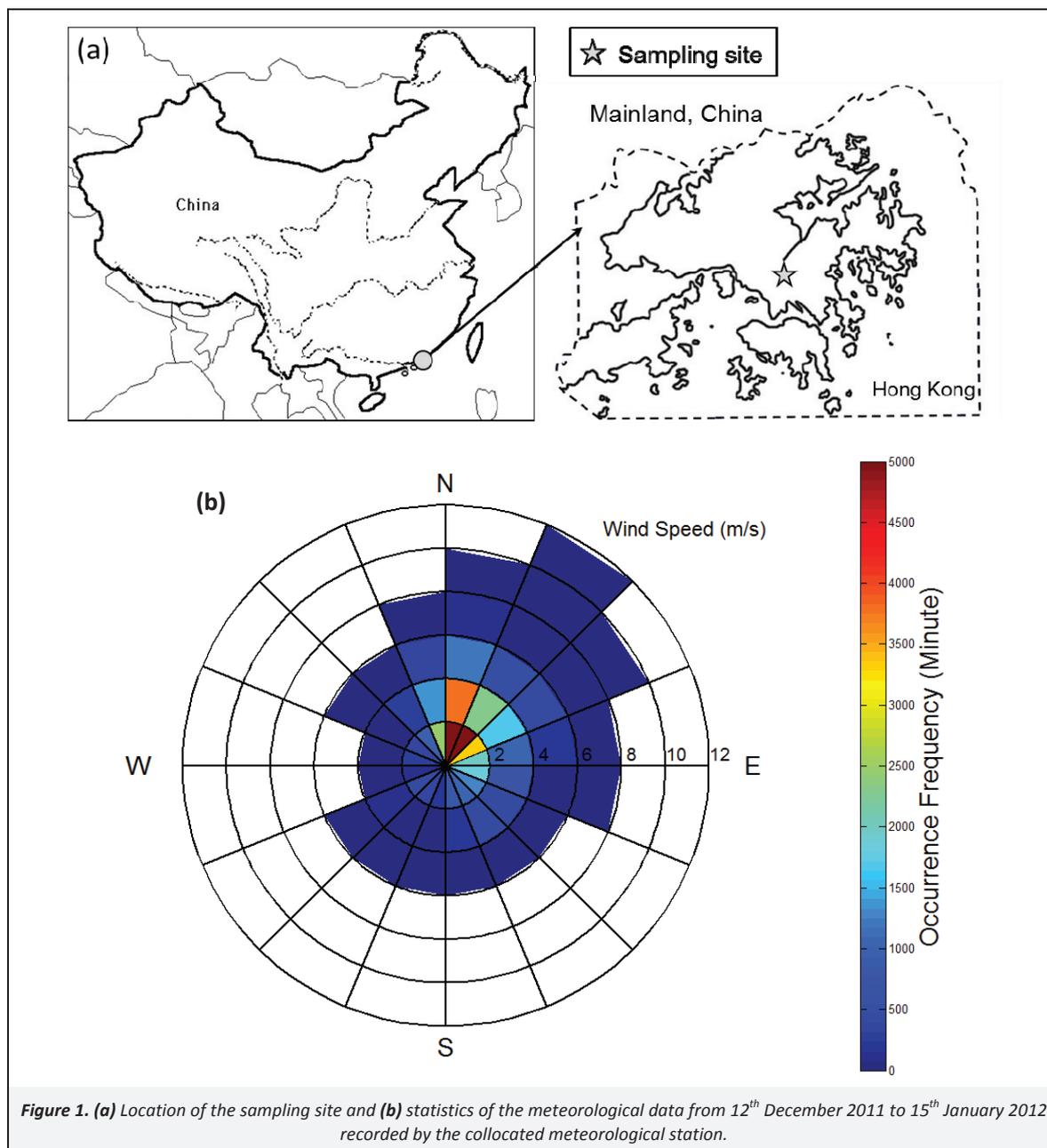
2.3. Chemicals and materials

Multi–element standard solutions for ICP were purchased from Fluka (Mo, USA). Calibration standards were prepared by diluting the stock solution with Milli–Q water or 10% nitric acid with the similar matrix in samples from 0.005 to 5 mg L^{-1}. All stock solutions were stored at 4 °C prior to use. Nitric acid (65%) and hydrochloric acid fuming (37%) were obtained from Merck KGaA (Germany). National Institute of Standards and Technology (NIST) Standard reference material (SRM) 2709a is a San Joaquin Soil (NIST, USA) and it was used in the study to evaluate the performance of acid digestion procedures. The argon used in Inductively Coupled Plasma (ICP) with purity ≥99.995% purchased from Hong Kong Linde Ltd.

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

The acid–digested and water–extracted samples were divided into two halves to analyze the total and water soluble metal concentrations, respectively. The concentrations of five major elements; Na, K, Ca, Mg, and Fe in liquid samples were determined using ICP–OES due to their high concentrations and spectral interference from the plasma gas as well as chloride from matrices in MS detection. The analysis was carried out using an Optima 2100 DV system (Perkin Elmer, USA) in scanning mode, with ion lenses tuned for maximum sensitivity. The plasma flow was set at 15 L min^{-1}, auxiliary flow at 0.3 L min^{-1}, and nebulizer flow at 0.8 L min^{-1}. The RF power was set at 1 300 Watt and flow rate of pump at 1.00 mL min^{-1}. Analytical drifts were corrected by spiking with five analytes using 1.0 mg L^{-1} standard solution.

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

Inductively Coupled Plasma Mass Spectrometry was used to determine the trace metal concentrations of Al, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, V, and Zn with a 7500cx system (Agilent, USA). Parameters were set at RF power (W) 1 600; carrier flow at 0.93 L min^{-1}; makeup gas flow at 0.24 L min^{-1}; sample pump rate at 1.0 rps and nebulizer pump rate at 0.2 rps. Analytical drifts of the instrument were monitored using a spiked 100 μg L^{-1} standard solution at regular intervals for Al and 10 μg L^{-1} for other analytes during sample determination.

Figure 1. (a) *Location of the sampling site and* **(b)** *statistics of the meteorological data from 12th December 2011 to 15th January 2012 recorded by the collocated meteorological station.*

2.6. Method development

The external eight–point calibration curves were first established using ICP standards ranging from 0.005 mg L^{-1} to 0.5 mg L^{-1} for trace metals and 0.05 mg L^{-1} to 5 mg L^{-1} for other metals to determine the linearity of detection. The limit of detection (LOD) was defined as three times of the standard deviation among ten replicates of a known low–level spike–added sample. The limit of quantification (LOQ) was defined as three times of LOD. During sample preparation, analytes may be lost in the liquid extraction processes. Thus, recovery was used to determine the acidic extraction efficiency of the method and to evaluate the interference on the analytes. The recoveries (%) of analytes were determined using standard reference materials (SRM) to detect digestion performance and to represent actual aerosols or significant aerosol components. In addition the PM samples collected from the winter campaign, six blank filters were selected to determine the background of concentration of filters for these two size fractions.

2.7. Upper continental crust enrichment factor

Upper continental crustal enrichment factors (CEFs) of the metals are frequently used to evaluate the contribution of anthropogenic sources to the PM bound metals. In this study, CEFs were calculated for all elements by dividing their relative abundance in a PM sample by their average abundance in the upper continental crust (UCC) (Taylor and McLennan, 2009). Since normalization to a reference element is applied in the calculation of CEFs (Birmili et al., 2006), aluminum was chosen as the reference element for this study because of its stability in chemical analysis.

$$\text{CEFs} = \left(\frac{\text{metals}}{\text{Al}}\right)_{\text{PM}} \bigg/ \left(\frac{\text{metals}}{\text{Al}}\right)_{\text{crustal}} \tag{1}$$

where, (metals/Al)$_{\text{PM}}$ is the ratio of metals and Al in PM samples while (metals/Al)$_{\text{crustal}}$ is the reference ratio from upper continental crust (Taylor and McLennan, 2009). An example of calculation of CEFs values is presented in the Supporting Material (SM). Typically,

CEFs values greater than 10 indicate that the elements have a non–crustal source and are enriched elements while CEFs values that are less than 10 indicate a significant crustal source (Chester et al., 2000; Cheung et al., 2011).

3. Results and Discussion

3.1. Method validation and performance: linearity, recovery, LOD, and LOQ

The correlation coefficients (R^2) of the external calibration for all analytes were higher than 0.997, offering a good linearity ($R^2>0.995$) for external standard analysis using ICP–MS and ICP–OES. The efficiency of acid–digestion recovery was evaluated by including SRM in the sample preparation following the same extraction and analysis protocol. Overall, very good recovery efficiency has been achieved for Cd, Co, Pb, Cu, Ni, Zn, V, Cr, Mg, Ca and Fe with an average ratio of 99.4% in the range of 83% and 112%. Figure S1 (see the SM) shows the correlation between the SRM metals concentration from NIST and the acid–digested metals concentration with a slope of 0.97 and regression coefficient of 0.9970. The recoveries for majority of the elements with efficiency higher than 80% are obtained. These values are higher than those reported by other researchers (Birmili et al., 2006; Canepari et al., 2008; Celo et al., 2011). The recovery of Cr was 86% in our developed method, which was much higher than that of 46% reported by Celo et al. (2011). For Al, recovery was 50%, which was very robust against any matrix effect. Al is associated with siliceous materials of airborne PM and literature results by acid digestion has always shown an unsatisfactory result (Canepari et al., 2008; Celo et al., 2011). After repeating the test several times, the recoveries of aluminum were very consistent at 50–55% with good reproducibility. Based on the test matrix results, the limits of quantification (LOQ) were 30 µg L^{-1} for Al and Fe, 0.3 µg L^{-1} for Cd, 100 µg L^{-1} for Ca, 10 µg L^{-1} for Mg, and 3 µg L^{-1} for others.

3.2. PM$_{2.5}$ and coarse PM concentrations

Figure 2 shows the weekly PM$_{2.5}$ and coarse PM mass concentrations during the winter sampling campaign, with an average concentration of 45.5±9.9 and 9.6±3.4 µg m^{-3}, respectively. ANOVA tests results showed that average PM$_{2.5}$ mass concentration is significantly higher than that of coarse PM ($p<0.01$). PM$_{2.5}$ is the major component of PM$_{10}$ mass and its average concentration was about 5.5 times higher than those of coarse PM across the sampling period. Hong Kong is located at the coast of the South China region and influenced by sub–tropical oceanic climate, with low monthly rainfall during winter from December to March. The dry period together with regional transport of pollution from the mainland China often contributed to high PM concentration in winter in Hong Kong (Guo et al., 2003). The weekly PM$_{2.5}$ concentrations are consistently higher than the World Health Organization (WHO) air quality guidelines of 25 µg m^{-3} for 24–hour average.

To locate the source origin of the air during the sampling period, a wind rose map was plotted as shown in Figure 1b using meteorological data collected from a co–located weather station (Vantage Pro2 weather station with standard radiation Shield, Davis Instrument) during the five week sampling period. Prevailing north to northeasterly winds were observed indicating the impact of regional transport of air parcel from mainland China to Hong Kong, which is a typical wintertime meteorological feature in Hong Kong as reported in the literature (Guo et al., 2003; Ho et al., 2003; Louie et al., 2005). In addition, there was a considerable occurrence of low wind speed conditions, below 4 m s^{-1}, which suggested partial contribution of local source emissions to the particulate pollutants during the winter time.

3.3. Concentration of metals in size–segregation PM

Table 1 shows the weekly metals concentrations in PM$_{2.5}$ and coarse PM, and their mass fraction ratios in each size mode during the sampling period. The abundance of the metals with a decreasing trend in PM$_{2.5}$ was: Fe>Zn>Ca>Al>Pb>Mg>Cu>Mn>V>Ni =Cr>Cd>Mo>Co; whereas the trend in coarse particles was: Ca>Fe> Al>Mg>Zn>Pb>Mn>Cu>Cr>V>Cd>Ni>Mo=Co. No Co was detected in either PM$_{2.5}$ or coarse PM, and Mo was not detected in coarse PM fraction but showed trace levels close to LOD.
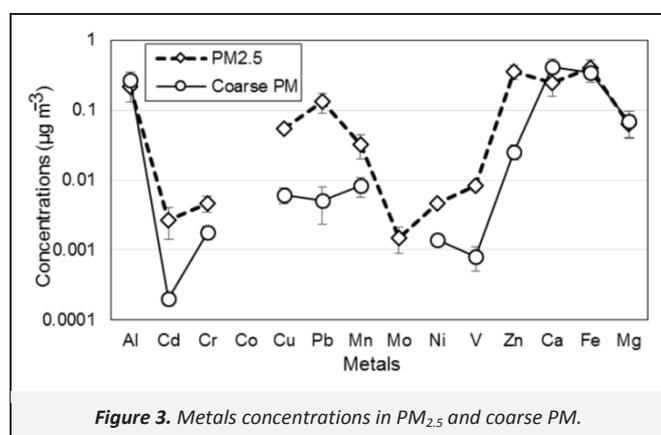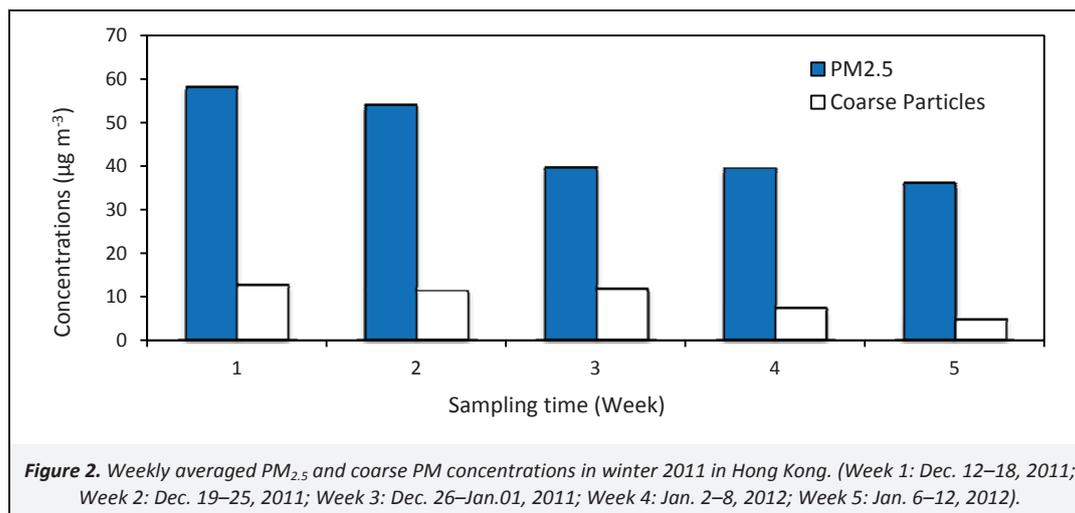
Figure 3 shows the distribution of the metals in PM$_{2.5}$ and coarse PM in logarithmic scale for contrasted visualization of the difference. Overall, the distribution profiles have similar patterns between the two size fractions as shown in Figure 3, and Al, Ca, Fe and Mg showed similar concentrations. These metals are major components of crustal materials (Pakbin et al., 2011) and their presence in coarse PM is associated with the road suspension or abrasion processes (Lough et al., 2005). Other metals, i.e., Cd, Cr, Cu, Pb, Mn, Ni, V, Zn, displayed much higher concentration levels in PM$_{2.5}$ than in coarse PM, among which, Cd, Pb, V and Zn have a PM$_{2.5}$/coarse PM ratio above 10 (Table 1). The contrast of their distribution in PM$_{2.5}$ indicate their combustion origins from vehicle exhaust emissions that form Aitken and Rees accumulation mode particles (Ning and Sioutas, 2010).

Table 1. *Concentrations of metals (µg m^{-3}) in PM$_{2.5}$ and coarse PM during five weeks sampling*

Metals	2011/12/12		2011/12/19		2011/12/26		2012/01/02		2012/01/09		Average		Std. Dev.		Ratio [a]
	PM$_{2.5}$	Coarse	PM$_{2.5}$	Coarse	PM$_{2.5}$	Coarse	PM$_{2.5}$	Coarse	PM$_{2.5}$	Coarse	PM$_{2.5}$	Coarse	PM$_{2.5}$	Coarse	
Al	0.3079	0.3739	0.3079	0.3337	0.1704	0.2166	0.1693	0.2399	0.1217	0.194	0.2154	0.2716	0.0867	0.0781	0.8
Cd	0.0044	0.0002	0.0036	0.0001	0.0019	0.0001	0.0019	0.0002	0.0016	0.0001	0.0027	0.0002	0.0013	0.00004	15.9
Cr	0.0053	0.0021	0.0063	0.0021	0.0032	0.0014	0.0042	0.0014	0.0042	0.0021	0.0047	0.0018	0.0012	0.0004	2.5
Co	N.A. [b]	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Cu	0.0603	0.0063	0.0434	0.0049	0.0561	0.0042	0.054	0.0063	0.054	0.0085	0.0535	0.0061	0.0062	0.0016	8.8
Pb	0.1894	0.0099	0.1598	0.0049	0.1122	0.0035	0.1005	0.0035	0.0942	0.0035	0.1312	0.0051	0.0415	0.0028	25.8
Mn	0.0466	0.0113	0.0444	0.0106	0.0233	0.0071	0.0254	0.0078	0.0212	0.0049	0.0322	0.0083	0.0123	0.0026	3.9
Mo	0.0021	N.A.	0.0021	N.A.	0.0011	N.A.	0.0011	N.A.	0.0011	N.A.	0.0015	N.A.	0.0006	N.A.	N.A.
Ni	0.0042	0.0014	0.0053	0.0014	0.0042	0.0014	0.0042	0.0014	0.0053	0.0014	0.0047	0.0014	0.0006	N.A.	3.3
V	0.0074	0.0011	0.0095	0.0011	0.0074	0.0007	0.0074	0.0007	0.0095	0.0004	0.0083	0.0008	0.0012	0.0003	10.6
Zn	0.4561	0.0339	0.4	0.0268	0.3238	0.0265	0.3069	0.0226	0.2646	0.0169	0.3503	0.0253	0.0768	0.0062	13.8
Ca	0.3028	0.5048	0.3589	0.5002	0.2098	0.4621	0.2012	0.3414	0.1473	0.2243	0.244	0.4066	0.0852	0.1214	0.6
Fe	0.5267	0.4734	0.5115	0.3926	0.2886	0.2727	0.3811	0.3347	0.2948	0.2321	0.4005	0.3411	0.1144	0.0959	1.2
Mg	0.0768	0.0744	0.0814	0.0744	0.0761	0.1058	0.0489	0.0578	0.0288	0.0293	0.0624	0.0684	0.0227	0.0279	0.9

[a] *Ratio of PM is equal to the ratio of average five weekly concentrations of PM$_{2.5}$/coarse PM.*

[b] *N.A.: not available.*

Figure 2. Weekly averaged PM$_{2.5}$ and coarse PM concentrations in winter 2011 in Hong Kong. (Week 1: Dec. 12–18, 2011; Week 2: Dec. 19–25, 2011; Week 3: Dec. 26–Jan.01, 2011; Week 4: Jan. 2–8, 2012; Week 5: Jan. 6–12, 2012).

Figure 3. Metals concentrations in PM$_{2.5}$ and coarse PM.

In addition to the comparison with concentration profiles, the metal ratios is also one important parameter for sources identification of metals, particularly of heavy metals in the atmosphere (Birmili et al., 2006). In the literature, V and Ni ratios have been used as an indicator of heavy oil combustion related sources from ship emissions or power production (Clayton and Koncz, 1994) because V and Ni are usually the most abundant metals in crude oil in the form of metalloporphyrins and non–porphyrin species (Filby, 1994). The concentrations of V and Ni in PM$_{2.5}$ and coarse PM, with the ratio of V/Ni, are shown in Table 2. PM$_{2.5}$ fractions of V and Ni dominate the mass distribution in PM$_{10}$ and it is noted that the ratio of V/Ni in PM$_{2.5}$ was nearly constant across all the five weeks, between 1.76 and 1.79, while it changed from 0.29 to 0.79 in coarse PM. Mueller et al. (2011) reviewed the particulate air pollution due to marine emissions and indicated a consistent ratio of V/Ni from ocean going vessels. Pandolfi et al. (2011) reported a ratio of V/Ni around 3 in both coarse PM and PM$_{2.5}$ in the Bay area of Algeciras in Southern Spain. Another study by Agrawal et al. (2009) also found that ambient V and Ni concentrations in PM$_{2.5}$ in Southern California decreased with increasing distance from the ports of Los Angeles and Long Beach. In this study, a consistent ratio of V/Ni around 1.8 was observed in PM$_{2.5}$ during the winter campaign suggesting a stable source of these metals during winter time while coarse PM V/Ni ratio was significantly lower. Although the reported ratio in this study is lower than those in port cities in literature, it is possible that the V and Ni contents in heavy oil vary greatly from batch to batch and from different origins of the crude oil (Zaki et al., 1989; Mueller et al., 2011), and a direct comparison of local marine emission profile is expected to warrant a better estimation of the marine emission contribution to local air quality. Since Hong Kong is an international port city with intensive marine transport near the coast, further studies on the identification of such source signature from the local marine emissions are needed.

3.4. Crustal enrichment factors

Figure 4 shows the upper continental crustal enrichment factors (CEFs) for the metals in both PM$_{2.5}$ (Figure 4a) and coarse PM (Figure 4b). The calculation of enrichment factor was based on Al as reference after correction for 50% extraction efficiency evidenced by very stable reproducibility. Since CEFs are obtained from elements when their abundance in a PM sample is divided by their average abundance in the upper continental crust, the CEFs can be used as a parameter for evaluation of the accumulation of metals contributed by anthropogenic origins in aerosol particles. For PM$_{2.5}$, majority of the metals have CEFs higher than 10: CEFs of Cd, Pb were higher than 1 000 and CEFs of Zn, Mo, and Cu were higher than 100; whereas the CEFs of V, Cr, Ni and Mn were only slightly over 10. For the coarse particles, majority of the metals have CEFs below 10 with only Pb, Zn and Cu larger than 10, and Cd larger than 100 (Figure 4b). A common practice when using CEFs is to expect a CEF of 1 as the background value and CEFs>10 as the indicative of PM sources different from crustal material, e.g., from anthropogenic sources (Birmili et al., 2006). The CEF values between 1 and 10 indicate a mixed contribution of metals from crustal materials or anthropogenic sources. For example, Fe is found to originate from railway steel abrasion emissions (Gehrig et al., 2007), while it also appears in background aerosols since it is a common component of crustal material (Hueglin et al., 2005).

The sampling site in the present study is a typical urban site surrounded by roadway and railway traffic and close to the major industrial district with port activities (Ning et al., 2013). Cd, Pb, Zn and Cu have been found to be consistently high in CEFs values in both PM$_{2.5}$ and coarse PM showing strong evidence of their anthropogenic origins. These metals are closely related to both combustion emission source and brake attrition or tire wearing related sources (Sternbeck et al., 2002), producing aerosol emission in PM$_{2.5}$ and coarse mode, respectively. For example, Cd and Cu are attributed to lube–oil emission and vehicle brake attrition, while Pb may come from the gasoline and lube–oil, brake pads and lead wheel weights (Lough et al., 2005). Out of the high CEFs metals, Cd and Pb are classified by the U.S. EPA as air toxics, emphasizing the importance of controlling vehicle emissions in urban area with intensive roadway traffic. Comparing PM$_{2.5}$ and coarse PM, the CEFs metals in PM$_{2.5}$ for most of the reported elements were about 10 times higher than those in coarse PM as shown in Figure 4, clearly indicating metals with anthropogenic origins largely reside in PM$_{2.5}$ fraction and it may play a significant role in metal–associated health effects.
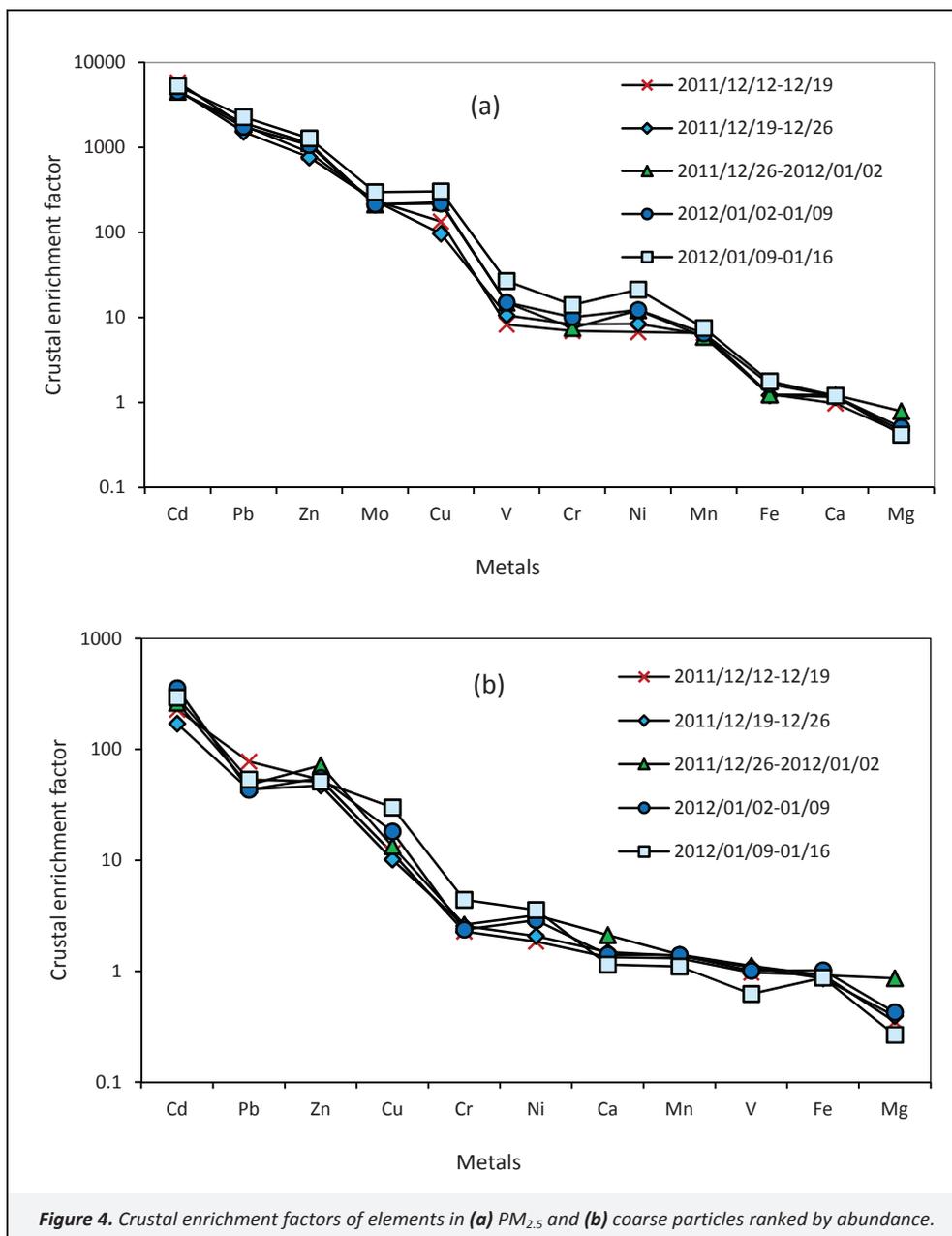
Figure 4. *Crustal enrichment factors of elements in (a) PM$_{2.5}$ and (b) coarse particles ranked by abundance.*

Table 2. *Ratio of metals mass concentrations between vanadium and nickel*

	Ni (µg m^{-3})		V (µg m^{-3})		Ratio	
	PM$_{2.5}$	Coarse PM	PM$_{2.5}$	Coarse PM	PM$_{2.5}$	Coarse PM
2011/12/12	0.0042	0.0014	0.0074	0.0011	1.76	0.76
2011/12/19	0.0053	0.0014	0.0095	0.0011	1.8	0.76
2011/12/26	0.0042	0.0014	0.0074	0.0007	1.76	0.5
2012/01/02	0.0042	0.0014	0.0074	0.0007	1.76	0.5
2012/01/09	0.0053	0.0014	0.0095	0.0004	1.8	0.25
Average	0.0046	0.0014	0.0083	0.0008	1.78	0.55

3.5. Water solubility of metals in PM$_{2.5}$ and coarse PM

While evaluating impact of metals on health effect, only the soluble fraction of metals is likely to play a role due to its bioavailability (Birmili et al., 2006). The definition of solubility depends sensitively on the speciation method, and a few investigations in literature have used approaches by comparing water and acid extracted metals (Gutierrez–Castillo et al., 2005;

Birmili et al., 2006). In this work, the water solubility of the metals was determined by the ratio of the water–extracted metals concentration and those from strong acid digestion. Figure 5 shows the average solubility of reported metals in PM$_{2.5}$ and coarse PM in percentages and error bar represents the standard deviation of the ratios for each metal. The water soluble mass fraction of metals in PM$_{2.5}$ and coarse PM is statistically different, especially for Mg, Mn, Pb, Cu, Al and Fe ($p < 0.01$). Detailed water soluble metals concen-

trations are listed in Table S1 for $PM_{2.5}$ and Table S2 for coarse PM (see the SM). The solubility distribution for each metal is plotted from the highest to lowest level based on the metals in $PM_{2.5}$, showing the comparison of solubility for $PM_{2.5}$ with that for coarse PM for each metal. The water solubility ratios ranged from 1.9% to 92.0% for the measured metals with very large variation indicating the importance of bioavailability to understand the impact of metals on public health (Figure 5, Tables S1 and S2). The water solubility of metals in $PM_{2.5}$ is mostly higher than those in coarse PM, except for Ca. The most soluble elements in $PM_{2.5}$ were Zn>Ca>Cd>V>Mg>Cu with their solubility higher than 60%; the least soluble elements were Cr, Al, Co. Co could not be detected in water extracted and acid digested matrix. The results in coarse particle indicated that Zn, Ca and Cd are the most soluble species with solubilities higher than 50%. Although Fe is the most abundant transition metal in $PM_{2.5}$, the solubility is significantly lower than other trace level transition metals, such as Zn ($p<0.01$) and Cd ($p<0.01$), which highlights the importance of characterizing the metals bioavailability while evaluating the impact of PM metals on health effects.

The solubility of metals in $PM_{2.5}$ could be divided into three groups, high (Zn, Ca, Cd, V, Mg, Cu>60%); medium (Pb, Mn, Ni, Mo, Fe between 20–60%); and low (Cr, Al<20%). In coarse PM, the high one included Zn, Ca, Cd (>60%); medium Mg, Mn, Pb, Cu (20–60%); and low Al and Fe (<10%). A significant size–dependent trend was found for certain elements, such as Al, Fe, Mo, V, Cr, and Ni. For example, more Fe was found in soluble forms in fine particles while insoluble fractions dominated in coarse PM indicating the different chemical states of the metals in different size fractions either due to different source emissions or atmospheric processes altering its chemical states. It is worth noting that metals with high insoluble fraction are largely components of mineral ash, which indicates their existence as metal oxides such as silicon, iron and aluminum–containing compounds. For example, a significant amount of Fe in crustal materials is present in its insoluble form as oxides (Fe_2O_3, Fe_3O_4) (Ghio et al., 1999; Canepari et al., 2008). Compared to the results with previous studies, the solubility of Zn, Cd, Pb, Mn and Cu were in good agreement within a more soluble range (Espinosa et al., 2002; Birmili et al., 2006). However, some other metals have much higher solubility than those reported in the literature (Espinosa et al., 2004; Birmili et al., 2006). For example, higher water solubility ratios are obtained in this study, i.e. 77.2–82.7% for Ca, 73.5–81.0% for Cd and 61.1–78.6% for V in the present work compared to 39.7% for Ca, 30.9% for Cd and 50.4% for V in

the previous work (Espinosa et al., 2002). This is possibly because the different methods were used for water extraction and acid digestion among studies (i.e. time period of water extraction, concentration and matrix of acids) that yield variation of recovery efficiency for metals with different chemical states such as carbonates, oxides, and metals bound to organic matter (Espinosa et al., 2002).

4. Conclusion

Size–segregated weekly atmospheric $PM_{2.5}$ and PM_{10} samples were collected in a typical urban site in Hong Kong during winter between late 2011 and early 2012. Dominant wind from North and North–East directions was observed during the sampling period showing the contribution of regional transport to local air pollution in Hong Kong in winter time. Fe, Zn, Ca, Al and Pb are the most abundant metals in $PM_{2.5}$ while Ca, Fe, Al and Mg in coarse PM. The distribution of metals in $PM_{2.5}$ and coarse PM are similar in pattern but different in magnitudes with Cd, Cr, Cu, Pb, Mn, Ni, V, Zn claiming much higher portion in $PM_{2.5}$. Consistent V/Ni ratio of 1.8 in $PM_{2.5}$ was found throughout the sampling period, suggesting their stable sources either from regional transport or from local marine emissions. Upper continental crustal enrichment factor analysis of the metals displayed much higher values in $PM_{2.5}$ than coarse PM which clearly indicate dominant anthropogenic source contribution to $PM_{2.5}$ metals with mostly from traffic related emissions. Due to the limited source profiles of PM metals available in literature, a comprehensive source apportionment investigation is not feasible in this study. The identification of metal sources based on the crustal enrichment factor and relative ratios is more of qualitative nature. The water solubility ratios of the reported metals displayed very large variation, especially for transition metals, with Zn, Cd, V and Cu being the most soluble and Cr, Fe and Ni being the least, highlighting the importance of bioavailability in understanding the impact of transition metals on particle toxicity. Coarse PM and $PM_{2.5}$ also showed different solubility profiles for the measured metals as a result of their different chemical forms either due to different source emissions or atmospheric processes altering its chemical states. The findings from the present study demonstrated a large variation of water solubility of metals in urban aerosols in different size fractions and also highlighted solubility as an important metric for considering the relation between metals and adverse health effects in epidemiological and toxicological studies.

Figure 5. *Water solubility ratios of metals in PM$_{2.5}$ and coarse PM in Hong Kong.*
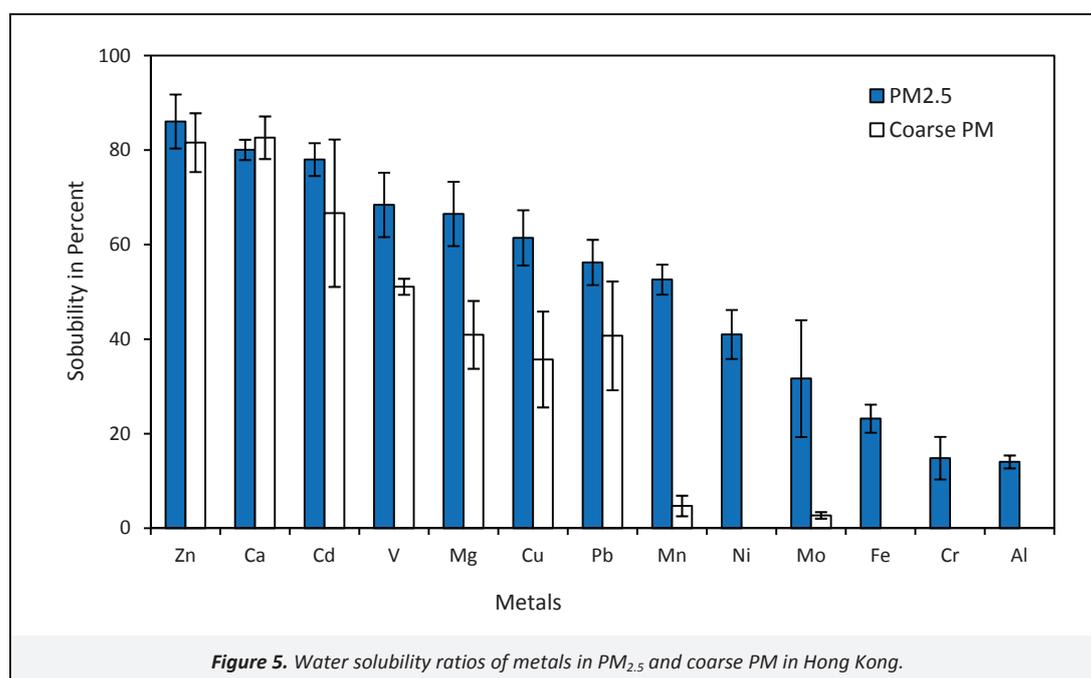
Acknowledgment

Supporting Material Available

The correlation of SRM metals concentration and acid–digested metals concentration (Figure S1), Water soluble mass fraction of metals of PM$_{2.5}$ in Kowloon Tong for five week determination (Table S1), Water soluble mass fraction of metals of coarse particles in Kowloon Tong for five week determination (Table S2), Example calculation of CEFs values. This information is available free of charge via the internet at http://www. atmospolres.com.

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