

# Concentration Distribution and Bioaccessibility of Trace Elements in Nano and Fine Urban Airborne Particulate Matter: Influence of Particle Size

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**Abstract** Trace elements, especially those associated with fine particles in airborne particulate matter (PM), may play an important role in PM adverse health effect. The aim of this paper is to characterize elements in a wide particle size range from nano (57–100 nm) to fine (100–1,000 nm) and to coarse (1,000–10,000 nm) fractions of two urban PM samples collected in Ottawa. Size-selective particle sampling was performed using a micro-orifice uniform deposit impactor, and element concentrations were determined in each different size fraction by inductively coupled plasma-mass spectrometry. A general trend of increasing element concentration with decreasing aerodynamic diameter was observed for elements V, Mn, Ni, Cu, Zn, Se, and Cd, indicating they were predominately concentrated in the nanoparticle size range. Other elements including Fe, Sr,

Mo, Sn, Sb, Ba, and Pb were predominately concentrated in the fine-size range. Increased concentration of elements in the nano and fine particle size range is significant due to their ability to penetrate into the deepest alveolar area of the lungs. This was confirmed by the calculation of median concentration diameters, which were less than 800 nm for most of the investigated elements. Particle size distribution and element correlation analysis suggest that the elements concentrated in the nano- and fine-size fractions originated mainly from vehicular combustion and emission. Long-range airborne transport and soil or road dust resuspension may also contribute. Particle size had an important effect on element bioaccessibility for the studied urban PM samples showing a general trend of increasing element bioaccessibility with decreasing particle size. These results emphasize the importance of acquiring information on nano and/or fine PM-bound elements and their bioaccessibilities for accurate element and PM exposure assessment.

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## 1 Introduction

Trace element analysis of airborne particulate matter (PM) is an important factor for assessing air quality

and health risk (Rasmussen 2004). Many elements, such as V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb are widely distributed in PM and, therefore, are suspected to be an important source of PM toxicity (Davidson and Osborn 1986; Nriagu and Pacyna 1988). Concentrations of transition metals (e.g., V, Cr, Mn, Fe, Ni, Cu, Zn) have received particular attention due to their direct links to lung inflammation and damage (Claiborn et al. 2002; Osonio-Vargas et al. 2003). Elemental PM components have been reported to produce and release inflammatory mediators by respiratory tract epithelial cells and/or to catalyze oxidative stress resulting in potential tissue injury (Carter et al. 1997; Donaldson et al. 1997; Kadiiska et al. 1997; Ghio et al. 1999; Lingard et al. 2005).

An increasing number of studies are being conducted on the particle size distribution of PM-associated metals as this is considered one of the most important aspects for the risk assessment of trace elements and their potential adverse effects. Particle size has been reported to influence or control many critical factors including element toxicity, atmospheric transport distance, and deposition rate (Allen et al. 2001). Information on particle size distribution will be of great benefit to determine the chemical and physical processes affecting aerosols (Wall et al. 1988) and to assess atmospheric lifetime and transboundary air pollution, and it can be used to obtain element speciation information as some trace elements and their compounds are prevalent in the coarse fractions whereas others are mainly bound to fine particles (Müller et al. 2001; Herner et al. 2006). Particle size and chemical compositions of PM are crucial factors for human health since the efficiencies of inhalation, respiratory deposition, and bioavailability are dependent upon these factors (Hinds 1999; Zereini et al. 2005). Recently, more attention has been drawn to fine and nanoparticles because there is evidence that fine-grained particles have more potential adverse effects than coarser ones (Donaldson et al. 1998; Allen et al. 2001; Kittelson et al. 2004; Lin et al. 2005; Niu et al. 2008). Coarse inhalable particles may be deposited mostly in the upper respiratory tract whereas fine particles can travel deeper into the lungs. Generally, the particle size fractions of <800, 800–1,300, 1,300–2,700, 2,700–6,700, and >6,700 nm can reach the alveolar, alveo-bronchial, bronchial, tracheo-bronchial, and extrathoracic regions, respectively (Samara and Voutsas 2005). Particle size and trace element concentration can also assist in determining source relation-

ship and apportionment (Williams et al. 2003). Nanoparticles are attributed mainly to mobile sources (automobiles and diesel trucks), other combustion processes (e.g., incinerators or residential/industrial heating systems), and the nucleation of organic gases (Seinfeld and Pandis 1998; Cabada et al. 2004; Kittelson et al. 2004; Lin et al. 2005). Atmospheric dispersion, dilution, condensation, evaporation, coagulation, and deposition processes all influence particle number concentration and particle size distributions from nano to fine fractions (AQEG 2005; Samara and Voutsas 2005; Zereini et al. 2005). Coarse-grained particles are usually attributed to natural or mechanical processes such as wind-blown soil, marine aerosols, and road dust resuspension.

Toxicological studies have suggested that it is the soluble trace element content instead of the total element content of PM that has more direct links to harmful effects (Costa and Dreher 1997; Ghio et al. 1999; Adamson et al. 2000; Prieditis and Adamson 2002; Heal et al. 2005). Thus, investigations of the soluble or extractable elements in PM have attracted much more attention in this field of study (Niu et al. 2007a). Partial and sequential extractions are commonly used to determine elemental associations with various fractions (Tessier et al. 1979; Espinosa et al. 2002; Heal et al. 2005; Niu et al. 2007a). For example, soluble Zn concentration in airborne PM has been found to be a factor in the mouse lung response (Adamson et al. 2000), and water extractable Fe, V, and Ni have been reported to be the primary determinant of acute inflammatory infection (Costa and Dreher 1997). The production of radicals by soluble elements and their mediated Fenton chemical reaction is the primary pathway to generating oxidants, where particle size plays an important role in element bioaccessibility and, therefore, finally in bioavailability and toxicity (Donaldson et al. 1998; Shi et al. 2003; Lingard et al. 2005).

There are many studies on particle size distribution of trace elements in PM and their related health effects (Allen et al. 2001; Bilos et al. 2001; Singh et al. 2002; Lin et al. 2005; Zereini et al. 2005; Birmili et al. 2006; Niu et al. 2010) but limited studies of their bioaccessibility. The aim of this paper is to investigate the concentration, particle size distribution (coarse-, fine-, and nano-sized particulates), and bioaccessibility of trace elements in urban PM collected at the Environmental Health Centre (EHC) of Health Canada in Ottawa, Canada. The particle size

effect on element bioavailability and, therefore, the potential health risk of exposure through inhalation are addressed. Associations between trace elements and specific sources are also discussed for coarse, fine, and nanoparticle fractions.

The EHC samples have been used in lung, heart, and allergy studies (Vincent et al. 1997, 2001; Kooter et al. 2003; Steerenberg et al. 2003). For example, inhalation toxicology of urban ambient PM has been investigated in detail using bulk EHC-93 sample (Vincent et al. 2001), and lung damage has been observed after instillation with EHC particles (Prieditis and Adamson 2002; Kooter et al. 2003). Pulmonary injury and inflammation have been suggested to be caused by exposure to the transition metals especially soluble metal components such as Cu and Zn in EHC-PM (Prieditis and Adamson 2002). Apart from inflammation-driven systemic effects, ambient airborne EHC-PM can exert direct changes on cardiac function causing cardiovascular impairment (Vincent et al. 2001). The allergenic study of EHC-PM indicated that at the same PM dose, PM from different fractions (coarse and fine) was shown to induce different effects on ovalbumin-induced allergic responses (Steerenberg et al. 2003), indicating the important role of particle size distribution.

## 2 Experimental

### 2.1 Sampling and Mass Measurement

Ambient urban air particle samples, EHC-93 and EHC-2K (collected using identical methodologies at the same sampling location from 1992–1993 (Vincent et al. 2001) and 1999–2000, respectively, for an integration of temporal changes over a 24-month sampling period) were obtained from the filtration system of the EHC in Ottawa, Canada, and were size fractionated using a micro-orifice uniform deposit impactor (MOUDI; Model 110, MSP Co., Minneapolis, MN) at a flow rate of 30 Lmin<sup>-1</sup> into 10 nominal cut sizes: 10,000, 5,600, 3,200, 1,800, 1,000, 560, 320, 180, 97, and 57 nm. To simplify the analysis of the results, fractions were grouped into three size ranges (nm): coarse (1,000–10,000), fine (100–1,000), and nano (57–100).

The Teflon filters used in the MOUDI were pre-conditioned for 24 h inside a custom-designed chamber

(Archimedes M3™; Rasmussen et al. 2008) with automated controls set at a constant air temperature (21±0.2°C) and constant relative humidity (RH, 40%±0.5%). Filters were weighed before and after loading using a Mettler UMX2 microbalance which sits inside the chamber on top of a stable marble bench within a soft-walled clean room at Health Canada. The long-term stability of the controls in the facility exceeds requirements of USEPA (1998) guidelines for mass measurement of airborne PM, which specify that RH and temperature must not vary more than ±5% and ±2°C, respectively, over 24 h. Numerous other environmental factors which may cause unacceptable errors in the gravimetric analysis of airborne PM, including static electricity and air buoyancy, are eliminated or minimized in the Archimedes M3™ chamber (Rasmussen et al. 2008).

### 2.2 Filter Digestion, Extraction, and Multi-Element Determination

For element bioaccessibility determination, a two-step extraction was employed. The soluble metal fraction was extracted under clean laboratory conditions using 0.01 M ammonium acetate (AA) at pH 7 (modified after Thomassen et al. 2001) to simulate the neutral lung environment. The loaded filter sample or blank filter was placed into a 15-mL polypropylene centrifuge tube with 10 mL of AA extraction solution. The tube was then sealed and submerged for 2 h in a shaking water bath at 37°C (1 h shaking followed by 1 h no shaking). Extractants were cooled to room temperature, centrifuged at 3,500 rpm for 20 min, and separated for element determination. The same filter containing the remaining non-soluble sample fraction was then ultrasonically digested using a HF–HNO<sub>3</sub> acid mixture in a hot water bath (60°C) for 5–7 days, with two 30-min ultrasonication intervals (modified after Jalkanen and Häsänen 1996).

A microwave-assisted acid digestion approach was used for single-step total element concentration. The Teflon filters with the MOUDI-deposited dust samples were carefully handled to minimize contamination (Rasmussen et al. 2006, 2007; Niu et al. 2007b, 2010). Procedural blank filters were handled identically to the samples. After conditioning and weighing, the sample or blank filters were then digested, using a Milestone ETHOS Microwave Labstation (Milestone Inc., Shelton, CT, USA) for high-pressure microwave-

assisted digestion. The filters were first placed into clean 100 mL PTFE vessels with a mixture of 8 ml ultra pure  $\text{HNO}_3$  (Seastar Chemical Inc.) and 2 mL  $\text{H}_2\text{O}_2$  (Merck, Suprapur), and were then digested in the microwave by a 50 min programmed digestion (ramp to 180°C in 20 min; ramp to 220°C in 10 min; hold at 220°C for 20 min).

Multi-element analysis was performed using a Perkin Elmer ELAN DRC II inductively coupled plasma-mass spectroscopy (ICP-MS) for the digested samples with the following operational parameters: RF power 1,100 W, plasma gas flow 15  $\text{Lmin}^{-1}$ , nebulizer gas flow 0.88–0.92  $\text{Lmin}^{-1}$ , auxiliary gas flow 1.2  $\text{Lmin}^{-1}$ , sample uptake 1  $\text{mL min}^{-1}$ , and dwell time 100 ms.

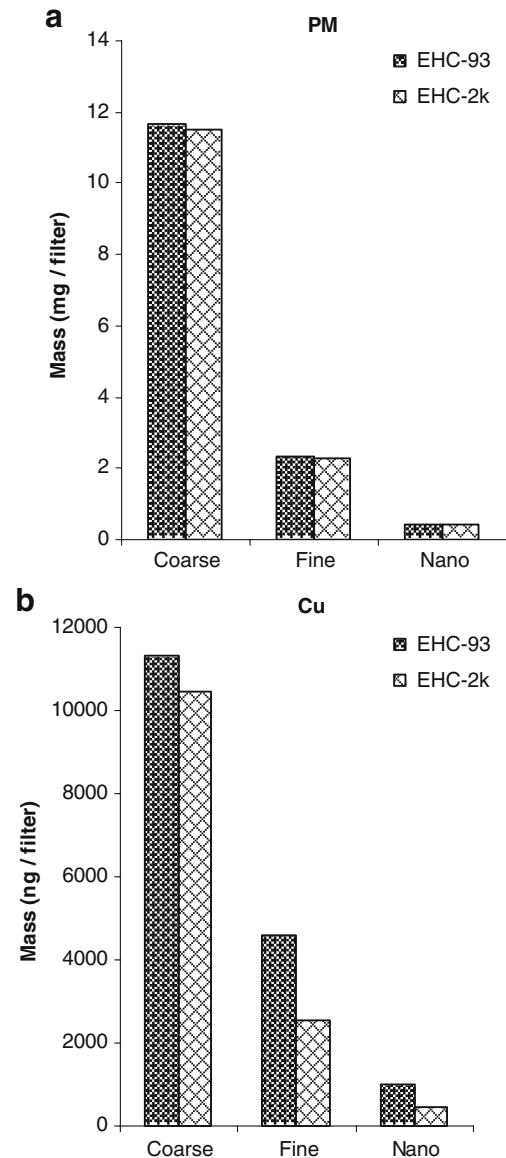
### 2.3 Quality Assurance

The certified reference materials (CRMs) employed for quality control were urban PM (NIST 1648) and coal fly ash (NIST 1633b). These CRMs were used to monitor the digestion recovery efficiency and the accuracy and reproducibility of the ICP-MS measurements. Elemental recoveries from 87% to 102% were achieved. Filter blanks were taken during each step of the procedure, including sampling, conditioning, and weighing as well as ICP-MS measurements. Eight to nine procedural blanks, consisting of the same acid mixture and dilution factors as the samples, were included to calculate the method limit of detection (LOD) and limit of quantitation (LOQ). The guideline given in SW846 for the determination of method detection limits (USEPA 1994) was followed to obtain the LOD and LOQ by multiplying the standard deviation of the measured concentrations of the eight or nine procedural blanks by three and ten, respectively.

## 3 Results and Discussion

### 3.1 PM and Element Mass Distribution

The PM mass distributions of EHC-93 and EHC-2K as a function of particle size are given in Fig. 1a. Both EHC-93 and EHC-2K show the same distribution pattern: the mass is concentrated in the coarse size fraction and decreases with decreasing particle size, showing the lowest mass in the nano-size fraction. Correlation analysis between PM mass distributions of EHC-93 and EHC-2K produces an excellent trend



**Fig. 1** PM (a) and element (b) mass distributions of EHC-93 and EHC-2K samples. Particle size (nm): coarse (1,000–10,000), fine (100–1,000), and nano (57–100)

line, with  $R^2=0.99$  ( $n=10$ ) and a slope of 1.0, which indicates that there is no significant difference between the mass distribution of these two EHC samples. The element mass detected by ICP-MS shows the same distribution patterns (Fig. 1b with Cu as an example) observed for the PM mass, indicating a direct association between PM and the PM-bound elements.

Although in this study and in the literature (Allen et al. 2001; Cabada et al. 2004; Lin et al. 2005; Samara and Voutsas 2005; Zereini et al. 2005; Niu

et al. 2008), the PM and elements only contribute a small part of the total mass for the finer particle size fractions (fine and nano), the finer particles account for nearly all of the aerosol number concentration in the urban atmosphere (Seinfeld and Pandis 1998). Compared to coarse particles, these finer particles can remain airborne for long periods of time (Kettles and Shilts 1994; QUARG 1996; Cabada et al. 2004), can be transported long distances, and can be inhaled deeper than other particles into the lungs (alveolar or alveo-bronchial). Thus, the potential health impacts of human exposures to fine particles are important for risk assessment. Note also, as will be discussed below, the patterns of element concentration distribution in the EHC PM are totally different from the patterns of PM mass distribution. The elements are found to be concentrated in the finer size fractions. Hence, attention to fine and nanoparticles for EHC-like PMs would be helpful in the exposure assessment of elements and their potential health effects to obtain more meaningful and realistic assessment results.

### 3.2 Median Values and Element Concentration Ranges

The median values and concentration ranges of the elements analyzed in EHC-93 and EHC-2K samples obtained for the ten size fractions are presented in Table 1. Among the investigated elements in the EHC-93 samples, Fe is the most abundant with a

median of 16,150  $\mu\text{g g}^{-1}$ , followed by Zn and Pb (10,478 and 8,848  $\mu\text{g g}^{-1}$ , respectively). Manganese, Cu, Sn, and Ba show moderate abundance with medians between 401 and 1,042  $\mu\text{g g}^{-1}$ , approximately 1 to 1.5 orders of magnitude lower than that of Fe. Elements with lower median values, 150 to 250  $\mu\text{g g}^{-1}$ , include V, Ni, and Sr, whereas those with the lowest medians, from 12.6 to 15.5  $\mu\text{g g}^{-1}$ , include Se, Mo, Cd, and Sb. For most of the abundant elements, Fe, Zn, and Pb, concentrations vary over a large range, mostly indicating their concentration distribution into different particle size fractions. For elements of lower abundance, the concentration range varies between elements, some (Ni, Cu, Se, and Sn) present larger variations, whereas others do not. Iron and Ba are crustal elements (Kettles and Shilts 1994): their abundance may imply, in part, soil or road dust-related sources. High concentrations of these elements have also been related to vehicular emissions (Watson et al. 2001). Thus, the interpretation of elemental sources requires information about particle size distribution (see discussion below).

Similar to EHC-93, median values of Fe, Zn, and Pb and Ca, Mn, and Cu are high and moderate, respectively, in EHC-2K (Table 1). However, median values and element concentration ranges show some differences for some of the elements. Iron and Ba show an increase in concentration, Zn decreases, but Mn, Cu, and Pb concentrations are generally stable

**Table 1** Element median concentration and concentration range values for EHC-93 and EHC-2K

Element	LOD	LOQ	EHC-93		EHC-2K	
			Median <sup>a</sup>	Range	Median	Range
V	1.8	6.1	162±21	56–189	98.4±14.0	46.0–120.9
Mn	0.8	2.6	505±75	287–597	506±48	279–610
Fe	14.1	47.1	16,150±2,102	8,776–18,808	22,624±3,840	13,471–28,670
Ni	29.0	96.5	251±195	46–853	269±200	58–37,041
Cu	5.9	19.7	1,042±109	445–1,419	977±32	538–1,210
Zn	7.7	25.7	10,478±971	4,946–12,255	3,622±94	1,979–4,753
Se	7.5	24.9	12.6±14.4	nd–289	8.0±3.4	nd–31.9
Sr	5.9	19.6	244±30	172–269	222±11	135–259
Mo	1.0	3.4	12.8±3.8	nd–17.0	25.6±2.2	nd–47.7
Cd	8.4	28.2	14.8±2.8	6.5–34.4	10.1±6.9	nd–89.1
Sn	2.0	6.7	898±146	294–1,088	269±195	111–388
Sb	1.4	4.6	15.5±0.8	nd–19.6	40.9±10.7	nd–71.2
Ba	2.4	8.1	401±42	190–584	702±22	273–1,068
Pb	12.2	40.6	8,848±753	4,224–12,026	7,837±502	3,878–11,909

LOD limit of detection (nanogram per filter);  
LOQ limit of quantitation (nanogram per filter);  
nd not detected

<sup>a</sup>Median plus standard deviation ( $\mu\text{g g}^{-1}$ ). Median and range are obtained from ten particle size (nm) fractions (10,000, 5,600, 3,200, 1,800, 1,000, 560, 320, 180, 97, and 57)

from the EHC-93 to the EHC-2K samples. Changes in median and concentration ranges are large for the elements Fe, Zn, Mo, Sn, Sb, and Ba for EHC-2K samples. This may indicate some variations in emission sources in EHC-2K as compared with that in EHC-93. In addition, the aging of aerosols and the long distance transport of particulate elements (Natusch et al. 1974; Rasmussen 1994, 1998) will also have an effect on the differences in element concentration and/or on the particle size distribution or both. Depending on the individual element, these changes may or may not affect their distributions in different particle size fractions. Also, note that the absence of a change in median value or a change in concentration range does not suggest that the concentration of elements among the different particle sizes will remain the same. Elements with the same median value or the same concentration range may show different particle size distributions.

### 3.3 Size Distribution

#### 3.3.1 EHC-93 Samples

The distribution of elements in the three size fractions of EHC-93 is shown by the light bars in Fig. 2. The distribution for transition metals V, Mn, Ni, Cu, Zn, Cd, and for the metalloid Se, in different particle size fractions exhibited the reverse trend found for the mass distribution (Fig. 1b). That is, their concentrations increase as the particle size decreases from coarse to nano (Fig. 2). This observation is helpful for risk assessment of trace elements in PM due to the potential role of inhaled transition metals in oxidative stress, DNA damage, or lung cancer (Natusch et al. 1974; Hlavay et al. 1992; Costa and Dreher 1997; Donaldson et al. 1997; Kadiiska et al. 1997; Ghio et al. 1999; Adamson et al. 2000; Shi et al. 2003; Lingard et al. 2005). This finding shows the importance of measuring elements in the fine and nano range in the exposure assessment of PM particles like EHC-93. The distributions for other elements (Fe, Sr, Sn, Sb, Ba, and Pb) show that their concentrations also increase as particle size decreases from the coarse- to fine-grain size but decrease slightly in the nano-size fraction (Fig. 2).

In general, all of the elements tend to be concentrated in either nano- or fine-size fractions that can ultimately enter the alveolar areas of the lung. The overall predominance of all investigated elements in the finer-grained particle size fractions in the present study also

suggests common anthropogenic sources. Combustion processes are normally the major source of finer particles (Seinfeld and Pandis 1998; Cabada et al. 2004; Kittelson et al. 2004; Lin et al. 2005). In some cases, natural sources, such as gas-particle conversion reactions, wind-blown soil, and road dust resuspension, also contribute significantly to the finer-grained particles (Kleeman and Cass 1998; Rasmussen 1998). In Ottawa, in the vicinity of the EHC sample location, vehicular-related combustion and emissions are most probably the main sources of the finer PM-bound element concentrations, as there are no nearby industrial or static combustion sources. Most of the elements in this study such as V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Sb, and Pb are suspected to be related to vehicular emissions including tire wear or break lining materials. In fact, the similar elements (Cr, Mn, Ni, Cu, Zn, Cd, Ba, and Pb) have been reported to be associated with gasoline/diesel fuels and engine exhausts in Taiwan (Chen 2002; Lin et al. 2005). Copper, Fe, Mn, Zn, Ba, and Pb were also observed to be the main pollutants emitted by vehicles in Florence, Italy (Monaci et al. 2000); whereas Cu, Zn, Mo, and Sb were attributed to diesel soot, abraded tire material, and rubbed-off brake linings, respectively, in Cologne, Germany (Weckwerth 2001).

Table 2 presents the Pearson correlation coefficient ( $r$ ) of the element concentration for all particle size fractions (coarse, fine, and nano). The values  $r \geq 0.75$  are highlighted to show the stronger correlations. The best associations ( $0.75 \leq r \leq 0.96$ ) exist between V, Mn, Cu, Zn, Se, and Ba supporting the interpretation of a common traffic-related source. This strong correlation still remains in the finer particle size fractions (fine and nano) for V with Cu, Zn, and Se but no longer with Mn and Ba as shown in Table 3. The loss of a strong association of V with Mn and Ba in the finer size fractions may indicate an additional source such as resuspension of roadside or soil dust. Note that Sr, Mo, and Pb also show a strong correlation with Fe when all particle fractions are considered (Table 2). The strongly correlated elements with Fe increase to seven (Mn, Sr, Mo, Sn, Sb, Ba, and Pb) when only the finer fractions are considered (Table 3). The lack of association of Fe with other elements when all particle sizes are considered implies that Fe in the coarse particles may have multiple sources. These sources may be ascribed to vehicular sources (mechanical wear or grinding in engines) and resuspension of soil or dust. The lack of association between Ni and any other



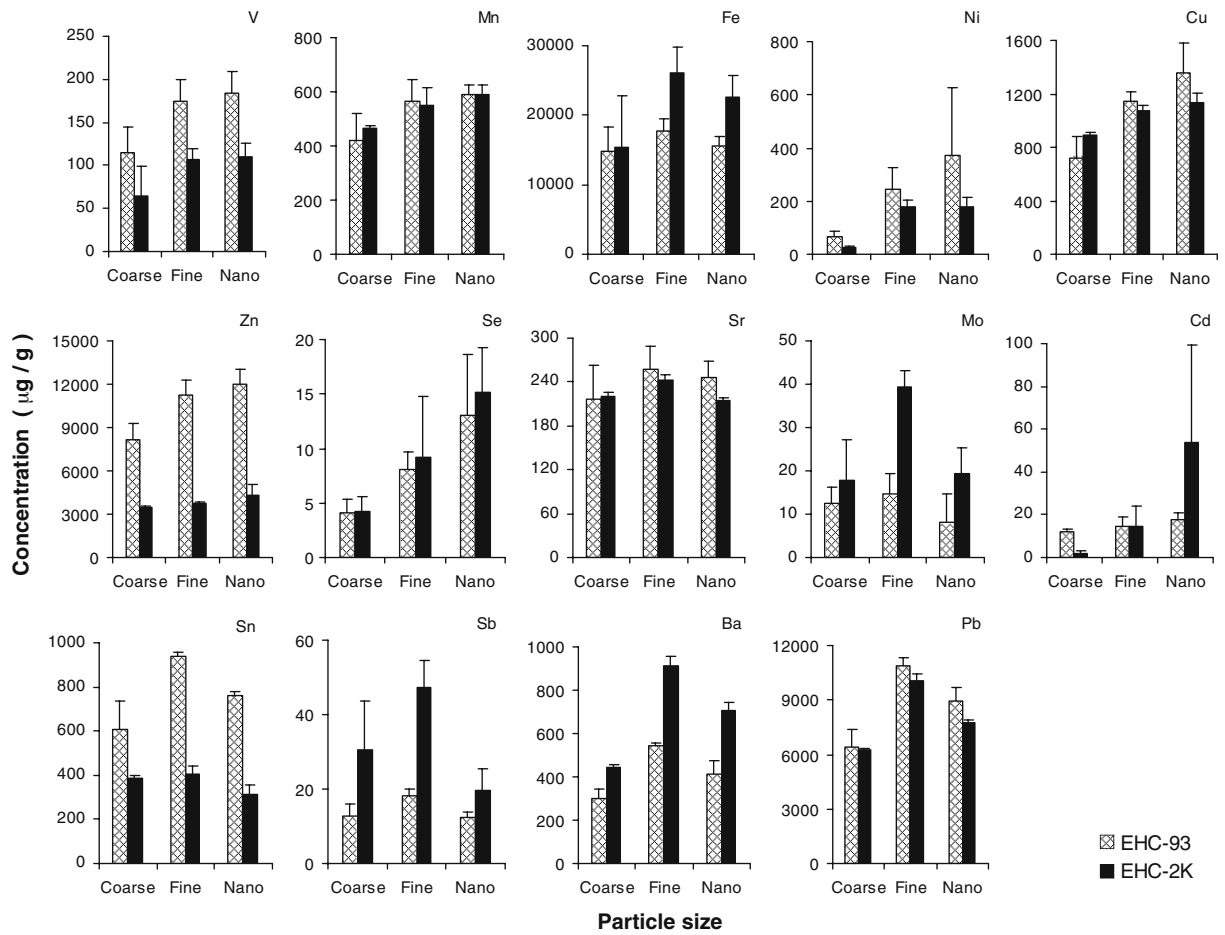


Fig. 2 Distribution of element concentrations for EHC-93 and EHC-2K for the three grouped particle size fractions

Table 2 Element correlation coefficients for EHC-93 in all particle fractions combined (coarse, fine, and nano)

	V	Mn	Fe	Ni	Cu	Zn	Se	Sr	Mo	Cd	Sn	Sb	Ba
Mn	<b>0.90</b>												
Fe	0.25	0.62											
Ni	0.05	0.13	0.12										
Cu	<b>0.95</b>	<b>0.86</b>	0.17	0.26									
Zn	<b>0.97</b>	<b>0.91</b>	0.29	0.19	<b>0.97</b>								
Se	<b>0.90</b>	0.74	0.03	0.15	<b>0.88</b>	<b>0.82</b>							
Sr	0.38	0.71	<b>0.88</b>	0.22	0.39	0.51	0.09						
Mo	-0.10	0.31	<b>0.77</b>	0.12	-0.06	0.04	-0.28	<b>0.83</b>					
Cd	0.59	0.27	-0.42	0.20	0.59	0.47	<b>0.77</b>	-0.42	-0.74				
Sn	0.58	<b>0.79</b>	0.70	-0.11	0.52	0.67	0.25	<b>0.87</b>	0.60	-0.28			
Sb	0.10	0.40	0.64	-0.06	0.11	0.26	-0.20	<b>0.84</b>	<b>0.84</b>	-0.70	<b>0.84</b>		
Ba	<b>0.83</b>	<b>0.95</b>	0.68	-0.14	0.72	<b>0.80</b>	0.63	0.71	0.36	0.12	<b>0.84</b>	0.47	
Pb	0.69	<b>0.91</b>	<b>0.76</b>	-0.02	0.65	0.74	0.47	<b>0.87</b>	0.62	-0.12	<b>0.91</b>	0.69	<b>0.94</b>

**Table 3** Element correlation coefficients for EHC-93 in fine particle fractions (fine and nano)

	V	Mn	Fe	Ni	Cu	Zn	Se	Sr	Mo	Cd	Sn	Sb	Ba
Mn	0.41												
Fe	-0.18	<b>0.79</b>											
Ni	0.64	0.31	-0.24										
Cu	<b>0.77</b>	0.32	-0.29	<b>0.92</b>									
Zn	<b>0.76</b>	0.56	-0.03	<b>0.88</b>	<b>0.93</b>								
Se	<b>0.91</b>	0.07	-0.48	0.63	0.67	0.60							
Sr	-0.12	<b>0.84</b>	<b>0.89</b>	0.10	0.03	0.30	-0.43						
Mo	-0.12	<b>0.83</b>	<b>0.88</b>	0.08	0.01	0.30	-0.42	<b>0.99</b>					
Cd	0.67	-0.36	-0.75	0.34	0.47	0.22	<b>0.82</b>	-0.79	-0.81				
Sn	-0.33	0.71	<b>0.90</b>	-0.07	-0.20	0.09	-0.58	<b>0.97</b>	<b>0.97</b>	-0.91			
Sb	-0.37	0.62	<b>0.77</b>	0.02	-0.12	0.17	-0.58	<b>0.93</b>	<b>0.95</b>	-0.92	<b>0.97</b>		
Ba	0.04	<b>0.88</b>	<b>0.97</b>	-0.14	-0.15	0.09	-0.28	<b>0.84</b>	<b>0.83</b>	-0.57	<b>0.81</b>	0.65	
Pb	0.00	<b>0.91</b>	<b>0.92</b>	0.12	0.04	0.32	-0.31	<b>0.98</b>	<b>0.97</b>	-0.71	<b>0.94</b>	<b>0.87</b>	<b>0.91</b>

element in the entire particle size range combined (Table 2) indicates it probably has multiple sources including traffic emissions from catalysts used in gasoline/diesel vehicles (Richard 2001), roadside dust resuspension, and long-range transport (Rasmussen 1998). The strong correlations between Ni, Cu, and Zn in the finer particle size fraction (Table 3) and the previously observed long-range transport of Ni and Zn in atmospheric particles (Allen et al. 2001; Singh et al. 2002) support this hypothesis.

The median concentration diameters (MCDs) of the elements were calculated from cumulative distributions of the element concentrations (Myers 1997) as shown in Fig. 3, using Cu and Pb as examples. All of the results listed in Table 4 show that the elements with the lowest MCDs are Se, Ni, and Cd (0.13–0.27  $\mu\text{m}$ ); those with moderate MCDs are Cu, V, Zn, Ba, Pb, and Mn (0.3–0.8  $\mu\text{m}$ ); and those with the largest MCDs include Fe, Co, Sr, Mo, and Sb (0.8–1.2  $\mu\text{m}$ ). Nickel and Cd show the largest MCD variation as indicated by their large standard deviation. This large MCD variation for Ni and Cd suggests multiple sources. The variation also supports the observation that Ni is strongly affected by aerosol dynamics including particle condensation, aggregation, and deposition (Lyons et al. 1993).

From the MCD results, it is noted that most of the elements in atmospheric aerosols are in the accumulation mode (<1  $\mu\text{m}$ ) which add to the significance of the contributions of long-range transport of these elements. The small MCDs indicate that, if inhaled, most of the particle-bound V, Ni, Cu, Zn, Sr, Cd, Sn, Ba, and Pb particles may penetrate into the deepest

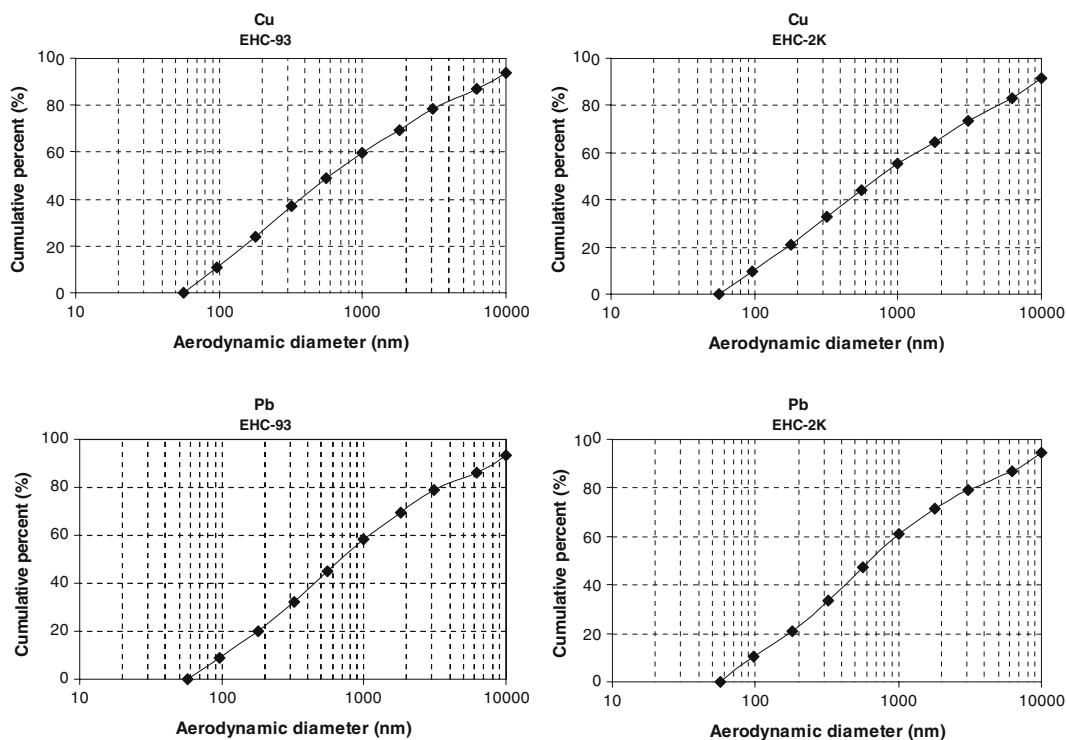
alveolar fractions, whereas most Fe, Mo, and Sb may be deposited into the alveo-bronchial fractions. Both of these scenarios are important, given the potential toxicity and role of these elements in processes leading to lung damage (Carter et al. 1997; Donaldson et al. 1997; Kadiiska et al. 1997; Ghio et al. 1999; Claiborn et al. 2002; Osonio-Vargas et al. 2003; Rasmussen 2004; Lingard et al. 2005). Note that the atmospheric abundance of an element in the nano-fraction is important for evaluation of respiratory effects. That is, even where the nano-fraction is relatively lower than the fine fraction for an element such as Fe, its atmospheric abundance may be such that the quantity penetrating into the deepest alveolar fraction is consequential.

### 3.3.2 EHC-2K Samples

The dark bars in Fig. 2 show the concentration distributions of trace elements for EHC-2K samples. Compared to the light bars for EHC-93 samples, the interesting concentration distribution trend still remains: element concentration increases as aerodynamic particle size decreases for V, Mn, Ni, Cu, Zn, Cd, and Se with maximum concentrations in the nano-size fraction. Other elements (Sn, Sb, Mo, Fe, Ba, Sr, and Pb) are dominated in the fine-size fraction. Thus, all the investigated elements in EHC-2K are concentrated either in the nano- or in the fine-size fractions similar to EHC-93.

Despite this general trend in EHC-2K samples, some significant differences occur for certain elements. Vanadium, Ni, Zn, Sn, and Sb show the largest changes





**Fig. 3** Cumulative percent concentration as a function of particle diameter for Cu and Pb in EHC-93 and EHC-2K samples

(Fig. 2). The overall concentrations of V, Zn, and Sn in EHC-2K are lower than those of EHC-93 by nearly 50% or more. The distribution trends are retained mostly for V and Zn but not for Sn, whose relative concentration in the nano-size fraction is decreased and in the coarse fraction it is increased, indicating a change in its particle size distribution. A significant change also occurs for concentrations of Sb and Mo but in the opposite direction of V, Zn, and Sn, showing a large concentration increase of Sb and Mo in EHC-2K as compared to the concentration in EHC-93. Correlation analysis (Tables 5 and 6) shows that the number of elements that are strongly associated with Zn has decreased from five (V, Mn, Cu, Se, and Ba) in EHC-93 (Table 2) to three (V, Mn, and Cu) in EHC-2K (Table 5) for all particle size fractions showing some changes in common sources for Se and Ba in EHC-2K. The strong correlation between Zn and Cu, Mn, and V suggests that Zn in EHC-2K is from vehicular emissions as it is widely accepted that these elements are associated with gasoline/diesel fuels (Monaci et al. 2000; Pleßow and Heinrichs 2001; Weckwerth 2001; Chen 2002; Lin et al. 2005; Birmili et al. 2006). Further data analysis of the finer particle size fractions

(fine and nano, Table 6) provides additional information for suggesting traffic-related sources of these elements. As indicated in Table 6, the correlation coefficient of Zn with Cu, Mn, and V in all particle size fractions (Table 5) decreases for Cu and Mn from 0.87 to 0.78 and 0.76, respectively, or significantly decrease for V from 0.86 to 0.45 in the finer particle size range reflecting difference (minor or not) in their sources when particle size decreases. Vanadium is most likely associated with vehicular diesel oil combustion (CECBP 2008) in the City of Ottawa, whereas Zn, Cu, and Mn may have additional contributions such as particles released from both tire and brake pad wear (Var et al. 2000; Marcazzan et al. 2003; Birmili et al. 2006).

Contrary to the nearly invariable distribution patterns for many elements (e.g., Se, Pb, Mn, V) in EHC-93 and 2K, the distribution patterns of Ni and Cd in EHC-2K show significant change (Fig. 2) as compared with that in EHC-93. Nickel exhibits a large concentration decrease and Cd increases in the nano-size fraction. In contrast, Cd is less enriched in the coarse-grained fraction relative to sample EHC-93. The increase in Cd may be due to vehicular-related contributions. Pacyna (1986) reported that Cd in the nano size comes mostly

**Table 4** MCDs for PM-bound elements in EHC-93 and EHC-2K

Element	MCD <sup>a</sup>	
	EHC-93	EHC-2K
Al	0.57±0.08	1.01±0.06
V	0.63±0.02	0.68±0.03
Cr	0.36±0.06	0.45±0.03
Mn	0.76±0.02	0.77±0.02
Fe	0.98±0.01	0.86±0.13
Co	1.15±0.15	0.61±0.43
Ni	0.27±0.24	0.07±0.00
Cu	0.56±0.04	0.68±0.08
Zn	0.69±0.06	0.74±0.13
As	1.01±0.02	1.02±0.37
Se	0.13±0.04	0.17±0.12
Sr	0.90±0.02	0.93±0.02
Mo	0.99±0.05	0.89±0.18
Cd	0.27±0.18	0.12±0.01
Sn	0.84±0.00	0.86±0.03
Sb	1.02±0.01	1.03±0.12
Ba	0.69±0.02	0.70±0.04
Pb	0.70±0.01	0.71±0.08

<sup>a</sup> Average values plus standard deviation, values in micrometer

from the exhaust emissions of both gasoline- and diesel-fuelled vehicles.

In summary, a common trend of particle size and element concentration distributions was found in EHC-93 and EHC-2K PM samples. However, some

elements (e.g., Ni, Cd, and Sn) do show pattern differences in size distribution whereas others (e.g., V, Fe, Zn, Mo, and Ba) only exhibit changes in concentration. These variations indicate that some temporal changes in sources of these two EHC samples might exist. Determining the source will require a full-source apportionment study. However, the aging process, including coagulation of the finer particles, may play a role. Surface soil re-entrainment as resuspended dust may play another role in such variations. If long-range transport is involved, the particle size distribution of PM and associated elements would be modified due to both the aging processes and the effect of their atmospheric pathways.

### 3.4 Particle Size Dependent Bioaccessibility

The chemical forms and particle size are two of the most important factors that influence element bioaccessibility (Hinds 1999; Rasmussen 2004; Zereini et al. 2005; Niu et al. 2008) and ultimately govern the bioavailability of the elements. Thus, testing of water solubility of particle-bound elements is commonly employed to provide more complete information for environmental and health-risk assessment (Thomassen et al. 2001). Nano and fine PM-bound elements and their solubilities (bioaccessibilities) are of particular interest due to the tendency of smaller particles to concentrate elements as indicated above in this study and their more direct linkages between oxidative stress and impaired lung function as compared with the coarse

**Table 5** Element correlation coefficients for EHC-2K in all particle fractions combined (coarse, fine, and nano)

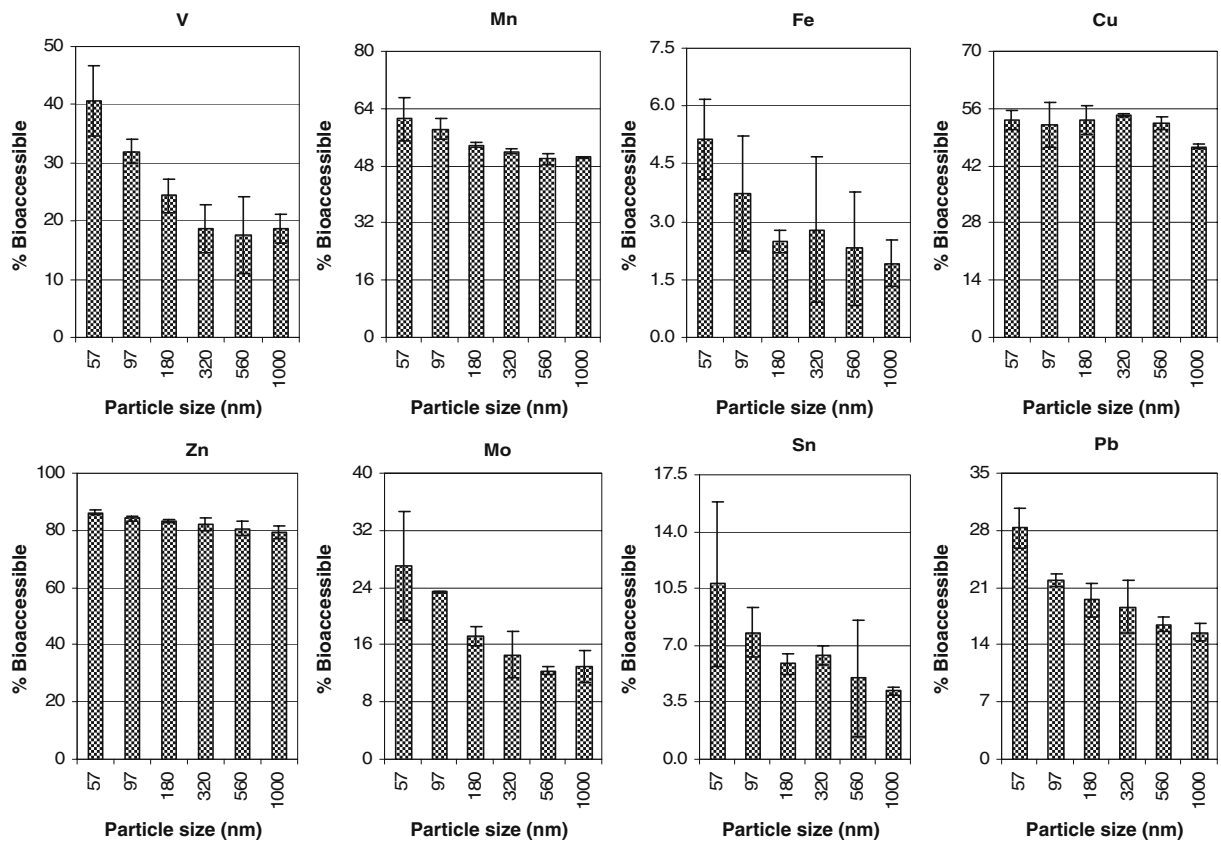
	V	Mn	Fe	Ni	Cu	Zn	Se	Sr	Mo	Cd	Sn	Sb	Ba
Mn	<b>0.96</b>												
Fe	<b>0.89</b>	<b>0.77</b>											
Ni	0.71	<b>0.79</b>	0.47										
Cu	<b>0.93</b>	<b>0.97</b>	0.69	<b>0.84</b>									
Zn	<b>0.86</b>	<b>0.87</b>	0.57	0.63	<b>0.87</b>								
Se	0.69	0.73	0.42	<b>0.81</b>	0.66	0.56							
Sr	<b>0.91</b>	0.51	0.64	0.36	0.61	0.42	-0.02						
Mo	<b>0.88</b>	0.61	<b>0.76</b>	0.40	0.67	0.43	0.09	<b>0.97</b>					
Cd	0.71	0.49	0.18	0.43	0.34	0.42	<b>0.79</b>	-0.48	-0.34				
Sn	0.44	0.42	0.35	0.27	0.50	0.32	0.11	<b>0.79</b>	<b>0.76</b>	-0.33			
Sb	0.61	0.34	0.45	0.21	0.45	0.32	-0.10	<b>0.91</b>	<b>0.85</b>	-0.57	<b>0.85</b>		
Ba	<b>0.93</b>	<b>0.83</b>	<b>0.98</b>	0.56	<b>0.78</b>	0.65	0.46	0.73	<b>0.83</b>	0.15	0.48	0.56	
Pb	<b>0.90</b>	<b>0.90</b>	<b>0.90</b>	0.60	<b>0.84</b>	0.66	0.59	0.64	<b>0.78</b>	0.31	0.57	0.47	<b>0.94</b>

**Table 6** Element correlation coefficients for EHC-2K in fine particle fractions (fine and nano)

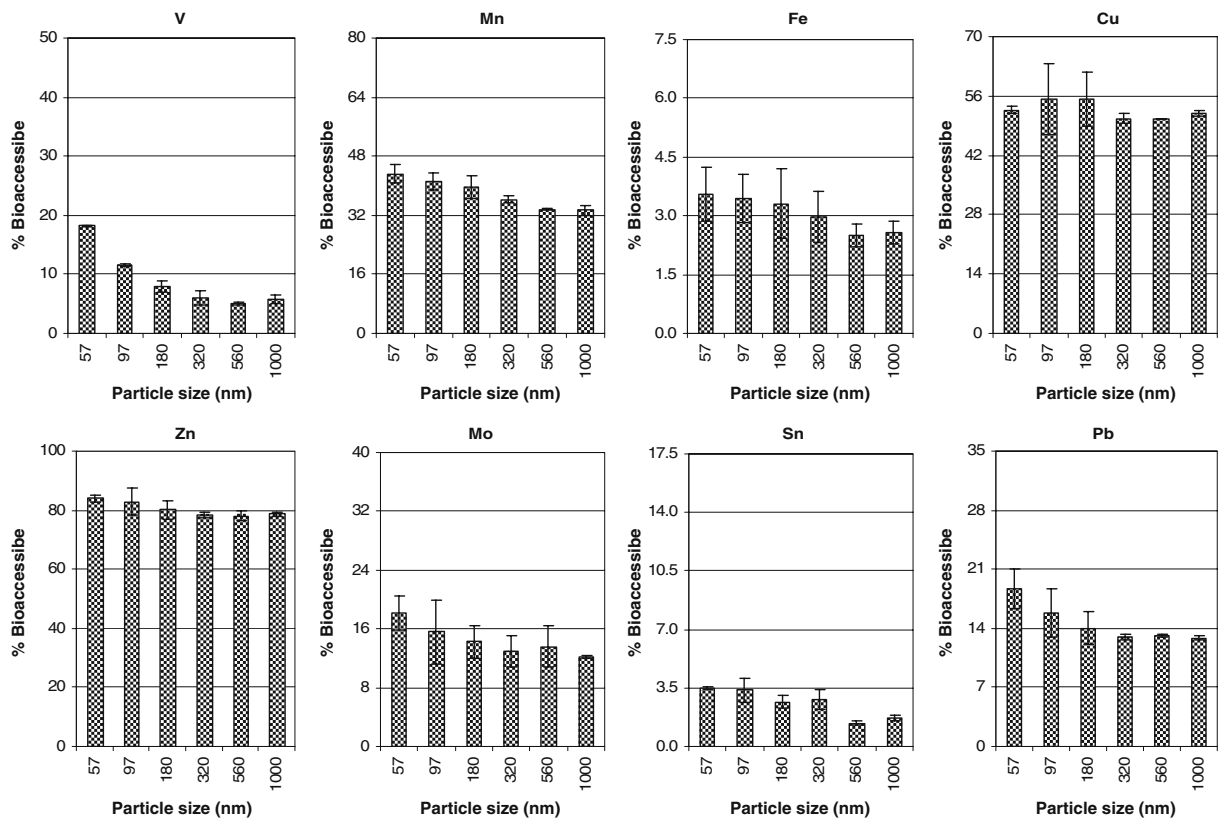
	V	Mn	Fe	Ni	Cu	Zn	Se	Sr	Mo	Cd	Sn	Sb	Ba
Mn	<b>0.89</b>												
Fe	0.26	0.19											
Ni	0.39	0.74	-0.23										
Cu	<b>0.83</b>	<b>0.96</b>	0.19	<b>0.81</b>									
Zn	0.45	<b>0.76</b>	-0.30	0.68	<b>0.78</b>								
Se	0.48	0.44	-0.43	0.65	0.32	0.26							
Sr	0.64	0.50	<b>0.82</b>	0.25	0.62	0.18	-0.33						
Mo	0.69	0.53	<b>0.87</b>	0.18	0.61	0.15	-0.33	<b>0.98</b>					
Cd	0.43	-0.05	-0.77	0.06	-0.24	0.12	0.67	-0.87	-0.83				
Sn	<b>0.81</b>	<b>0.79</b>	0.72	0.39	0.74	0.31	0.14	<b>0.81</b>	<b>0.86</b>	-0.44			
Sb	<b>0.84</b>	0.63	<b>0.82</b>	0.30	0.70	0.21	-0.20	<b>0.97</b>	<b>0.99</b>	-0.77	<b>0.89</b>		
Ba	0.57	0.50	<b>0.94</b>	0.07	0.51	0.04	-0.26	<b>0.93</b>	<b>0.97</b>	-0.74	<b>0.90</b>	<b>0.94</b>	
Pb	<b>0.76</b>	0.68	<b>0.79</b>	0.15	0.57	0.15	0.08	0.72	<b>0.80</b>	-0.37	<b>0.96</b>	<b>0.82</b>	<b>0.90</b>

PM-bound elements (Donaldson et al. 1998; Ghio et al. 1999; Allen et al. 2001, Osonio-Vargas et al. 2003; Kittelson et al. 2004). In this work, element bioaccessibility in EHC airborne particulate samples was assessed

using a “water soluble” extraction buffered at pH 7 to simulate the neutral lung environment (Thomassen et al. 2001) which was then compared with the total element digestion results.



**Fig. 4** Element bioaccessibility versus particle size for EHC-2K samples



**Fig. 5** Element bioaccessibility versus particle size for EHC-93 samples

Figure 4 shows element bioaccessibility as a function of particle size from nano to fine range for EHC-2K samples. The general trend of increasing element bioaccessibility with decreasing particle size is observed indicating that certain elements have the highest bioaccessibility in the nano-size range of EHC-2K urban air particles. Some elements show a steep increase as particle size decreases from fine to nano (e.g., V, Fe, Mo, Sn, and Pb), whereas others show gentle increase or little change with size (e.g., Mn, Cu, and Zn). The observation demonstrates the important role that particle size plays in both bioaccessibility and the refinement of human health-risk assessments for the inhalation pathway.

Figure 4 reveals that bioaccessibility can be element dependent. For example, some elements show very high percentages, such as Zn with 80% to 84% bioaccessibility (Fig. 4) and Cu with bioaccessibility ranging from 46% to 54%, indicating that most of nano and fine Zn-bound and about half of the Cu-bound particles are presented in PM as soluble or bioaccessible forms.

Some exhibit moderate bioaccessibility such as Pb (from 16% to 29%) and V (from 18% to 41%). Others have low bioaccessibility such as Fe (2–5%) and Sn (4–11%). The comparative pulmonary toxicity study of various elements in urban dust by Prieditis and Adamson (2002) showed that the capability of elements to induce lung injury is on the order of  $Zn > Cu > V, Pb,$  and  $Fe,$  which is consistent with the general bioaccessibility order in this study ( $Zn > Cu > V > Pb > Fe$ ). This observation indicates that studies of relative element bioaccessibility may assist in understanding factors related to inhalation toxicology.

The general trend in element bioaccessibility in EHC-93 samples (Fig. 5) is similar to that in EHC-2K, indicating particle size-dependent concentration and bioaccessibility distributions are generally the same. However, differences in bioaccessibility values for some elements (V, Mn, Mo, Sn, and Pb) are observed. This difference indicates some possible variations in speciation (i.e., different physical or chemical forms) of these elements between EHC-2K and EHC-93.

#### 4 Conclusions

Particle size is observed in this study to be a key factor affecting both element concentration distribution and element bioaccessibility and is thus a critical parameter for accurately assessing health effects of the EHC-type urban air particles. The element concentration distribution revealed that V, Mn, Ni, Cu, Zn, Se, and Cd in EHC PM samples exhibited the relative highest mass concentrations in the nano size (<100 nm) and the lowest concentrations in the coarse size (>1,000 nm). For these elements, a general trend of increasing element concentrations as aerodynamic particle size decreases was observed. Other elements (Fe, Pb, Ba, Sn, Sb, Mo, and Sr) predominantly occur in the fine-size fraction (100–1,000 nm). The fact that nano or fine particulate-bound elements were found to dominate in the EHC-93 and EHC-2K samples collected in an area of the City of Ottawa without nearby industrial sources suggests that the main sources of these elements are vehicular combustion and emission, perhaps with some contribution from long-range transport and roadside dust resuspension. The results also underscore the importance of future investigations into nano and fine particle-bound elements in PM and settled dust for improved urban exposure-related health-risk assessments.

As in the case of the total concentration distributions, similar trends were also observed for element bioaccessibility studies in the nano- and fine-particle fractions: element bioaccessibility values increase with decreasing particle size. It would appear that bioaccessibility is both particle size- and element-dependent. These results further demonstrate the importance of considering particle size and element speciation effects for future improvements in exposure assessment.

The general concentration trend was consistent for elements in EHC samples collected during different years. However, the comparison between EHC-93 and EHC-2K samples indicated that there were some differences in total element concentrations and/or particle size distributions for certain elements, indicating possible source variations during these two sampling periods. Aging-related aggregation or long-range transport processes, which have been generally accepted as the cause of fine particle mass variations, may also partly account for relative elemental concentration changes between different sampling periods. Changes in windblown soil or road dust resuspension may also contribute to such variations.

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