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Heavy metals in urban roadside soils, part 1: effect of particle size fractions on heavy metals partitioning

Received: 13 January 2006
Accepted: 22 March 2006
Published online: 13 April 2006
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Abstract Urban roadside soils are important environmental media for assessing heavy metal concentrations in urban environment. However, among other things, heavy metal concentrations are controlled by soil particle grain size fractions. In this study, two roadside sites were chosen within the city of Xuzhou (China) to reflect differences in land use. Bulk soil samples were collected and then divided by particle diameter into five physical size fractions, 500–250, 250–125, 125–74, 74–45, < 45 μm . Concentrations of metals (Ti, Cr, Al, Ga, Pb, Ba, Cd, Co, Cu, Mn, Ni, V, Zn, Mo, As, Sb, Se, Hg, Bi, Ag) were determined for each individual fraction. These metals could be roughly classified into two groups: anthropogenic element (Pb, Ba, Cd, Cu, Zn, Mo, As, Sb, Se, Hg, Bi, Ag) and lithophile element (Ti, Cr, Al, Ga, Co, Mn, Ni, V) in terms of values of enrichment factor. As expected, higher concentrations

of anthropogenic heavy metals (Cu, Zn, Mo, As, Hg, Bi, Ag) are observed in the finest particle grain size fraction (i.e. < 45 μm). However, heavy metals Se, Sb and Ba behave independently of selected grain size fractions. From the viewpoint of mass loading, more than 30% of the concentrations for all anthropogenic heavy metals are contributed by the particle grain size fractions of 45–74 μm at site 1 and more than 70% of the concentrations for all heavy metals are contributed by the particle grain size fractions of 45–74 and 74–125 μm at site 2. These results are important for transport of soil-bound heavy metals and pollution control by various remedial options.

Keywords Grain size fraction · Heavy metal partitioning · Urban roadside soils · Loading · XRD · Xuzhou · China

Introduction

In recent years, public attention has been focused increasingly on environmental pollution and its effect on man and other creatures. Among the various pollutants, heavy metals are particularly important in their action (Ratha and Sahu 1993). Urban roadside soils are the “recipients” of large amounts of heavy metals from a variety of sources (e.g. vehicle emissions, coal burning waste, etc.) and accordingly the heavy metals in urban

roadside soils can be used as tracers of urban environmental pollution. However, the concentration of heavy metals in soils is controlled by the particle sizes, as it is reported that accumulation of heavy metals is inversely related to particle size (Forstner 1980). Finer particles, due to their high specific area, adsorb more heavy metals. Thus, analysis of effect of particle size fractions on heavy metal concentrations is very important in urban pollutant studies because: (1) the particles themselves are pollutants, and size distribution is an important factor

that influences particle transportability. The particles with aerodynamic diameters under $100\ \mu\text{m}$ can be transported by “suspension” and the finest among them ($< 10\ \mu\text{m}$) may remain airborne for a long time (De Miguel et al. 1997); (2) some metals are preferentially adsorbed to finer particles and it is important for modeling and policy implementation to know which particle sizes are dominant in transporting pollutants (Ratha and Sahu 1993); (3) fine heavy metal-containing particles exhibit a more serious threat to health. Fine particles are more soluble than coarser ones due to the increasing surface area (Lin et al. 1998). Fine particles are more likely to traverse the gastric mucosa and be more efficiently adsorbed (Hemphill et al. 1991).

The objectives of the present study are to quantify anthropogenic heavy metal concentrations in different particle size fractions and to compute their enrichment factors (Efs) and mass loadings for individual fraction in urban roadside soils. These results are important for managing the heavy metal transport in soils.

Materials and methods

Study area

Xuzhou is in the northwestern part of Jiangsu, one of the provinces of China, the geographical position is $33^{\circ}43' - 34^{\circ}58' \text{N}$, $116^{\circ}22' - 118^{\circ}40' \text{E}$. Xuzhou is an important center of historic and modern day industrial activities where coal provided fuel for manufacturing.

In the present study, two roadside sites were chosen within the city of Xuzhou to reflect differences in land use within an urban setting (Fig. 1). The first (designated Site 1) is in the area near the Xuzhou steel-iron plant and

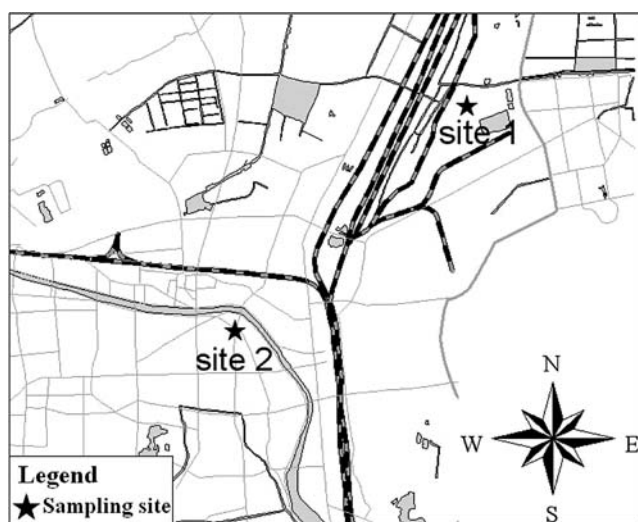


Fig. 1 Study area and sampling sites

with heavy truck traffic going to and from the steel-iron plant. The second site (Site 2) is near the city center in an area with mostly automobile traffic.

Sampling and analysis

Two surface soil samples (depth = 0–10 cm) were collected from the two sites. At each sampling point, three sub-samples, each with a $20\ \text{cm} \times 20\ \text{cm}$ surface, were taken and then mixed to obtain a bulk sample. Such a sampling strategy was adopted to reduce the possibility of random influence of urban waste. Samples were collected with a stainless steel spatula and kept in PVC packages. These two bulk samples were initially sieved through a $1,000\ \mu\text{m}$ to remove coarse sand and then divided by particle diameter into five physical size fractions, 500–250, 250–125, 125–74, 74–45, $< 45\ \mu\text{m}$. The weights of each size fraction were recorded and percent distribution of weights in each size calculated.

Two bulk ($< 1\ \text{mm}$) soil samples were analyzed for: sand ($50 - 2,000\ \mu\text{m}$), silt ($2 - 50\ \mu\text{m}$) and clay ($< 2\ \mu\text{m}$) using Coulter Laser equipment. Samples were stirred and ultrasound used to facilitate particle dispersion (Navas and Machin 2002); total organic carbon (TOC) by chromic acid digestion; pH_{water} on a 5 g to 25 ml slurry using an PHS-3C pH-meter; and carbonate content (total inorganic carbon, TIC) by back titrating an excess of 0.5 M HCl added to 1 g of sample with 0.5 M NaOH (Sutherland 2003).

The elemental concentrations for Ti, Cr, Al, Ga and Pb were determined by X-ray fluorescence spectrometry (XRF, Philips PW1400 apparatus), on bulk sample pressed, boric-acid backed pellets. The accuracy of determinations was checked by using certified reference materials. Ba, Cd, Co, Cu, Mn, Ni, V, Zn and Mo concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS). The elements As, Sb, Se, Hg, Bi and Ag were determined by inductively coupled plasma atom emission spectrometry (ICP-AES). All calibration standards were prepared in the acid matrix used for the soil samples. Caution was used in preparing and analyzing samples to minimize contamination from air, glassware and reagents, which were all of suprapur quality. Replicated measures of certified reference materials, reagent blanks and duplicated soil samples were used to assess contamination and precision.

X-ray diffraction (XRD) was used to determine sample mineralogy, especially the clay mineral types. Sample preparation started by putting 2–3 g of sample in a beaker filled with 200 mL of water. After stirring, the suspension was left for 45 min. The clay minerals, which were floating close to the surface, were caught with a pipette and transferred onto a glass slide. The sample was left to air dry. One set of slides was air dried,

a duplicate set was glycolated, and another set was heated to 350 and to 550 to differentiate clay minerals. XRD analysis of soil was carried out for mineral phase identification by XRD instrument (D/Max-3B), made by Rigaku Co. Japan, using Cu-K α . All samples were run at a tube voltage of 35 kV and 30 mA. Scanning velocity and sampling spacing for qualitative analysis are 4°/min and 0.02°, respectively. Scanning velocity and sampling spacing for quantitative analysis are 2°/min and 0.02°, respectively.

Results and discussion

Physicochemical properties

The physicochemical properties of bulk soil samples from the two sites are determined and the results are shown in Table 1. With the exception of TOC and soil texture, the physicochemical properties of soil samples from the two sites studied are almost similar.

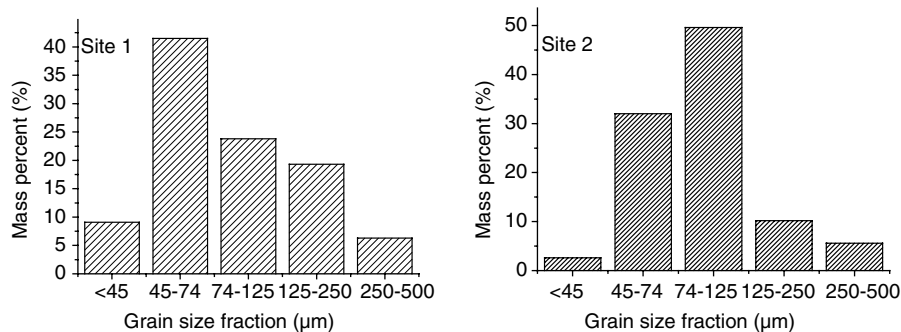
Mass percentages were calculated to exhibit particle sizes effect on distribution particles. As shown in Fig. 2, approximately 75% of all particles are smaller than 125 μm for soil samples from site 1 and approximately 84% from site 2. The soil particles finer than 125 μm are easily transferred into the closest watershed with urban runoff (Benoit and Rozan 1999) or into the atmosphere by wind and contribute heavy metal pollution.

Table 1 Physicochemical parameters of two bulk soil samples (< 1 mm) from two sites

| | PH | TOC (%) | TIC (%) | Soil texture (μm) | | |
|--------|------|---------|---------|--------------------------------|----------|--------------|
| | | | | < 2 (%) | 2–50 (%) | 50–1,000 (%) |
| Site 1 | 7.69 | 3.68 | 10.3 | 2.3 | 37.8 | 59.9 |
| Site 2 | 7.70 | 10.15 | 9.98 | 5.7 | 59.4 | 34.9 |

TOC Total organic carbon, TIC total inorganic carbon

Fig. 2 Mass percentages as a function of grain size of soil samples



Mineralogy

The XRD patterns of the two bulk soil samples from two sites are shown in Fig. 3. The clay mineralogy of the soil from the two sites is not significantly different and the major mineralogical phases identified in soils are illite, kaolinite, chlorite and illite-montmorillonite interstratified minerals. Quantitative analysis (Table 2) shows nearly 50% of clay is illite, the remainder is kaolinite, illite-montmorillonite interstratified minerals and chlorite.

Enrichment factors

To identify heavy metals introduced into the environment as a result of human activities, it is common practice to calculate the enrichment factor of a heavy metal X (EF_x) in the sampled material with respect to its natural abundance in the regional background, according to the following algorithm: $EF_x = (X/E_{ref})_{sample} / (X/E_{ref})_{background}$, where X is the concentration of the element of interest and E_{ref} the reference element for normalization. Generally, E_{ref} is chosen among elements of definite natural origin (Al, Ti, Sc, etc). If an EF is greater than unity, this indicates that the element is more abundant in the soil relative to that found in the regional background. However, EFs less than 2 may be not considered significant although they are an indicator of metal accumulation, because such small enrichments may arise from differences in the composition of local soil material and reference regional background used in EF calculations. In the present study, Ti is used as reference element and if the EF values are greater than 2, in this case, they are considered to be soil pollution for related metals.

Enrichment factors for anthropogenic heavy metals at the various grain size fractions from the two sites are shown in Fig. 4. Interestingly, although the higher concentrations for most of the heavy metals are found in finer size fraction (i.e. < 45 μm) (see the below), the higher values of EFs are observed in coarse particle size

Fig. 3 X-ray diffraction patterns of bulk soil samples from sites 1 and 2

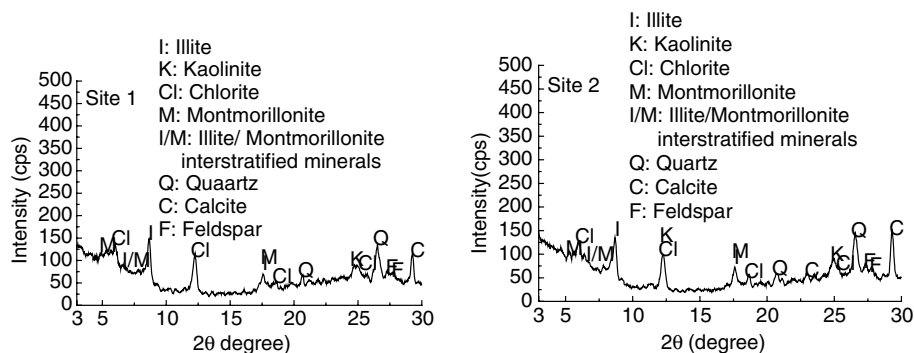


Table 2 Quantitative analysis of clay minerals

| | Chlorite | Kaolinite | Illite | I/M ^a |
|--------|----------|-----------|--------|------------------|
| Site 1 | 14 | 22 | 45 | 19 |
| Site 2 | 16 | 21 | 48 | 15 |

^aIllite/Montmorillonite inter-stratified minerals

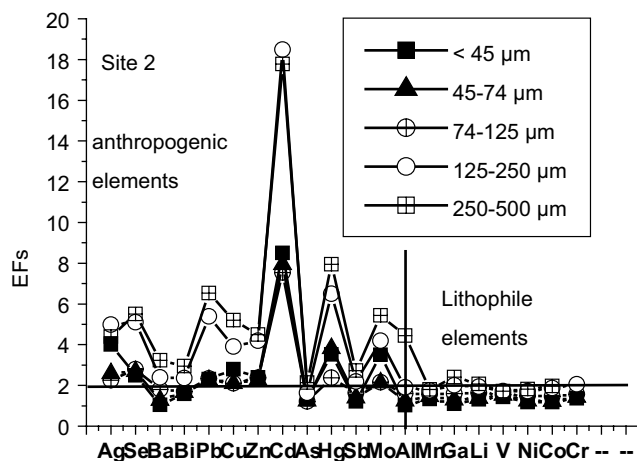
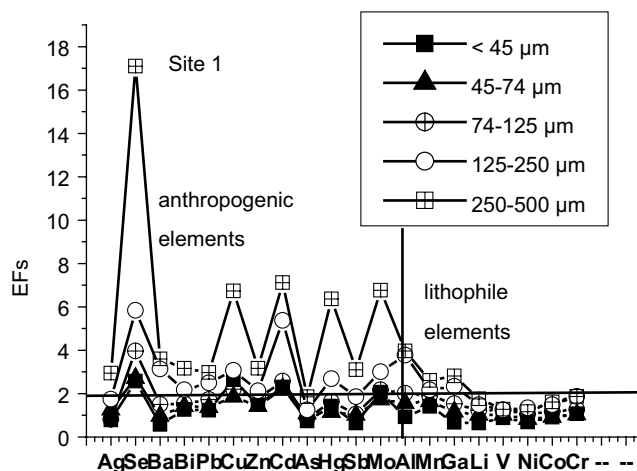


Fig. 4 Enrichment factors of heavy metals at the various grain size fractions (Ti as reference element)

fraction (i.e. 250–500 μm). This is mainly attributed to different enrichment properties for reference element, Ti, at various particle size fractions. The finer particle size fraction, the more the Ti concentration. In addition, heavy metals from the studied sites can be roughly classified into two groups in terms of EFs values: anthropogenic elements and lithophile elements. The first group of heavy metals (Ag, Se, Ba, Bi, Pb, Cu, Zn, Cd, As, Hg, Sb, Mo) shows EFs are greater than 2 at almost various grain size fractions, indicating these metals are mainly derived from anthropogenic sources. The second group has EFs in the range of 0.5–2, showing that these heavy metals are not significantly enriched with respect to regional background and an anthropogenic contribution can be excluded. Accordingly, in the next section, only the first group of heavy metals is discussed.

Effect of grain size fractions on heavy metal partitioning

Heavy metal partitioning as a function of grain size is very important for transport of soil-bound heavy metals and pollution control by various remedial options. Figure 5 shows the relative heavy metal concentrations in the five grain size fractions from the two sites. As expected, most of the heavy metals (Ag, Bi, Cu, Zn, Cd, As, Hg, Mo) exhibit a substantial accumulation in the finest particles. Such a pattern is usually attributed to the increase in specific surface area and concomitant increase in the proportion of reactive substrates (Sutherland 2003). However, Se, Ba and Sb are inclined to be enriched in the coarse soil particles from site 1 and behave relatively evenly at various particle size fractions from soil sampled at site 2. With regard to Pb and Cd, the effects of particle grain size fractions on concentrations are also different. The fact that Pb exhibits a substantial accumulation in the coarse soil particles at site 2 is agreement with the results of Varrica et al. (2003) in the study of roadway dust of Palermo, Italy.

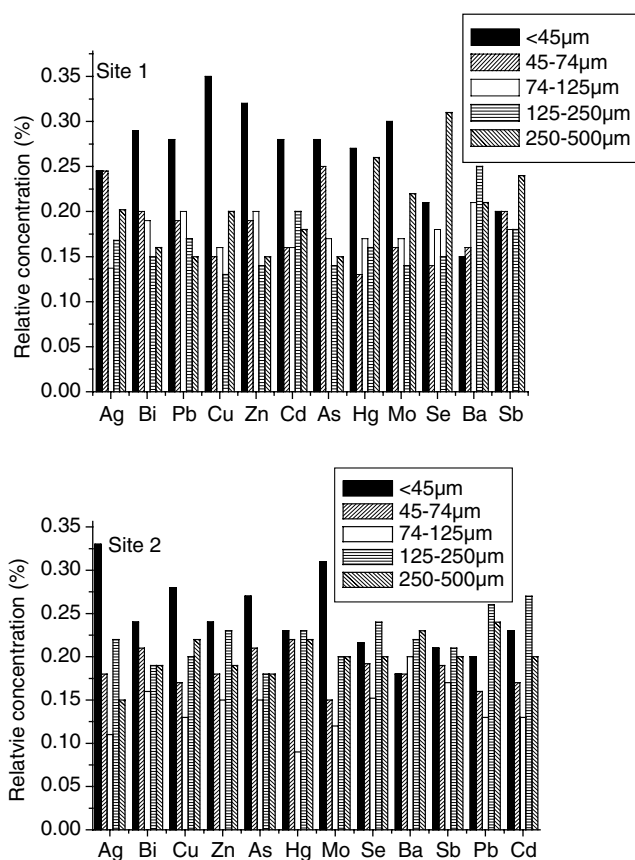


Fig. 5 Relative heavy metal concentrations in five fractions from the two sites

Heavy metal loadings

The most important index of contamination is the mass loading of heavy metals in a given grain size fraction (Sutherland 2003). Loading combines heavy metal concentrations, on a grain size basis, with data on the mass percent. The equation used for computing heavy metal

loadings on a grain size fraction basis ($GSF_{loading}$) (Sutherland 2003) was:

$$GSF_{loading} = 100 \times \left[\frac{HM_i \times GS_i}{\sum_{i=1}^5 HM_i \times GS_i} \right], \quad (1)$$

where HM_i is the heavy metal (i) concentration in an individual grain size fraction (e.g. $< 45 \mu\text{m}$) in mg/kg , with five classes per sample; and GS_i is the mass percentage of an individual fraction, which has limits of 0–100%. The summation of $GSF_{loading}$ values for an individual sample = 100%.

The mass loadings for heavy metals from each particle grain size group were calculated and are shown in Table 3. As far as soil samples from site 1 are concerned, more than 30% of the concentrations for all studied heavy metals are contributed by the particle grain size fractions of 45–74 μm while all other grain size particles almost equally contribute total heavy metal concentrations. More than 70% of the concentrations for all heavy metals are contributed by the particle grain size fractions of 45–74 and 74–125 μm , while the coarse fraction (250–500 μm) and the finest fraction ($< 45 \mu\text{m}$) account for only less than 10% of the heavy metals stored in soils from the site 2, respectively. As mentioned above, these soil particles finer than 125 μm could be problematic in that they are easily transferred into surface waters or into the atmosphere. The results are of importance for managing heavy metal transport.

Conclusions

Effects of particle grain size fractions on partitioning for heavy metals are different. For Cu, Zn, Mo, As, Hg, Bi and Ag, higher concentrations are found in the finest particle grain size fraction (i.e. $< 45 \mu\text{m}$). However, for heavy metals Se, Sb and Ba, the concentrations are independent of various particle grain size fractions to

Table 3 Heavy metal mass loadings (%) of five grain size fractions (μm) from two sites

| | Site 1 | | | | | Site 2 | | | | |
|----|--------|-------|--------|---------|---------|--------|-------|--------|---------|---------|
| | < 45 | 45–74 | 74–125 | 125–250 | 250–500 | < 45 | 45–74 | 74–125 | 125–250 | 250–500 |
| Ag | 11.1 | 50.45 | 16.14 | 16.14 | 6.29 | 5.5 | 36.9 | 37.2 | 14.68 | 5.49 |
| Se | 11.7 | 34.47 | 25.16 | 17.15 | 11.67 | 3.15 | 34.5 | 42.4 | 13.7 | 6.3 |
| Ba | 7.3 | 34.1 | 26.2 | 25.57 | 6.83 | 2.37 | 29.1 | 50.5 | 11.3 | 6.58 |
| Bi | 13.5 | 43.0 | 23.2 | 15.16 | 5.16 | 3.4 | 36.1 | 43.4 | 11.2 | 5.69 |
| Pb | 15.54 | 48.4 | 30.3 | 20.5 | 5.68 | 3.22 | 32.1 | 39.5 | 16.8 | 8.3 |
| Cu | 18.3 | 37.36 | 22.2 | 14.28 | 7.27 | 4.49 | 34.3 | 40.9 | 12.9 | 7.4 |
| Zn | 15.8 | 42.63 | 26.34 | 14.7 | 4.9 | 3.6 | 34.4 | 42.5 | 13.4 | 6.1 |
| Cd | 13.6 | 37.5 | 21.5 | 20.9 | 6.4 | 3.6 | 34.2 | 38.4 | 16.8 | 6.9 |
| As | 12.1 | 50.4 | 19.7 | 13.2 | 4.59 | 3.9 | 37.2 | 42.8 | 10.3 | 5.7 |
| Hg | 14.8 | 33.3 | 23.7 | 18.3 | 9.9 | 3.8 | 42.1 | 31.1 | 15.1 | 7.9 |
| Sb | 10.3 | 46.35 | 23.52 | 19.31 | 0.48 | 2.9 | 33.5 | 46.5 | 11.2 | 5.9 |
| Mo | 15.7 | 37.5 | 23.67 | 15.13 | 7.97 | 5.4 | 33.3 | 39.8 | 13.9 | 7.6 |

some extent. More than 30% of the concentrations for all anthropogenic heavy metals are contributed by the particle grain size fractions of 45–74 μm at site 1 and more than 70% of the concentrations for all heavy metals are contributed by the particle grain size fractions

of 45–74 and 74–125 μm at site 2 from the mass loading viewpoint. These results are of importance for transport of soil-bound heavy metals and pollution control by various remedial options.

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