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ORIGINAL ARTICLE

Relationships between heavy metals and iron oxides, fulvic acids, particle size fractions in urban roadside soils

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Abstract Urban roadside soils are the ''recipients'' of large amounts of heavy metals from a variety of sources including vehicle emissions, coal burning waste and other activities. The behavior of heavy metals in urban roadside soils depends on the occurrence as well as the total amount. Accordingly, knowledge of the interactions between heavy metals and other constituents in the soil is required to judge their environmental impact. In this study, correlations of heavy metal concentrations (Pb, Zn, Cu, Ag, Se, Ni, Cr and Ba) to iron extracted using dithionite–citrate–bicarbonate (DCB) buffer (Fe_{DCB}), fulvic acids and particle size fractions were examined from the Xuzhou urban roadside soils. Heavy metals except for Cr and fulvic acids had a positive significant correlation with Fe_{DCB}, indicating these metals and fulvic acids are principally associated with the surfaces of iron oxides of the soils. Significant positive correlations were also found between the contents of fulvic acids and heavy metals, showing these heavy metals (especially for Cu, Ni and Cr) form stable complexes with fulvic acids. Such finding is of importance with regard to the increased mobilization of heavy metals, e.g., into freshwater ecosystems. Ag, Se and Cr are independent of particle size fractions because of their low concentrations of Ag and Se in the studied soils. Pb, Zn, Cu, Ba and Ag are mainly enriched in the finer soil particles (especially < 16 μm).

Keywords Dithionite–citrate–bicarbonate buffer extraction · Iron oxides · Fulvic acids · Particle size fraction · Urban roadside soils · Xuzhou · China

Introduction

Roadside soils have long been known to contain high levels of heavy metals, especially lead. There is general agreement that these metals decrease in concentration with depth and distance from the roadway. What is less certain is the form in which the metals occur and consequently how easy they are to remobilize (Turer and Maynard 2003). From a policy perspective, the question is, how serious is the hazard posed by these metals? In this study, the relationships between fulvic acids, particle sizes and Fe oxides and heavy metals have been examined.

Soil organic matter is composed of humic substances (fulvic acids and humic acids) and non-humic substances. Fulvic acids are organic substances, which predominantly have lower molecular weights than humic acid, usually not more than 5,000 g mol^{-1}, and are often called dissolved organic carbon (DOC). DOC comprises amino acids, aliphatic acids, peptides and sugars and their polymers. These low molecular weight materials have a different behavior from humic acids in many ways, the most important difference being that they are dissolved in aqueous media in the range of pH normally found in soils, along with the metals that they have bound. DOC is often reported to reduce metal

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adsorption on solid-state soil constituents by either competing more effectively for the free metal ions and forming organo-metallic complexes or being preferentially adsorbed onto the solid phase (Guisquiani et al. 1998). Some workers have concluded that DOC may facilitate the transport of heavy metals (Jardine et al. 1992; Guisquiani et al. 1992; Li and Shuman 1997). The movement of heavy metals is of great importance because it involves the risk of groundwater contamination and deterioration of drinking water quality. An important role for organic matter in controlling heavy metal distribution is suggested by the work of Al-Chalabi and Hawker (2000) on roadside soils of Brisbane, Australia. Their data set shows much stronger correlations between lead and organic carbon than for traffic volume, carbonate carbon, depth or clay content. The anthropogenic lead, Zn and Cu are strongly correlated to the amount of organic matter in the highway soils (Turer and Maynard 2003). Unpolluted soils apparently do not show this pattern. For example, Tack et al. (1997) reported low correlation coefficients for organic carbon versus Cu, Pb and Zn, in the range 0.2–0.4, for unpolluted soils in Flanders. However, to the authors' knowledge, the relationships between fulvic acids and heavy metals are scarce on urban roadside soils.

The concentration of heavy metals in soil is also controlled by particle sizes, as it is reported that sorption 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 particle size distribution is very important in urban pollutant studies (Vermette et al. 1987) because: (1) the particles themselves are pollutants, and size distribution is an important factor that influences particle transportability. Particles with aerodynamic diameters under 100 μm can be transported by "suspension" and the finest among them (<10 μm) 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). In addition, Fe oxides are abundant in soils and are important soil components influencing the remobilization of heavy metals. Iron oxide particles in metal-contaminated soils have been found to contain particularly high concentrations of metals (Langen and Hoberg 1995). In case of lead and zinc, Jones (1987) states that hydrous Fe oxides may be more readily associated with zinc than with lead. The concentrations of heavy metals and spatial distributions have been reported elsewhere (Wang et al. 2005). In this study, only the results of comparison of fulvic acids, particle sizes and iron oxides with heavy metals on the Xuzhou urban roadside soils have been reported.

Materials and methods

Study area

Xuzhou is in the northwestern part of Jiangsu, one of the provinces of China, the geographical position being 33°43′–34°58′N, 116°22′–118°40′E. Xuzhou (China) is an important center of historic and modern day industrial activities where coal provides the fuel for manufacturing.

Sampling and analysis

A total of 21 topsoil samples (depth = 0–10 cm) were collected within the city of Xuzhou (Fig. 1).

At each sampling point, three sub-samples, each with a 20 × 20 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. All samples were collected with a stainless steel spatula and kept in PVC packages. The soil samples were air-dried and sieved through a 1 mm sieve. All bulk topsoil samples (<1 mm) were analyzed for particle size fractions using Coulter Laser equipment. Samples were stirred and ultrasound used to facilitate particle dispersion (Navas and Machin 2002). Fulvic acids were extracted by chromic acid digestion. Extractable Fe was determined using dithionite–citrate–bicarbonate (DCB) buffer (Fe_{DCB}) for total oxides, hydroxides and oxyhydroxides (Bolton and Evans 1996).

The elemental concentrations for Ba, Cu, Ni, Zn and Pb were measured by inductively coupled plasma mass spectrometry (ICP-MS). The elements Se, Ag and Cr 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 good quality. Replicated measures of standard reference materials (ESS-1 and ESS-2 were provided by China Environ-

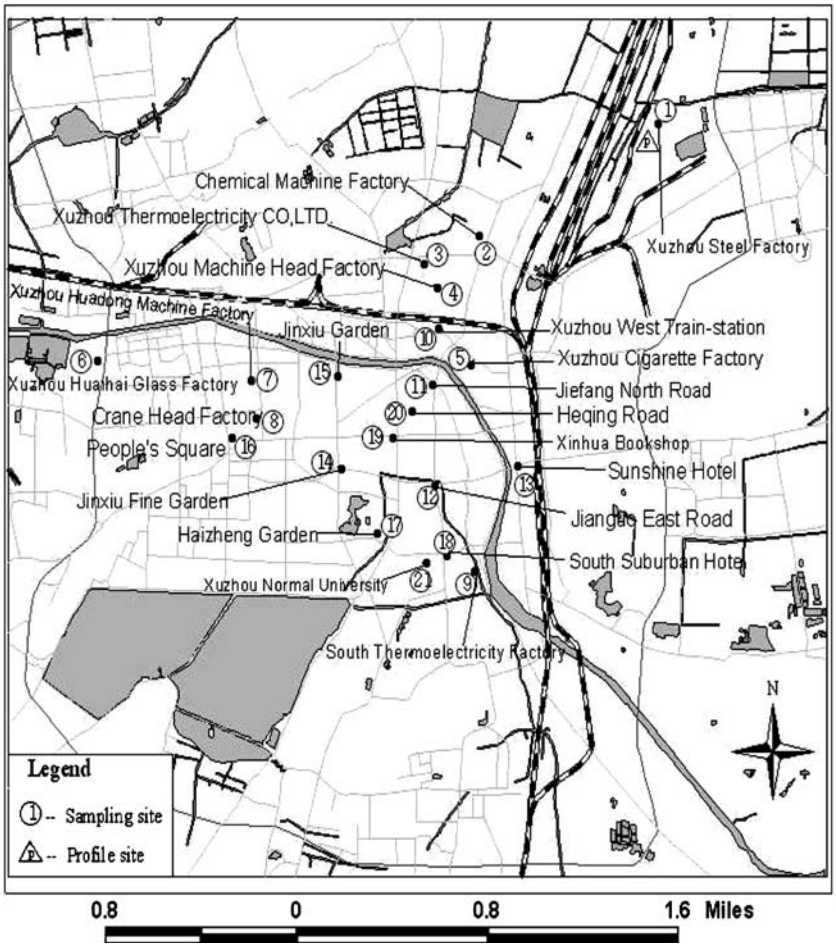

Fig. 1 Map of the Xuzhou city with location of sampling sites of soils

mental Monitoring General Station), reagent blanks and duplicated soil samples (approximately 10 of the total number of soil samples were used for this purpose) randomly selected from the set of available samples were used to assess contamination and precision. The analytical precision, measured as relative standard deviation, was routinely between 5 and 6%, and never higher than 10%.

Results and discussion

Relationship between iron and heavy metals

Fe oxides, extracted using *DCB* buffer, consist usually of hematite (Fe_2O_3), goethite (α-FeOOH), lepidocrocite (γ-FeOOH) and others. These iron oxides can adsorb some heavy metal ions and accordingly control their activities and transport in soils to a certain extent. Figure 2 shows that significant positive correlations are observed between Pb, Zn, Cu, Se, Ag, Ba and Fe_{DCB} while weak correlation is observed between Cr and Fe_{DCB}. This difference may result from different anthropogenic sources for heavy metals studied. Previous researches have shown that the heavy metals (Pb, Zn, Cu, Se, Ba, Ag and Ni) are mainly derived from traffic emissions while Cr is derived from coal burning in the studied areas (Wang et al. 2005). From another point of view, the significant correlation between heavy metals and Fe_{DCB} also indicates that these heavy metals may mainly enrich the surface of Fe oxides while Cr may also be associated with other constituents of the soils. As far as Pb, Cu and Zn are concerned, the correlation of Pb against Fe_{DCB} is more significant than that of Cu and Zn, indicating iron oxides have a particularly strong affinity for Pb adsorption. This is in accordance with the result obtained by Brümmer (1986).

Relationship between fulvic acids and heavy metals

Fulvic acids are more soluble than humic acids, tending to be removed from solution via precipitation with acids and polyvalent cations (Rieuwerts et al. 1998). These soluble fulvic acids may either remain in solution having a low affinity for the adsorbent or

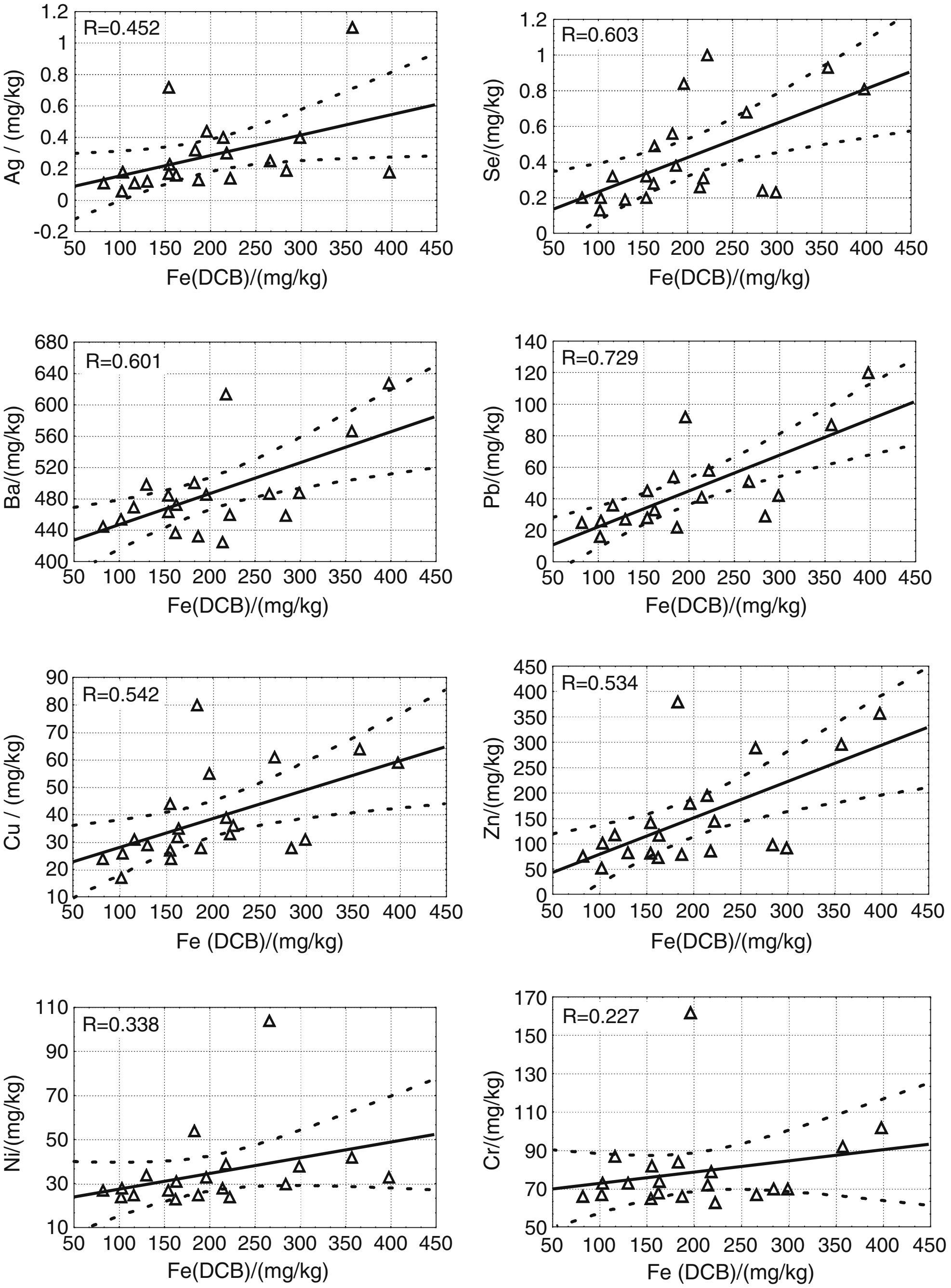

Fig. 2 Scatter plots between heavy metals (mg/kg) and $\mathrm{Fe_{DCB}}$ (mg/kg)

become adsorbed to the adsorbent (e.g., clays and Fe and Mn oxides). Figure 3 shows that there is significant correlation between the contents of fulvic acids and $\mathrm{Fe_{DCB}}$, indicating fulvic acids in the soils are probably adsorbed onto the surfaces of iron oxides. On the other hand, organic ligands on fulvic acids behave as soft Lewis bases, while metals are soft acids and consequently they tend to form complexes. As we all know, metal salts of fulvic acids are readily soluble and that this component may be a major factor in the mobilization of heavy metals in soils. The fact that significant correlations exist between heavy metals and fulvic acids is indicative of complexation between them. Such finding is of importance with regard to the increased mobilization of heavy metals, e.g., into freshwater ecosystem. As far as Pb, Cu and Zn are concerned, correlation of Cu against fulvic acids is more significant than that of Pb and Zn, showing that copper ions in the soil solutions can form more stable complexes than lead and zinc ions. This is in agreement with the previous researches (Rieuwerts et al. 1998).

Fig. 3 Scatter plots between heavy metals (mg/kg) and fulvic acid (%)

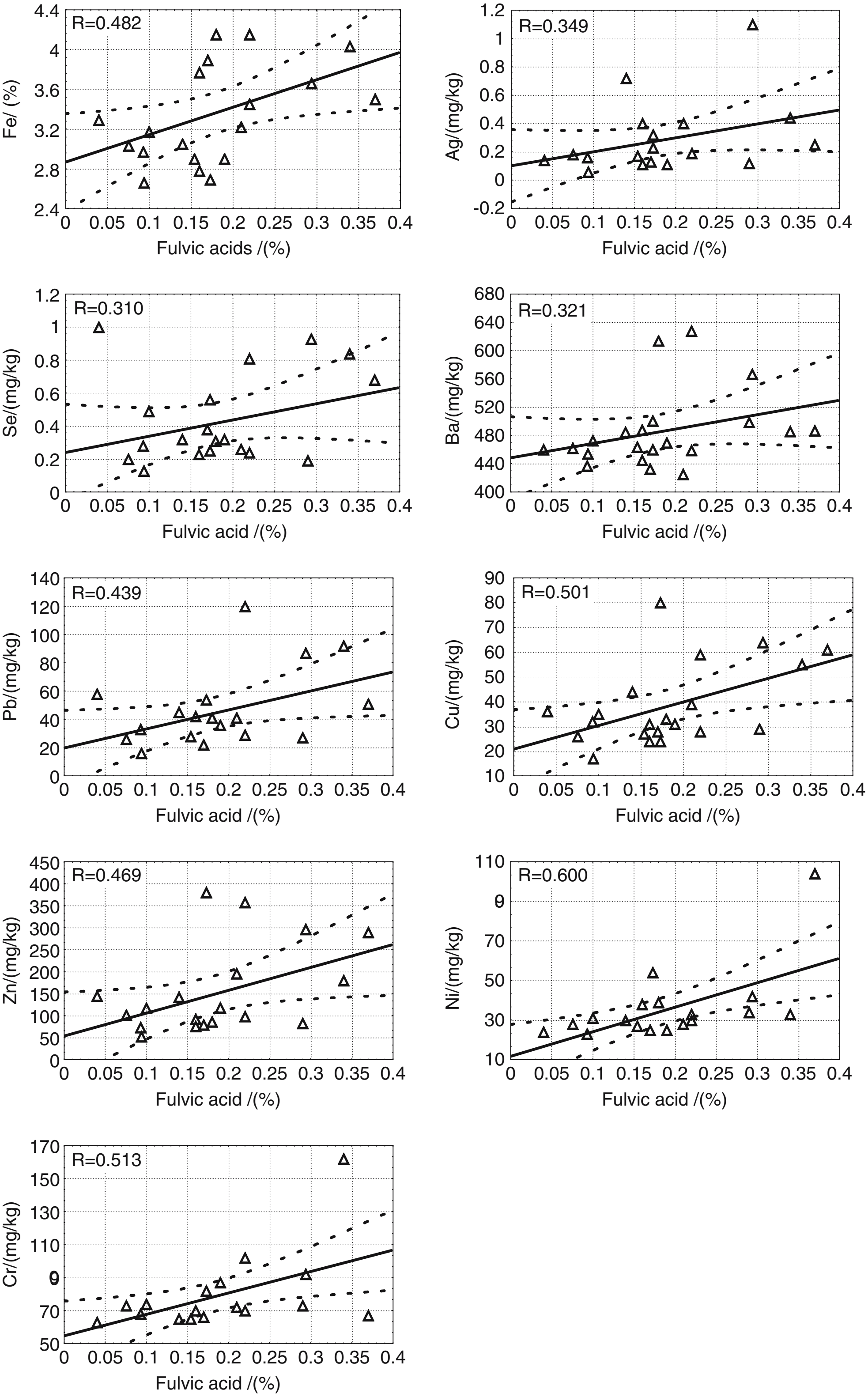

Table 1 Pearson correlation coefficients between particle size fractions and heavy metals

Particle size (μm)	Ag	Se	Ba	Pb	Cu	Zn	Ni	Cr
< 2	0.13	–0.068	0.562**	0.280	0.246	0.141	0.294	0.006
2–4	0.009	–0.031	0.580**	0.284	0.263	0.164	0.371	0.004
4–8	0.034	0.046	0.566**	0.367	0.371	0.286	0.403	0.016
8–16	–0.006	0.044	0.471*	0.342	0.335	0.267	0.412	–0.026
16–32	0.005	–0.207	0.225	–0.043	–0.014	–0.111	0.159	–0.147
>32	0.043	0.013	–0.599*	–0.319	–0.167	–0.100	–0.241	–0.006
< 4	0.011	–0.052	0.572**	0.282	0.254	–0.152	0.329	0.005
< 8	–0.052	–0.058	0.554**	0.277	0.236	0.159	0.354	–0.003
< 16	–0.107	–0.048	0.527**	0.276	0.235	0.176	0.374	–0.018
< 32	–0.240	–0.102	0.273	0.182	0.135	0.114	0.299	–0.063

*Significant correlation at 0.05 levels and **significant correlation at 0.01 levels

Relationship between particle size fractions and heavy metals

The relationships between particle size fractions and heavy metals are shown in Table 1. As far as Ag and Se are concerned, no correlations are found for all particle size fractions and this may be due to the low concentrations for these two metals in the studied soils. Ba, Pb, Cu, Zn and Ni are mainly enriched in finer soil particle sizes (especially <16 μm). Such pattern is usually attributed to the exponential increase in specific surface area and concomitant increase in the proportion of reactive substrates (Sutherland 2003). In case of Cr, no significant correlation is observed, but reasonable interpretation is not obtained.

Conclusions

The relationships between heavy metals (Pb, Cu, Zn, Se, Ag, Ba, Ni, Cr) and iron oxides, fulvic acids as well as particle size fractions were examined from the Xuzhou urban roadside soils. The main conclusions derived from this study are: (1) significant correlations exist between Fe_{DCB} and heavy metals except for Cr because of different anthropogenic sources; (2) fulvic acids in the soils are mainly adsorbed onto the surfaces of iron oxides and form stable complexes with heavy metals (especially Cu, Cr and Ni), showing that these heavy metals can be readily desorbed into freshwater ecosystems; (3) Pb, Cu, Zn, Ba and Ag are principally enriched in finer soil particles while Se, Ag and Cr are independent of particle size fractions in the studied soils.

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