

Speciation of heavy metals in garden soils: evidences from selective and sequential chemical leaching

Zhongqi Cheng · Leda Lee · Sara Dayan ·
Michael Grinshtein · Richard Shaw

Received: 12 April 2010 / Accepted: 2 March 2011 / Published online: 25 March 2011
© Springer-Verlag 2011

Abstract

Purpose Gardening (especially food growing) in urban areas is becoming popular, but urban soils are often very contaminated for historical reasons. There is lack of sufficient information as to the bioavailability of soil heavy metals to plants and human in urban environments. This study examines the relative leachability of Cr, Ni, As, Cd, Zn, and Pb for soils with varying characteristics. The speciation and mobility of these metals can be qualitatively inferred from the leaching experiments. The goal is to use the data to shed some light on their bioavailability to plant and human, as well as the basis for soil remediation.

Materials and methods Selective and sequential chemical leaching methods were both used to evaluate the speciation of Cr, Ni, As, Cd, Zn, and Pb in soil samples collected from New York City residential and community gardens. The sequential leaching experiment followed a standard BCR four-step procedure, while selective leaching involved seven different chemical extractants.

Responsible editor: Jean Louis Morel

Electronic supplementary material The online version of this article (doi:10.1007/s11368-011-0351-6) contains supplementary material, which is available to authorized users.

Z. Cheng (✉) · L. Lee · S. Dayan · M. Grinshtein
Environmental Sciences Analytical Center, Department of Earth
and Environmental Sciences, Brooklyn College of The City
University of New York,
Brooklyn, NY 11210, USA
e-mail: zcheng@brooklyn.cuny.edu

R. Shaw
USDA-NRCS NYC Soil Survey,
1000 South Ave,
Staten Island, NY 10314, USA

Results and discussion The results from selective and sequential leaching methods are consistent. In general, very little of the heavy metals were found in the easily soluble or exchangeable fractions. Larger fractions of Cd and Zn can be leached out than other metals. Lead appears predominantly in the organic or carbonate fractions, of which ~30–60% is in the easily soluble organic fraction. Most As cannot be leached out by any of the extractants used, but it could have been complicated by the ineffective dissolution of oxides by ammonium hydroxylamine. Ni and Cr were mostly in the residual fractions but some released in the oxidizable fractions. Therefore, the leachability of metals follow the order Cd/Zn > Pb > Ni/Cr.

Conclusions Despite of the controversy and inaccuracy surrounding chemical leaching methods for the speciation of metals, chemical leaching data provide important, general, and easy-to-access information on the mobility of heavy metals in soils, which in turn relates to their potential bioavailability to plant uptake and human health risk. Such data can be used to guide risk assessment of different metals and develop effective remediation strategies.

Keywords Chemical leaching · Garden soil · Heavy metals · Speciation

1 Introduction

Soil is known as one of the most important biogeochemical sinks for contaminants. Urban soils can often contain dangerous levels of heavy metals, posing significant health risks if not properly dealt with. For example, preliminary survey in New York City based on about 250 garden soil

samples yielded a median Pb concentration of 550 ppm (Cheng and Shaw 2009), significantly higher than the 400 ppm limit set by the United States Environmental Protection Agency for children's play areas (USEPA, Toxic Substances Control Act Section 403).

There is renewed interest in cultivating the small patches of lands in urban settings for food, as the society is moving to achieve a more sustainable urban environment and a greener economy. Growing vegetables and fruits in residential backyards and community gardens not only produces much needed food, but also brings many aspects of social, economical, health, and cultural benefits that cannot be undervalued. These efforts are vital in helping municipalities build local food systems to reduce reliance on the long, fossil fuel-dependent supply lines stretching from centralized farms to local supermarkets. However, gardening activities increase human's contact with contaminants in the soil, therefore the health risks need to be better understood. Studies have shown that urban soils can be an important pathway for heavy metal exposure (e.g., Mielke and Reagan 1998; Mielke et al. 1999). In many cases, children, who are among the group highly sensitive to contamination, are encouraged to participate in gardening activities. This has added to the urgency to understand the link between soil contamination and associated risks in urban settings.

Identification of the chemical forms, or namely speciation, of heavy metals in soils is the first step in assessing their mobility, bioavailability to plants, as well as toxicity to animals and human. It is generally known that the total concentration of a metal is not a good indicator of its health risk. The risk only exists if the contaminant enters the body via one of the exposure pathways, such as ingestion and inhalation. The degree to which a metal can be uptake by plants or absorbed by human body is dependent upon many factors, and one of the most important controls is the phase (s) where the metal resides. Metals reside in different phases and vary in potential to be mobilized. Speciation can be inferred by sequential extraction of the soil with chemical reagents designed to extract the elements bound in, or associated with, a particular soil phase (Kaplan and Yaman 2009). Sequential extraction can be time and labor intensive, often requires several days to complete a sequence. By comparison, selective extractions are simple and cost-effective methods for the investigation of labile metals in soils. Although the selectivity of a certain reagent is limited, many types of reagents can be used and the results can be integrated to derive more detailed speciation information.

It is generally recognized that the ability of chemical leaching methods to predict soil heavy metal speciation is limited. For urban soils in particular, many phases in soils are anthropogenic and therefore may not behave similarly

to naturally present minerals or components. The chemicals often attack several phases to various degrees rather than being "selective." The leaching rates of metals are dependent upon time duration of leaching, soil to extractant ratio, particle size, and whether equilibration has been reached. In some cases, re-adsorption and precipitation of the metals can even lead to false conclusions (Nirel and Morel 1990; Scheckel et al. 2003). Many new techniques have been developed in recent years that allow better and more accurate understandings of the speciation of metals in soil, mostly using instrumental methods for phase characterization in soil (D'Amore et al. 2005; Rao et al. 2008). These methods have advantages of identifying exact mineral phases where the heavy metals reside, and can be compared to chemical leaching to reach more precise conclusions on metal speciation. However, better metal speciation results still do not directly lead to better bioavailability or bioaccessibility predictions. In fact, chemical leaching may be a better predictor for bioavailability because it is applied to bulk soil and reflecting the overall leaching rate from multiple phases, which is closer to real world situations. For human health risk assessments, *in vitro* and *in vivo* experiments are commonly used. For plant uptake, a new approach using "Diffusive Gradient in Thin Film" was developed for *in situ* direct measurements. In addition, Sinaj et al. (2004) used isotopic technique to quantify and compare Zn that can be leached by various chemicals (*E* values) to actual plant uptake (*L* values). Echevarria et al. (1998) used isotopic exchange kinetics to study the pool of Ni in soil that was phytoavailable.

Despite of the obvious shortcomings and pitfalls associated with some chemical leaching techniques for metal speciation, they are easy to perform, affordable, and have been widely used to assess the mobility of metal contaminants in soils and sediments (e.g., Gomez et al. 2000; Joksi et al. 2005; Maiz et al. 1997). One of the most commonly used sequential extraction procedures is the BCR (Community Bureau of Reference of the European Commission, now the Standards, Measuring and Testing Programme) method. The BCR procedure aims to fractionate metals into the operationally defined phases of acid-extractable, reducible, oxidizable, and residual, with each of the steps targeting metals in different phases (Table 1). This procedure has been tested against reference standards and several different matrices (e.g., Sutherland and Tack 2003; Larner et al. 2006).

This study combines selective and sequential chemical leaching techniques to investigate the speciation of heavy metals in garden soils collected from the New York City area. For historical reasons, multiple sources have contributed to the soil heavy metal contamination in New York City, adding complications to metal distributions in different phases. We used the original BCR procedure for the

Table 1 Comparison of sequential and selective leaching and their respective fractions

Fractions	Sequential leaching	Selective leaching
Exchangeable and weakly absorbed fractions Carbonate fraction	Step I (0.11 M acetic acid)	1.0 M KNO ₃ for exchangeable and weakly absorbed fractions 1.0 M ammonium acetate, pH=4.8; or 1.0 M CH ₃ COOH for carbonate, exchangeable, and weakly absorbed fractions
Oxide/reducible fraction	Step II (0.1 M NH ₂ OHHCl, pH=2)	0.04 M NH ₂ OHHCl for Mn oxide fraction (and some carbonate) 1.0 M NH ₂ OHHCl for Fe oxide fraction (and some carbonate)
Organic fraction	Step III (8.8 M H ₂ O ₂ then 1 M NH ₄ Ac at pH=2, for organic and oxidizable fractions)	0.1 M Na ₂ EDTA for organic (and some carbonate?) bound fractions 0.2 M Na ₄ P ₂ O ₇ for easily soluble organic bound and exchangeable fractions

sequential leaching of eight soil samples of different types, and seven reagents for the selective leaching of 16 samples. The results from selective leaching and sequential leaching are compared. The data is intended to provide general insights into the speciation and mobility of these heavy metals in garden soils. Implications on plant and human bioavailability, as well as soil remediation strategies are also discussed.

2 Methods

The soil samples used in this study were selected from a collection of about 250 garden soil samples deposited at the Environmental Sciences Analytical Center (ESAC) at Brooklyn College. These soil samples represent a range of physical and chemical properties ([Electronic Supplementary Material](#)) that occur in urban garden soils. The pH, organic content, and salt content ranged 5.1–7.0, 3.2–14%, and 41–627 ppm, respectively. The soils are mainly loamy sand and sand. In general, those with higher Pb content were selected, with total Pb concentrations ranged from 423 to 2,586 ppm. Other metal concentrations in the studied soil samples are given in [Supplementary Information](#).

These soil samples were sent to ESAC by gardeners from the New York City area intended for heavy metal screening. The samples were collected from surface to up to 25–30 cm (i.e., 6–8 in.) depth. The gardeners were instructed to collect soil from several locations spread within each garden, thoroughly mix them, and remove stones and plant fragments, before packing about 200–300 g into plastic bags and sending it to the lab for soil testing. The samples were air dried and briefly disaggregated, without further grounding or sieving before being used for selective and sequential leaching experiments.

2.1 Sequential extraction

A subset of eight samples was subject to sequential extraction, using a slightly modified four-step procedure recommended by BCR (European Commission 1997).

1. *Exchangeable and carbonate fractions.* Approximately 5 g of each soil was put into 50 mL centrifuge tubes, into which 40 mL of 0.11 M acetic acid solution was added. The centrifuge tubes were tightly capped, laid on their sides and agitated on the shaker at room temperature for 16 h, followed by centrifugation. About 10 mL of the supernatant was saved for analysis by an Inductively Coupled Plasma Mass Spectrometer (ICP-MS); the remaining solution was carefully poured off and was discarded. About 20 mL of deionized water was then added to the tube and shaken for ~20 min, followed by centrifugation. Again about 10 mL of supernatant was saved and the remaining supernatant was carefully decanted.
2. *Reducible fractions.* Forty milliliters of a 0.1-M hydroxylammonium chloride solution (pH adjusted to 2.0 with HCl) was added to the tubes with residual samples and shaken at room temperature for ~17 h. The samples were centrifuged and 10 mL of the leachate was saved for ICP-MS analysis and the remaining supernatant discarded. The samples were then washed with 30 mL of deionized water followed by centrifugation. Again 10 mL of supernatant was saved and the remaining supernatant discarded.
3. *Oxidizable and organic fractions.* A total of 30 mL of 30% hydrogen peroxide was used for each sample to flush the samples from the 50 mL centrifuge tubes into Teflon beakers. The samples were then left at room temperature, uncovered, for about 10 min before being

placed into an 80°C water bath to evaporate to dryness. The evaporation process took approximately 2.5–3 h. Then 50 mL of the 1.0 M ammonium acetate solution was used to flush the dried residue from the glass beakers into 50 mL centrifuge tubes. The samples were then left for about 16 h and were agitated briefly prior to centrifugation. Then 10 mL of supernatant was saved for ICP-MS analysis and the rest discarded. Each sample residue was agitated with 20 mL of deionized water and centrifuged, and 10 mL of supernatant was saved and the remaining supernatant decanted.

4. **Residual fraction.** Twenty milliliters of a 1:1 solution of 15.8 M nitric acid and 30% hydrogen peroxide solution was used to rinse the samples into glass beakers and the beakers were put on a hotplate to evaporate. The temperature of the hotplate started at 65°C and eventually increased to 185°C. Twenty milliliters of 1.0 M HNO₃ solution was added to the dried residue and used to wash any remaining material into 50 mL centrifuge tubes from which a 1-mL aliquot was centrifuged. Then 50 µL of the supernatant was diluted for ICP-MS analysis.

2.2 Selective leaching

A total of 16 samples were selected for the selective leaching experiments. Among them, four were different size fractions (<120 µm, 120–250 µm, 250–500 µm, and 0.5–2 mm) of the same soil sample (S0609-40). The selective extracts were obtained by shaking 1.0 g of soil sample with 5.0 mL of different reagents separately. Seven different leaching solutions were used: (1) 1.0 M KNO₃; (2) 0.04 M NH₂OH·HCl solution; (3) 1.0 M NH₂OH·HCl solution; (4) 0.1 M Na-EDTA; (5) 1.0 M acetic acid; (6) 0.2 M sodium pyrophosphate; and (7) ammonium acetate with pH adjusted to 4.8. The target phases of these reagents are listed in Table 1.

The mixtures of soil sample and extracting agent were placed in 25 mL scintillation vials, tightly capped and placed on a shaker for 4–5 h. This time duration for equilibration was chosen because in previous experiments we observed that the leaching rates of metals from soils by 10% HCl were dependent upon time of equilibration. The equilibrium appeared to be reached by 4 h. A 1-mL aliquot was then taken from each vial, centrifuged, and 0.1 mL of the supernatant was then diluted for metal concentration determination.

2.3 Total heavy metal analysis for soil samples

The total heavy metal concentrations of soil samples were measured using an acid digestion method (adapted from US

EPA Method 3050B) followed by ICP-MS determination (US EPA Method 6020A). Soil samples were first dried at 105°C, ground in a mortar, and passed through a 2-mm sieve. The samples were then digested using mixed acids (HNO₃–HF–HCl) in Teflon vessels on hotplate. A small aliquot of the digest was centrifuged and the supernatant was diluted for ICP-MS analysis. Standard Reference Material NIST-2702 (inorganic marine sediment) was used for external quality control.

2.4 ICP-MS determination

For leachates and digested samples, a Perkin Elmer Dynamic Reaction Cell Inductively Coupled Plasma Mass Spectrometer was used to measure the concentrations of Pb, As, Cr, Ni, Cd, Zn, Fe, and Mn. An internal standard element Ge was used to correct for instrument drift.

3 Results and discussion

A comparison of the sequential and selective leaching methods and their respective target fractions are given in Table 1 to aid in the results presentation and discussion. For each metal, the percent of recovery is calculated relative to the amount in the air-dried soil sample. For sequential leaching, a comparison of recovery rates for different metals and different leaching steps are illustrated in Fig. 1, where the mean and 1-σ standard deviation of eight samples are presented. For selective leaching, such comparisons are tabulated in Table 2 where the mean of recovery rates for all 16 samples are shown, and in Fig. 2 where boxplots of recovery rates are used to illustrate the

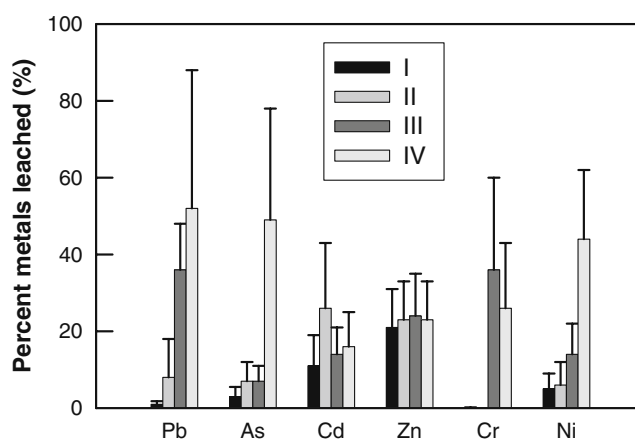


Fig. 1 Mean percentage of heavy metals that can be leached during the four-step sequential leaching. The mean was based on the eight samples, with one standard deviation also indicated on the plot. For each element, the four bars from left to right correspond to leaching rates of the four sequential leaching steps in the modified BCR method

Table 2 Mean recovery rate (%) of heavy metals by selective leaching of different reagents

Fractions	Pb	As	Cd	Cr	Ni	Zn
1.0 M KNO ₃	0.4	0.4	3	0.5	1.0	2.0
0.04 M NH ₂ OH·HCl	0.1	0.8	4	0.1	0.8	2.3
1.0 M NH ₂ OH·HCl solution	11	7	37	0.6	4	16
0.1 M Na-EDTA	72	17	49	7	12	33
1.0 M acetic acid	33	3	28	9	4	19
0.2 M sodium pyrophosphate	23	14	26	8	5	20
1.0 M ammonium acetate (pH adjusted to 4.8)	4	3	21	3	6	21

variations among samples. Significant variations exist among samples, different metals, as well as different leaching solutions and sequential extraction steps.

Finer fractions of the same soil contain higher contents of studied metals (Table 3 and [Electronic Supplementary Material](#)). It is interesting that, based on the results from the four-step sequential leaching experiment, Pb recovery rates are lower for the finer fractions (Table 3). Trends for other metals, however, are not clear ([Electronic Supplementary Material](#)). Lead has its unique anthropogenic sources (e.g., gasoline Pb, paint Pb) that could have contributed to the

different leaching behavior than other metals. Madrid et al. (2008) observed higher metal availability (extraction with EDTA) for the clay fraction than the whole soil, while this is not the case for bioaccessibility (SBET extraction).

3.1 Exchangeable or weakly absorbed fractions

The readily exchangeable fraction, also known as non-specifically adsorbed fraction, can be released by equilibrating with cations such as K⁺, Ca²⁺, Mg²⁺, and NH₄⁺ that displace the metals weakly bound electrostatically on

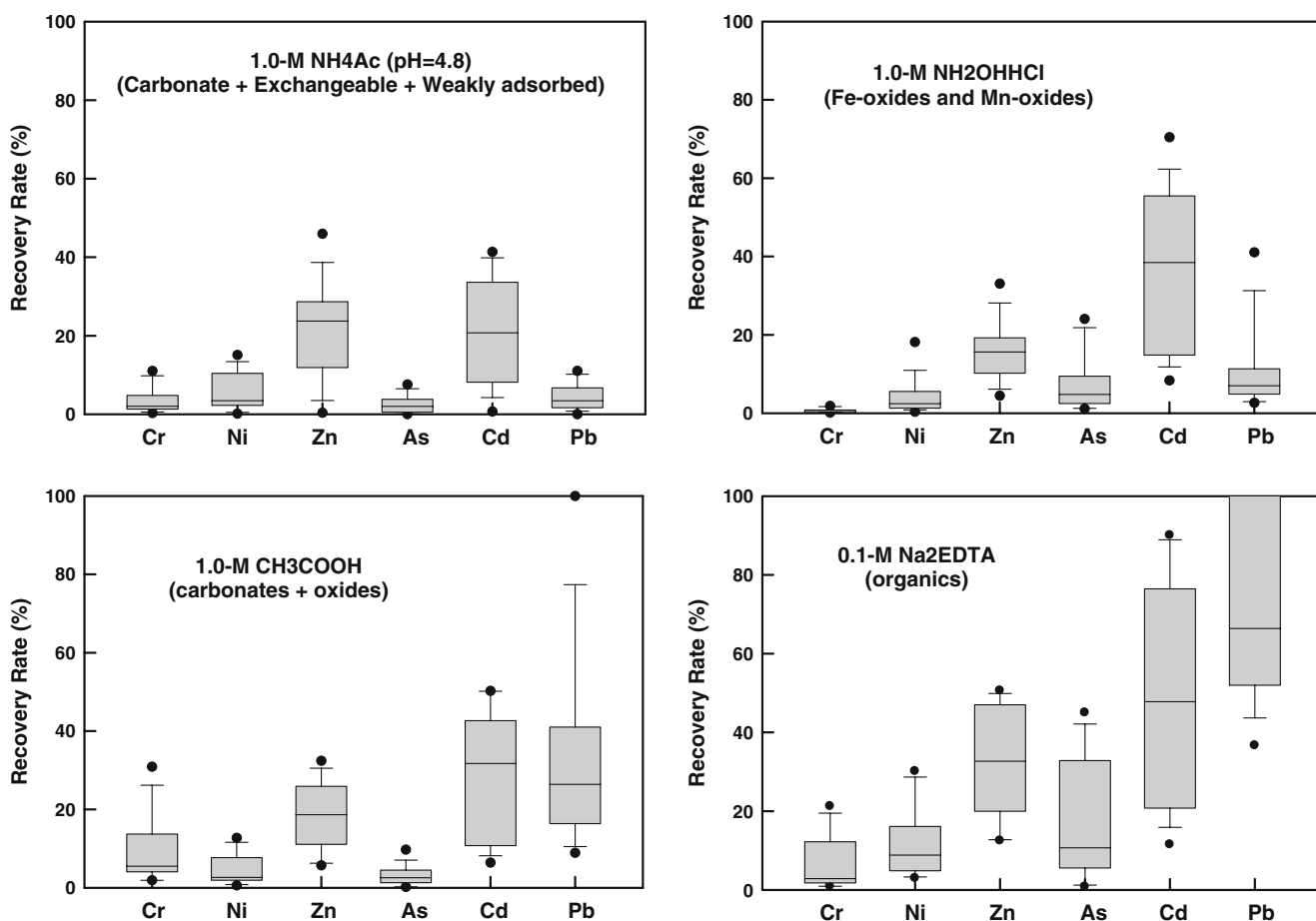


Fig. 2 Box plots of metal recovery rates for Cr, Ni, Zn, As, Cd, and Pb. The lines inside the boxes are mean values, and the lower and upper boundaries of the box indicate 25 and 75 percentile of the sample size ($n=16$)

Table 3 Comparison of Pb recovery rates during the four-step sequential leaching experiment for the four size fraction of the same soil sample

Sample ID	Soil fractions	TOC (%)	Total Pb (ppm)	Step 1 (%)	Step 2 (%)	Step 3 (%)	Residual (%)
S0609-40A	<120 μm	14	2,586	0.5	1.1	25	74
S0609-40B	120–250 μm	13	2,009	0.7	3.5	30	66
S0609-40C	250–500 μm	8.6	1,189	1.5	16.0	46	37
S0609-40D	0.5–2 mm	4.5	1,915	2.1	13.0	44	42

Soil pH is 6.7, salt content is 239 ppm

organic or inorganic sites (Rao et al. 2008). In the current selective leaching experiment this fraction is estimated by the 1 M KNO_3 solution. The mean percentages of metal in this fraction are below 1% for all metals except for Cd and Zn, which are still no more than 3% (see Table 2). It should be noted that the mean for Cd and Zn are biased by three samples that showed exchangeable or weakly absorbed fractions as high as 15%, while for most other samples these values are below 1%.

3.2 Carbonate fraction

The carbonate phase is a loosely bound phase and liable to change with environmental conditions, in particular to low pH. The time required for complete dissolution of carbonates depends on several factors such as particle size and type and amount of carbonate in the sample. According to the BCR scheme, the first step of sequential leaching used a weak acetic acid at 0.11 M for 16 h to dissolve the carbonate and liberate the metals bound in this mineral. The measured concentrations in leaching solutions should be a combination of carbonate fraction and the exchangeable and weakly absorbed fractions (see Table 1). Nevertheless, the metal fractions that can be leached by 0.11 M acetic acid are small (<5% on average), with the exception to Cd (11%) and Zn (21%). In selective leaching, 1 M ammonium acetate (pH adjusted to 4.8) and 1.0 M acetic acid were both used to evaluate the fractions of carbonate-bound metals in soil samples. The results from ammonium acetate leaching are consistent with what is found with 0.11 M acetic acid (see Table 2 and Fig. 2). However, with the 1 M acetic acid much larger fractions of Pb (9–100%) are released into the solution. Stronger acidity might have leached out metals from other fractions such as oxides, but it is also likely that the weaker acetic acid did not dissolve all the carbonates. In urban environment some soils can contain significant amount of carbonates (e.g., cement from construction debris). In weaker acids the dissolution rates of some carbonates can be very slow, and these carbonates can contain significant amount of Pb. Several other studies also found low recovery rates using ammonium acetate and acetic acid (e.g., Kaplan and Yaman 2009; Larner et al. 2006).

3.3 Reducible fraction (Fe or Mn hydroxides)

The acidified NH_2OHHCl (i.e., ammonium hydroxylamine hydrochloride) solution at high concentrations releases the metals from Mn and Fe oxides (Rao et al. 2008). The amorphous oxyhydroxides of Fe and Mn strongly absorb trace elements, initially in exchangeable forms, but with time are increasingly transformed to less mobile, specifically absorbed forms. The original BCR method used a 0.1 M hydroxylammonium chloride at pH=2 (as was used for the sequential leaching in this study). However, it was argued that such dilute NH_2OHHCl (0.1 M) only releases metals from Mn oxide phases with little attack on Fe oxide phases. The optimized BCR method increased the hydroxylamine chloride concentration to 0.5 M and decreased the pH to 1.5. For selective leaching, we used a 1-M NH_2OHHCl to release metal fractions on the amorphous Fe oxide phase. It should be noted that the low pH of NH_2OHHCl leaching solutions could also lead to the dissolution of carbonate phases in soil, thereby releasing metals in the carbonate fraction.

The results from sequential leaching of urban garden soils indicate that heavy metals associated with the Mn oxide phases are relatively small, with the exception of Cd (19–46%) and Zn (12–35%; see Fig. 1). This is consistent with what is observed for selective leaching with 0.04 M NH_2OHHCl (see Table 2). Increasing the NH_2OHHCl concentration to 1 M significantly increased the amount of metals released into solution, especially for Pb (11%) and As (7%; see Table 2 and Fig. 2). This suggests that there is an appreciable fraction bound to amorphous Fe oxides.

In the sequential leaching, little Fe was released into the solution (<4% of total soil Fe for all samples, with an average of 1.7%) in comparison to the much higher fraction of Mn being released (45–59%). In the selective leaching experiment, similar observations can be made where 0.04 M solution released little Fe (0.1%) and on average only 10% of Mn. In comparison, the 1 M NH_2OHHCl solution released on average 3% of Fe and 21–60% of Mn (Fig. 3). In both cases the low percentages of Fe released into the liquid phase suggest that the majority of Fe in the soil is not in the easily reducible amorphous state. The efficiency of Fe and Mn extractions by different concen-

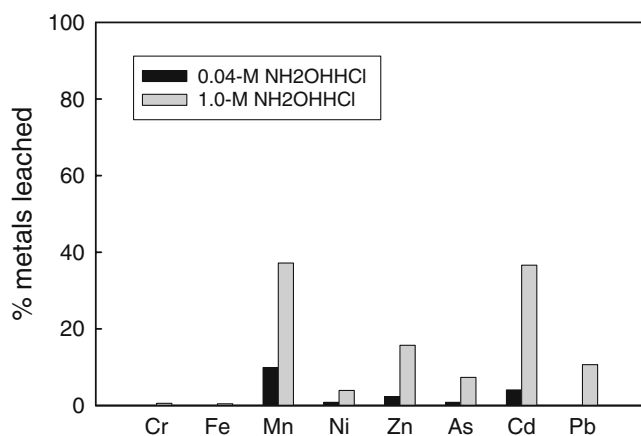


Fig. 3 Comparison of the fraction of metals that resides with Mn and Fe oxides. Theoretically, the weaker hydroxylamine solution (0.04 M) will dissolve the amorphous Mn oxide phases, while the more concentrated reagent (1.0 M) will attack also the Fe oxide fraction

trations of NH_2OHHCl is a measurement of how different oxide phases are dissolved—which probably controls the release of other metals associated with the oxides. There was some question about the consistency of hydroxylamine for the dissolution of Fe. Davidson et al. (2004) showed that while ammonium oxalate offers superior dissolution of iron-containing matrix components, it should not be used if calcium or lead concentrations are to be measured due to rapid precipitation of oxalates from solution.

3.4 Organic-bound fraction

The organic fraction released in the oxidizable step of the sequential extraction is not considered as mobile or available since it is thought to be associated with stable high molecular weight humic substances that release small amounts of metals in a slow matter. The sulfide phase can also be oxidized and release heavy metals in its mineral structure. It can be observed that during this step significant amounts of Pb, Cr, and Ni are released, with mean fractions at 36%, 36%, and 14%, respectively (see Figs. 1 and 2).

A 0.1-M Na-EDTA solution was also used to evaluate the organic-bound metal fractions (see Table 1). EDTA can displace metals from insoluble organic and organometallic complexes in addition to those absorbed on inorganic soil components because of its strong complexing ability (Kaplan and Yaman 2009). Metals in carbonate fractions can potentially be displaced as well. In addition to Cd and Zn, a high percentage of Pb (average 72%) is extracted by Na-EDTA. Appreciable amounts of As (17%), Ni (12%), and Cr (7%) were also leached out (see Table 2 and Fig. 2).

An alternative approach uses sodium or potassium pyrophosphate (0.1 M at pH=10) to disperse colloidal organic material by complexing the flocculating Ca, Al, or Fe cations. This fraction is more selective for the easily

soluble organic fraction, metals associated with humic and fulvic acids (Kaplan and Yaman 2009). Figures 4 and 5 compare the fractions of Pb, Cd, and Zn that can be leached out by 0.1 M EDTA and those with 0.2 M $\text{Na}_2\text{P}_4\text{O}_7$. Good correlations are observed for all three metals. Judging by the linear relationships, 30–60% of organic and carbonate-bound Pb is in the easily soluble organic fraction, while for Cd and Zn this fraction is about 50%.

3.5 Comparison of mobility for different metals

Lead is rather immobile in natural conditions considering the fact that little Pb can be found in the exchangeable or weakly absorbed form. Most of the Pb can be extracted by Na-EDTA (37–100%), which suggests the dominance of organic- and/or carbonate-bound fractions. The fact that a large percentage of Pb is complexed by organics is confirmed by the large amounts of Pb released (22–46%) during the oxidizable step (Step III, see Table 1) of sequential leaching, where organics were oxidized by H_2O_2 and Pb was subsequently displaced by NH_4Ac . Denys et al. (2007) suggest that in high carbonate samples a significant fraction of Pb could be associated with the sulfur compartment, and this fraction can be released in the oxidizable step as well. The carbonate fraction of Pb appears to be small based on the leaching with 0.1 M acetic acid or ammonium acetate (pH=4.8). But as discussed earlier the carbonate content of soils can vary greatly, thereby stronger acids and longer time may be required to obtain accurate assessment.

More than 85% of arsenic was left in the residual fraction during sequential leaching. Similarly, only Na-EDTA and $\text{Na}_4\text{P}_2\text{O}_7$ solutions can extract more than 10% of As. Arsenic is the only oxyanion in the list of metals

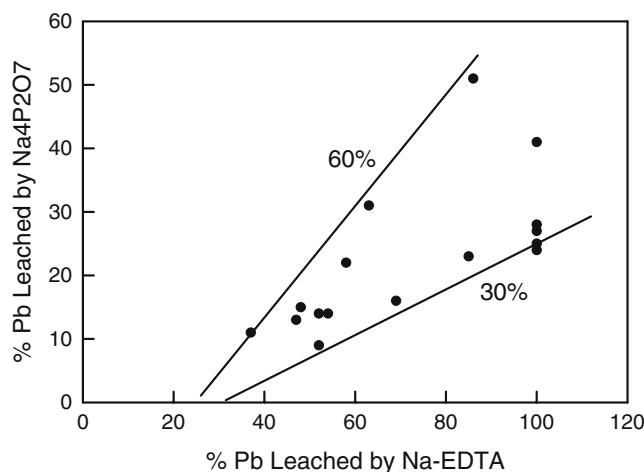


Fig. 4 Comparison of %Pb that can be leached out by 0.2 M Na-EDTA solution (corresponds to organic fraction and carbonate fraction) and that by 0.2 M $\text{Na}_4\text{P}_2\text{O}_7$ solution (corresponds to easily soluble organic fraction and exchangeable fraction)

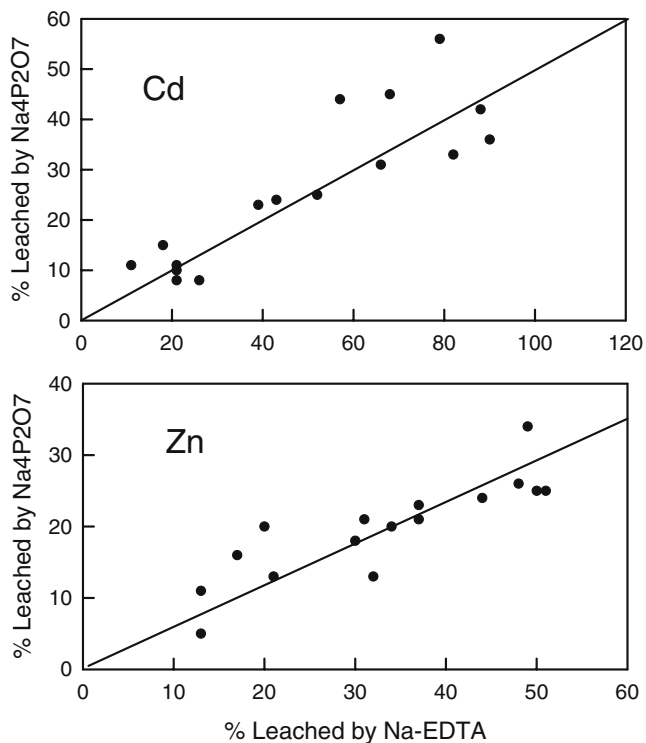


Fig. 5 Comparison of %Cd and %Zn that can be leached out by 0.2 M Na–EDTA solution (corresponds to organic fraction and carbonate fraction) and that by 0.2 M Na₄P₂O₇ solution (corresponds to easily soluble organic fraction and exchangeable fraction)

examined in this study. Wenzel et al. (2001) also showed that NH₄NO₃, NaOAc, NH₂OH·HCl, and EDTA were not effective in extracting As from urban soils. Instead, a 0.2-M ammonium oxalate solution (pH=3.25) was used to dissolve amorphous and poorly crystalline Fe and Al oxides, while the same solution combined with ascorbic acid was used to dissolve the crystalline Fe and Al oxide phases. Their results showed that recovery of As from these two sequential leaching steps were ~40% and ~30%, respectively. Arsenate is very similar to phosphate in terms of chemical properties; therefore it is strongly bound to Fe, Mn, or Al oxides and cannot be displaced by nitrate, acetate, or EDTA. The majority of As can only be released when the oxides are dissolved. The relatively poor ability of NH₂OH·HCl solution for dissolving Fe and Mn oxides (as discussed earlier) lead to the low recovery of As. Nevertheless, Fe, Mn, and Al oxides are known to be a sink for arsenate and arsenite, the two most common inorganic As forms. In reducing environments As tends to be mobilized and transported by groundwater. It should also be noted that one of the main sources for As is from pesticide application, where As is often in the form of lead arsenate. Lead arsenate is a very stable compound, where As likely will not be leached by any of the above chemical solutions.

Much higher fractions of Cd and Zn are readily available for ion exchange in comparison to other metals (see Fig. 1

and Table 2). Cd and Zn appear to be more evenly distributed among carbonate, organic, and oxide fractions. Half of the Na–EDTA extractable Cd and Zn are easily soluble or exchangeable, suggesting relative high mobility for these two metals. Gerard et al. (2001) used ¹⁰⁹Cd to study the uptake of Cd by three different plants, and they found that more than 50% of the total soil Cd was isotopically exchangeable within 90 days even under a high soil pH condition.

Cr and Ni in soils are generally in stable forms. Selective leaching with Na–EDTA, 1 M acetic acid, or 0.2 M Na₄P₂O₄ can only release small amounts of Cr and Ni (see Table 2 and Fig. 2). Echevarria et al. (1998) used isotopic exchange method and also found that the quantity of Ni available for plants, which can be estimated by DTPA extraction, was rather low. However, the oxidizable step of sequential leaching extracted on average 36% (range from 9% to 66%) of Cr and 14% (range from 7% to 25%) of Ni. This could suggest that some Cr and Ni were in the sulfide phase—which can be liberated by oxidizing rather than complexing or competitive adsorption.

4 Implications

4.1 Plant uptake

Heavy metals can be accumulated in edible vegetables and fruits that can pose a health risk to humans. On the other hand, at high levels many heavy metals can be toxic to plant growth. The rate of plant uptake of trace metals is dependent on environmental, genetic, and toxicological factors. Toxic metal ions are thought to be taken up in the same way as essential micronutrients, like Cu²⁺ and Mn²⁺ (Ross 1994), where the form of metal taken up by the plant is the uncomplexed or free metal ion (M²⁺; Hamon 1995).

Our investigation of natural garden soils suggests that very little of the heavy metals exist in readily exchangeable or weakly adsorbed forms. It should be mentioned, however, that the availability of metals to plants are also dependent upon time, plant species, as well as soil conditions. For example, isotopic exchange methods revealed that Zn extracted by dilute neutral salts such as NaNO₃, CaCl₂, and KCl represent only small parts of soil available Zn (Sinaj et al. 2004). The results also showed that the quantity of isotopically exchangeable Zn can be extrapolated up to 3 months (which is a period relevant to the nutrition of annual crops) in acidic soils, while more research is needed for alkaline soils.

Should environmental conditions change the release of metals bound in certain phases can be appreciable. For example, carbonate-bound metals can be mobilized under low pH conditions, and metals associated with the Fe and

Mn oxide phases will be released into soil solution under reducing or low pH environments. Under normal soil conditions, the bioavailability of heavy metals to plant uptake is expected to be low. This is especially true in the case of Pb, Cr, Ni, and As. Even for Cd and Zn, only in very rare cases more than 10% of these metals are readily available for uptake. It can be argued that plant uptake of metals is a long-term process and over time the accumulation can be significant, but measurements of toxic metals in vegetables and fruits have generally revealed low concentrations and are several orders of magnitude lower than the soils. Hough et al. (2004) assessed potential risk of heavy metal exposure from consumption of home produced vegetables by urban populations, and concluded that food grown on 92% of the urban area presented minimal risk to the average person subgroup. Some plants do have tendency to hyperaccumulate metals, however, likely through a very different mechanism. A new approach using “Diffusive Gradient in Thin Film” was developed for in situ direct measurements of metal bioavailability to the plants (International Network for Acid Prevention 2002). The device is placed in equilibration with soil solution for extended period of time—which simulates metal transfer into soil roots.

4.2 Soil remediation

The fact that metals are unevenly distributed in different phases in soil provides an opportunity to effectively manage the soil to minimize their mobility. Immobilizing the metal contaminants can lower plant uptake rates and minimize the risk of groundwater pollution. To accomplish this, remediation of the soil must limit the amount of bioavailable, e.g., free ions or weakly sorbed forms and transform them into precipitations or more stable compounds. For example, maintaining a neutral to slightly basic soil pH is important to ensure that the carbonate-bound metals are held in check. Phosphate can bind most metals to form compounds that are very stable. Clays and zeolites can provide extra strong sorption sites to reduce the amount of free ions in solution. Soil amendments showed promising results in the laboratory and in some field studies (e.g., Gworek 1992; Mench et al. 1994; Rebedea and Lepp 1995; Culligan et al. 2001; Querol et al. 2006; Kumpiene et al. 2008; Lee et al. 2009). On the other hand, to make phytoremediation more effective, strong chelating reagents such as EDTA has been used to mobilize Pb—which mostly exists in the organic- and carbonate-bound fractions.

Increasing organic matter content can assist in binding metals thereby reducing their mobility. For example, Bassuk found that different types of organic material can help to reduce lead uptake by lettuce (Bassuk 1986). However, some other researchers suggested that organically

complexed and even inorganically complexed metals can potentially cross the soil membrane, therefore increasing the metals’ bioavailability. Lead introduced to plants as Pb–EDTA entered plants more easily and was more mobile within the plant compared to the unchelated, free metal ion (Huang et al. 1997; Cunningham and Berti 1997). Addition of mulch and compost has been a common practice to mitigate soil contamination, and in the meantime in addition to increase soil fertility. More research is clearly needed to better understand the effects of organic content on plant uptake of heavy metals.

4.3 Bioavailability and human health risk

The soil heavy metal speciation data suggest that soil ingestion is probably a much more important pathway for human health risk in comparison to the threat from eating vegetables and fruits grown in contaminated soils. This issue is likely to be very important to gardeners who have extensive contact with contaminated soil, therefore have higher probability to inhale, ingest, and breathe in soil dust. Vegetables and fruits not washed thoroughly can also contain appreciable amount of soil particles. In addition, incidental ingestion is known to be a problem for children. Soil dust is a significant source of Pb in urban environments. Our results, as well as several other recent studies, showed that fine soil fractions, which are the main source for dust, tend to have much higher concentrations of heavy metals than bulk soil (Biasioli and Ajmone-Marsan 2008; Wang et al. 2006).

When contaminated soil particles are ingested, they are extracted sequentially by saliva, gastric fluid, intestinal fluid, bile, and rigorous physical mixing and grinding in the process. The low pH condition (pH=2 or lower) in gastric acid is very favorable for the release of metals in the carbonate, organic, and oxide phases. Our results show that metals in these phases constitute the majority of Pb, Cd, and Zn in the garden soil samples we analyzed (see Table 2 and Fig. 2). A new study has found that even the sulfide-bound fraction of Pb (extracted with 7N HNO₃) can be bioavailable (Denys et al. 2007). This means that a majority of the heavy metals in ingested soil are biologically accessible to human absorption.

In fact, many in vitro extraction experiments have generally shown that large percentages of heavy metals in soils can be bioavailable or bioaccessible. US EPA considers that >75% of Pb in cerussite or oxide phases is bioavailable. In vitro extraction (SBET method) of fine particles of some urban soils by Madrid et al. (2008) also showed high bioaccessibility for Pb (19–83%), Zn (24–83%), and Ni (5–86%). In another study of urban playground soils, As bioaccessibility ranged from 10% to 29% (Ljung et al. 2007).

5 Conclusions

Despite of the controversy and inaccuracy surrounding chemical leaching methods for the speciation of metals, they provide important, general, and easy-to-access information on the mobility of heavy metals in soils, which in turn relates to their potential bioavailability to plant uptake and human health risk. Large variability is observed among different soil samples and among different elements for metal speciation, but some general conclusions can be drawn from the selective and sequential leaching experimental data. In general, little heavy metals are exchangeable or weakly adsorbed onto soil particles, suggesting that metals in soil are generally not highly bioavailable in nature. For Pb, organic and carbonate are the two most dominant phases. Metals in these two phases can become bioavailable if conditions are favorable. The percentages of Cr and Ni that can be leached out are much less (<15% on average), suggesting that they could reside in minerals of natural origin (i.e., the serpentine bedrock in Brooklyn and Staten Island) that have not been broken down. Similar to Cd, significant fractions of Zn exists in carbonate, organic, and Fe oxide phases. Therefore, based on the selective and sequential leaching experiments, the mobility of metals in soil is in the order of: Zn/Cd>Pb>Cr/Ni.

Acknowledgments We want to thank the numerous gardeners who sent their soil samples in for screening of heavy metal contents. Public attention to our soil screen program was also assisted by The New York Times and CBS Evening News. Discussions with scientists and educators from the Brooklyn Botanic Garden have contributed to our understanding of the urban soils and plant uptake of metals. Comments and suggestions from Prof. Jean Louis Morel and two anonymous reviewers were very helpful in improving this manuscript.

References

- Bassuk NL (1986) Reducing lead uptake in lettuce. *Hortsci* 21 (4):993–995
- Biasioli FM, Ajmone-Marsan F (2008) Availability and bioaccessibility of metals in fine particles of urban soils. *Arch Environ Contam Toxicol* 55:21–32
- Cheng Z-Q, Shaw R (2009) Heavy Metal Contamination in New York City Garden Soils. In: Abstract presented at the 5th International conference on Soils of Urban, Industrial, Traffic, Mining, and Military Areas. New York, pp 30–31
- Culligan CN, Yong RN, Gibbs BF (2001) Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Eng Geol* 60:193–207
- Cunningham SD, Berti WR (1997) Phytoextraction or in-place inactivation: Technical, economic and regulatory considerations of soil lead issue. In: Iskandar IK, Hardy SE, Chang AC, Pierzynski GM (eds) Proceedings of extended abstracts from the fourth international conference on the biogeochemistry of trace elements
- Davidson CM, Hursthouse AS, Tognarelli DM, Ure AM, Urquhart GJ (2004) Should acid ammonium oxalate replace hydroxylammonium chloride in step 2 of the revised BCR sequential extraction protocol for soil and sediment. *Anal Chim Acta* 505(2):193–199
- D'Amore JJ, Al-Abed SR, Scheckel KG, Ryan JA (2005) Methods for speciation of metals in soils: a review. *J Environ Qual* 34:1707–1745
- Denys S, Caboche J, Tack K, Delalain P (2007) Bioaccessibility of lead in high carbonate soils. *J Environ Sci Health A* 42:1331–1339
- Echevarria G, Morel JL, Fardeau JC, Leclerc-Cessac E (1998) Assessment of phytoavailability of nickel in soils. *J Environ Qual* 27:1064–1070
- European Commission (1997) BCR Information Reference Materials
- Gerard E, Echevarria G, Sterckeman T, Morel JL (2001) Cadmium availability to three plant species varying in Cd accumulation pattern. *J Environ Qual* 29:1117–1123
- Gomez A, Giraldez I, Sanchez-Rodas D, Morales E (2000) Selectivity assessment of a sequential extraction procedure for metal mobility characterization using model phases. *Talanta* 52:545–554
- Gworek B (1992) Lead inactivation in soils by zeolites. *Plant Soil* 143:71–74
- Hamon R, Lorenz S, Holm PE, Christensen TH, McGrath SP (1995) Changes in trace metal species and other components of the rhizosphere during growth of radish. *Plant Cell Environ* 18:749–756
- Hough RL, Breward N, Young SD, Crout NMJ, Tye AM, Moir AM, Thorton I (2004) Assessing potential risk of heavy metal exposure from consumption of home-produced vegetables by urban populations. *Environ Health Perspect* 112(2):215–221
- Huang JW, Chen J, Serti WR, Cunningham SO (1997) Phytoremediation of lead-contaminated soils: role of synthetic chelates in triggering lead hyperaccumulation in plants. In: Iskandar IK, Hardy SE, Chang AC, Pierzynski GM (eds) Proceedings of extended abstracts from the fourth international conference on the biogeochemistry of trace elements
- International Network for Acid Prevention (2002) Diffusive Gradients in Thin-films (DGT) A technique for determining bioavailable metal concentrations. Available at http://www.inap.com.au/public_downloads/Research_Projects/Diffusive_Gradients_in_Thin-films.pdf
- Joksi AS, Katz SA, Horvat M, Radmila MR (2005) Comparison of single and sequential extraction procedures for assessing metal leaching from dredged coastal sediments. *Water Air Soil Pollut* 162(1–4):265–283
- Kaplan O, Yaman M (2009) Selective and sequential extraction of lead in soil samples and plant parts taken from a serpentine and copper mining area. *Atom Spectr* 30(1):1–9
- Kumpiene JK, Lagerkvist A, Maurice C (2008) Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—a review. *Waste Manage* 28:215–225
- Larner BL, Seen AJ, Townsend AT (2006) Comparative study of optimized BCR sequential extraction scheme and acid leaching of elements in the certified reference material NIST 2711. *Anal Chim Acta* 556:444–449
- Lee SH, Lee JS, Choi YJ, Kim JG (2009) In situ stabilization of cadmium-, lead-, and zinc-contaminated soil using various amendments. *Chemosphere* 77:1069–1075
- Ljung K, Oomen A, Duits M, Selinus O, Berglund M (2007) Bioaccessibility of metals in urban playground soils. *J Environ Sci Health A* 42:1241–1250
- Madrid F, Biasioli M, Ajmone-Marsan F (2008) Availability and bioaccessibility of metals in fine particles of some urban soils. *Arch Environ Contam Toxicol* 55:21–32
- Maiz I, Esnaola V, Millan E (1997) Evaluation of heavy metal availability in contaminated soils by a short sequential extraction procedure. *Sci Total Environ* 206:107–115
- Mench MJ, Didier VL, Laffler M, Gomez A, Masson P (1994) A mimicked in-situ remediation study of metal-contaminated soils with emphasis on Cd and Pb. *J Environ Qual* 23:58–63

- Mielke HW, Reagan PL (1998) Soil is an important pathway of human lead exposure. *Environ Health Perspect* 106(1):217–229
- Mielke HW, Gonzales CR, Smith MK, Mielke PW (1999) The urban environment and children's health: soil as an integrator of lead, zinc, and cadmium in New Orleans, Louisiana, USA. *Environ Res* 81:117–129
- Nirel PV, Morel FM (1990) Technical note: pitfalls of sequential extractions. *Water Res* 24:1055–1056
- Querol X, Alastueya A, Moreno N, Alvarez-Ayusob E, García-Sánchez A, Camaa J, Ayora C, Simón M (2006) Immobilization of heavy metals in polluted soils by the addition of zeolitic material synthesized from coal fly ash. *Chemosphere* 62(2):171–180
- Rao CRM, Sahuquillo A, Sanchez JFL (2008) A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace metals in soils and related materials. *Water Air Soil Pollut* 189:291–333
- Rebedea I, Lepp NW (1995) The use of synthetic zeolites to reduce plant metal uptake and phytotoxicity in two polluted soils. *Environ Geochem Health* 16:81–88
- Ross SM (1994) Toxic metals in soil-plant systems. John Wiley and Sons, New York
- Scheckel KG, Impellitteri CA, Ryan JA, McEvoy T (2003) Assessment of a sequential extraction procedure for perturbed lead contaminated samples with and without phosphorus amendments. *Environ Sci Technol* 37:1892–1898
- Sinaj S, Dubois A, Frossard E (2004) Soil isotopically exchangeable zinc: a comparison between e and L values. *Plant Soil* 261:17–28
- Sutherland RA, Tack FMG (2003) Fractionation of Cu, Pb and Zn in certified reference soils SRM 2710 and SRM 2711 using the optimized BCR sequential extraction procedure. *Advan in Environ Res* 8:37–50
- US EPA, Office of Solid Waste and Emergency Response (1996) Superfund Soil Screening Guidance: Quick Reference Fact Sheet, EPA/540/F-95/041
- Wang HH, Li LQ, Wu XM, Pan GX (2006) Distribution of Cu and Pb in particle size fractions of urban soils from different city zones of Nanjing, China. *J Environ Sci* 18(3):482–487
- Wenzel WW, Kirchbaumer N, Prohaska T, Stingeder G, Lombic E, Adriano DC (2001) Arsenic fractionation in soils using an improved sequential extraction procedure. *Anal Chim Acta* 436:309–323