Release of cadmium, copper and lead from urban soils of Copenhagen

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ABSTRACT

We studied the bonding and release kinetics of Cd, Cu and Pb from different soils in the older metropolitan area of Copenhagen. Total Cd, Cu and Pb concentrations were elevated 5–27 times in the urban soils compared to an agricultural reference soil, with Cd and Pb in mainly mobilisable pools and Cu in strongly bound pools. The soils were subjected to accelerated leaching studies in $Ca(NO_3)_2$ or HNO_3 solutions resulting in release up to 78, 18 and 15% of total Cd, Cu and Pb soil concentrations over a period of 15 weeks. The relative initial Cd and Pb release rates increased 10 fold when pH decreased 2 and 3 units, respectively, while increases in Cu release rates were only seen at pH below 4. The total leachable Cu and Pb pools were higher in urban soils compared the agricultural reference soil but not for Cd.

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1. Introduction

Soils serve as the most important sink for heavy metal pollutants in the terrestrial ecosystem. Heavy metals are important pollutants in urban areas and their presence is therefore an important indicator of human exposure to heavy metals. Studies conducted in many parts of the world in both developed and developing countries report on the content, distribution, origin, extractability and solid phase speciation of heavy metals in urban soils (e.g. Lee et al., 2005; Kartal et al., 2006; Davidson et al., 2006; Riga-Karandinos et al., 2006; Wong et al., 2006). A large-scale survey of urban park soils compared to rural soils in Hong Kong showed that the mean concentrations of Cu and Zn in urban soils (24.8 and 168 mg kg^{-1}, respectively) were at least four and two times higher than those of rural soils, while the mean Pb concentration of urban soils (90 mg kg^{-1}) was one magnitude higher than that of rural soils (8.7 mg kg^{-1}) (Wong et al., 2006; Li et al., 2001). Lead represents a classical example as concentrations in urban soils often exceed 100 mg kg^{-1} which can be compared to median concentrations for Danish clay soils of 12 mg kg^{-1} (Larsen et al., 1996; Davidson et al., 2006). Typical sources to lead contamination are traffic related including leaded petrol, lead containing particles from roads, tyres and brakes, but also coal combustion and industrial emission can contribute significantly to the lead emission (Andersen et al., 1978; Wåhlin et al., 2006; Grosbois et al., 2012; Kuang et al., 2013). Also

the contents of Cu, Zn and in certain cases Cd, show elevated concentrations in urban soils (Lu et al., 2003; Manta et al., 2002; Imperato et al., 2003). Soil metal contents are usually reported to be highest in oldest part of cities depending on land use, where heavily trafficked areas and industrial areas have higher contents than soils in parks, recreational areas and allotments (Ljung et al., 2006; Davidson et al., 2006; Zhang et al., 2005; Ajmone-Marsan and Biasioli, 2010; Charlesworth et al., 2011).

High contents of heavy metals in urban soils pose an ecosystem and health risk as the metals may migrate to groundwater and rivers either in solution or as particulate material (Ge et al., 2000; Jensen et al., 2009). However, despite the high contents of heavy metals in urban soils the mobility or leachability is often not very high due to relatively strong bonding (Madrid et al., 2004; Sauvé et al., 1997). However, some studies show that the potential mobility and associated risk of heavy metal pollutants may be higher in urban soils compared to rural and agricultural soils (Mingkui et al., 2003; Krasnodebska-Ostrega et al., 2004; Zhao and Li, 2013).

Urban soil materials differ from rural soils not only with respect to the level of contamination, but also with respect to general soil properties which may affect the bonding of the contaminants. Urban soils usually have higher contents of organic matter, may have high CEC, base saturation and pH if influenced by building material, and they generally are rich in nutrients, in particular phosphorus, but also nitrogen and potassium (Jim, 1998; Mingkui et al., 2003; Zhang et al., 2011). Often they are more compacted and have higher bulk densities, lower hydraulic conductivities and poorer aeration status than rural soils (Scharenbroch et al., 2005). A

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correlation between heavy metal contents and content of soil organic carbon has often been found (Madrid et al., 2004; Ruiz-Cortes et al., 2005; Turer et al., 2001; Madrid et al., 2006). The high soil pH often seen in urban soils also gives rise to strong bonding of metals to soil particles by surface adsorption and precipitation processes (Sauvé et al., 2000).

Many sequential extraction studies have been carried out to characterise metals pools which can be leached with different chemical solutions and thereby determine their potential mobility (Tokalioglu and Kartal, 2003; Davidson et al., 2006; Gál et al., 2008; Madrid et al., 2008; Cheng et al., 2011). Despite the limitations and inaccuracy related to sequential extractions such methods offers general information on the potential mobility of heavy metals from a soil under different chemical and physical conditions (Cheng et al., 2011). Relevant changing chemical conditions may be concentrations of organic chelators, acidification, and shift in soil aeration status which may mobilise heavy metals (Ge et al., 2000; Strobel et al., 2005; Zhang et al., 2012). Leaching with water or dilute acids gives further insight into metal bonding and lability, and the approach is useful in risk evaluation (Sukreeyapongse et al., 2002; Strobel et al., 2005).

The aim of the present study was to investigate the Cd, Cu and Pb contamination, bonding strength and potentially leachability of different urban surface soils from the older metropolitan area of Copenhagen. Sequential extractions and leaching tests over 15 weeks with dilute calcium nitrate and nitric acid solutions were carried out in batch experiments. The data are useful for evaluation of risks of Cd, Cu and Pb leaching under changing soil conditions caused by for example change in land use.

2. Materials and methods

2.1. Soil samples

Five top soils (0–10 cm) were sampled from the City of Copenhagen urban area (U1–U5) and one non-contaminated agricultural reference soil (A6) was sampled in the rural area outside Copenhagen. Descriptions of the sampling sites are given in Table 1. The five urban soil samples represent urban sites of Copenhagen, which are not consolidated nor covered. The current land uses are city road side, park, private gardens and allotment gardens.

2.2. Soil characterisation

In the laboratory soil samples were air-dried at room temperature and roots, visible plant remains and anthropogenic materials were removed. Then, the samples were sieved through a 2.0 mm stainless steel sieve, and kept in polyethylene bottles. Soil pH was determined potentiometrically by means of a combination electrode in a suspension of soil and 10 mM $CaCl_2$ at a soil:solution ratio of 1:2.5. Organic carbon was determined by dry combustion at 1250 °C in oxygen (ELTRA, CS 500). Inorganic carbon was determined by the volumetric calcimeter method as described by Allison and Moddie (1965). Total N was determined by the Kjeldahl method, total P by 6 M H_2SO_4 extraction of ignited samples (Mehta et al., 1954), and soil texture was

determined by the Bouyoucos method (Bouyoucos, 1927). Oxalate extractable aluminium and iron was determined according to Schwertmann (1964), while cation exchange capacity (CEC) and exchangeable cations were determined using the ammonium acetate method (pH 7) and atomic absorption spectroscopy for determination of Na, K, Mg and Ca (Stuanes et al., 1984).

The pseudo-total content of heavy metals was determined by strong acid digestion of finely ground samples. Approximately 0.5 g soil was treated with 10 mL concentrated HNO_3 in a microwave for 0.5 h, according to US-EPA method 3051A followed by metal analysis by graphite furnace atomic absorption spectroscopy (GFAAS) (Perkin Elmer 5100, Zeeman 5100) (USEPA, 1991). Blank samples and the certified reference material Montana soil 2711from the National Institute of Science and Technology (NIST) were included for quality assurance. The BCR sequential extraction procedure by Rauret et al. (1999) was used to differentiate between four pools of bonded heavy metals differing with respect to bonding modes: i) water and acid soluble pool, ii) reducible fraction, iii) oxidisable fraction, and iv) residual fractions. The BCR extractions were carried out in triplicates. Graphite furnace atomic absorption spectroscopy (GFAAS) was used to determine Cd, Cu and Pb concentrations in the extracts.

2.3. Release

The release of Cd, Cu and Pb from the 6 soils was studied at room temperature by repeated leaching with either 10 mM HNO_3 or 1 mM $Ca(NO_3)_2$ – a method similar to the one described by Strobel et al. (2005). The two leaching solutions were used in order to assess shifts in metal leachability as a function of soil acidification. A 50 mL polycarbonate centrifuge tube containing 5 g air dry soil and 25 mL of 10 mM HNO_3 or 1 mM $Ca(NO_3)_2$ solution was placed on a shaking table (36 strokes min^{-1}) for 15 weeks. At end of each week the centrifuge tubes were centrifuged at 1000 g for 20 min, and 20 mL of supernatant were removed and used for analysis of Cd, Cu, and Pb, total dissolved organic carbon (TOC) and pH. 20 mL of new leaching solution was added to the centrifuge tubes, and the leaching continued. Cadmium, Cu and Pb in the acidified supernatants were determined by GFAAS, pH determined (Metrohm 691 Meter, Electrode 6.0202.110) and TOC quantified using a TOC analyser (Shimadzu TOC-500). All experiments were carried out in triplicates.

2.4. Data treatment

The concentrations of Cd, Cu and Pb determined in the release experiments were used for calculating cumulated release (Q) according to:

$$Q_i = \frac{1}{m}\left(c_i \cdot V_{extr1} + \sum_2^n (c_i \cdot V_{extr} + (c_{i-1} - c_i) \cdot V_{rem})\right) \tag{1}$$

where m is the mass of soil used (5 g), V_{extr1}, V_{extr} and V_{rem} are 0.025, 0.020 and 0.005 L respectively, and c_i is the concentration of heavy metal in solution at time "i". Initial release rates were determined as the slope of linear regressions of the cumulated release versus time for week 1–3. The relative release rates for the different metals were calculated as the release rates divided by the pseudo-total metal content.

3. Results and discussion

3.1. Soil location and properties

The locations and general characteristics of the six soils are presented in Table 1. The clay content ranged between 10 and 28%

Table 1
Soil sample locations and characteristics.

Sample ID	Sample location description	Clay[a] (wt-%)	Silt[a] (wt-%)	pH ($CaCl_2$)	CEC (cmol(+)/kg)	Calcite (g $CaCO_3$/kg)
U1	Old university park and garden area. Sampled from unplanted soil only 1 m from main city street area.	28	12	7.38 ± 0.01	14.0 ± 0.3	61.4 ± 3.2
U2	City allotment garden located near railway. Sampled from soil surface with no vegetation.	14	18	6.93 ± 0.01	14.0 ± 0.2	52.6 ± 1.4
U3	Road side verge of primary city road. Sampled in the grass covered verge between the car lane and the asphalt-paved bicycle lane.	12	22	6.38 ± 0.05	15.0 ± 0.2	-[b]
U4	Old city house garden located next to city road. Sampled from soil surface with almost no vegetation.	10	24	6.60 ± 0.03	12.1 ± 0.1	-
U5	Old public city park with old beech trees. Sampled from soil surface with almost no vegetation below trees.	10	22	3.45 ± 0.00	11.9 ± 0.3	-
A6	University experimental farm location from outside the Copenhagen. Agricultural reference soil.	10	20	5.26 ± 0.01	6.16 ± 0.02	-

[a] Clay: <2 μm; silt: 2–50 μm.
[b] -: No calcite found.