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Effects of soil water content and organic matter addition on the speciation and bioavailability of heavy metals

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ABSTRACT

The mobility and bioavailability of cadmium, copper, lead and zinc were evaluated in three soils amended with different organic materials for two moisture regimes. Agricultural and reclamation activities impose fresh inputs of organic matter on soil while intensive irrigation and rainstorm increase soil waterlogging incidence. Moreover, scarcity of irrigation water has prompted the use of greywater, which contain variable concentrations of organic compounds such as anionic surfactants.

Soils added with hay, maize straw or peat at 1% w/w were irrigated, at field capacity (FC) or saturated (S), with an aqueous solution of the anionic surfactant Aerosol 22 (A22), corresponding to an addition of 200 mg C/kg soil/day. Soil solution was extracted after one month and analysed for total soluble metals, dissolved soil organic matter and UV absorbance at 254 nm. Speciation analyses were performed with WHAM VI for Cd, Cu, Pb, and Zn. For selected scenarios, metal uptake by barley was determined.

Metal mobility increased for all treatments and soils ($Pb > Cu > Cd \geq Zn$) compared to control assays. The increase was significantly correlated ($p < 0.05$) with soil organic matter solubilisation for Cd ($R = 0.68$), Cu ($R = 0.73$) and Zn ($R = 0.86$). Otherwise, Pb release was related to aluminium solubilisation ($R = 0.75$), which suggests that Pb was originally co-precipitated with Al–DOC complexes in the solid phase. The effect of A22 in metal bioavailability, determined as free ion activities (FIA), was mainly controlled by soil moisture regime. For soil 3, metal bioavailability was up to 20 times lower for soil amended with hay, peat or maize compared to soil treated only with A22. When soil was treated with A22 at FC barley yield significantly decreased ($p < 0.05$) for the increase of Pb ($R = 0.71$) and Zn ($R = 0.79$) concentrations in shoot, while for saturated conditions such uptake was up to 3 times lower.

Overall, metal bioavailability was controlled by solubilisation of soil organic matter and formation of metal-organo complexes.

1. Introduction

The distribution and speciation of metals in soil are worldwide altered by human activities. Agricultural practices such as application of organic amendments or irrigation with wastewaters introduce organic compounds in soil that affects the reactivity, solubility and bioavailability of metals, compromising environmental health and crop nutrition. Several studies have demonstrated that addition of organic materials to soil have a moderate effect on the mobility of metals, e.g. manure (Walker et al., 2003), peat (Gondar et al., 2006) or crop-straw (Mohamed et al., 2010). Otherwise, anionic surfactants reach the soil mainly with waste discharges and can increase metal leaching by direct complexation (Mulligan et al., 2001) or by solubilisation of soil organic matter (Hernandez-Soriano et al., 2011a). Anionic surfactants are widely present in wastewaters applied for irrigation, originated from domestic households (Wiel-Shafran et al., 2006).

Organic matter content in soil is crucial for the proper uptake of certain elements that are essential for healthy crop development, e.g. copper (Cu) (Alloway, 2005) and zinc (Zn) (Alloway, 2008). However, the beneficial impact of organic inputs can be lessened by the potential enhancement of the bioavailability of elements with unknown metabolic function, e.g. cadmium (Cd) (Smeyers-Verbeke et al., 1978), which is a powerful enzyme inhibitor and considered an extremely significant pollutant, due to its great solubility in water (Kabata-Pendias, 2011). Organic amendments can also enhance lead (Pb) uptake, which metabolic role in plants has been widely discussed (Sharma and Dubey, 2005; and references therein). Nevertheless, Pb is situated first in the ranking of environmental toxic threats (Watanabe, 1997), and impacts the health of more than ten million people in the world (http://www.blacksmithinstitute.org/).

Currently, it is well established that the total concentration of metal in soil does not constitute a reliable indicator of the potential

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risk of toxicity (McLaughlin et al., 2000). Thus, the mobility of metals is properly related to the total concentration of metal in solution, i.e. the free ion as well as metal complexes and metal-bearing colloids (Degryse et al., 2009). Moreover, metal bioavailability is directly related to the speciation of the metals in solution (Nolan et al., 2003; Inaba and Takenaka, 2005). The evaluation of plant uptake generally focus on economically important crops such as barley (*Hordeum vulgare* L.), which also constitutes an excellent model plant for metal uptake (Flores-Meza, 2008).

The objectives of this work were (1) to determine the mobility and bioavailability of Cd, Cu, Pb and Zn in soils under different moisture regimes and amended with common sources of organic matter; and (2) to relate metal bioavailability to organic matter solubility and metal speciation in the soil solution.

2. Material and methods

2.1. Soils characterization

Three soils with a range of properties (Table 1) were selected for this study. Soils were enriched with metals from atmospheric emissions (1) non-ferrous smelters (2, 3) and exceed the Dutch intervention values (CLEA, 2011) for Cd (soils 1) and Pb (soils 2 and 3). Total C concentrations were determined by dry combustion using a CN analyser (VarioMax). The total metal concentrations were determined by aqua-regia digestion. Metal concentrations in the digests were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 3300 DV). Two internal standards (a polluted and an unpolluted soil) were analysed with each digestion. These standards were verified against a soil sample with certified metal concentration (sewage sludge-amended soil, CRM 143 from the Central Bureau of Reference of the European Union). The recovery of the metals studied for these internal lab standards was always between 90% and 110%. The soil pH was measured in 0.01 M $CaCl_2$ (soil:solution ratio, 1:5) after shaking of the soil for 1 h and settling for 30 min. The silver–thiourea method was used to measure the CEC and exchangeable cations at the soil pH.

2.2. Incubation experiment

Soils were sieved at 2 mm and air dried. Subsets of 200 g were homogeneously amended with organic materials (peat, maize straw or milled hay) at 1% w/w, placed in plastic pots and incubated at 25 °C in the darkness. Irrigation was performed with Milli-Q (control) or an aqueous solution of the anionic surfactant Aerosol 22, at a rate corresponding to the addition of 200 mg C kg^{-1} soil/day. Soils were incubated at field capacity (FC) or saturated (S) for one month. Each treatment was carried out in duplicate. The anionic surfactant Aerosol 22 (tetrasodium N(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate), was purchased from Sigma Aldrich. Aerosol 22 was selected for this study because it has been previously reported to enhance metal solubility (Hernandez-Soriano et al., 2010). Characteristics of interest are: molecular weight, 653; critical micellar concentration (CMC), 0.653 g L^{-1}; pH 8 at 1 CMC.

Table 1
Selected physical and chemical properties, total and soluble content of Cd, Cu, Pb and Zn of soils.

Soil	S1	S2	S3
Location	Hungary	France	Belgium
pH	7.48	6.81	7.13
OC[a] (%)	2.7 (28)	6.5 (200)	2.3 (110)
SUVA[b]	15	57	35
CEC ($cmol_c\ kg^{-1}$)	25	26	15
Sand (%)	32	13	35
Silt (%)	23	69	53
Clay (%)	45	18	12
Cd[c]	118 (38)	1.1 (16)	0.6 (2)
Cu[c]	21 (7)	57 (114)	17 (86)
Pb[c]	n.d.	5550 (398)	5460 (291)
Zn[c]	48 (15)	245 (95)	74 (90)
Al[c]	(20)	(120)	(70)

n.d. = non-determined.
[a] Numbers in brackets correspond to soil organic matter in solution (mg L^{-1}).
[b] Specific UV-absorbance (SUVA) (L g^{-1} cm^{-1}).
[c] Aqua-regia extractable metal content (mg kg^{-1}). Numbers in brackets correspond to total soluble metal (μg L^{-1}).

2.3. Pore water analysis

Soil solution was extracted from control and amended and/or irrigated soils after incubation, through centrifugation using the 'double chamber' method (10 min at 3000 *g*) (Bufflap and Allen, 1995). After centrifugation, the soil solution was immediately filtered through a 0.45-μm filter and the pH was measured. The solutions were analysed for soluble metal concentrations by ICP-OES and for dissolved organic carbon (DOC) using a TOC-analyser (Analytical Sciences Thermalox). Total DOC comprises carbon corresponding to soil soluble organic matter plus the carbon in solution due to the presence of A22, for the corresponding treatments. The approach presented did not allow differentiating native soil organic carbon from that added with hay, maize or peat inputs. However, since the specific UV-Absorbance (SUVA) of A22 (0.245 L g^{-1} cm^{-1}) largely differs from that of soil-derived DOC (Table 1), the DOC concentration equivalent to solubilised soil organic matter (DOC_{soil}) can be estimated from the UV absorbance at 254 nm and the measurements of total DOC according to Eq. (1). Further description of this approximation is provided elsewhere (Hernandez-Soriano et al., 2011a).

$$[DOC_{soil}] = \frac{A^{254} - SUVA_{surf} \cdot [DOC]}{SUVA_{soil} - SUVA_{surf}}. \quad (1)$$

2.4. Emergence and growth test

Ten uniform, undressed seeds of barley were evenly placed in plastic cylindrical pots filled with soil (200 g, dry weight basis). There were four replicates per treatment. Soils were fertilized with 50 mg P kg^{-1} soil as KH_2PO_4 and 100 mg N kg^{-1} as KNO_3. Pots were covered with a thin layer of polyethylene beads to prevent excessive moisture loss and placed in a growth cabinet, with a 16 h/8 h day/night cycle (20 °C/16 °C) at 70% humidity.

The emergence of the seeds was recorded after 2 days and seedlings were thinned to give a total of five evenly spaced seedlings per pot. After 14 additional days of growth, shoot biomass was removed and the dry mass of the shoots was determined after oven drying at 70 °C for 16 h.

For all the assays, total concentration of Cd, Cu, Pb and Zn (and other elements) in barley shoots was analysed by ICP-OES following digestion with HNO_3.

2.5. Data analysis

The speciation analysis of the solutions collected upon incubation was carried out using the speciation model WHAM VI (Tipping, 1994), as described by Van Laer et al. (2006).

The relationship between variables was determined by regression analysis. For all tests, correlation was considered significant for $p<0.05$. Statistical analysis was performed with the software package SPSS 17.0 (Illinois, USA).