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Organic matter and salinity modify cadmium soil (phyto)availability

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ABSTRACT

Although Cd availability depends on its total concentration in soil, it is ultimately defined by the processes which control its mobility, transformations and soil solution speciation. Cd mobility between different soil fractions can be significantly affected by certain pedovariables such as soil organic matter (SOM; over formation of metal-organic complexes) and/or soil salinity (over formation of metal-inorganic complexes). Phytoavailable Cd fraction may be described as the proportion of the available Cd in soil which is actually accessible by roots and available for plant uptake. Therefore, in a greenhouse pot experiment Cd availability was observed in the rhizosphere of faba bean exposed to different levels of SOM, NaCl salinity (50 and 100 mM) and Cd contamination (5 and 10 mg kg^{-1}). Cd availability in soil does not linearly follow its total concentration. Still, increasing soil Cd concentration may lead to increased Cd phytoavailability if the proportion of Cd^{2+} pool in soil solution is enhanced. Reduced Cd (phyto)availability by raised SOM was found, along with increased proportion of Cd-DOC complexes in soil solution. Data suggest decreased Cd soil (phyto)availability with the application of salts. NaCl salinity affected Cd speciation in soil solution by promoting the formation of $CdCl_n^{2-n}$ complexes. Results possibly suggest that increased Cd mobility in soil does not result in its increased availability if soil adsorption capacity for Cd has not been exceeded. Accordingly, chloro-complex possibly operated just as a Cd carrier between different soil fractions and resulted only in transfer between solid phases and not in increased (phyto) availability.

1. Introduction

There is a special interest in understanding the processes which control cadmium (Cd) mobility and phytoavailability at the soil-plant interface, and especially in agricultural soils. High Cd level in agricultural soils is usually resulting from anthropogenic activities (e.g. application of phosphate fertilizers) (McLaughlin et al., 1999; WHO, 1992). Available Cd soil fraction may be defined as the proportion of the total concentration which is available for the uptake by organisms. Accordingly, soil phytoavailable Cd fraction may be described as the proportion of available Cd in soil which is actually accessible by roots and available for plant uptake. Although depends on its total concentration, Cd soil availability is ultimately regulated by the processes which control its mobility in soil. Soil Cd contamination is followed by a cascade of reactions with soil surfaces and the concentration of Cd in the soil solution depends on numerous interrelated processes (oxidation-reduction, precipitation/dissolution, adsorption/desorption, inorganic and organic complex formation) (Romić, 2012). Cd sorbed on soil mineral surfaces is bound by reversible adsorption (Cullen and Maldonado, 2013), making it relatively available between different soil fractions and suggesting its mobilization under certain environmental conditions. Soil parameters important in controlling Cd chemistry and bioavailability are pH, soil mineralogy and SOM, but also the existence of other trace metals which may compete with Cd for the adsorption sites in soil (Lu and Xu, 2009). For instance, at lower soil pH values, hydrogen ions adsorbed to soil particles increase the positive charge on inorganic and organic soil components and thus resulting in weaker adsorption of positively charged metal ions, e.g. Cd^{2+} (Kirchmann and Eriksson, 2011). Furthermore, Appel and Ma (2002) found that although Cd(II) is a closed-shell cation that favours coulombic-type reactions and whose sorption is expected to increase with increased cation exchange capacity (CEC) induced by raised SOM content, sorption of Cd (and Pb) in three tropical soils depended more on soil mineralogy than organic matter content. But still, soil organic matter (SOM) has an important two-sided role in metal mobility: particulate organic matter retains trace metals (TMs) through the formation of complexes with metals, decreasing thus their mobility (Matijević et al., 2014a), and dissolved organic carbon (DOC) can actually increase TMs mobility due to formation of metal-DOC complexes in soil solution (Kirchmann and Eriksson, 2011), which are not as strongly bound to soil particles as Cd^{2+}. Moreover, plants can uptake Cd-DOC complexes (Hamon et al., 1995), but at the same time their formation lowers the concentration of

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free metal ion in soil solution, the most available Cd form for plant uptake (Degryse et al., 2012). Thus, Cd soil (phyto)availability depends on its chemical speciation (form), which is in a very close function of pH and the presence of organic and inorganic ligands in the soil solution (McLaughlin et al., 1997; Smolders et al., 1998; Ondrasek et al., 2009).

Plant Cd uptake can be considered as a threshold for Cd entry from the terrestrial environment into the food chain. And although Cd has a no known essential function for plants, it is readily absorbed by plant roots and even translocated to aerial parts (i.e. fruits) (Smolders, 2001). In addition, the problem of secondary (anthropogenic) soil salinization caused by poor quality irrigation water is raising worldwide (FAO and ITPS, 2015), and although being more expressed in southern regions of the world, this process is increasingly affecting European agricultural land as well. Increased soil salinity amongst other negative effects on agricultural production, may affect TMs availability in soil, especially Cd. For example, soil NaCl salinity may influence Cd mobility by the formation $CdCl_n^{2-n}$ complexes. Formation of such complexes reduces the activity of Cd^{2+} in soil solution, but at the same time Cd-chloride complexes are more loosely bound to soil particles and therefore may enhance Cd mobilization (Ghallab and Usman, 2007). Chlorides are highly mobile in soil, and among all TMs, Cd readily forms rather stable complexes with chloride ligands (McLaughlin and Singh, 1999), eventually affecting its adsorption reactions with soil surfaces and thereby soil mobility. Cd complexes with chlorides have also been recognized as phytoavailable. Cd originating from $CdCl_n^{2-n}$ complexes may enter roots directly and/or dissociating from the chloro-complex after reaching binding sites on the root surface and entering cells as Cd^{2+} (Crea et al., 2013).

Faba bean (*Vicia faba* L.) is one of the major cool season grain legume crops produced worldwide for food and feed because of high yield and protein content (Daur et al., 2010). Soils suitable for faba bean cultivation are neutral to slightly alkaline good structured soils with relatively high clay content (Matthews and Marcellos, 2003). According to our previous research, faba bean (cv. Aguadulce) proved to be a rather salt tolerant horticultural crop (Matijević et al., 2014b), an important trait in a selection of a model plant for study of combined plant stressors, one of which is increased soil salinity. Faba bean has been frequently used in research of cadmium toxicity to plants as well (Foltête et al., 2012).

Defining soil parameters which control TMs soil availability is of major importance for estimating and limiting their uptake by crops. These studies enable prevention of over- and under-estimation of risks in terms of food safety when using contaminated soils for agricultural production. Therefore, the present study is focused on the effects of increased level of SOM, salinity and Cd contamination on Cd soil (phyto)availability.

2. Material and methods

2.1. Applied treatments and experimental design

A greenhouse pot experiment was carried out from April to June in 2012, at the experimental station of the Faculty of Agriculture University of Zagreb, Croatia. Faba bean (*Vicia faba* L. cv. Aguadulce) seeds were sown in polystyrene cups containing peat soil and after three weeks uniform seedlings were transplanted into pots (one plant per pot). Pots were containing 2 soil types with different SOM content: (i) alluvial soil type sampled from cultivated land in a Croatian Mediterranean region (SOM_0) and (ii) the same alluvial soil with added peat (4:1 v/v; SOM_1). Alluvial soil prior the experiment was purged from roots and other plant parts, fragmented and passed through a 1 cm mesh. Peat used for the experiment was a commercially produced fine structured (0–5 mm) black sphagnum peat (Potgrond P, Klasmann) used in growing young vegetable plants. SOM_0 and SOM_1 soil types (initially containing 0.45 ± 0.01 mg kg^{-1} Cd) were spiked with Cd at two levels: 5 mg kg^{-1} (Cd_5) and 10 mg kg^{-1} (Cd_{10}). In short, $Cd(NO_3)_2 \times 4H_2O$ solution was initially added to 5 L of uncontaminated soil batches to be then mixed and homogenized with adding uncontaminated soils every five days in increasing amounts required to obtain a soil spiked with the treatment amounts of Cd. During the next 30 days of incubation the soils were mixed daily to improve homogeneity. Control (Cd_0) treatment without added Cd was also used in the experiment. During the experiment, all pots were fertigated using automatic drip irrigation system with a basic nutrient solution (Poly-Feed Drip 20-20-20) at the concentration of 2 g L^{-1}. Also, NaCl salinity was applied to pots through the irrigation system at 3 NaCl levels: $NaCl_0$ as control (without added NaCl), $NaCl_{50}$ (control + 50 mM NaCl) and $NaCl_{100}$ (control + 100 mM NaCl). The fertigation rate and frequency was the same for all the treatments and adjusted to the climatic conditions in the greenhouse. Split-split-plot experimental design with 3 blocks was applied in this study (Fig. 1). In each block, the main plots were assigned to 2 SOM (SOM_0 and SOM_1), the sub-plots were randomly assigned to 3 NaCl salinity ($NaCl_0$, $NaCl_{50}$, $NaCl_{100}$), and sub-sub-plots to 3 Cd (Cd_0, Cd_5, Cd_{10}) levels.

Fig. 1. Experimental setup.

2.2. Sampling, soil and plant tissue analysis

Five weeks after salinity treatment started sampling of soils was performed: soil from three pots of the same treatment was merged, mixed thoroughly and representative samples were taken. Soil samples were air-dried, passed through a 0.5 mm mesh and subjected for detection of next parameters: pH and electrical conductivity (in a 1:5 soil/water ratio), soil organic carbon (C_{org}) by sulfochromic oxidation (ISO 14235, 1998), calcium carbonate ($CaCO_3$) by the volumetric calcimeter method after HCl attack, and a particle size distribution by the pipette method after disaggregation in sodium pyrophosphate (ISO 11277, 2009). Samples were also digested in aqua regia (ISO 11466, 1995) applying the microwave technique on a MARSXpress system (CEM) for elemental detection (Cd, Cu, Ca, Mg, P, S, Fe, Mo, Mn and Zn) by inductively coupled plasma optical emission spectroscopy (Vista MPX AX, Varian), whereas Na and K concentrations were determined by atomic emission spectroscopy (Atomic Absorption Spectrometer 3110, Perkin-Elmer). All concentrations were calculated on the basis of dry weight of samples (105 °C, 24 h). Quality control procedure consisted of reagent blanks, duplicate samples and several referenced soil samples with similar matrix from the inter-laboratory calibration program (Houba et al., 1996). Maximum allowable relative standard deviation between replicates was set to 10%. Data for the soil total element concentrations which were not significantly affected by any of the experiment treatments are not shown (K, Mg, Cu, Zn). Soil solution element concentrations were determined in a saturated soil water extract: Na and K concentrations by atomic emission spectroscopy (Atomic Absorption Spectrometer 3110, Perkin-Elmer); P, Cl^-, NO_3^-, NH_4^+ and SO_4^{2-} by continuous flow auto-analyzer (San++ Continuous Flow Analyzer,