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Soil physical characteristics after EDTA washing and amendment with inorganic and organic additives

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ABSTRACT

Soil washing has been established as suitable remediation technology, with most research focused on metal removing efficiency and toxic effect on plants, less on the influence on soil physical characteristics, which was the focus of this study. In soil column experiment highly contaminated soil and soil washed with EDTA, mixed with additives (gypsum, hydrogel, manure, peat) were tested. White clover was used as a soil cover. Yield, metal concentration in soil and plant, aggregate fractionation and stability, saturated hydraulic conductivity and soil water retention of the soil were measured. Soil washing decreased metal concentration in soil and plants, but yield of white clover on remediated soil was significantly lower compared to the original soil. Significant differences in water retention characteristics, aggregate fractionation and stability between original and remediated soil have been determined. Gypsum, hydrogel and peat increased plant available water, manure and peat increased yield on remediated soil.

1. Introduction

Due to several degradation processes, the area of arable land suitable for plant production is reducing. At the same time the global demands for food, livestock feed and energy are increasing (Nonhebel and Kastner, 2011). Global governance of soil resources (Montanarella and Vargas, 2012) as well as revitalizations and remediation of degraded areas seem to be the necessary action for sustainable development. Soils degraded by metal pollution cover several million ha and represent a world-wide problem. Intensive search of solutions for metal polluted soils and ways for their safe use for plant production has been undergoing in past few decades. Different remediation technologies have been investigated including: phyto-extraction (Van Nevel et al., 2007), enhanced phyto-extraction (Meers et al., 2004), physical separation and chemical extraction technologies (Dermont et al., 2008). Negative effects of in situ chelate application (Nowack et al., 2006) lead to intensive research of ex-situ remediation procedures. Use of chelating agents for ex-situ soil washing proved to be efficient method for reduction of metal content in the soil. Different chelating agents were tested, most frequent EDTA, which proved to be efficient, available and low cost (Lestan et al., 2008). Development of method for chelant recycling as well as possibility of cleansing and total reuse of the spent washing solution as process water made soil washing method environmentally acceptable (Pociecha and Lestan, 2012; Voglar and Lestan, 2012). Remediation significantly reduced concentration of Pb, Cd and to lesser extent also of Zn in roots of Chinese cabbage (*Brassica rapa* L.) but did not entirely prevent toxic metals accumulation in *B. rapa* leaves (Jelusic et al., 2013). Yield of *B. rapa* grown on remediated soil was reduced comparing to control soil even though measurement of net photosynthesis, stomatal conductance and transpiration did not prove negative effect of remediated soil on plants' fitness. Negative side-effects of the EDTA application to soil on plant yield and short-term effect on viability of soil microorganisms were reported also by other authors (Grcman et al., 2001). Possible explanations were toxic effect of metal- EDTA complexes, lack of metal micronutrients leached during soil washing and changed physical properties of soil. These results indicate that while toxic metals removal efficiency is promising, the cumulative effect of novel remediation technology on soil properties and functioning must be carefully examined before any attempt of field-scale application.

Previous research focused mainly on soil chemical properties and (eco) toxicology of metals which remained in the soil after remediation. In this study, changes of soil physical properties after EDTA-soil washing were evaluated. It was expected that remediation process, especially intensive mixing of the soil slurry and soil compression after de-watering (Voglar and Lestan, 2012),

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significantly deteriorate physical properties of soil. Furthermore, different soil additives with capacity to improve the physical characteristics of remediated soil were tested in a soil column experiment. Plant roots are integral part of soil system with significant effect on soil physical properties and water regime. Therefore, white clover (*Trifolium repens* L.), which is suitable plant for revitalization of degraded soils (van Eekeren et al., 2009), was used to provide soil cover.

2. Materials and methods

2.1. Soil properties

Contaminated soil (3730 mg Pb, 2140 mg Zn and 25.8 mg Cd kg^{-1} dry soil) was collected from the upper 30 cm layer of a managed vegetable garden in the Meza Valley, Slovenia (49°26′46″ N, 10°10′55″ E). The origin of soil contamination is more than 500 years tradition of lead mining and smelting in the area (Souvent, 1992). For soil analyses samples were air-dried and sieved to 2 mm (ISO 11464, 2006). Soil pH was measured in a 1/2.5 (*v*/*v*) ratio of soil and 0.01 M $CaCl_2$ suspension (ISO 10390, 2005). Soil samples were analyzed for organic matter by modified Walkley–Black titrations (ISO 14235, 1998), cation exchange capacity (CEC) as a sum of base cations measured after soil extraction with ammonium acetate (pH = 7) and extractable acidity determined with $BaCl_2$ method (Soil Survey Laboratory Methods Manual, 1992), soil texture by the pipette method (ISO 11277, 2009). Total nitrogen was determined by dry combustion (ISO 13878, 1998). Carbonates were determined volumetrically after soil reaction with HCl (ISO 10693, 1995), easily extractable P (P_2O_5) and K (K_2O) colorimetrically after ammonium lactate extraction (Leskošek, 1993). Results for original and remediated soil are shown in Table 1. For metal analyses air-dried samples were ground in an agate mill, sieved to 150 μm and digested in *aqua regia* solution consisting of HCl and HNO_3 in a 3:1 ratio (*v*/*v*) (ISO 11466, 1995). Metals were measured by flame (acetylene/air) atomic absorption spectrometry (AAS, Varian AA240FS, ISO 11047, 1998).

Contaminated soil was washed with EDTA by the procedure described in Voglar and Lestan (2012). In short, 75 kg of soil was extracted with 75 L of EDTA solution (60 mmol Na_2-EDTA kg^{-1} of dry soil) in a concrete mixer for 2 h, pH of the solution within the remediation process was 7.4. Sand and oversize material (particles >2 mm) were separated on a wet sieve and washed separately with tap water. The soil suspension was separated from the spent soil washing solution in a chamber filter press (filter cloth thickness 0.6 g cm^{-2}, air permeability 22 dm^3 dm^{-2} min^{-1}) and densely packed soil (bulk density 1.7 g cm^{-3}) was repeatedly rinsed within the press with high pressurized tap water (8 bar) to remove all EDTA-mobilized toxic metals species (until no Pb, Zn and Cd was detected in the used rinsing solution). EDTA and combined used washing and rinsing solution were recycled as described by Pociecha and Lestan (2012). Soil washing reduced metals concentrations to 1540, 1790 and 11.3 mg kg^{-1} dry soil for Pb, Zn and Cd respectively (Table 1). Part of the excluded particles (<5 mm) were returned and mixed with the sieved soil. In the final stage of the soil preparation, amorphous soil mass was rubbed through a sieve with desired mesh size. In our experiment we used 5 mm mesh sieve, thusly predetermining aggregate size.

Table 1
Average soil properties and standard deviations (SD, n = 3) of the original and remediated soil used in the experiment.

Variables/properties and units	Original	SD	Remediated	SD
Clay (%)	39.2	3.7	48.5	4.7
Silt (%)	49.4	4.8	41.0	3.9
Sand (%)	11.4	0.9	10.5	1.0
pH	6.6	0.1	6.9	0.1
$CaCO_3$ (%)	21.7	1.1	21.8	1.0
Organic matter (%)	7.8	0.2	7.7	0.2
Available P_2O_5 (mg 100 g^{-1})	135	9	150	10.5
Available K_2O (mg 100 g^{-1})	13.2	0.9	10.9	1.1
Cation exchange capacity (mmolc 100 g^{-1})	31.3	1.1	30.9	1.9
Base saturation (%)	78.3	2.3	81.9	2.5
Exchangeable Ca (mmolc 100 g^{-1})	19.2	1.2	18.7	1.6
Exchangeable Mg (mmolc 100 g^{-1})	5.0	0.08	4.2	0.13
Exchangeable K (mmolc 100 g^{-1})	0.29	0.02	0.22	0.01
Exchangeable Na (mmolc 100 g^{-1})	0.12	0.01	2.27	0.05
Exchangeable acidity	6.8	0.1	5.6	0.4
Pb (mg kg^{-1})	3730	150	1540	60
Zn (mg kg^{-1})	2140	40	1790	30
Cd (mg kg^{-1})	25.8	1.1	11.3	0.5
Cu (mg kg^{-1})	51.8	2.2	42.2	2.5
Mo (mg kg^{-1})	40.6	1.9	9.8	0.5
Mn (mg kg^{-1})	767	22	381	10
Ni (mg kg^{-1})	25.8	1.2	25.4	1.2
Co (mg kg^{-1})	11.4	0.2	7.9	0.2
Fe (%)	2.77	0.01	2.85	0.01
As (mg kg^{-1})	25.4	0.5	25.6	0.6
Cr (mg kg^{-1})	27	3.2	32	4.0
Al (%)	1.55	0.01	1.65	0.01
Hg (mg kg^{-1})	0.32	0.04	0.35	0.03

2.2. Growth column experiment

The experiment was conducted in a greenhouse from June 2011 until March 2012. Cylindrical columns (20 cm high, diameter 15.3 cm) used for experiment were equipped with adjustable drainage for saturated hydraulic conductivity measurements (*K*-value determination). To homogenize the soil material, i.e. avoid large soil structural aggregates, which could have impeded the small size experiment (*K*-value determination, soil bulk density), original and remediated soils were sieved prior to column packing (8 mm mesh sieve). Organic (manure, peat), inorganic (gypsum, hydrogel) additives were added to the soil. For both soils six treatments were set: control (no plant, no additives), control plant (plant, no additive), gypsum (plant, gypsum, equivalent 8 t ha^{-1}), manure (plant, manure equivalent 30 t ha^{-1}), peat (plant, peat 5% mass) and hydrogel (plant, hydrogel equivalent 1.2 t ha^{-1}). Hydrogel, used in the experiment, was super absorbent polymer intent for use in agriculture (polyacrylate – polyacrylamide copolymer). Gypsum, hydrogel and peat were devoid of any macro nutrients. Manure contained 422.4 mg 100 g^{-1} plant available P_2O_5 and 244.8 mg 100 g^{-1} plant available K_2O. Metal content in gypsum and hydrogel were very low (Pb <10 mg kg^{-1}, Zn <40 mg kg^{-1} and Cd <0.2 mg kg^{-1}). Concentrations of Pb, Zn and Cd were 15.8 mg kg^{-1}, 323 mg kg^{-1} and <0.2 mg kg^{-1}, respectively, for manure, and 20.7 mg kg^{-1}, 148 mg kg^{-1} and <0.2 mg kg^{-1}, respectively, for peat.

Columns were filled with soil mixtures to initial soil bulk density of 1.1 g cm^{-3}. The bottom of the column was filled with drainage inert sand (2–5 mm) over mesh that prevented soil particle loss through the outlet. Soil in all treatments was fertilized with 150 mg N and K kg^{-1} soil as NH_4NO_3 and K_2SO_4, respectively. Soil columns were stabilized for eight weeks and sown with white clover (*T. repens*) as a test plant to make columns with original and remediated soil more reliable model of field conditions. White clover is fitting for the size of the experimental columns as it develops a relatively shallow root system and at the same time stimulates the ecosystem services of water infiltration and supply of nutrients (van Eekeren et al., 2009). During this period and prior to the first determination of *K*-value soil columns were saturated with water and left to drain several times to stabilize conditions. During the experiment soil columns were considered to be falling head permeameters, on each hydraulic conductivity was calculated using a modification (Gardiner and Sun, 2002) of the falling head method of Klute and Dirksen (1986). Falling head method determines hydraulic conductivity (*K*-value) through a soil of a depth L by measuring the time (t) required for the hydraulic head to drop from one known level (h_0) to another known level (h_1) using the following equation:

$$K = (L/t)\ln((h_0 + L)/(h_1 + L)) \quad (1)$$

For each determination of the *K*-value the measurement was replicated five times and average was calculated, *K* was measured once a month. 30 h before each *K*-value measurement columns were saturated with water, first with capillary rise, then till the edge of the column using drainage outlet to saturate column from below. Prior to and after saturation dry and wet soil surface level was measured to determine soil bulk density and potential shrinkage or swelling. When plants developed, white clover was cut before *K*-value measurement to determine plant yield (Nov, Dec, Jan). Total plant yield was calculated as sum of dry mass in three cuts. Dry root mass was determined from one half of the column.

Columns were irrigated every second day with 100 mL per column (July–October) and biweekly in winter (November–January) (equivalent of 5 mm). At the end of the experiment shoots and roots were harvested, separated, and thoroughly washed with deionized water. All plant samples were dried at 35 °C to a constant weight and ground in a titanium centrifugal mill. Ground plant tissues (250–300 mg dry weight) were acid-digested (65% HNO) using microwave heating, left to cool down and diluted to a volume of 25 mL with deionized water. Metals Pb, Zn, Cd were analyzed by flame (acetylene/air) atomic absorption spectrometry (AAS, Varian AA240FS).

Soil of each column was sampled for aggregate size distribution, aggregate stability (Kemper and Rosenau, 1986; Bissonnais et al., 2002) and soil water retention analyses. For determination of aggregate size distribution soil was oven dried at 25 °C, then sieved through sieves with mesh size 8, 4, 2, 1 and 0.5 mm in one go, fractions were weighted. Wet sieving with single sieve method (Kemper and Rosenau, 1986) was used for determination aggregate stability of two size fractions (1–2, and 2–4 mm). Soil aggregates (4.0 g) were placed on a sieve with mesh size of 0.25 mm, wetted and then shaken in a can containing distilled water for 3 min using a wet sieving apparatus (Eijkelkamp, Netherlands). Mass of disintegrated soil aggregates (m_d) was determined after being oven-dried at 55 °C to constant weight. Residue of the soil aggregates above mesh was then shaken in a can containing 0.1 M NaOH for 8 min on a wet sieving apparatus to exclude non soil particles (skeleton,