Int. J. Environ. Sci. Technol. (2015) 12:2765–2776
DOI 10.1007/s13762-014-0713-x

ORIGINAL PAPER

Impact of various amendments on immobilization and phytoavailability of nickel and zinc in a contaminated floodplain soil

S. M. Shaheen · J. Rinklebe · M. H. Selim

Received: 15 April 2014 / Revised: 17 October 2014 / Accepted: 10 November 2014 / Published online: 4 December 2014

Abstract The immobilization of toxic metals in soils using amendments is a cost-effective remediation technique for contaminated soils. Therefore, this study aimed to assess the efficiency of various amendments to immobilize nickel (Ni) and zinc (Zn) in soil and reduce their phytoavailability. A greenhouse pot experiment was established with a contaminated agricultural floodplain soil. The soil was treated with activated carbon (AC), bentonite (BE), biochar (BI), cement bypass kiln dust (CBD), chitosan (CH), coal fly ash (FA), limestone (LS), nano-hydroxyapatite (HA), organo-clay (OC), sugar beet factory lime (SBFL), and zeolite (Z) with an application rate of 1 % (0.2 % for HA) and cultivated by rapeseed (*Brassica napus*). After plant harvesting, the soil was analyzed for water-soluble and geochemical fractions of Ni and Zn. Additionally, both metals were analyzed in the aboveground biomass. Application of the amendments increased significantly the biomass production of rapeseed compared to the control (except for OC, HA, and FA). Water-soluble Ni and Zn decreased significantly after adding the amendments (except OC, Z, and CH). The SBFL, CBD, LS, BE, AC, and BI were most effective, resulting in a 58–99 and 56–96 % decrease in water-soluble Ni and Zn, respectively. The addition of SBFL, CBD, and LS leads to the highest decreasing rate of concentrations of Ni in plants (56–68 %) and Zn (40–49 %). The results demonstrate the high potential of CBD, SBFL, LS, BE, AC, and BI for the immobilization of Ni and Zn in contaminated floodplain soils.

Keywords Low-cost immobilizing agents · Nano-hydroxyapatite · Organo-clay · Rapeseed · Remediation · Toxic metals

Introduction

Contamination of agricultural soils by potentially toxic metals (PTMs) threatens food safety and disturbs ecosystems (Shaheen et al. 2013a; Srinivasarao et al. 2014). Many floodplain soils are highly contaminated with PTMs (Rinklebe et al. 2007; Shaheen and Rinklebe 2014; Rinklebe and Shaheen 2014). Nickel (Ni) and zinc (Zn) are PTMs found in contaminated soils (Overesch et al. 2007; Rennert and Rinklebe 2010; Taghipour et al. 2013). Metals can become mobilized, leading to soil and groundwater contamination that increase the possibility of entering into the food chain and finally into the human body (Taghipour et al. 2013; Shaheen et al. 2014a, b, c). Thus, remediation of PTMs in contaminated soils has received increasing attention and is an important issue for adequate environmental management (Ok et al. 2011a; Castillo et al. 2014; Shaheen et al. 2015).

Choosing an adequate remediation technique—which should be in accordance with the prevailing site characteristics, types and concentration of pollutants, and the further use of the contaminated soil—is therefore required to limit the risk of polluted soils to organisms and for

S. M. Shaheen
Department of Soil and Water Sciences, Faculty of Agriculture, University of Kafrelsheikh, 33 516 Kafr El-Sheikh, Egypt

S. M. Shaheen · J. Rinklebe (✉)
Department D, Soil- and Groundwater-Management, University of Wuppertal, Pauluskirchstraße 7, 42285 Wuppertal, Germany
e-mail: rinklebe@uni-wuppertal.de

M. H. Selim
School of Plant, Environmental, and Soil Sciences, Louisiana State University, Baton Rouge, LA 70803, USA

reclamation of the contaminated site. In situ immobilization of PTMs is a remediation technology based on adding easily available amendments to polluted soils, aiming to reduce the solubility of metals in the soil without altering their total concentrations (Ok et al. 2011b; Lee et al. 2013; Shaheen et al. 2015). Immobilization of metals in soil is promising because of its simplicity and effectiveness, in situ applicability, and low cost (Varrault and Bermond 2011; Ahmad et al. 2012). Over the past 5 years, the term "green remediation" has been extensively used. Green remediation is the practice of considering environmental impacts of remediation activities at every stage of the remedial process to maximize the net environmental benefit of a cleanup (Tomasevic et al. 2013). For this reason in this paper, various by-products were used as soil amendments and/or immobilizing agents and bioenergy crop such as rapeseed to achieve the so-called green concept.

Common amendments such as liming materials and phosphates were used as immobilizing agents for PTMs in soils (Gonzalez-Alcaraz et al. 2013; Bolan et al. 2013). However, there is an increasing demand for new, applicable, and economic amendments. Those materials should have a high sorption capacity; they should be abundant, available, biodegradable, and inexpensive in order to use them as low-cost-effective amendments for on-site remediation of metal-contaminated soils. Moreover, it would be desirable if they originate from renewable sources (Ashraf et al. 2013; Dumbrava et al. 2014).

Coal fly ash (FA), limestone (LS), sugar beet factory lime (SBFL), and cement bypass kiln dust (CBD) are important wastes (Shaheen et al. 2013b, 2014d, e, f). The safe recycling of these wastes in agriculture is considered a sound alternative both environmentally and economically. Several studies have been conducted to evaluate the capabilities of these wastes and various by-products, i.e., biochar (BI), activated carbon (AC), and chitosan (CH), to remove metals from aqueous solutions and wastewaters (Shaheen et al. 2013b, 2014e). However, no attempts have been made to study the efficiency of CH, BI, SBFL, and CBD for the immobilization of PTMs especially in contaminated floodplain soils because there are very few studies which have been seek for an adequate in situ remediation using different amendments which can be applied for floodplain soils. Thus, here we are dealing with emerging and alternative soil amendments to assess their potentiality to immobilize Ni and Zn in a contaminated floodplain soil. However, before those technologies are applied in the field, many factors affecting the metal immobilization by these amendments should be investigated. Therefore, we chose to conduct this relatively short-term pot experiment for one season as a first step toward identifying in a concise manner the stabilizing potential of the tested amendments before planning to move to a field-scale trial. Hence, the objectives of the present work were (1) to study the impact of various emerging amendments, i.e., BI, CH, HA, and OC, and several low-cost alternative soil amendments such as AC, BE, CBD, FA, LS, SBFL, and Z on the water-soluble and the geochemical fractions of Ni and Zn in a contaminated floodplain soil, and (2) to assess the effectiveness of these amendments on the phytoavailability and the uptake of Ni and Zn by rapeseed plants.

The novelty of this study is that we examined an emerging amendments, i.e., BI, CH, HA, and OC, and a variety of low-cost amendments and by-products, i.e., AC, BE, CBD, FA, LS, SBFL, and Z, that were not tested as immobilizing agents for toxic metals, i.e., Ni and Zn, in contaminated floodplain soil like our soil and that are not restricted on a particular geographical locality. Additionally, the use of plants, which are not for direct food consumption and of high economic value, e.g., bioenergy crops such as rapeseed, as test crop in this metal-contaminated soil is an issue worth evaluating where this soil is used as grassland. The motivation of our study was that the obtained results will be required to answer both scientific and practical questions regarding the suitability and efficiency of the studied amendments for the in situ remediation of the toxic metals Ni and Zn in contaminated floodplain soils.

Materials and methods

Sampling site

Soil samples were collected from a floodplain at the lower course of the Wupper River close to the confluence into the Rhine River. The study site is located near the town Leverkusen, about 20 km to the north of Cologne, Germany (E 2570359, N 5661521; 51°4′0.48″N, 6°4′0.48″E). The site is under agricultural use as grassland. The study site is flooded periodically by the Wupper River, usually in spring time. The catchment area of the Wupper River encompasses 814 km^2. The soil is classified as Eutric Fluvisols according to IUSS-FAO (2014) and highly contaminated with PTMs (Frohne et al. 2011, 2014).

Sampling and analysis of the soil

The soil was collected from 26 to 40 cm depth since this horizon reveals the highest contamination. About 400 kg soil was collected from an area 4 m^2. The sampling was performed in eight replicates of about 50 kg, which were pooled to one composite sample. Soil material was homogenized, air-dried, and crushed handily. Soil properties, particle size distribution, and oxides concentration were determined according to standard methods (Blume et al. 2011). Total C (C_t) and N_t were measured with dry combustion and thermal conductivity detection using a C/N/S-Analyser (Vario EL Heraeus, Analytik Jena, Jena, Germany). Inorganic C was quantified by dry combustion and IR detection with a C-MAT 550 (Stroehlein). Soil organic C was calculated as the difference between C_t and inorganic C. Separate subsamples were digested in a microwave system (Milestone MLS 1200 Mega, Germany) for pseudo total metal concentrations (US EPA 3051a 2007). Available concentrations of Ni and Zn were extracted by ammonium bicarbonate-diethylene triamine pentaacetic acid (AB-DTPA) (Soltanpour and Schwab 1977). The total and available metal concentrations in the soil were quantified by ICP-OES (details see below).

Collection and analysis of the amendments

The CH was obtained from the Egyptian Petroleum Research Institute and was prepared from the shrimp shells. The sugar beet factory lime was obtained from the wastes around the sugar beet factory in El-Hamoul, Kafr El-Sheikh Governorate, Egypt. Cement bypass kiln dust was brought from Tourah Portoland cement factory, Cairo, Egypt. Activated carbon was obtained from Sigma-Aldrich (purity above 95 %) and sieved to a particle size of 0.18 mm (US mesh size 80) in diameter. Biochar was collected from company of TERRA PRETA e.K., Berlin, Germany. The name of the biochar product is TERRA PRETA, and it is composed of bio-charcoal, humus, clay, alumina, shell limestone, perlite, microorganisms, and organic fertilizer. Bentonite was collected from IBECO HT-X, S&B Industrial Minerals GmbH. Zeolite is a natural clinoptilolith–zeolithe powder (<20 µm) without any amendments in pharmaceutical quality; it is commercially available via Zeolith-Bentonit-Versand.de, Chemnitz, Germany. Nano-hydroxy apatite was obtained from Sigma-Aldrich, Hoagland's No.2 Basalt Salt Mixture, USA. Fly ash was collected from the Ruhr industrial region, Germany. Limestone was collected from the Wuppertal region, Germany. Organo-clay MRM is a sulfur impregnated form of Organo-clay PM-199.

The pH of the amendments was measured in deionized water (1:2 H_2O for inorganic materials and 1:5 H_2O for organic materials). Total calcium carbonates were determined by using Collins calcimeter. Total metal concentrations were digested with aqua regia (DIN ISO 11466 1997). The studied (pseudo)total metal concentrations in the studied sorbents were quantified by ICP-OES (details see below).

Pot experiment

The influence of the amendments on the immobilization and bioavailability of Ni and Zn to the rapeseed (*Brassica napus*) was investigated in a greenhouse pot experiment using the contaminated floodplain soil. The studied amendments (except HA) were applied to the soil at a rate of 10 g kg^{-1} soil, equivalent to 20 Mg ha^{-1}, assuming a bulk density of 1.33 g cm^{-3} at field and a depth of incorporation of 15 cm. Nano-hydroxyapatite was applied to the soil at a rate of 2 g kg^{-1}. In a portion of 3 kg of each air-dried sample, we added 30 g of each of the ten amendments (AC, BE, BI, CBD, CH, FA, LS, OC, SBFL, and Z) and 6 g of HA which were placed into 20-cm-diameter and 25-cm-height pots. A complete randomized block design was composed of twelve treatments (eleven amendments plus one control) with three replicates each. This design resulted in a total of 36 pots (1 soil × 12 treatments × 3 replicates × 1 plant). The soil and each amendment were mixed thoroughly and placed in the pots. The pots were irrigated with approximately 1L deionized water to reach a moisture content of about 60 % of the field capacity. One week after the amendment applications, rapeseed was planted. Rapeseed was used in this study as test plant due to its ability to tolerate high levels of PTMs in soils and due to their use as bioenergy plant. Thirty seeds (later thinned to 25) were sown in each pot. During the germination period, soil moisture was maintained at 80 % of field capacity and after thinning was raised to field capacity. The pots were irrigated with deionized water. The moisture content was kept at field capacity by weighting the pots every day and adding the lost water. Two and 5 weeks after the germination, the pots were irrigated with 300 ml of a nutrient solution containing 0.8 g NH_4NO_3 L^{-1} and 0.4 g K_2HPO_4 L^{-1} (solution pH = 7.22). The plants were harvested 8 weeks after seeding where the aboveground biomass was removed from the pots.

Preparation and analyses of plant and soil samples

The aboveground biomass was thoroughly washed with 1 mM HCl and dried to constant weight at 70 °C in a forced draft oven. The dry biomass was recorded, and then, the samples were ground to fine powder in a stainless steel grinder and stored in plastic bags until analysis. One gram of plant material was dry-ashed in a muffle furnace at 450 °C for 5 h and extracted with 20 % hydrochloric acid (Jones et al. 1991), and Ni and Zn concentrations were measured by ICP-OES (see below).

As for the soil samples, after harvesting they were taken out of the pots, air-dried, passed through a 2-mm sieve and analyzed for pH, water-soluble extractable, and the geochemical fractions of Ni and Zn. Soil pH was measured (1:1 H_2O). Water-soluble Ni and Zn were extracted by deionized water in 1:1 extraction ratio. 30 g of soil samples was equilibrated with 30 mL of deionized water in 50-mL centrifuge tubes (pre-weighed) for 2 h on a reciprocating shaker at room temperature. After equilibration, the samples were centrifuged at 5,000 rpm for 20 min and the supernatant was filtered through a Whitman no. 42 filter paper. The non-residual chemical fractions of Ni and Zn were extracted by a sequential extraction method based on the work of Tessier et al. (1979) and proposed by Sánchez-Martín et al. (2007) to characterize the partitioning of Ni and Zn in the soil. The method used discriminates the metals into soluble + exchangeable [F1: 1 M NH_4OAc (pH 7.0), sorbed and bound to carbonate (F2: 1 M NH_4OAc adjusted to pH 5 with HOAc), Fe–Mn oxide bound (F3: 0.175 M $(NH_4)_2C_2O_4$ and 0.1 M $H_2C_2O_4$, and organically bound (F4: 0.1 M $Na_4P_2O_7$)]. Separation between steps was by decantation of the supernatant after centrifugation at 5,000 rpm for 20 min. The concentrations of Ni and Zn in the digested soil and plant samples, as well as the concentrations of available form and the different metal fractions after extractions of the soil, were measured by ICP-OES (Ultima 2, Horiba Jobin-Yvon, Unterhaching, Germany). A 4-point calibration was performed with standard solutions (CertiPur, Merck) diluted in deionised water. Each sample was measured in three replications. The concentrations were calculated on the basis of dry weight of samples (105 °C, 24 h).

Quality control and statistical analysis

Quality control of the extraction efficiency of total metals was performed using certified soil reference materials (BRM No. 13 and BRM No. 10a) obtained from the German Federal Institute for Materials Research and Testing (BAM). The average recovery was 104 % for Ni and 99 % for Zn. In all measurements, blanks, triplicate measurements of metals in extracts, and analyses of certified reference materials for each metal (Merck) were routinely included for quality control, according to ISO/IEC 17025 for laboratory accreditation. Additionally, a test of recovery was carried out at five different concentration levels (1,000, 100, 50, 25, and 12.5 $\mu g\ L^{-1}$) as an internal quality control. The average relative standard deviation (RSD) was less than 3 %. The detection limits were 28 $\mu g\ L^{-1}$ for Al, 10 $\mu g\ L^{-1}$ for As, 2.7 $\mu g\ L^{-1}$for Cd, 7.0 $\mu g\ L^{-1}$ for Co, 7.1 $\mu g\ L^{-1}$ for Cr, 5.4 $\mu g\ L^{-1}$ for Cu, 6.2 $\mu g\ L^{-1}$ for Fe, 1.4 $\mu g\ L^{-1}$ for Mn, 12 $\mu g\ L^{-1}$ for Mo, 10 $\mu g\ L^{-1}$ for Ni, 40 $\mu g\ L^{-1}$ for Pb, 60 $\mu g\ L^{-1}$ for S, 75 $\mu g\ L^{-1}$ for Se, 7.5 $\mu g\ L^{-1}$ for V, 1.8 $\mu g\ L^{-1}$ for Zn. Maximum allowable relative standard deviation between replicates was set to 5 % for soil and 8 % for plant analyses. Statistical analyses were performed using the analysis of variance (ANOVA) and Duncan's multiple range tests to compare the means of the treatments at a level of significance of $P < 0.05$ using the SPSS 22 package.

Results and discussion

Characterization of the soil and the amendments

Basic properties and metal concentrations in the soil are presented in Table 1. The soil texture was dominated by silt. The soil was weakly acidic, contained high organic carbon, and showed a moderate cation exchange capacity (CEC). The soil exhibited higher concentrations of iron (Fe) oxides than manganese (Mn) oxides. The amorphous Fe and Mn (oxalate extractable) values were relatively low compared to the crystalline form (CBD extractable), suggesting that the majority of Fe and Mn existed in crystalline form. In general, the soil has elevated total concentrations of the elements. Concentrations of the elements exceeded the precautionary values of the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV 1999). In addition, the values of the elements studied (except V) were found to be higher than the maximum allowable soil concentrations. Moreover, the values of As, Cr, Cu, Pb, Se, and Zn were higher than the upper limit of the trigger action values for PTMs in agricultural soils as reported by Kabata-Pendias (2011), implying harmful soil alterations need remediation. Concerning to Ni and Zn, the soil has elevated concentrations of Ni (80.96 mg kg^{-1}) and Zn (1,324.0 mg kg^{-1}) (Table 1). Total concentrations of the metals exceeded the precautionary values (15–70 for Ni and 150–200 for Zn) of the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV 1999). Also, the values were found to be higher than the maximum allowable soil concentrations (20–60 for Ni and 100–300 for Zn) and the trigger action values (75–150 for Ni and 200–1,500 for Zn) as reported by Kabata-Pendias (2011). However, the Ni concentrations are lower than many serpentine soils which contain high geogenic Ni levels (Licina et al. 2010; Antić-Mladenović et al. 2011). The metal availability as extracted using AB-DTPA seems high especially for Zn. Increase in total Ni and Zn concentration in the studied soil may be due to the contamination of the water and sediments of Wupper River by these metals from anthropogenic activities (Frohne et al. 2011, 2014).

Selected properties and (pseudo)total metal concentrations in the amendments are presented in Table 2. Most of the amendments were alkaline; the pH ranged from 7.8 in CH to 12.6 in CBD except for BI (6.6) and OC (6.7). The LS and SBFL recorded the highest total carbonate concentrations (82.4 and 98.5 %, respectively). Bentonite, OC, Z, BE, FA, and CBD showed high concentrations of Al and Fe. Organo-clay has the highest concentration of sulfur. Concentrations of Ni and Zn in the amendments were relatively low (Table 2).

Table 1 Properties and metal concentrations of the studied soil

Properties	Unit	Concentrations
Sand	[%]	6
Silt		92
Clay		2
Electric conductivity	[μSm^{-1}]	54.5
pH	(1:1 H_2O)	6.71
Total carbonates	[%]	b.d.l.
Total carbon		7.06
Total nitrogen		0.354
Total inorganic carbon		0.003
Total organic carbon		7.05
Total phosphorus		0.098
Cation exchange capacity	[$cmol_{(+)}kg^{-1}$]	15.10
Exchangeable-K		0.10
Exchangeable-Na		0.10
Exchangeable-Ca		13.1
Exchangeable-Mg		2.41
Iron (Fe)–Manganese (Mn) oxides		
Fet	[%]	4.375
Fed		3.553
Feo		2.524
Fe_o/Fe_d	ratio	0.710
Mnt	[%]	0.100
Mnd		0.091
Mno		0.086
Mn_o/Mn_d	ratio	0.950
(Pseudo)total metal(loid) concentrations		
Al	[mg kg^{-1}]	18,469.7
As		90.8
Cd		8.1
Co		20.4
Cr		490.3
Cu		3,044.1
Ni		80.96
Pb		412.1
S		994.1
Se		14.6
V		43.0
Zn		1,324.0
AB-DTPA-extractable Ni and Zn		
Ni Zn	[mg kg^{-1}]	2.04
Zn		17.09

Total sand (2–0.063 mm); total clay (<2 µm). Fe_t and Mn_t = total Fe and Mn; Fe_d and Mn_d = citrate-bicarbonate-dithionate extractable Fe and Mn; Fe_o and Mn_o = ammonium oxalate-oxalic acid extractable Fe and Mn

b.d.l. below detected limit, *AB-DTPA* ammonium bicarbonate-diethylene triamine pentaacetic acid

Impact on soil pH

Soil pH was weakly acidic to neutral. Cultivation of rapeseed decreased the pH from 6.7 in the experimental soil (ES) to 6.3 in the cultivated non-amended soil (control) probably as a result of the plant rhizosphere acidic impact. Application of the amendments except for OC and Z increased the soil pH compared to control. The highest increasing rate of soil pH was for SBFL and LS followed by BE, CBD, and AC. The SBFL and LS increased the soil pH from 6.3 to 7.5, while OC decreased it to 6.0. Soil pH was mainly affected by the pH of the amendments, where CBD, SBFL, LS, BE, and AC had higher pH values (Table 2), indicating that these amendments (especially the highly alkaline) may have a beneficial effect on plant growth and Ni and Zn solubility in the studied soil.

Impact on dry biomass yield

Application of the amendments except for OC, HA, and FA increased rapeseed dry biomass yield significantly compared to control (Fig. 1). The highest increasing rate was for CBD followed by SBFL, LS, BI, CH, AC, BE, and Z. The CBD increased dry biomass yield by about sixfold, while OC decreased it by 25 %. The higher yields in the alkaline and organic amendment-treated soils might be attributed to the improved soil pH, physical conditions by the supply of OM, and additional nutrients from the amendments. For example, the increase in biomass yield in the case of SBFL-treated soil could be explained by its high concentrations of macronutrient especially phosphorus (Sims et al. 2010; Shaheen and Tsadilas 2013).

Impact on water-soluble and geochemical fractions of Ni and Zn

Cultivation of rapeseed decreased significantly the water-soluble Ni and increased significantly water-soluble Zn (Figs. 2, 3). These results suggest that, in case of Zn, the plant growth caused a pronounced increase in the water-soluble fraction pattern for the control soil. These changes can be explained with the interaction of root exudates with the surroundings solids. Excretion of root exudates, which contain organic acids, amino acids, sugars, and high molecular weight compounds, increases the solubility of metals in the rhizosphere (Malandrino et al. 2011).

In comparison with the non-amended soil, the water-soluble concentrations of Ni and Zn in the amended soils decreased significantly with the amendments except for OC and Z with Ni (Fig. 2) and OC, CH, and Z with Zn (Fig. 3).

Table 2 Selected characteristics and (pseudo)total metal concentrations in the studied amendments

Amendments	AC	BE	BI	CBD	CH	FA	HA	LS	OC	SBFL	Z
pH [H_2O]	11.0	10.3	7.3	12.6	7.8	9.9	10.8	9.2	6.7	8.7	8.0
Total CO_3	4.5	10.5	6.77	19.8	n.d.	0.35	n.d.	98.5	b.d.l.	82.4	1.2
Metal concentration [mg kg^{-1}]											
Aluminum	n.d.	11,911.9	12,400	11,810.8	204.1	11,950.7	n.d.	403.6	11,952.1	1,705.2	11,905.2
Iron	n.d.	17,777.3	8,500	8,394.1	1,284.3	17,930.9	n.d.	475.3	3,256.1	849.3	6,115.9
Manganese	n.d.	497.1	300	143.8	70.7	311.6	n.d.	158.9	191.8	84.1	104.5
Nickel	n.d.	7.0	11.7	9.7	28.2	42.0	n.d.	0.7	7.0	36.0	0.91
Sulfur	n.d.	5,750.2	2,200	11,405.6	136.4	2,144.7	n.d.	76.7	38,718.2	2,025.2	0.21
Zinc	n.d.	45.7	71.7	86.5	5.1	102.0	n.d.	4.8	36.9	14.3	22.1

AC activated carbon, *BE* bentonite, *BI* biochar, *CBD* cement bypass kiln dust, *CH* chitosan, *FA* coal fly ash, *HA* Nano-hydroxyapatite, *LS* limestone, *OC* organo-clay, *SBFL* sugar beet factory lime, *Z* Zeolite, *n.d.* not determined

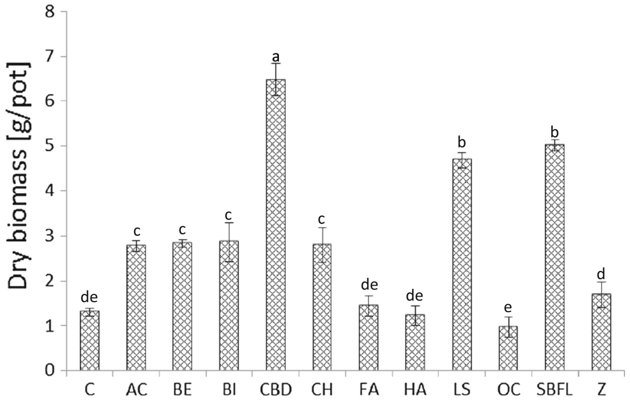

Fig. 1 Impact of soil amendments on the dry biomass yield of rapeseed. *C* control, *AC* activated carbon, *BE* bentonite, *BI* biochar, *CBD* cement bypass kiln dust, *CH* chitosan, *FA* coal fly ash, *HA* nano-hydroxyapatite, *LS* limestone, *OC* organo-clay, *SBFL* sugar beet factory lime, *Z* zeolite. Values accompanied by different letters are significantly different within columns at the level ($P < 0.05$)

The extent of the decrease in metal solubility, however, differed among the two metals and amendments used. The decreasing rate of water-soluble Ni was higher than Zn. Nearly 100 % of water-soluble Ni was decreased by AC, BI, CBD, FA, HA, LS, and SBFL compared to the control. Bentonite and CH decreased water-soluble Ni by 58.7 and 11.1 %, respectively, compared to the control. In contrast, OC increased significantly water-soluble Ni by 138.1 % compared to the control (Table 3). The water-soluble concentrations of Zn decreased by about 95, 92, 89, 83, 74, 56, 30, and 26 % by CBD, SBFL, LS, BE, AC, BI, FA, and HA, respectively, compared to the control. In contrast, OC increased the water-soluble Zn by 196 % compared to the control. Non-significant differences were recorded between the control and Z and CH treatment for soluble Ni and Zn (Figs. 2, 3; Table 3). Seaman et al. (2001) also found that hydroxyapatite was effective in decreasing the solubility of Ni.

Concentrations of soluble + exchangeable Zn (F1) were higher than Ni (Figs. 2, 3). Nickel and Zn in F1 were significantly decreased by the amendments (except for OC and Z). The amendments decreased soluble + exchangeable Ni and Zn by a relatively similar decreasing percentage (Table 3). The average decreasing percentages were about 74, 73.5, and 68 % by SBFL, CBD, and LS, respectively. Bentonite, AC, and BI showed the second efficiency order and decreased F1 of Ni and Zn by about 30, 26.5, and 20.5 %, respectively. The CH, FA, and HA decreased the concentrations of soluble + exchangeable Ni and Zn by about 11.5 %. In contrast, OC increased soluble + exchangeable Ni and Zn by 25 and 18 %, respectively, compared to the control (Table 3). Non-significant differences were recorded between the control and Z and CH treatment for soluble + exchangeable Ni and Zn (Figs. 2, 3; Table 3).

Cultivation of rapeseed decreased significantly the concentrations of Ni and Zn in the sorbed and bound to carbonate fraction (F2) (Figs. 2, 3). This could be explained by the relative decrease in pH after the cultivation resulting in dissolving the carbonate fraction of both metals (especially Zn). These changes can be explained by the interaction of root exudates with the surrounding solids in the rhizosphere. These organic compounds in the rhizosphere might lead to an increase in the microbiological activities which enables roots to mobilize the easily mobilizable metal fraction (sorbed and bound to carbonates) by acidification and redox changes. Therefore, the relative acidification in the rhizosphere might increase the soluble fraction and decrease the sorbed and carbonate fraction of Zn (Malandrino et al. 2011).

In comparison with the control, the F2 of Ni in the amended soils decreased significantly (except for CBD). Bentonite, HA, and BI showed the highest decreasing rate of Ni (about 54 %). Activated carbon, CH, and FA showed the second efficiency order and decreased the exchangeable Ni concentrations of about 30 %. The F2 of Ni was decreased about 7, 14, and 22 % by Z, LS, and SBFL,

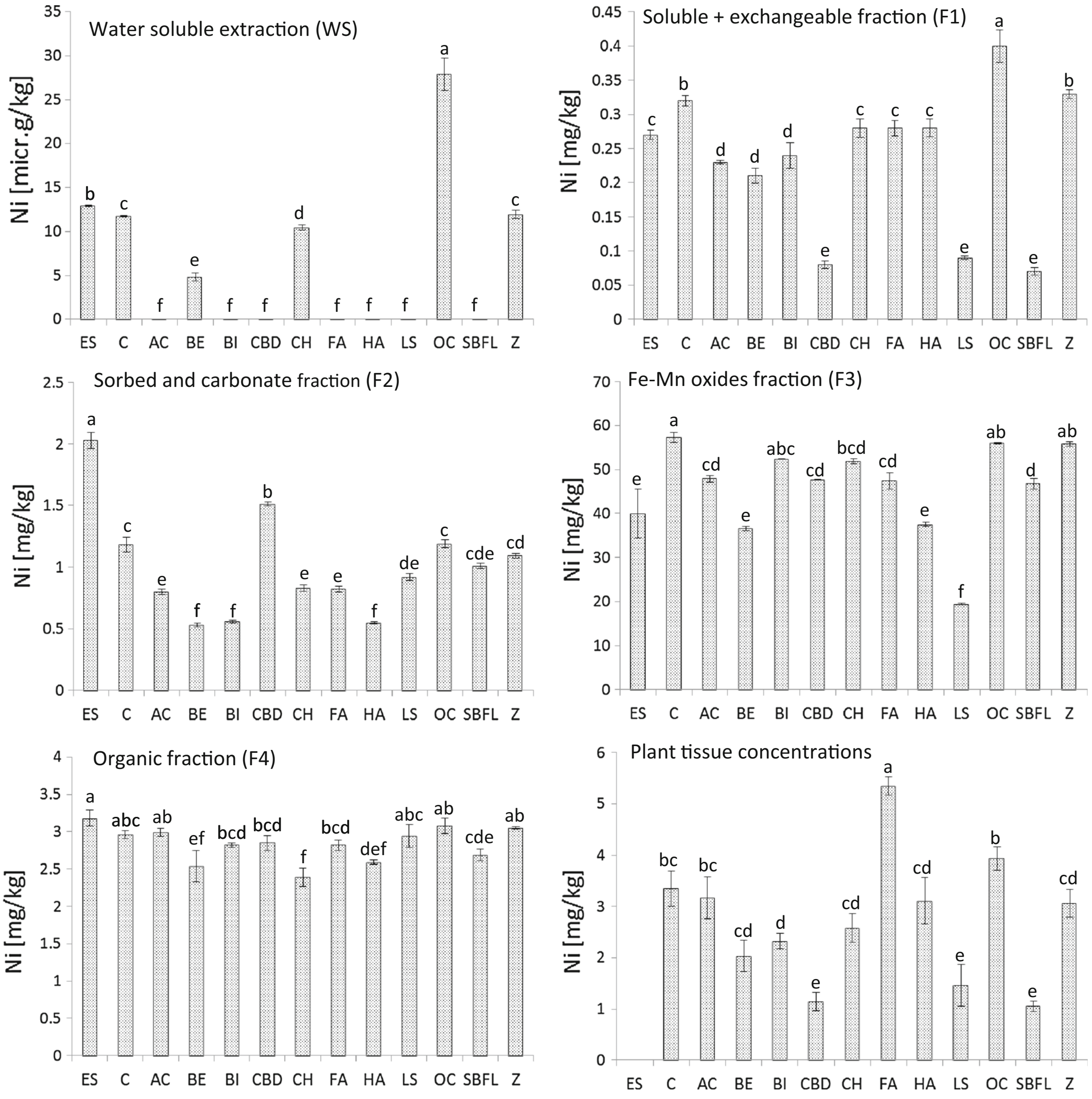

Fig. 2 Impact of soil amendments on the water-soluble and geochemical fractions of Ni in the soil and on the plant tissue concentrations of Ni in the grown rapeseed. *ES* experiment soil, *C* control, *AC* activated carbon, *BE* bentonite, *BI* biochar, *CBD* cement bypass kiln dust, *CH* chitosan, *FA* coal fly ash, *HA* nano-hydroxyapatite, *LS* limestone, *OC* organo-clay, *SBFL* sugar beet factory lime, *Z* zeolite. Low detection limit = 0.005 mgL^{-1}. Values accompanied by different letters are significantly different within columns at the level ($P < 0.05$). Please notice the different scales

respectively. In contrast, CBD increased F2 of Ni about 28 % compared to the control (Table 3). Although BE, HA, and BI decreased the concentration of sorbed Zn by about 7–20 %, the other amendments increased it by an increasing percentage ranged from 11 to 38 %. The CBD showed the highest increasing percentage (38 %), while AC, CH, FA, LS, OC, SBFL, and Z showed increasing percentages ranged from 11 to 16 % (Table 3).

The amendments decreased significantly the oxide fraction (F3) of Ni and Zn compared to the control with a similar rate (Figs. 2, 3). The LS showed the highest decreasing rate of Ni and Zn (67.5 %). Bentonite and HA showed the second efficiency order and decreased oxide fraction of Ni and Zn by about 32 %. The oxide fraction of Ni and Zn was decreased by about 11–18 % by AC, CH, CBD, FA, and SBFL. The lowest decreasing percentages (2–8 %) were recorded with Z, OC, and BI (Table 3).

The variations in the organic fraction (F4) of Ni and Zn after adding the amendments were narrow and not significant in most cases (Figs. 2, 3; Table 3). These results imply that the impact of the studied amendments on the organic bound fraction of both metals is relatively small compared to the soluble, exchangeable, and oxide fractions.

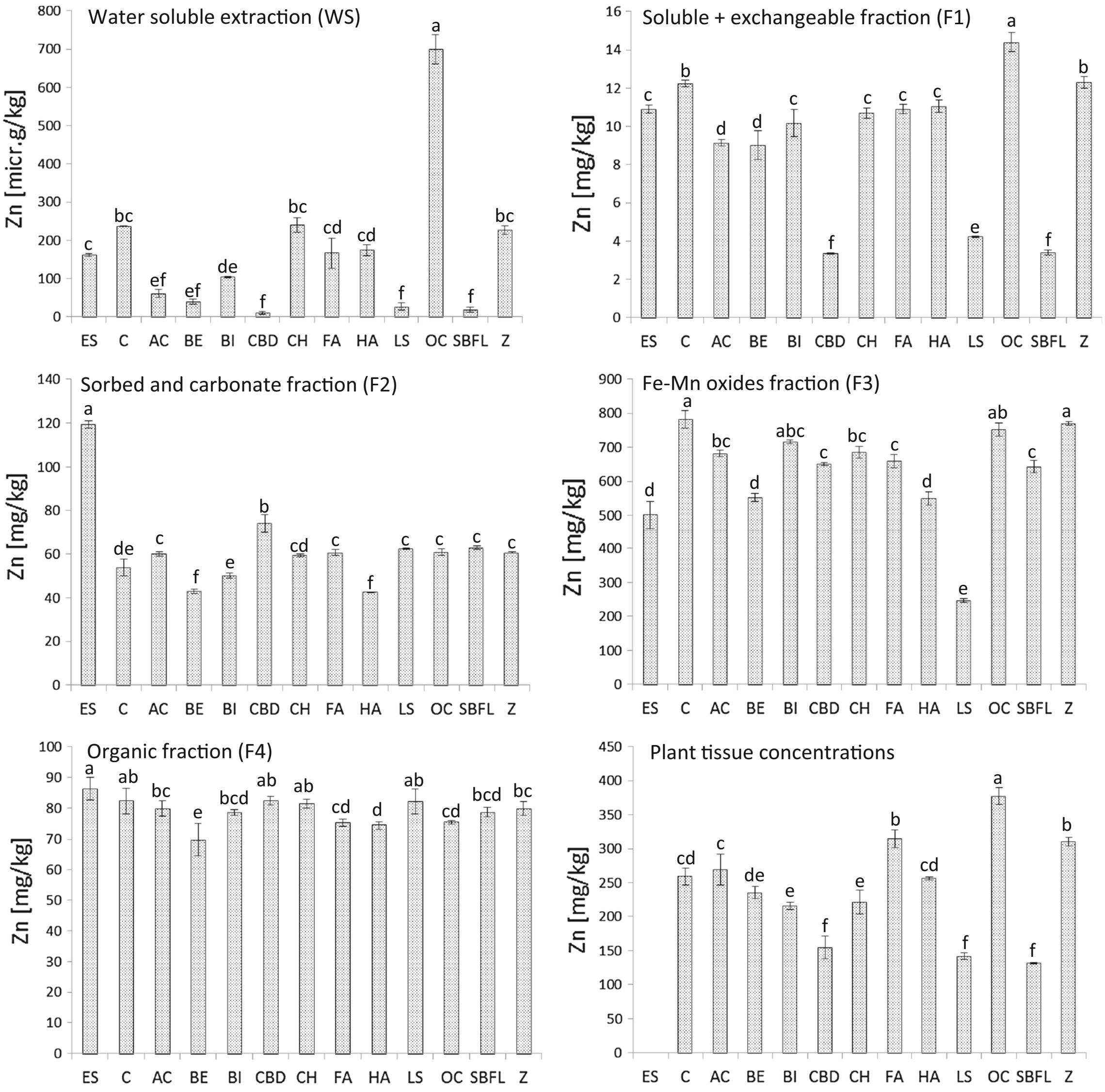

Fig. 3 Impact of soil amendments on the water-soluble and geochemical fractions of Zn in the soil and on the plant tissue concentrations of Zn in the grown rapeseed. *ES* experiment soil, *C* control, *AC* activated carbon, *BE* bentonite, *BI* biochar, *CBD* cement bypass kiln dust, *CH* chitosan, *FA* coal fly ash, *HA* nano-hydroxyapatite, *LS* limestone, *OC* organo-clay, *SBFL* sugar beet factory lime, *Z* zeolite. Values accompanied by different letters are significantly different within columns at the level ($P < 0.05$). Please notice the different scales

Impact of amendment types on metal solubility and mobilization

The SBFL, CBD, and LS showed the highest decreasing percentage of water-soluble and soluble + exchangeable Ni and Zn followed by BE, AC, BI, FA, and HA (Table 3). Thus, these alkaline materials can be used to treat Ni- and Zn-contaminated soils, decreasing their solubility due to their high pH which increases soil pH and enhances precipitation and sorption of metals in the treated soil (Hale et al. 2012). The high efficacy of SBFL in decreasing solubility and mobilization of Ni and Zn might be caused by its high alkalinity and high content of total calcium carbonates (Table 2). Therefore, SBFL increased soil solutions' pH more than one unit, which decreased metals solubility due to enhanced sorption and/or precipitation, where the sorption of metal cations is strongly dependent on pH (Gonzalez-Alcaraz et al. 2013).

The high efficacy of CBD in decreasing the mobilization of Ni and Zn could be explained by its high alkalinity (pH = 12.6, Table 2), high carbonates content (20 %), surface area, and oxides content. Furthermore, the metals might be decreased by CBD, presumably due to sorption/precipitation reactions (Shaheen et al. 2013b). The relatively high efficiency of BE in decreasing the solubility and mobilization of Ni and Zn might be due to sorption of Ni and

Table 3 Impact of soil amendments on the increasing/decreasing percentage of water-soluble and each fraction, and the plant tissues concentrations of Ni and Zn in the treated soil compared to the control

Treatment	Nickel						Zinc					
	WS	F1[a]	F2[b]	F3[c]	F4[d]	Plant tissue conc.	WS	F1[a]	F2[b]	F3[c]	F4[d]	Plant tissue conc.
AC	99.91	28.13	32.20	16.40	−1.01	5.37	74.43	25.27	−11.71	12.78	3.04	−3.78
BE	58.74	34.38	55.08	36.13	14.19	39.40	83.47	26.17	20.26	29.36	15.19	9.24
BI	99.91	25.00	52.54	8.55	4.73	30.75	56.17	16.76	6.69	8.41	4.62	16.83
CBD	99.91	75.00	−27.97	16.75	3.72	65.97	95.73	72.69	−37.73	16.86	0.00	40.41
CH	11.08	12.50	29.66	9.42	19.26	22.99	−1.35	12.59	−10.41	12.40	1.09	14.75
FA	99.91	12.50	30.51	17.10	4.73	−59.70	29.63	10.87	−12.64	15.72	8.63	−21.22
HA	99.91	12.50	53.39	34.55	12.50	7.16	26.37	9.65	20.82	29.75	9.60	1.12
LS	99.91	71.88	22.03	66.14	0.68	56.42	88.80	65.41	−15.99	68.46	0.12	45.34
OC	−138.11	−25.00	−0.85	2.27	−4.05	−17.61	−195.73	−17.66	−13.20	3.82	8.38	−45.38
SBFL	99.91	78.13	14.41	18.32	9.12	68.66	92.10	72.20	−16.91	17.75	4.50	49.31
Z	−1.79	−3.13	7.63	2.62	−3.04	8.66	4.35	−0.57	−12.64	1.52	2.92	−19.49

Increasing/decreasing percentage = control−treatment/control*100 (data calculated from Fig. 2 for Ni and Fig. 3 for Zn) (−): increasing (+): decreasing

WS water-soluble extraction, *AC* activated carbon, *BE* bentonite, *BI* biochar, *CBD* cement bypass kiln dust, *CH* chitosan, *FA* coal fly ash, *HA* nano-hydroxyapatite, *LS* limestone, *OC* organo-clay, *SBFL* sugar beet factory lime, *Z* zeolite

[a] F1 = soluble + exchangeable fraction, [b] F2 = sorbed and carbonate fraction, [c] F3 = Fe–Mn oxides fraction, [d] F4 = organic fraction

Zn on the surface of BE or fixation of metal as a result of precipitation, physical entrapment in clay lattice wedge zones, or strong sorption at the exchange sites (Sdiri et al. 2014). Because soil pH is the most important factor that governs the solid solution equilibria of metals in soils, the effect of addition of BE on soil pH was significant where it increased soil pH from 6.3 to 6.9. Application of FA decreased significantly the concentrations of water-soluble and soluble + exchangeable Ni and Zn compared to the control, possibly due to its high alkalinity (pH 9.89; Table 2) and its high content of sesquioxides. In this respect, Tsadilas et al. (2009) stated that FA may increase the available surface area for element sorption, increase the pH of acidic soils, and render most cationic metals less mobile.

Among the organic amendments, AC showed the highest efficiency in decreasing the water-soluble and soluble + exchangeable concentrations of Ni and Zn compared to the control followed by BI and CH (Table 3). Carbonaceous sorbents such as activated carbon have been shown to have a very high affinity and capacity for sorbing metals (Lehmann 2007; Shaheen et al. 2014e). The high pH value for AC (Table 2) could explain its ability to reduce the solubility and mobilization of Ni and Zn. An increase in soil pH determines the success of immobilization of PTMs in the contaminated soils since the solubility and availability of PTMs in soils can be decreased at high soil pH (Lee et al. 2013). In combination with soil pH, the addition of organic materials, such as in AC, reduces the bioavailability of Ni and Zn by forming stable complexes with humic substances (Srivastava et al. 2008).

Biochar decreased significantly the solubility of Ni and Zn compared to control despite its low pH (Figs. 2, 3). Biochar has a large surface area and can thus reduce the bioavailability of metals and organic compounds (Zhang et al. 2013). We have observed a strong reduction in the soluble Ni concentrations compared to Zn, indicating a strong tendency of AC and BI to retain this metal (Table 3). The structure of BI might explain some of the effects. It is thought that oxidation of BI occurs most rapidly on their outer surfaces, followed by interior pores, which might result in differential element retention between surface and interior sites as a result of shifting CEC for example (Beesley et al. 2011). Zinc, which was much more abundant in water soluble fraction and present in higher concentrations than Ni may have been retained both to outer surfaces and, when those retention sites were effectively saturated, further adsorbed to the network of pores and fissures that form biochar's complex inner microstructure (Beesley and Marmiroli 2011). Such differential metal retention and leaching effects are related to pore sizes, outer, and inner surfaces of biochar (Singh et al. 2010). Biochar has proven to be effective at decreasing high concentrations of soluble Ni and Zn originating from a contaminated soil (Beesley et al. 2011; Ahmad et al. 2014).

Chitosan shows a different behavior concerning water-soluble and soluble + exchangeable Ni and Zn concentrations. In contrast to the other amendments, the impact of CH on the decrease in the soluble + exchangeable fraction of Ni and Zn was higher than the soluble form (Figs. 2, 3). The low efficiency of CH in decreasing water-soluble Ni and Zn could be explained by its low impact on soil pH, since its application decreased soil pH slightly. The relatively high efficacy of CH in decreasing the potential mobility (F1) of Ni and Zn could be explained by the special sorption properties of CH. The principal characteristics of CH that may affect its sorption properties are its deacetylation degree, crystallinity, and to a lesser extent molecular weight. Therefore, it should be mentioned that sorption properties of CH are due to its composition and the presence of active (functional) groups. Particularly, the large amount of amino and hydroxyl groups in CH leads to the high sorption efficiency of metals (Kamari et al. 2011; Shaheen et al. 2013a, b).

In contrast, the application of OC increased the water-soluble and soluble + exchangeable Ni and Zn concentrations compared to the control (Figs. 2, 3), which could be due to the relatively low pH (Table 2), which decreased soil pH from 6.32 to 6.05. This effect was particularly obvious for Zn where its concentration in OC was relatively high compared to Ni. Statistical analyses revealed that both water-soluble and exchangeable concentrations of Ni and Zn correlated negatively with soil pH, while exchangeable concentrations were more affected.

The amendments with high content of $CaCO_3$ (i.e., SBFL, CBD, and LS) increased the carbonate bound fraction of Ni and Zn. There was a special strong effect on Zn, with consistent increase in F2 of this metal indicating a strong tendency of SBFL, CBD, and LS to retain this metal. In most cases and especially with the liming materials, the decrease in water-soluble and exchangeable Ni and Zn in the amended soils resulted in an increase in the carbonate fraction (especially Zn).

Impact on plant tissues concentrations

Concentrations of Zn in rapeseed were higher than Ni (Figs. 2, 3). This probably occurs because Zn was present at high concentrations in the studied soil and, hence, it was preferentially assimilated by plants. Metal concentrations in the rapeseed were below critical values. The plant tissue concentrations of Ni and Zn decreased significantly in the treated soil (1.05 mg kg^{-1} for Ni and 130.0 mg kg^{-1} for Zn with SBFL) by the amendments (except FA and OC treatments) as compared to the control (3.35 mg kg^{-1} for Ni and 259 mg kg^{-1} for Zn) (Figs. 2, 3). Concentrations of Ni showed higher (5.4–68.6 %) decreasing percentage than Zn (1.1–49.3 %) with the amendments. The SBFL, CBD, and LS showed the highest decreasing rate of Ni and Zn. The decreasing percentages varied from 56 to 68 % for Ni and from 40 to 49 % for Zn by SBFL, CBD, and LS. Bentonite, BI, and CH showed the second efficiency order and decreased concentrations of Ni by 39, 30, and 23 % and concentrations of Zn by 9, 16, and 14 %, respectively (Table 3). The AC and HA did not affect significantly the concentrations of Ni and Zn compared to the control. Zeolite showed a different trend for the two metals, where it decreased the concentrations of Ni by 9 % while it increased the concentrations of Zn by 19 % (Table 3). In contrast to the other amendments, FA and OC increased the concentrations of Ni by 60 and 18 % and concentrations of Zn by 21 and 45 % compared to the control. We assume that the competition between the high concentrations of Ca, Al, and Fe in FA (Table 2) and the sorbed Ni and Zn might increase the release and desorption of Ni and Zn to the soil solution in an available form for plant uptake. In this respect, Selim and Zhang (2013) reported that competition among various element species for available sorption sites on soil matrix surfaces can enhance the mobilization of contaminants in the soil environment.

Our results suggest that SBFL, CBD, LS, and BE had the most important role in decrease in the concentrations of Ni and Zn compared to control. The decrease in Ni and Zn in the SBFL, CBD, and LS treatments is probably due to the ability of these amendments to increase soil pH and decrease metal solubility and mobilization. Fine particles of $CaCO_3$ in LS, SBFL, and CBD can cause the precipitation of Ni and Zn especially under the high pH values. Statistical analyses showed that plant tissue concentrations of Ni and Zn correlated negatively with soil pH. In this respect, Gagnon et al. (2013) found that liming using several alkaline residuals and by-products increased soil pH and decreased Zn and Cd bioavailability to the grown plants.

The negative charge of BE surfaces may electrostatically adsorb Ni and Zn on their exchangeable sites or retain Ni and Zn (e.g., by entrapping Ni and Zn in the clay lattice wedge zones). Biochar and CH treatment caused a decrease in the concentration of Ni and Zn. Chitosan decreased significantly the mobile fraction (F1) of Ni and Zn which decreased the plant uptake of both metals compared to the control. This implies that CH is able to retain metal ions, perhaps on its surfaces. Chitosan key property is the presence of amino groups ($–NH_2$) and to some extent hydroxyl groups (–OH). The decrease in Ni and Zn in the BI treatment is probably due to the presence of high OM amounts in BI what increases the soil retention capacity. For example, Kabata-Pendias (2011) reported that the Ni and Zn phytoavailability can be decreased in soils amended with OM and alkaline materials due to sorption, complexation, co-precipitation, or a combination of the three mechanisms.

Conclusion

Our aim was to assess the efficiency of the emerging amendments, BI, CH, HA, and OC, and a variety of low-cost amendments and by-products, i.e., AC, BE, CBD, FA, LS, SBFL, and Z, to immobilize Ni and Zn and to reduce their bioavailability in a contaminated floodplain soil using a sequential extraction procedure and plant uptake. Based on our results, we conclude that among the studied amendments, CBD, LS, SBFL, BE, AC, BI, and CH increased rapeseed biomass yield and decreased significantly the solubility and plant tissues concentrations of Ni and Zn compared to the control. Among the emerging amendments, the BI and CH showed a relatively high efficiency in immobilizing of Ni and Zn than HA and OC. Application of the HA with the application rate 0.2 % is too low for metal immobilization. Organo-clay increased the mobilization and uptake of Ni and Zn, which might be useful for an enhancing the removal of both metals from the soil using bioenergy crops like rapeseed.

In CBD, SBFL, and LS cases, the decrease in the water-soluble and soluble + exchangeable Ni and Zn concentrations in the amended soils resulted in an increase in the sorbed and bound to carbonate fraction (especially Zn). These results underscore the benefit of the geochemical fractionation method in assessing the efficiency of soil in situ remediation technique and, more generally, in assessing trace metal mobilization of the soil. In this scenario, it is essential to individuate a simple and cost-effective remediation technique that allows the reduction in metal assimilation from contaminated soils by plants. The chemical immobilization of Ni and Zn by SBFL, CBD, LS, BE, BI, and CH proposed in this study demonstrated to meet those requirements. This highlights their potential for an adequate use as immobilizing agents for Ni and Zn in contaminated soils in the immediate future. However, although the achieved results in the pot experiments might be considered as levels close to field conditions, a verification of the efficiency of the recommended amendments at field conditions is requested in future. Moreover, assessment of the stability of these immobilizing agents under aerobic and anaerobic conditions will be recommended in the future studies.

Acknowledgments We thank the German Academic Exchange Foundation (Deutscher Akademischer Austauschdienst, DAAD), GERSS Fellowship; Code number A1291166 and WAP program; Code number A/14/05113) and the Egyptian Science and Technology Development Fund (STDF-STF; Project ID: 5333) for financial support of the postdoctoral scholarship of the first author at the University of Wuppertal, Germany. The authors thank C. Vandenhirtz, F. Seufzer, D. Theiss, and M. Langerhans-Muhlack for their technical assistance, and Mr. J. Olsta, CETCO Company, USA, for kindly providing the organo-clay.

References

Ahmad M, Hashimoto Y, Moon DH, Lee SS, Ok YS (2012) Immobilization of lead in a Korean military shooting range soil using eggshell waste: an integrated mechanistic approach. J Hazard Mater 209–210:392–401

Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D, Vithanage M, Lee SS, Ok YS (2014) Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99:19–33

Antić-Mladenović S, Rinklebe J, Frohne T, Stärk HJ, Wennrich R, Tomić Z, Ličina V (2011) Impact of controlled redox conditions on nickel in a serpentine soil. J Soils Sedim 11:406–415

Ashraf A, Nadeem S, Sharif S, Ansari TM, Munir H, Mahmood A (2013) Study of hybrid immobilized biomass of Pleurotus sajor-caju and Jasmine sambac for sorption of heavy metals. Int J Environ Sci Te. doi:10.1007/s13762-013-0471-1

BBodSchV (1999) Bundes-Bodenschutz- und Altlastenverordnung (BBodSchV) vom 12. Juli 1999 [Federal Soil Protection and Contaminated Sites Ordinance dated 12 July 1999]

Beesley L, Marmiroli M (2011) The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. Environ Pollut 159:474–480

Beesley L, Moreno-Jiménez E, Gomez-Eyles JL, Harris E, Robinson B, Sizmur T (2011) A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. Environ Pollut 159:3269–3282

Blume H-P, Stahr K, Leinweber P (2011) Bodenkundliches Praktikum. Springer Spektrum, Akademischer Verlag, Heidelberg. 3. Aufl

Bolan ND, Mahimairaja S, Kunhikrishnan A, Naidu R (2013) Sorption–bioavailability nexus of arsenic and cadmium in variable-charge soils. J Hazard Mater 261:725–732

Castillo VA, Barakat MA, Ramadan MH, Woodcock HL, Kuhn JN (2014) Metal ion remediation by polyamidoamine dendrimers: a comparison of metal ion, oxidation state, and titania immobilization. Int J Environ Sci Te 11(6):1497–1502

DIN ISO Norm 11466 (1997) Soil quality, extraction of trace elements soluble in aqua regia

Dumbrava A, Birghila S, Munteanu M (2014) Contributions on enhancing the copper uptake by using natural chelators, with applications in soil phytoremediation. Int J Environ Sci Te. doi:10.1007/s13762-013-0467-x

Frohne T, Rinklebe J, Diaz-Bone RA, Du Laing G (2011) Controlled variation of redox conditions in a floodplain soil: impact on metal mobilization and biomethylation of arsenic and antimony. Geoderma 160:414–424

Frohne T, Rinklebe J, Diaz-Bone RA (2014) Contamination of floodplain soils along the Wupper River, Germany, with As Co, Cu, Ni, Sb, and Zn and the impact of pre-definite redox variations on the mobility of these elements. Soil Sedim Contam Int J 23:779–799

Gagnon B, Ziadi N, Robichaud N, Karam A (2013) Metal availability following paper mill and alkaline residuals application to field crops. J Environ Qual 42:412–420

Gonzalez-Alcaraz MN, Conesa HM, Alvarez-Rogel J (2013) When liming and revegetation contribute to the mobilisation of metals: learning lessons for the phytomanagement of metal-polluted wetlands. J Environ Manage 116:72–80

Hale B, Evans L, Lambert R (2012) Effects of cement or lime on Cd Co, Cu, Ni, Pb, Sb and Zn mobility in field-contaminated and aged soils. J Hazard Mater 199–200:119–127

IUSS-FAO (ed) (2014) World reference base for soil resources. Vol. 106. World Soil Resources Reports. FAO, Rome

Jones Jr, Wolf JB, Mills HA (1991) Plant analysis handbook: a practical sampling, preparation, analysis, and interpretation guide. Micro-Macro Publishing, Athens

Kabata-Pendias A (2011) Trace elements in soils and plants, 4th edn. CRC Press, Boca Raton

Kamari A, Pulford ID, Hargreaves JJ (2011) Binding of heavy metal contaminants onto chitosans—an evaluation for remediation of metal contaminated soil and water. J Environ Manage 92:2675–2682

Lee SS, Lim JE, Abd El-Azeem SAM, Choi B, Oh S, Moon DH, Ok YS (2013) Heavy metal immobilization in soil near abandoned mines using eggshell waste and rapeseed residue. Environ Sci Pollut Res 20:1719–1726

Lehmann J (2007) A handful of carbon. Nature 447:143–144

Licina V, Antic-Mladenovic S, Kresovic M, Rinklebe J (2010) Effect of high Nickel and Chromium background levels in serpentine soil on their accumulation in organs of a perennial plant. Commun Soil Sci Plan 41:1–15

Malandrino M, Abollino O, Buoso S, Giacomino A, Gioia C, Mentasti E (2011) Accumulation of heavy metals from contaminated soil to plants and evaluation of soil remediation by vermiculite. Chemosphere 82:169–178

Ok YS, Kim SC, Kim DK, Skousen JG, Lee JS, Cheong YW, Kim SJ, Yang JE (2011a) Ameliorants to immobilize Cd in rice paddy soils contaminated by abandoned metal mines in Korea. Environ Geochem Hlth 33:23–30

Ok YS, Lee SS, Jeon WT, Oh SE, Usman ARA, Moon DH (2011b) Application of eggshell waste for the immobilization of cadmium and lead in a contaminated soil. Environ Geochem Hlth 33:31–39

Overesch M, Rinklebe J, Broll G, Neue HU (2007) Metals and arsenic in soils and corresponding vegetation at Central Elbe river floodplains (Germany). Enviro Pollut 145:800–812

Rennert T, Rinklebe J (2010) Release of Ni and Zn from contaminated floodplain soils under saturated flow conditions. Water Air Soil Pollut 205:93–105

Rinklebe J, Shaheen SM (2014) Assessing the mobilization of cadmium, lead, and nickel using a seven-step sequential extraction technique in contaminated floodplain soil profiles along the central Elbe river, Germany. Water Air Soil Pollut 225:2039. doi:10.1007/s11270-014-2039-1

Rinklebe J, Franke C, Neue HU (2007) Aggregation of floodplain soils as an instrument for predicting concentrations of nutrients and pollutants. Geoderma 141:210–223

Sánchez-Martín M, García-Delgado M, Lorenzo L, Rodríguez-Cruz M, Arienzo M (2007) Heavy metals in sewage sludge amended soils determined by sequential extractions as a function of incubation time of soils. Geoderma 142:262–273

Sdiri AT, Higashi T, Jamoussi F (2014) Adsorption of copper and zinc onto natural clay in single and binary systems. Int J Environ Sci Te 11(4):1081–1092

Seaman JC, Arey JS, Bertsch PM (2001) Immobilization of nickel and other metals in contaminated sediments by hydroxyapatite addition. J Environ Qual 30:460–469

Selim HM, Zhang H (2013) Modeling approaches of competitive sorption and transport of trace metals and metalloids in soils: a review. J Environ Qual 43:640–653

Shaheen SM, Rinklebe J (2014) Geochemical fractions of chromium, copper, and zinc and their vertical distribution in soil profiles along the Central Elbe River, Germany. Geoderma 228–229:142–159

Shaheen SM, Tsadilas CD (2013) Phosphorus sorption and availability to canola grown on an Alfisol amended with various soil amendments. Commun Soil Sci Plan 44:89–103

Shaheen SM, Tsadilas CD, Rinklebe J (2013a) A review of the distribution coefficient of trace elements in soils: influence of sorption system, element characteristics, and soil colloidal properties. Adv Colloid Interface Sci 201–202:43–56

Shaheen SM, Eissa F, Ghanem KM, Gamal El-Din H, Al-Anany F (2013b) Heavy metals removal from aqueous solutions and wastewaters by using various by products. J Environ Manage 128:514–521

Shaheen SM, Rinklebe J, Rupp H, Meissner R (2014a) Lysimeter trials to assess the impact of different flood-dry-cycles the dynamics of pore water concentrations of As, Cr, Mo, and V in a contaminated floodplain soil. Geoderma 228–229:5–13

Shaheen SM, Rinklebe J, Rupp H, Meissner R (2014b) Temporal dynamics of soluble Cd Co, Cu, Ni, and Zn and their controlling factor in a contaminated floodplain soil using undisturbed groundwater lysimeter. Environ Pollut 191:223–231

Shaheen SM, Rinklebe J, Frohne T, White J, DeLaune R (2014c) Biogeochemical factors governing Co, Ni, Se, and V dynamics in periodically flooded Egyptian north Nile delta rice soils. Soil Sci Soc Am J 78:1065–1078

Shaheen SM, Tsadilas CD, Hooda PS (2014d) Opportunities and challenges in the use of coal fly ash for soil improvements—a review. J Environ Manage 145:249–267

Shaheen SM, Eissa F, Ghanem KM, Gamal El-Din H, Al-Anany F (2014e) Metal ion removal from industrial wastewaters by sorption on activated carbon, cement kiln dust, and sawdust. Water Environ Res 86(7). doi:10.2175/WERD1300382.1

Shaheen SM, Shams MS, Ibrahim SM, Elbehiry FA, Antoniadis V, Hooda PS (2014f) Stabilization of biosolids by using various by-products: Impact on soil properties, biomass production, and bioavailability of copper and zinc. Water Air Soil Pollut 225(7). doi:10.1007/s11270-014-2014-x

Shaheen SM, Tsadilas CD, Rinklebe J (2015) Immobilization of soil copper using organic and inorganic amendments. J Plant Nutr Soil Sci (in press)

Sims AL, Windels CE, Bradley CA (2010) Content and potential availability of selected nutrients in field applied sugar beet factory lime. Commun Soil Sci Plan 41:438–453

Singh B, Singh BP, Cowie AL (2010) Characterisation and evaluation of biochars for their application as a soil amendment. Aust J Soil Res 48:516–525

Soltanpour PN, Schwab P (1977) A new soil test for simultaneous extraction of macro- and micro-nutrients in alkaline soils. Commun Soil Sci Plan 8:195–207

Srinivasarao Ch, Gayatri RS, Venkateswarlu B, Jakkula VS, Wani SP, Kundu S, Sahrawat KL, Rajasekhara Rao BK, Marimuthu S, Gopala Krishna G (2014) Heavy metals concentration in soils under rainfed agro-ecosystems and their relationship with soil properties and management practices. Int J Environ Sci Technol 11(7):1959–1972

Srivastava VC, Mall ID, Mishra IM (2008) Adsorption of toxic metal ions onto activated carbon: study of sorption behaviour through characterization and kinetics. Chem Eng Process Process Intensif 47:1269–1280

Taghipour H, Mosaferi M, Armanfar F, Gaemmagami SJ (2013) Heavy metals pollution in the soils of suburban areas in big cities: a case study. Int J Environ Sci Te 10:243–250

Tessier A, Campbell PGC, Blsson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 52:45–53

Tomasevic DD, Dalmacija MB, Prica M, Dalmacija BD, Kerkez DV, Becelic-Tomin MR, Roncevic SD (2013) Use of fly ash for remediation of metals polluted sediment—green remediation. Chemosphere 92:1490–1497

Tsadilas CD, Shaheen SM, Dimitrios G, Samaras V, Hu Z (2009) Influence of fly ash application on Copper and Zinc sorption by acidic soil amended with biosolids. Commun Soil Sci Plan 40:168–179

United State Environmental Protection Agency (USEPA) (2007) Microwave assisted acid digestion of sediments, sludges, soils, and oils, vol 3051A

Varrault G, Bermond A (2011) Kinetics as a tool to assess the immobilization of soil trace metals by binding phase amendments for in situ remediation purposes. J Hazard Mater 192:808–812

Zhang X, Wang H, He L, Lu K, Sarmah A, Li J, Bolan NS, Pei J, Huang H (2013) Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. Environ Sci Pollut Res. doi:10.1007/s11356-013-1659-0