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RESEARCH ARTICLE

Evaluation of soil amendments as a remediation alternative for cadmium-contaminated soils under cacao plantations

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Abstract Elevated plant-available cadmium (Cd) in soils results in contamination to cacao (*Theobroma cacao* L) beans. Effectiveness of vermicompost and zeolite in reducing available Cd in three cacao-growing soils was studied under laboratory conditions. Sorption–desorption experiments were conducted in soils and amendments. Cadmium was added at 0 or 5 mg kg^{-1} (spiked), then, amendments were incorporated at 0, 0.5, or 2 %. Amended soils were incubated at room temperature for 28 days. Plant-available Cd was determined using 0.01 M $CaCl_2$ (WSE) and Mehlich 3 (M3) extraction procedures in subsamples taken from individual bags at six time intervals. Soils and amendments displayed different sorption characteristics and a better fit was attained with Freundlich model ($R^2 > 0.82$). Amendments were ineffective in reducing extractable Cd in non-spiked soils. In Cd-spiked soils, vermicompost at 2 % significantly reduced WSE-Cd ($P < 0.01$) from 3.36, 0.54, and 0.38 mg kg^{-1} to values lower that instrument's detection in all the three soils and significantly diminished M3-extractable Cd ($P < 0.05$) from 4.62 to 4.11 mg kg^{-1} in only one soil. Vermicompost at 0.5 % significantly decreased WSE-Cd ($P < 0.01$) from 3.04 and 0.31 to 1.69 and 0.20 mg kg^{-1}, respectively, in two soils with low sorption capacity for Cd. In contrast, zeolite failed to reduce WSE- or M3-extractable Cd in all studied soils. A negative correlation occurred between soil pH and WSE-Cd ($r > -0.89$, $P < 0.01$). The decrease in WSE-Cd appears to be associated with the increase in pH of the vermicompost-amended soils.

Keywords Cacao-growing soils · Plant-available Cd · Single extraction · Vermicompost · Zeolite

Introduction

Excessive concentration of cadmium (Cd^{2+}) in terrestrial environments endangers the sustainability of the surrounding ecosystems (Alloway 2013; Campbell 2007; Kabata-Pendias 2011). Such elevated concentration could affect plants by hindering basic metabolic processes and/or tainting harvestable organs, in consequence, contaminating the food web (Bian et al. 2013; Chavez et al. 2015 Marschner 2012). Various crops such as grains, vegetables, and tubers have been reported to accumulate high levels of Cd in edible parts (Hu et al. 2013; Liu et al. 2013); moreover, Cd has been reported in chocolate from the use of Cd-rich cacao beans (Yanus et al. 2014; Zarcinas et al. 2004). The accumulation of Cd in plant organs has been strongly linked to the surfeit of Cd in soils (Chavez et al. 2014; Karaca 2004).

Cadmium is a non-degradable pollutant, which easily moves from highly soluble to less soluble fractions and vice versa. Soil remediation rises as a viable tool to reduce the solubility of Cd, thus preventing excessive uptake and

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accumulation of Cd in plants (Hooda 2010; Kirkham 2006; Park et al. 2011). Chemical stabilization using soil amendments is one of the most applied in situ strategies (Kirkham 2006; Lee et al. 2009; Park et al. 2011; Sebastian and Prasad 2014).

One of the first steps towards chemical stabilization is the selection of the "finest" amendments. Batch equilibrium experiments, in which absorbents are tested for their ability of retaining Cd in solution, offer a simple and reliable screen tool for identifying potential materials for reducing bioavailable Cd in soil (Bohn et al. 2001; Degryse et al. 2009; Essington 2015). Isotherm non-mechanistic models are then applied to the dataset for quantitative description of retention capacity and affinity of Cd to the amendments. In this context, Langmuir and Freundlich equations are the two most used models (Degryse et al. 2009; Elzinga et al. 1999). One of the major limitations with batch experiments is the sensitivity of sorption data to experimental conditions (background electrolyte solution, pH and ionic strength, temperature, initial concentration range, etc.) (Essington 2015). Therefore, comparison between experiments should be carefully conducted.

The application of soil amendments is considered as a cost-effective remediation strategy for overcoming Cd pollution in agricultural soils (Houben et al. 2012; Kirkham 2006). In most successful cases, the modification of soil pH is significantly related to immobilization of Cd in soils (Hooda 2010; Houben et al. 2013; Kirkham 2006). Indeed, increasing pH is consistently correlated with lower availability of Cd in soil (Bian et al. 2013; Houben et al. 2013; Kirkham 2006). Several mechanisms are involved in the reduction of plant-available Cd in high-pH soils: (ad) sorption, precipitation, complexation, redox reaction, and metal-organic ligand formation are the major processes impairing the availability of Cd (Houben et al. 2012; Park et al. 2011). Ideally, the applied amendment should have this liming effect in soils thereby the removal of Cd in soil solution through chemical stabilization is favored.

The effects of organic amendments, such as composts, humic acids, manures, biochars, and vermicomposts, in reducing labile Cd in soils have been increasingly investigated (Bian et al. 2013; Jordão et al. 2011; Liu et al. 2009; Rosen and Chen 2014). Vermicompost, also known as earthworm compost, is a multipurpose soil conditioner that improves several physical-chemical characteristics in soils, i.e., soil pH, cation exchange capacity (CEC), organic carbon, water holding capacity, and soil aeration (Kaushik and Garg 2004; Lazcano et al. 2008). A comparative advantage of vermicomposting over traditional composting is the retention of heavy metals (including Cd) in earthworms bodies, thus reducing inputs of metals to soils (Shahmansouri et al. 2005). Application of vermicompost has been reported to decrease plant-available Cd in agricultural soils (Abbaspour and Golchin 2011; Jordão et al. 2011; Mudhoo et al. 2012).

Mineral amendments are regularly used in agricultural practices. Calcium carbonates ($CaCO_3$) are widely utilized in managing acidic soils. Because of the liming capacity, this amendment has been tested in the immobilization of soil Cd (Houben et al. 2012; Lee et al. 2009). Another broadly apply mineral conditioner is zeolite, a natural or synthetic phyllosilicate that has a high specific surface area, cation exchange, and water holding capacity. These characteristics can improve the sorption of cations, such as Cd (Ming and Boettinger 2001). Wingenfelder et al. (2005) reported a higher Cd sorption capacity of Na-zeolite (synthetic) over natural-zeolite. Similarly, Zenteno et al. (2013) studied the potential of several amendments in reducing Cd in batch experiments and reported a superior performance of zeolite as compared to other amendments. In addition, Hamidpour et al. (2010) reported a lower available Cd in soils amended with zeolite as compared to soils amended with bentonite, and this reduction in soil Cd availability resulted in lower metal content in corn shoots and roots.

In a recent study, Chavez et al. (2015) monitored the concentration of Cd in cacao (*Theobroma cacao* L) farms in southern Ecuador and reported that all of the sampled sites had total soil-Cd content (surface layer) above permissible level for agricultural soils (0.43 mg kg^{-1}). Twelve out of the 19 sampled farms had a bean-Cd concentration exceeding safety standards for cacao beans (European Union, 0.6 mg kg^{-1}). A practical remediation alternative for these Cd-bearing soils is imperative for reducing uptake and accumulation of Cd in cacao beans. The objective of this research was to evaluate the effectiveness of low-cost soil amendments in reducing plant-available Cd in three contaminated cacao-growing soils under laboratory conditions.

Materials and methods

Characterization of soils and amendments

Soil samples were collected from the surface layer (0–15 cm) of three cacao farms located in southern Ecuador. Soils varied in their basic physical-chemical properties and background Cd content. Two amendments were tested in this study: vermicompost and zeolite. Vermicompost was obtained from a local cacao farm and was produced from cattle manure and harvest residues. Zeolite was purchased from a local supplier. Soils and amendments were air dried and sieved through a 0.5-mm screen prior to treatments.

Physical-chemical characteristics were measured in triplicates for both soils and amendments. The pH and electrical conductivity (EC) were measured with a pH/conductivity meter (Fisher Accumet® AB200) in a solid to DI water ratio of 1:2; total carbon (C) and nitrogen (N) content was determined by combustion method using a C-N analyzer (Vario MAX CN

Macro Elemental Analyzer, Hanau, Germany); effective cation exchange capacity (CEC_E) was obtained from the sum of basic cations displaced by 1 M NH_4AOC at pH 7 (Sumner and Miller 1996). Total recoverable Cd was determined for soils and amendments using 3050B acid-digestion procedure (USEPA 1996). Treatment means and standard errors of the analyzed properties are presented in Table 1.

Sorption–desorption experiment and adsorption models

Batch experiments were conducted to investigate the sorption and desorption characteristics of Cd in the soils and amendments. In 50-mL centrifugation tubes, soils (2 g each) or amendment samples (0.5 g each) were equilibrated with 40 mL of 0.01 M $CaCl_2$ electrolyte solution at room temperature (25 °C) for 24 h in a reciprocating shaker at 100 rpm (Excella E24, NewBrunswick Scientific^{TM}). Cadmium was added as [$Cd(NO_3)_2$] at 0, 2, 4, 6, 8, and 10 mg kg^{-1} for soils, and 0, 5, 10, 30, 60, 120, 240, and 480 mg kg^{-1} for amendments. After equilibration, tubes were centrifuged at 2500 rpm for 5 min or until a clear solution was obtained, and aqueous solutions were passed through a 0.45-μm membrane filter prior to analysis of Cd concentration using ICP-OES (Ultima, JY Horiba Group, Edison, NJ, USA) in duplicates and triplicates for soils and amendments, respectively. The amount of Cd sorbed by soil or amendment was obtained by the difference in Cd concentration between the initial and equilibrium solution.

Data obtained from sorption experiments were fitted into the one- and double-site Langmuir and Freundlich models as follows:

$$q = \frac{bK_L C\mathrm{eq}}{(1 + K_L C\mathrm{eq})} \tag{1}$$

$$q = \frac{b_1 K_{L1} C\mathrm{eq}}{(1 + K_{L1} C\mathrm{eq})} + \frac{b_2\, K_{L2} C\mathrm{eq}}{(1 + K_{L2} C\mathrm{eq})} \tag{2}$$

and,

$$q = Kf\, C_{\mathrm{eq}}^{N} \tag{3}$$

In the one- and double-site Langmuir models (Eqs. 1 and 2, respectively), q refers to the amount of sorbed Cd per unit mass of soil or amendment (sorbents), Ceq is the concentration of Cd in equilibrium solution, b $(_{1,\ 2})$ and K_L $(_{1,\ 2})$ are adjustable parameters defining the sorption maxima and the binding energy-related constant, respectively. In the Freundlich model (Eq. 3), q and Ceq have similar meaning as Eqs. 1 and 2, Kf and N are positive adjustable parameters that are interpreted as the property of the sorbent and the heterogeneity of sorption sites, correspondingly (Elzinga et al. 1999; Essington 2015).

Desorption study was performed using 0.01 M $CaCl_2$ as background electrolyte solution other experimental conditions were maintained. The concentration of Cd in the desorbing solution was analyzed using the ICP-OES. The percentage of desorbed Cd in the total sorbed Cd was obtained from the slope of the linear relationship between the desorbed and sorbed Cd.

Soil incubation experiment and plant-available Cd determination

Soils and amendments were thoroughly mixed at three ratios and incubated at room temperature for 28 days. Soils (180 g each) were weighed into Ziploc bags (13 × 15 cm), Cd was spiked as [$Cd(NO_3)_2$] at two application rates: 0 (non-spiked) or 5 mg of Cd per kg^{-1} of soils. Soils were moistened to 70 % of their water holding capacity (WHC) with deionized water. The moist soils were pre-incubated for 2 days prior to incorporation of amendments. Subsequently, amendments and soils were thoroughly mixed at the following rates: 0 (control), 0.5, or 2 % (*w*/*w*). The treated soils were arranged in a complete randomized design (CRD) in triplicates. Ziploc bags were open periodically to facilitate gas interexchange; at each time, water content was monitored and adjusted if necessary.

The performance of the amendments in reducing plant-available Cd was evaluated by two single extraction methods: 0.01 M $CaCl_2$ and Mehlich 3 (M3). These procedures were applied in subsamples taken from individual bags at the intervals of 0, 3, 7, 14, 21, and 28 days after incubation. $CaCl_2$ (0.01 M) is a weak salt with a low extraction capacity (1:20 soil to solution ratio and 1 h equilibration time); this method accounts for the water soluble and exchangeable Cd (hereafter called WSE-Cd) and has been widely reported as a reliable

Table 1 Physical-chemical properties of the soils and amendments (mean ± SE)

Soil/amendment	Total recoverable Cd (mg kg^{-1})	M3-extractable Cd (mg kg^{-1})	Total C (%)	Total N (%)	CEC (cmols kg^{-1})	pH	EC (μS cm^{-1})
Soil 1	0.93 ± 0.06	0.18 ± 0.01	2.00 ± 0.01	0.16 ± 0.00	3.84 ± 0.25	4.92 ± 0.00	64.6 ± 0.89
Soil 2	0.89 ± 0.11	0.32 ± 0.01	1.77 ± 0.01	0.20 ± 0.01	8.86 ± 0.08	6.47 ± 0.02	81.2 ± 2.92
Soil 3	2.10 ± 0.00	0.75 ± 0.01	3.10 ± 0.05	0.37 ± 0.00	21.9 ± 0.07	6.62 ± 0.01	240.2 ± 11.8
Vermicompost	0.55 ± 0.07	ND	40.36 ± 0.02	12.36 ± 0.01	51.6 ± 0.12	4.30 ± 0.03	1139 ± 3.27
Zeolite	0.37 ± 0.06	ND	0.03 ± 0.00	0.21 ± 0.00	3.51 ± 0.10	5.50 ± 0.18	0.01 ± 0.00

tool for determining available Cd in soils (Amacher 1996; Degryse et al. 2003). Conversely, M3 is a very acidic solution (pH = 2) with a higher extraction power, as compared with neutral salts (1:10 soil to solution ratio and 5 min equilibration time); this method releases Cd attached to the organic-mineral phase of soil (Mehlich 1984). Simultaneously soil pH was monitored up to 60 and 75 days, due to its steady increase within the 28 days of incubation.

Quality control and quality assurance

Standard QA/QC laboratory procedures were performed throughout the analysis of solution samples. A calibration coefficient (R^2) of 0.9995 (or greater) was obtained for the standard curve in the ICP-OES prior to the analysis of samples. Recovery of spiked Cd (90–110 %) from a secondary source and the analysis of duplicates every 10 samples were included in the analytical procedure. The detection limit of ICP-OES for Cd was <2 μg L^{-1}.

Data treatment

Analysis of the data was conducted using JMP Pro 11 (SAS 2009). Means and standard errors (SE) were calculated for each variable. Means of sorbed Cd from the batch experiments were applied to the isotherm models. Analysis of variance (ANOVA) was conducted to compute the differences in plant-available Cd and soil pH among the different treatments and different sampling times using Duncan's multiple range test. The relationship between soil pH and extractable Cd was studied using a pairwise correlation analysis. Statistical differences were established at $P < 0.05$.

Results and discussion

Characteristics and properties of soil and amendments

Background Cd content and physical-chemical properties differed among the soils (Table 1). For instance, the highest total recoverable and M3-extractable Cd occurred in soil 3 (S3), whereas soil 1 (S1) and soil 2 (S2) had a similar total recoverable Cd, but a lower M3-extractable Cd was found in S1. Despite the different background Cd, the selected soils were considered polluted according to USEPA standards for agricultural soils (0.43 mg kg^{-1}), therefore remediation strategies should be implemented (USEPA 2002). In addition, total C, CEC$_E$, and soil pH were higher in S3 while CEC$_E$ and pH were lower in S1. Moreover, S2 had the lowest total C content and a soil pH similar to S3. These soil properties played a fundamental role in the fate of soil Cd.

Similarly to soils, physical-chemical properties varied between the two amendments (Table 1), due to the distinctive nature of the materials. Higher total C and total N were measured in the vermicompost than zeolite. CEC$_E$ was notably higher in vermicompost, but total recoverable Cd was lower in zeolite. Inherited physical-chemical properties of the amendments such as pH, CEC, exchangeable cations, and porosity have a significant effect on the immobilization of soluble Cd in soil (Hamidpour et al. 2010; Shaheen et al. 2012). Studies have been conducted to determine the suitability of these two amendments in the retention of soluble Cd. Jordão et al. (2011) studied the potential of vermicompost (derived from cattle manure) in retaining soluble Cd in Brazilian soils and reported a pH of 6.4, total C content of 15.21 g kg^{-1}, and total Cd of 0.57 mg kg^{-1} in their amendment. The vermicompost used in this study had a similar total Cd, higher total C and N, and a lower pH. Zenteno et al. (2013) reported a pH of 5.25 for vermicompost and 7.87 for zeolite, whereas total C in vermicompost was 5.11 g kg^{-1}, they concluded that zeolite had a greater potential for Cd immobilization.

Sorption characteristics of Cd in soils and amendments

Distinctive sorption characteristics were observed among the soils. Based on the q values (Fig. 1), S3 had the greatest sorption capacity, particularly at low Cd concentrations, in which nearly 100 % of the metal was retained into this soil. Sorption of Cd in this soil increased rapidly with equilibrium Cd concentration (Ceq) below 2 mg L^{-1} but plateau at higher Ceq. S2 had a lower sorption capacity for Cd than S3. At the highest Cd loading (10 mg L^{-1}), this soil retained about 61 % of the added Cd. On the contrary, at the highest Ceq, S1 only retained 24 % of the added Cd, likely because this soil had the lowest pH and CEC$_E$. In general, Cd sorption in the soils decreased in the following order: S3 > S2 >> S1. This trend may be attributed to the difference in physical-chemical properties like pH and CEC$_E$. Previous studies showed the importance of these soil properties in the retention of soluble Cd (He et al. 2005).

Based on the regression coefficients (R^2), the data fitted better on Freundlich model ($R^2 > 0.95$) than Langmuir model ($R^2 < 0.69$); however in S3, a good fit ($R^2 = 0.99$) was obtained with the double-site Langmuir model. The Kf and b values, obtained from the Freundlich or Langmuir models (Table 2), confirmed the decreased trend of Cd sorption capacity of the soils as S3 > S2 >> S1. The same decreasing fashion occurred with the binding energy-related constant (K_L), suggesting that the sorbed Cd was strongly retained in S3 and S2 but weakly in S1. The parameters obtained from the Freundlich model displayed a similar trend for the characteristics of sorbed Cd, Kf was much higher in S3 than S2 and S1, but N was comparable for the three soils. Desorption of Cd in the three soils supported the parameters reported by the isotherm models. Based on the slope of the linear equation, sorbed Cd in S1

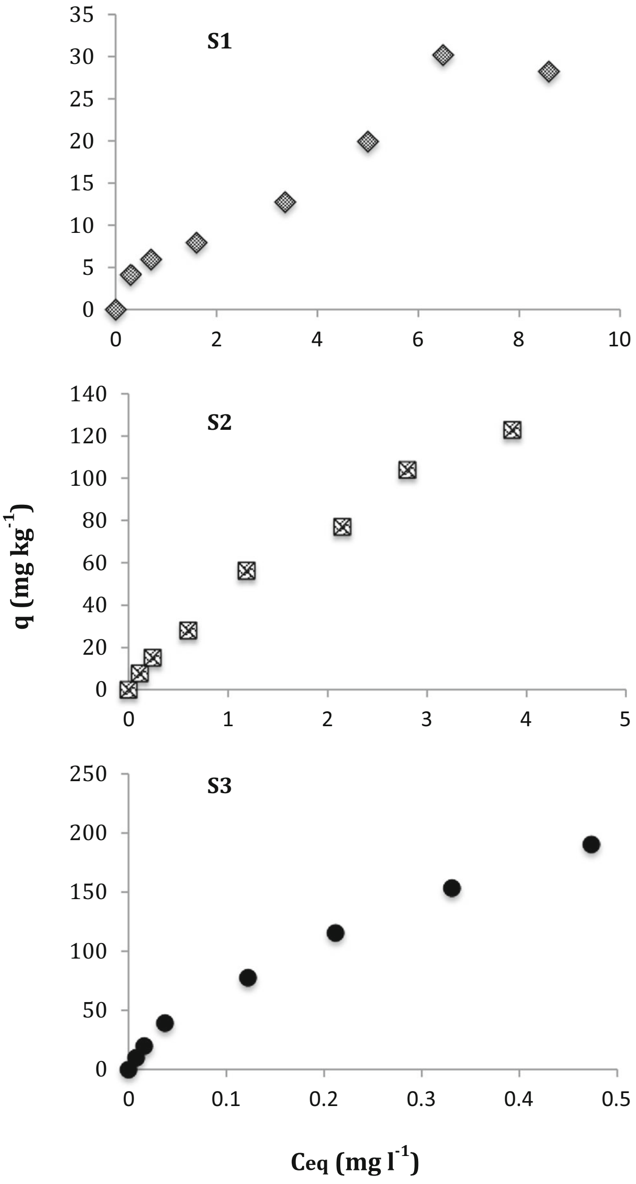

Fig. 1 Sorption isotherms characterizing the retention of Cd in three cacao-growing soils

and S2 was readily desorbed (0.94 and 047, $R^2 = 0.96$, 0.99, respectively), whereas the least desorbed Cd occurred in S1 (0.04, $R^2 = 0.95$).

Intensive studies have been conducted to understand Cd sorption in soils and its relation to Cd availability to plants. Adhikari and Singh (2003) investigated the absorption characteristics of five Indian soils exposed to increasing Cd concentration (Cd ranged from 0 to 75 mg L^{-1}). Their data fitted the Freundlich model ($R^2 > 0.90$) better than the Langmuir model ($R^2 < 0.82$), whereas the Freundlich sorption-related constant (*Kf*) ranged from 1.99 to 4.16 (L kg^{-1}), and sorption maxima (*b*), as calculated by the simple Langmuir model, ranged between 55 to 90 mg kg^{-1}. These values are lower than those observed in the present study, with maximum absorption capacity of the soils ranged from 36.36 to 303.0 mg kg^{-1}, as calculated by the Langmuir model, whereas the Freundlich absorption-related constant *Kf* varied from 7.47 to 338.8 L kg^{-1}. Greater Cd maxima sorption capacities have been reported in other soils, the discrepancy may be explained by different experimental conditions, such as Cd loadings and pH of background solution (Covelo et al. 2007; He et al. 2005; Shaheen 2009).

Sorption characteristics of the two amendments were similar (Fig. 2). At low Cd initial concentrations (<10 mg L^{-1}), the two amendments had high affinity for Cd, but reached a “temporary” saturation at 120 mg L^{-1}. Thereafter, a sharp increase in Cd sorption occurred at Cd concentrations higher than 240 mg L^{-1}, which could be attributed to different sorption mechanisms such as surface precipitation. Langmuir model failed to describe the sorption data for both amendments; however, a good fit was attained with Freundlich model (Table 2). The absorption-related constants (*Kf*) were 8.72 and 3.80 L kg^{-1} for vermicompost and zeolite, respectively. The corresponding *N* values for the two amendments were 0.95 and 1.1. Higher *Kf* values may indicate the higher affinity of vermicompost for Cd; nevertheless, the two amendments had comparable *q* values at the same *C*eq (Fig. 2). The sorption of Cd into different soil conditioners has been reported

Table 2 Sorption–desorption parameters of Cd from the Freundlich and Langmuir models

Soils/amendments	Langmuir model			Freundlich model			Desorption	
	b (mg kg^{-1})	K_L (L mg^{-1})	R^2	*Kf* (L kg^{-1})	*N*	R^2	*X* (slope)	R^2
Soil 1	36.4	0.31	0.69	7.47	0.61	0.95	0.93	0.96
Soil 2	172	4.83	0.68	44.66	0.78	0.99	0.47	0.99
Soil 3[a]	19.9 $_{(1)}$ 303 $_{(2)}$	503 $_{(1)}$ 3.3 $_{(2)}$	0.99	338.8	0.70	0.99	0.04	0.95
Vermicompost	ND	ND	ND	8.72	0.95	0.83	0.69	0.89
Zeolite	ND	ND	ND	3.80	1.11	0.95	0.89	0.69

ND not determined

[a] Double-site Langmuir model was applied, then two *b* and K_L constants are reported and referred as (1) and (2), respectively

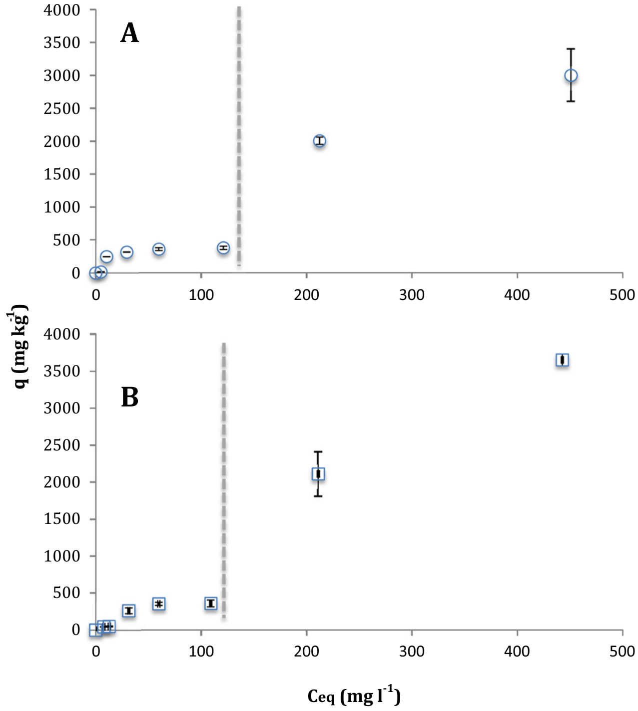

Fig. 2 Sorption isotherms characterizing the retention of Cd in vermicompost (**a**) and zeolite (**b**). *Bars* represent the standard error (SE) of three replicates. *Dotted line* represents the increase in Cd adsorption at Cd concentrations higher than 120 mg L^{-1}

previously. Zenteno et al. (2013) compared various mineral and organic soil amendments for in situ remediation of Cd-contaminated soils. Langmuir model was successfully applied to describe the sorption of Cd in the studied amendments. Previous studies reported a greater performance of zeolite and lime (minerals) over vermicompost and sugarcane filter cake (organics) in the retention of soluble Cd. The range of Cd in equilibrium solution was lower in their experiment (0–80 mg L^{-1}) than the present study (0–480 mg L^{-1}). Consequently, a much lower *q* was obtained in that study. Jordão et al. (2011) conducted a batch experiment of testing the sorption of Cd in two Brazilian soils amended with cattle manure-derived vermicompost. The sorption data fitted both Freundlich and Langmuir isotherm models successfully. This group reported a greater sorption of Cd in vermicompost and vermicompost-amended soils than control soils. Additionally, the sorption of Cd and the binding energy-related constants were improved in the vermicompost-amended soils.

Plant-available Cd in amended soils

The potential of amendment in reducing plant-available Cd was evaluated in a 28-day incubation study. Plant availability of Cd in soil was estimated with chemical extractions. In Cd-spiked soils, WSE-Cd ranged from 3.00 to 3.75, 0.67 to 0.36, and 0.39 to 0.28 mg kg^{-1}, in S1, S2, and S3, respectively, confirming the higher affinity of S3 and S2 than S1 for soluble Cd. This distinctive sorption capacity of soils for Cd supports the data in the previous section; hence, external inputs of Cd in S2 and S3 are quickly sorbed onto soil organic and mineral constituents, thus decreasing Cd bioavailability, whereas in S1 exogenous Cd is mostly soluble and readily available for plant uptake. In contrast with WSE-Cd, the concentrations of M3-extractable Cd were similar among the three soils and ranged from 4.43 to 4.93, 4.26 to 4.91, and 4.29 to 4.66 mg kg^{-1}, in S1 (Fig. 4), S2, and S3, respectively (data not shown for S2 and S3). The difference in WSE- and M3-extractable Cd indicates that the metal is mainly fixed into the organic-mineral phase of soils, which is not extractable to the 0.01 M $CaCl_2$ solution but released under acidic conditions. This finding is in line with previous results, which indicated that carbonates and organic matter were the major sink of Cd in the cacao-growing soils (Chavez et al. 2014).

The effectiveness of soil amendments in reducing soluble Cd in non-spiked soils could not be properly determined, mainly due to the inherited low water soluble and exchangeable Cd in the selected soils. However, in the Cd-spiked soils, WSE-Cd was significantly reduced ($P < 0.01$) in the vermicompost-amended soils during the incubation period, particularly at 2 % application rate (Fig. 3). In this treatment, WSE-Cd was significantly lowered after 7 days of incubation, as compared to the non-amended soils (control) ($P < 0.01$). In S1, this treatment reduced WSE-Cd by 47 and 92 % at the 7th and 14th day of incubation, respectively. In S2 and S3, WSE-Cd decreased by 67 and 58 %, respectively, at day 7. At day 14, the concentration of WSE-Cd was below detection limit (BDL) for the S2 and S3. Furthermore, the incorporation of vermicompost at 0.5 % significantly reduced the concentration of WSE-Cd in S1 and S3 ($P < 0.01$) but not in S2. In S1, WSE-Cd was declined by 29, 38, and 43 % at days 14, 21, and 28, respectively, in comparison with control; similarly in S3, 37, 58, 52, and 41 % of WSE-Cd was reduced at days 7, 14, 21, and 28, respectively. In contrast, the application of zeolite in Cd-spiked soils did not affect the concentration of WSE-Cd in any of the soils.

Except in S1, the addition of vermicompost or zeolite failed to reduce M3-extractable Cd during the incubation time. Vermicompost at 2 % in the spiked-S1 significantly reduced ($P < 0.05$) M3-extractable Cd by 8 and 7 % at days 21 and 28, respectively, as compared to control soils (Fig. 4). The poor performance of amendments in reducing M3-extractable Cd may be a result of the acidic nature (pH = 2) and extraction power of the M3 solution (Meers et al. 2007).

The application of vermicompost has been reported to effectively remove water-soluble Cd, and therefore, the incorporation of this amendment has been suggested for use in Cd-enriched soils. In addition, vermicompost could improve soil physical-chemical properties, consequently enhancing crop growth (Belliturk et al. 2015; Jordão et al. 2011; Mudhoo et al. 2012). Abbaspour and Golchin (2011) applied

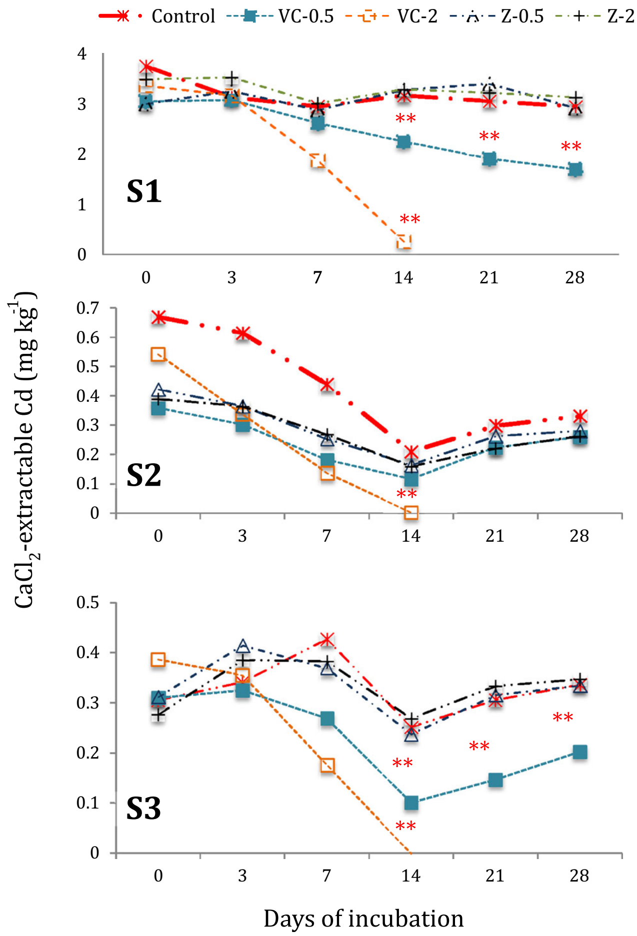

Fig. 3 Changes of water soluble and extractable Cd (WSE-Cd) with incubation time the three soils amended with vermicompost (*VC*) or zeolite (*Z*) at 0.5 and 2 %. *Double asterisks* (**) indicates significant difference at $P < 0.01$

vermicompost, zeolite, and di-ammonium phosphate (DAP) to immobilize heavy metals in contaminated soils in Iran and reported that DAP and vermicompost were superior amendments for decreasing WSE-Cd (extractable to 1 M NH_4NO_3), whereas the poorest performance occurred in zeolite-amended soils. Neither vermicompost nor zeolite reduced DTPA-extractable Cd. These results coincide with our findings that vermicompost was effective in reducing WSE-Cd, but failed to decrease M3-extractable Cd in some of the Cd-contaminated soils.

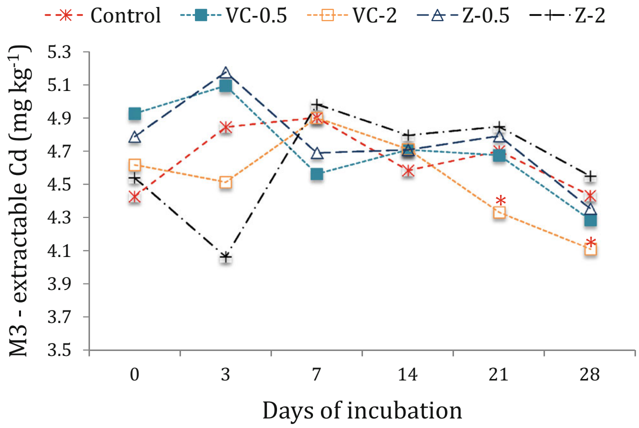

Fig. 4 Changes of Mehlich 3-extractable Cd with incubation time in soil 1 amended with vermicompost or zeolite at 0.5 and 2 %. *Single asterisk* (*) indicates significant difference at $P < 0.05$

The addition of organic amendments has been reported to ameliorate the toxicity of Cd in agricultural systems. Recently, biochars have been suggested as alternative amendment for Cd-contaminated soils. For instance, Houben et al. (2013) applied various rates of biochar in a highly Cd-contaminated soil and reported a reduction of 130 and 250 % in WSE-Cd (0.01 M $CaCl_2$) after 56 days of incubation; however, high biochar rates (5 and 10 %, respectively) were necessary. At a realistic field-applicable rate (1 %), no statistical differences were reported between the biochar-amended soils and control. Bian et al. (2013) evaluated the effect of biochar at two rates in reducing WSE-Cd (0.01 M $CaCl_2$) in rice fields in China. The application of 20 and 40 t ha^{-1} of biochar significantly lowered WSE-Cd in the studied fields and subsequently decreased Cd content in rice grains. The application of biochar is considered as a great alternative to alleviate Cd contamination in soils; unfortunately, this amendment is not produced or marketed in Ecuador. Moreover, vermicompost proved to be as promising as biochar in reducing WSE-Cd in Cd-contaminated soils of cacao-growing areas; at 2 % rate, this amendment significantly reduced plant-available Cd in all the studied soils.

The relationship between soil pH and WSE-Cd

Soil pH in the incubated soils was monitored along with plant-available Cd for the first 28 days of incubation period; however due to the drastic increase of pH in the vermicompost-amended soils, measurement of pH was extended to 60 and 75 days (Figs. 5 and 6). Initially, the addition of Cd (spiked) lowered soil pH, and the differences in pH between the spiked and non-spiked were 0.70, 0.56, and 0.37 units, respectively in S1, S2, and S3, as measured in the first subsampling point (0 day). Regardless of Cd addition, the incorporation of vermicompost at 2 % increased pH of all the amended soils after 75 days of incubation. This increase was statistically significant ($P < 0.01$), as compared to control after 7 days of incubation. In the non-spiked soils, the incorporation of vermicompost at 2 % raised pH in a magnitude of 3.07, 2.08, and 1.55 units in S1, S2, and S3, respectively. At the 0.5 % rate, the pH was significantly raised in S1 in a magnitude of 1.25 (Fig. 5). In the Cd-spiked soils, the addition of vermicompost at 2 % raised soil pH by 3.56, 2.50, and 2.05 units, in S1, S2, and S3, respectively, and by 1.87 unit at the 0.5 % rate in S1 (Fig. 6). At the 2 % rate, the maximum pH rise in vermicompost-amended soils occurred at day 60 and gradually decreased thereafter. Similar trend was observed at the

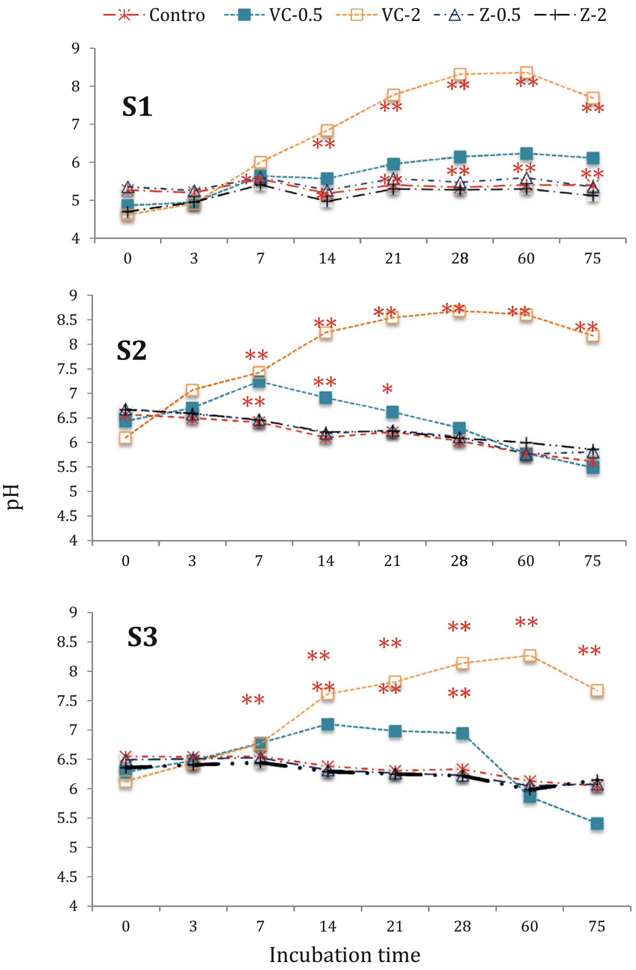

Fig. 5 Changes of pH in the non-spiked soil 1 (**a**), soil 2 (**b**), and soil 3 (**c**) during the incubation period. *Single asterisk* (*) and *double asterisks* (**) indicate statistical differences with control at $P < 0.05$, and 0.01, respectively

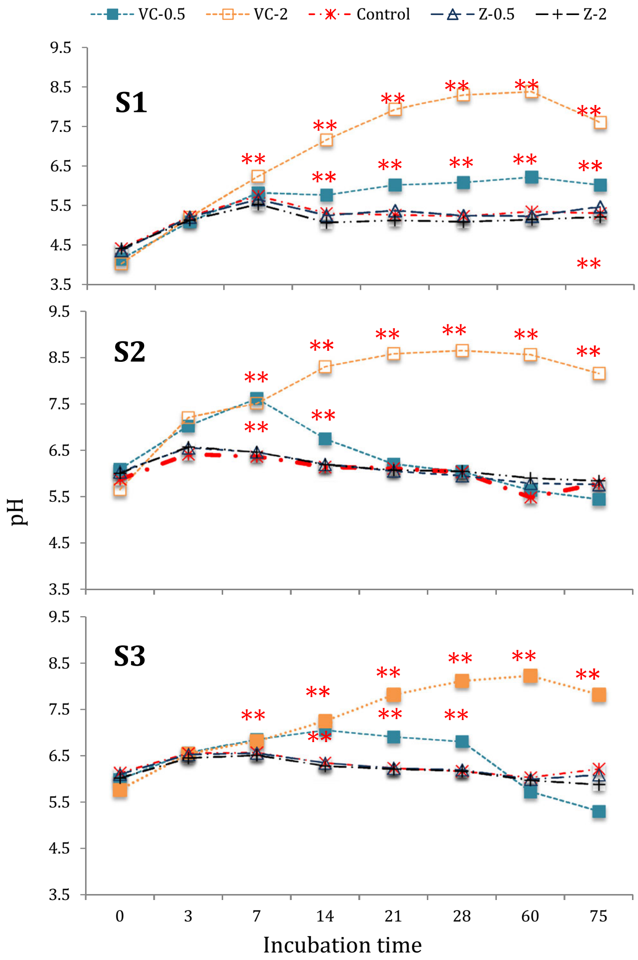

Fig. 6 Soil pH monitoring in Cd-spike soil 1 (**a**), soil 2 (**b**), and soil 3 (**c**) during 90 days of incubation time. *Double asterisks* (**) indicates statistical differences with control $P < 0.01$

0.5 % rate in S1, whereas in the other two soils vermicompost at 0.5 % increased soil pH for a short time but failed to maintain this rise during the 75-day period.

Due to the properties of the amendment, the increase of soil pH in the vermicompost-amended soils is likely related to nitrogen (N) mineralization, which is favored in the low C/N organic amendments (Table 1) (Robertson and Groffman 2007). The mineralization of organic N (from R-NH_2 to NH_4) produces hydroxides (OH^-), consequently raising the soil pH (Robertson and Groffman 2007; Xu et al. 2006). Some studies have elucidated the role of N mineralization in modifying soil pH. Xu et al. (2006) investigated the relationship between organic N mineralization and soil pH change by testing three acid soils ($pH < 4.9$) amended with several plant residues. These plant residues contained different N levels and varied in their pH level. They reported that soil pH had the highest and steady increase with the application of 15 g kg^{-1} of lucerene ($pH = 5.12$ and N 49.3 g kg^{-1}), the magnitude of the increment was up to 3.3 units and stabilized after 42 days of incubation. Additionally, the concentration of NH_4^+ in those lucerene-amended soils resembled the curve of soil pH change. Thereby, a strong relationship between NH_4^+ production and soil pH was reported. Authors concluded that N mineralization strongly affected soil pH, particularly in low C/N amendments. Our results strongly agree with those reported by Xu et al. (2006), similar pH increase occurred in the lucerene- and vermicompost-amended soils. This supports the hypothesis that mineralization of organic N significantly affects soil pH, which, in our study, ultimately altered Cd mobility in the vermicompost-amended soils.

In order to confirm the previous statement, a pairwise correlation analysis, using the data from 7 to 28 days, was conducted. A negative relationship between WSE-Cd and soil pH in all the soils occurred. The correlation coefficients (*r*) were −0.96, −0.89, and −0.92 ($P < 0.01$) for S1, S2, and S3, respectively. This finding suggests that increased soil pH is one of the major mechanisms responsible for the reduced WSE-Cd in the vermicompost-amended soils. In this context, the role of pH in modifying Cd mobility and solubility has been intensively studied (Karaca 2004; Park et al. 2011). For instance, Karaca (2004) reported a negative correlation ($r = -0.78$,

$P < 0.01$) between DTPA-extractable Cd and soil pH after amended with tobacco (*Nicotiana tabacum*) dust for 60 days. Application of chicken manure compost (CMC) reduced WSE-Cd (extracted by KNO_3) by 70 %, mainly due to a pH increase at high CMC application rate (Liu et al. 2009). The application of vermicompost in cacao-growing soils increased soil pH, which in turn reduced Cd mobility and possibly plant uptake.

One of the most used soil amendments for increasing soil pH and simultaneously decreasing plant-available Cd is lime, e.g., $CaCO_3$, $Ca(OH)_2$, etc. (Chaney et al. 2009; Hong et al. 2009; Tlustoš et al. 2006). Calcium hydroxide ($Ca(OH)_2$) was mixed at various ratios with a Cd-contaminated soil ($Cd > 2$ mg kg^{-1}) in South Korea, this soil was impacted by a long history of Zn smelting extraction. The application of $Ca(OH)_2$ reduced the concentration of 1 M NH_4OAc-extractable Cd by 50 % over the experimental period, a corresponding increase of 1.2 units in soil pH was reported. In addition, Cd concentration in leaves and roots of radish (*Raphanus sativa*, L.) significantly decreased with the application of 8 Mg of $CaOH_2$ ha^{-1} (Hong et al. 2009). In a containerized experiment, the application of 0.5 % of $CaCO_3$ increased soil pH by 1.6 units, which decreased 0.01 $CaCl_2$-extractable Cd by 50 %, as compared to control; consequently, a 40 % reduction in Cd content was reported in shoots and wheat grains (Tlustoš et al. 2006). In a naturally Cd-rich soil, the application of lime ($CaCO_3$) and zinc reduced the uptake and accumulation of Cd in lettuce. The application of 100 mg kg^{-1} of Zn and a pH of 7.08 lowered Cd content in lettuce from 12 to about 2 mg kg^{-1}, which is much lower than permissible levels for this crop (Chaney et al. 2009).

Conclusions

The sorption characteristics of the soils and amendments were described better by the Freundlich than the Langmuir isotherm model. S3 and S2 had a higher Cd sorption capacity due to a difference in physical-chemical properties. Soluble Cd in these soils was more quickly bound to soil components, as compared to S1. Both amendments had a similar sorption behavior; however, sorption constants obtained from the Freundlich model revealed a higher sorption capacity of Cd by vermicompost than zeolite. Incubation experiment confirmed the effectiveness of vermicompost over zeolite in Cd immobilization. Application of vermicompost at 2 % significantly reduced WSE-Cd in the studied soils with the maximum decrease occurring in the first 14 days of incubation. At a lower rate (0.5 %), vermicompost significantly diminished WSE-Cd in S1 and S3, but not S2. Vermicompost also reduced M3-extractable Cd in S1 at days 21 and 28 of incubation. The effectiveness of vermicompost in reducing WSE-Cd is related to a substantial increase in soil pH, which is likely due to the mineralization of organic N from the amended materials, similar to hydrolysis of urea. There was a negative correlation between WSE-Cd and pH in the amended soils.

These results indicate that vermicompost is a promising amendment for remediating Cd-contaminated soils of cacao-growing areas in southern Ecuador in addition to other benefits of improving soil quality. Nevertheless, the performance of this amendment in a plant-soil experiment is needed in order to propose this soil conditioner for field applications.

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