Research Article

Comparative Use of Soil Organic and Inorganic Amendments in Heavy Metals Stabilization

Agustina Branzini and Marta Susana Zubillaga

Department of Fertility and Fertilizers, University of Buenos Aires, Avenue San Martín 4453, 1417 Buenos Aires, Argentina

Correspondence should be addressed to Agustina Branzini, branzini@agro.uba.ar

Received 21 October 2011; Revised 20 January 2012; Accepted 25 January 2012

1. Introduction

Point source and diffuse contamination of soils by heavy metals (HMs) is an environmental problem worldwide. An important input pathway is anthropogenic activities, such as disposal of industrial and hazardous residues, mining activities, incidental accumulations, industries atmospheric deposition, energy generation, and agricultural chemicals [2, 3]. High proportion of the contamination is retained by soil particles, so that is why this system is considered a vulnerable environment to being contaminated [4]. In addition, there is an increasing interest in HM contamination as a result of a continuous accumulation on top soil, with elevated availability to organisms [5]. Therefore, high concentrations of HM and their potential toxicity may affect soil ecology, agricultural production, and water quality, implicating risks for environment and human health [6].

In Argentine, soil contamination has been mostly recorded in urban and periurban areas. Reference [7] indicated that concentrations of Cd, Cu, Pb, and Zn in urban soils exceeded the international standards referred to the human health, and according to [8], elevated levels of Cu, Pb, Cd, and Zn were found in horticultural soils of Buenos Aires. Contamination with Cu, Cr, Zn, As, Cd, Hg, and Pb occurred near the Ecological Reserve area of Buenos Aires, close to an automobile cemetery. Moreover, industrialized areas are affected by high Cu, Zn, and Cr concentrations in industrial effluents [9].

Heavy metals partition in contaminated soils is influenced by several chemical and biological reactions [10, 11]. Soils retain HM by sorption, precipitation, and complexation; such reactions reduce the metal mobility and bioavailability [2, 12, 13]. However, this natural attenuation process can be complemented by in situ application of chemical technologies, as organic and inorganic amendments [14]. In situ chemical immobilization is a cost-effective remediation approach that stabilizes HM in contaminated soil [15, 16]. Generally, these technologies reduce HM availability,
improve soil fertility, and increase plant growth [17, 18]. On one hand, organic amendments (compost) contain a high proportion of humified organic matter and could decrease HM bioavailability in soil, even though temporally and thus permitting the reestablishment of vegetation [19]. On the other hand, within the inorganic amendments, phosphate fertilizers are also effective in HM immobilization through formation of stable mineral HM phosphate [20]. The formation of these insoluble metal compounds, reduce their mobility through the soil profile and the pool available for biota [21]. In addition, the application of amendments simultaneously, could promote plant growth and biological activity of degraded soil [22].

The objective of this study has been to assess the distribution of three heavy metals (Cu, Zn, and Cr) as a mixture in contaminated soil, after applying biosolid compost (BC) and phosphate fertilizer (PF), both independently and in combination.

2. Materials and Methods

2.1. Soil Sampling. Typic Hapludoll soil representative from sandy Pampas (35°37′S, 61°22′W) (Tables 1 and 3) was chosen for the experiment. Five composite topsoil samples (0–20 cm depth) were randomly collected (10 individual samples). The sampled soil was air-dried and passed through a 2 mm sieve to obtain homogeneous particle size. Soil samples were enriched by adding metal solutions (CuCl₂·2H₂O, ZnSO₄·7H₂O, and H₂CrO₄), achieving final concentrations of 350 µg g⁻¹ copper (Cu), 700 µg g⁻¹ zinc (Zn), and 750 µg g⁻¹ chromium (Cr). This enrichment overcame the maximum levels of total HM established in agricultural soils by Argentinean legislation (Table 3). Wetting cycles (at field capacity) and air-drying every five days were performed, during a period of three months.

2.2. Greenhouse Experiment. The experiment consisted in 1 kg pots containing HM-enriched soil and two different amendments: Biosolid Compost (BC) (Tables 2 and 3) as organic amendment and superphosphate triples (PF) as inorganic amendment (100 Mg ha⁻¹ and 100 kg ha⁻¹ rate, resp.). The compost was enriched with sawdust as bulking agents and biosolids from sewage sludge treatment plant located in the north of Buenos Aires City (1:1, biosolid: sawdust ratio by volume). Samples of enriched soil were thoroughly mixed with the amendments resulting in four treatments: (i) Contaminated Soil (CSC) as control, (ii) Contaminated Soil + Phosphate Fertilizer (CSC + PF), (iii) Contaminated Soil + Biosolid Compost (CSC + BC), and (iv) Contaminated Soil + Phosphate Fertilizer + Biosolid Compost (CSC + PF + BC). The experiment was carried out in a completely randomized design with three replications per treatment. Destructive samplings were performed at two time points of the experiment: beginning (0 days) and end (190 days).

2.3. Soil Chemical Analysis. Sequential extraction procedure was performed on all samples from each pot (3 g in 50 cm³ polypropylene centrifuge tubes) to measure Cu, Zn, and Cr in different fractions after the application of BC and PF, separately and simultaneously, according to [23] methodology. This type of procedure has been successfully used for sludge-treated soils [24–26]. The procedure separates metals into four operationally defined fractions: soluble and exchangeable (EX), organic matter bound (OC), carbonate bound (CB), and residual (RES) (Table 4). After each extraction, the solution was separated from the solid by centrifugation at 3000 rpm for 45 min. The supernatant was decanted and filtered through Whatman N. 42 filter paper, and the wet residue in the tube was recorded. The pseudototal HM concentrations were determined by acid digestion with mixture of HCl, H₂SO₄, and HNO₃ [1]. Heavy metals contents of each supernatant were measured at two time points by flame atomic absorption spectrophotometer (AAS). Soil pH and electricity conductivity (EC) was measured using a mixture of soil and deionized water (1:2.5 m/v) with a glass electrode [27] in each time point.

2.4. Statistical Analysis. Treatments effects were determined by factorial arrangement of 4 × 2 (amendment levels and time points), according to the general linear model procedure of Statistics, version 8.0. Differences between means were separated using least significant differences (LSDs). Variances were stabilized when necessary by a logarithmic transformation of some data set. In addition, a simple linear correlation between these variables was performed.
Table 3: Heavy metals content (in ppm) of soil samples and composted biosolids, and the maximum levels of total heavy metals established by Argentinean law (Hazardous wastes regime: soil quality guide).

|                  | Typical Hapludoll |                     | Biosolid Compost |                  | Law 24051* |
|------------------|-------------------|---------------------|------------------|------------------|------------|
|                  | Available | Total | Available | Total |          |          |
| Cu               | 0.051    | 17.0  | 1.52     | 726.7 | 150–500  |
| Zn               | 0.040    | 38.2  | 0.65     | 1183.3 | 600–1500 |
| Cr               | <0.001   | 14.9  | 13.2     | 230.0  | 750       |

*Levels for soils with agricultural and industrial uses.

Table 4: Sequential extraction procedure of heavy metals from soil samples and operationally defined fractions.

| Phase/association | Abbr. | Step | Operational procedure |
|-------------------|-------|------|-----------------------|
| Soluble—exchangeable | EX    | 1    | 30 mL 0.1 M CaCl₂, shaken 16 h at room temperature |
| Organic matter—bound | OB    | 2    | 30 mL 0.5 M NaOH, shaken 16 h at room temperature |
| Carbonates—bound | CB    | 3    | 30 mL 0.5 M Na₂EDTA, shaken 1h |
| Residual | RES  | 4    | Estimated by summation of three fractions and the total content (acid digestion with hydrochloric, sulfuric, and nitric acids) [1] |

3. Results and Discussion

3.1. Distribution of HM in Soil Fractions. The distribution of Cu, Zn, and Cr in contaminated and remediated soils for both sampling dates is reported in Table 5. Heavy metals in contaminated and amended soils showed similar pattern of distribution between fractions. Furthermore, each metal was associated in a different way with soil components, as was expected. These differential trends are in agreement with other studies, which demonstrate that the adsorption process is metal specific [28, 29].

In particular, copper was mainly associated with soil organic matter (Table 5(b)) (P < 0.001), forming that make metals less available for plants [30]. Copper-organic matter association was slightly higher at the end of the experiment, especially with biosolid compost application (among 4 to 6%) in comparison with the other treatments. In agreement with [31], extraction procedure showed that in contaminated soils Cu was mostly present in the acid-soluble and reducible fractions, and in soil amendment with organic matter the soluble and exchangeable Cu fraction was reduced. A possible explanation for this result is the precipitation and complexation by the presence of stabilized organic matter in the compost, such as humic substances (Table 2) [16, 32]. These results corroborate other investigator findings which indicated that organic matter plays a fundamental role in controlling soil HM adsorption, being Cu the preferentially associated with the organic fraction [33]. On the other hand, [34] reported that extractable amounts of Cu were always very small, indicating a low contribute from soluble organic Cu complexes. However, in this pilot study the amount of Cu-EX was lower than 1% of total heavy metal content, and at the end of the experiment, compost and BC + PF treatments had more Cu in residual fraction, indicating greater Cu immobilization.

In all treatments, Zn was remained mostly in soluble and exchangeable fraction of soil as mobile Zn (P < 0.001). In contaminated soil without amendments (CSC) and with fertilizer application, Zn solubility increased by 15.4 and 8.4%, respectively, with experiment time. These results differ with [35], who demonstrated that leached Zn concentration decreased 5.92 ± 2.74 mg kg⁻¹ with phosphate amendment, as a result of immobilization by metal-phosphate precipitates. However, our results are in agreement with those of other studies, which confirm that this increase was possible associated with soil acidification [16, 36, 37]. It cannot be excluded that the simultaneous adding of metal cations could affect Zn adsorption, in agreement with [38], due to ion competition between Zn, Cu, and Cr [8]. Metals with high water solubility pose higher risk of leaching into groundwater. In fact, [39] established that, according to maximum leached concentrations (as a fraction of the total concentration in soil), Zn was the most mobile element in a sequence composite by Zn, Cu, As, and Cr. As a consequence, Zn may offer major environmental risk compared to other metals, since mobile Zn is immediately available for absorption by plants and soil biota in accordance [40, 41].

Chromium was initially adsorbed by soil carbonates as compared with soil organic matter (P < 0.001) [42, 43]. In contrast, at the end of the experiment, a Cr redistribution among fractions was observed and the Cr fraction organic associated to the soil organic matter increased by 10% in the BC treatment, as compared to the beginning of the experiment. This suggests that the addition of organic amendments could enhance the reduction rate of Cr (VI) to Cr (III) increasing it temporal immobilization in soil [44]. According to [34] Cr amounts associated with organic matter increase with the increasing extent of soil contamination, thereby suggesting high constants values of organic-Cr complexes. Moreover, these authors demonstrated that Cr undergoes a progressive insolubilization (organically bound Cr into insoluble Cr) in about 20 years. In this pilot experiment we cannot corroborate this ageing process due to the soil metal spiking approach and the relatively short incubation time.
Table 5: Distribution of copper (a), zinc (b), and chromium (c) in soil chemical fractions at two time points of the experiment: beginning (A) and end (B). Treatments: CSC: Contaminated Soil, CSC + PF: Contaminated Soil + Phosphate Fertilizer, CSC + BC: Contaminated Soil + Biosolid Compost, and CSC + PF + BC: Contaminated Soil + Phosphate Fertilizer + Biosolid Compost (Mean ± S.D., n = 3).

(a) Soluble and exchangeable Heavy metals concentration (mg kg⁻¹)

| Treatment              | Cu       | Zn        | Cr       |
|------------------------|----------|-----------|----------|
| CSC (A)                | 2.56 ± 0.8 | 553.00 ± 2.6 | 0.27 ± 0.0 |
| CSC (B)                | 4.25 ± 0.5 | 457.00 ± 47.6 | 0.54 ± 0.1 |
| CSC + PF (A)           | 4.70 ± 2.4 | 569.33 ± 77.5 | 0.53 ± 0.0 |
| CSC + PF (B)           | 5.14 ± 2.7 | 438.17 ± 77.9 | 0.64 ± 0.2 |
| CSC + BC (A)           | 3.72 ± 0.3 | 547.67 ± 67.2 | 0.43 ± 0.0 |
| CSC + BC (B)           | 3.75 ± 1.0 | 426.17 ± 68.0 | 0.50 ± 0.0 |
| CSC + PF + BC (A)      | 4.76 ± 0.7 | 557.33 ± 19.0 | 0.62 ± 0.1 |
| CSC + PF + BC (B)      | 4.95 ± 0.4 | 422.67 ± 23.1 | 0.79 ± 0.2 |

ANOVA
Amendments
Moment
/Amendments × moment ns ns ns

(b) Organic matter bound Heavy metals concentration (mg kg⁻¹)

| Treatment              | Cu       | Zn        | Cr       |
|------------------------|----------|-----------|----------|
| CSC (A)                | 183.27 ± 16.3 | 195.17 ± 6.7 | 32.63 ± 6.6 |
| CSC (B)                | 200.73 ± 7.2 | 115.73 ± 0.6 | 57.48 ± 2.9 |
| CSC + PF (A)           | 186.20 ± 12.6 | 141.33 ± 25.0 | 32.20 ± 2.7 |
| CSC + PF (B)           | 199.93 ± 18.7 | 110.80 ± 26.0 | 52.15 ± 10.6 |
| CSC + BC (A)           | 196.93 ± 13.4 | 193.33 ± 63.1 | 34.20 ± 7.4 |
| CSC + BC (B)           | 206.30 ± 16.3 | 172.50 ± 13.5 | 45.57 ± 6.9 |
| CSC + PF + BC (A)      | 202.00 ± 10.1 | 172.50 ± 13.5 | 28.87 ± 2.8 |
| CSC + PF + BC (B)      | 189.80 ± 3.7 | 126.20 ± 20.9 | 39.70 ± 0.8 |

ANOVA
Amendments
Moment
/Amendments × moment ns ns ns

(c) Carbonate bound Heavy metals concentration (mg kg⁻¹)

| Treatment              | Cu       | Zn        | Cr       |
|------------------------|----------|-----------|----------|
| CSC (A)                | 189.20 ± 12.6 | 330.33 ± 29.5 | 139.47 ± 5.1 |
| CSC (B)                | 183.97 ± 17.1 | 199.83 ± 19.3 | 152.13 ± 2.8 |
| CSC + PF (A)           | 183.90 ± 2.5 | 340.67 ± 11.6 | 138.20 ± 9.0 |
| CSC + PF (B)           | 166.73 ± 10.8 | 197.17 ± 29.5 | 143.83 ± 14.3 |
| CSC + BC (A)           | 190.53 ± 11.3 | 334.00 ± 84.3 | 123.73 ± 14.6 |
| CSC + BC (B)           | 150.85 ± 11.6 | 234.67 ± 26.3 | 145.95 ± 0.9 |
| CSC + PF + BC (A)      | 187.20 ± 9.8 | 317.67 ± 9.7 | 115.93 ± 11.6 |
| CSC + PF + BC (B)      | 162.30 ± 8.9 | 242.33 ± 44.7 | 143.47 ± 4.3 |

ANOVA
Amendments
Moment
/Amendments × moment ns ns ns
Residual Heavy metals concentration (mg kg$^{-1}$) 

|          | Cu    | Zn    | Cr    |
|----------|-------|-------|-------|
| CSC (A)  | 29.25 ± 2.5 | 39.6 ± 12.2 | 446.8 ± 1.0 |
| CSC (B)  | 20.76 ± 3.2 | 30.2 ± 5.8  | 466.28 ± 2.6 |
| CSC + PF (A) | 20.1 ± 8.3   | 123.4 ± 39.6 | 469.5 ± 6.0   |
| CSC + PF (B) | 39.52 ± 17.1 | 28.52 ± 5.6  | 616.02 ± 14.4 |
| CSC + BC (A) | 32.8 ± 14.4   | 113.2 ± 38.6 | 476.3 ± 12.4  |
| CSC + BC (B) | 50.18 ± 0.8   | 63.21 ± 2.6  | 496.43 ± 4.1  |
| CSC + PF + BC (A) | 31.2 ± 5.5    | 55.0 ± 4.4   | 431.5 ± 6.0   |
| CSC + PF + BC (B) | 45.67 ± 4.3   | 39.99 ± 2.6  | 543.13 ± 2.4  |

ANOVA

| Amendments       | * | * |
|------------------|---|---|
| Moment           | * | * |
| Amendments × moment | ns | ns |

Significance levels: $P < 0.05$; ns: not significant.

According to [45] and assuming that mobility and availability of Cu, Zn, and Cr are associated with their solubility and geochemical forms and that these HMs reduce in the order of extraction sequence, the apparent mobility and potential availability in the soil were Zn > Cu > Cr. In addition, [46] reported that in carbonate soils Cr, Cu, and Pb had higher affinity for the reactive solid phases than Ni, Zn and Cd. The active role of amorphous Al silicates and interaction between clays and organic matter from compost, with formation of organoclays, would have improved the soil adsorbing capacity and enhanced this HM competition [34].

3.2. Effect of Amendments Application on Soil Chemical Characteristics. Application of amendments improved the soil chemical characteristics (Figure 1). Initially, soil pH increased with the addition of both amendments, compared to untreated soil. Since these results were in agreement with those found in a previous study [47], this soil pH modification was slight (2.87% = BC and 2.87% = PF), and there was no correlation with HM bioavailability [48]. Soil acidification observed upon increasing of the experiment time for all treatments was possibly due to soil organic matter mineralization [49] and/or to H+ formation by the fertilizer solubilization [50]. Therefore, liming may be necessary to compensate potential soil acidification when using PF and BC application to reduce HM-contaminated soil [51]. Contrary to [52], we found that soil EC decreased significantly when organic amendment was added ($P = 0.044$), at the end of the experiment, and no correlation was found between the EC and heavy metals availability.

4. Conclusions

Results from this pilot experiment, showed that application of BC and PF in combination affected the partition of Cr, Cu, and Zn added to soil. In particular, BC and PF in combination reduced the solubility and mobility of Cu and Cr whereas Zn stabilization was increased through compost with or without PF application. The use of PF alone increased the available Zn. These results show that combination of organic and inorganic amendments are needed for immobilizing different metals of concern and
could provide a basis for future research about the existence of interactions between metals added simultaneously into the soil. However, the use of liming agents may be needed to buffer soil acidification on prolonged time scales.

References

[1] S. P. McGrath and C. H. Cunliffe, “A simplified method for the extraction of the metals Fe, Zn, Cu, Ni, Pb, Cr, Co and Mn from soils and sewage sludges,” Journal of the Science of Food and Agriculture, vol. 36, pp. 794–798, 1985.

[2] A. Kabata-Pendias, Trace Elements in Soils and Plants, CRC Press, Boca Raton, FlA, USA, 3rd edition, 2000.

[3] R. Schulin, F. Curchod, M. Mondeshka, A. Daskalova, and A. Keller, “Heavy metal contamination along a soil transect in the vicinity of the iron smelter of Kremikovtzi (Bulgaria),” Geoderma, vol. 140, no. 1-2, pp. 52–61, 2007.

[4] D. T. Pinhochet, J. A. Aguirre, and E. R. Quiroz, “Estudio de la lixiviación de Cadmio, Mercurio y Plomo en suelos derivados de cenizas volcánicas,” Agro Sur, vol. 30, no. 1, pp. 51–58, 2002.

[5] D. C. Adriano, Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals, Springer, New York, NY, USA, 2nd edition, 2001.

[6] J. A. Gómez del Rio, P. J. Morando, and D. S. Cicerone, “Natural materials for treatment of industrial effluents: Comparative study of the retention of Cd, Zn and Co by calcite and hydroxyapatite. Part I: batch experiments,” Journal of Environmental Management, vol. 71, no. 2, pp. 169–177, 2004.

[7] R. S. Lavado, M. B. Rodrigue, J. D. Scheiner et al., “Heavy metals in soils of Argentina: comparison between urban and agricultural soils,” Communications in Soil Science and Plant Analysis, vol. 29, no. 11–14, pp. 1913–1917, 1998.

[8] L. Giuffré, S. Ratto, L. Marbán, J. Schonwald, and R. Romaniuk, “Heavy metals risk in urban agriculture,” Ciencia del Suelo, vol. 23, no. 1, pp. 101–106, 2005.

[9] K. Plogeac, E. Guillon, and M. Aplincourt, “Competitive sorption of metal ions onto a north-eastern France soil: Isotherms and XAFS studies,” Geoderma, vol. 139, no. 1-2, pp. 180–189, 2007.

[10] M. B. McBride, Environmental Chemistry of Soils, Oxford University Press, New York, NY, USA, 1994.

[11] P. Sipos, T. Németh, V. K. Kiss, and I. Mohai, “Sorption of copper, zinc and lead on soil mineral phases,” Chemosphere, vol. 73, no. 4, pp. 461–469, 2008.

[12] A. P. D. Mora, J. J. Ortega-Calvo, F. Cabrera, and E. Madejón, “Changes in enzyme activities and microbial biomass after “in situ” remediation of a heavy metal-contaminated soil,” Applied Soil Ecology, vol. 28, no. 2, pp. 125–137, 2005.

[13] R. Clemente, D. J. Walker, and M. P. Bernal, “Uptake of heavy metals and As by Brassica juncea grown in a contaminated soil in Aznalcóllar (Spain): the effect of soil amendments,” Environmental Pollution, vol. 138, no. 1, pp. 46–58, 2005.

[14] M. Mench, J. Vaňgronsveld, C. Beckx, and A. Ruttens, “Progress in assisted natural remediation of an arsenic contaminated agricultural soil,” Environmental Pollution, vol. 144, no. 1, pp. 51–61, 2006.

[15] O. P. Shukla, U. N. Rai, and S. Dubey, “Involvement and interaction of microbial communities in the transformation and stabilization of chromium during the composting of tannery effluent treated biomass of Vallisneria spiralis L,” Bioresource Technology, vol. 100, no. 7, pp. 2198–2203, 2009.

[16] X. Cao, A. Wahbi, L. Ma, B. Li, and Y. Yang, “Immobilization of Zn, Cu, and Pb in contaminated soils using phosphate rock and phosphoric acid,” Journal of Hazardous Materials, vol. 164, no. 2-3, pp. 555–564, 2009.

[17] N. Calace, T. Campisi, A. Iacondini, M. Leoni, B. M. Petronio, and M. Pietroletti, “Metal-contaminated soil remediation by means of paper mill sludges addition: chemical and ecotoxicological evaluation,” Environmental Pollution, vol. 136, no. 3, pp. 485–492, 2005.

[18] R. Clemente, C. Almela, and M. P. Bernal, “A remediation strategy based on active phytoremediation followed by natural attenuation in a soil contaminated by pyrite waste,” Environmental Pollution, vol. 143, no. 3, pp. 397–406, 2006.

[19] P. Castaldi and P. Melis, “Growth and yield characteristics and heavy metals content on tomatoes in different growing media,” Communications in Soil Science and Plant Analysis, vol. 35, no. 1-2, pp. 85–98, 2004.

[20] J. Wright, J. L. Conca, and A. F. Slater, “PIMS with apatite II: a field scale demonstration on a lead contaminated soil,” in Stabilisation/Solidification Treatment and Remediation, A. Al-Tabbaa and J. A. Stegemann, Eds., Chapter 4, Taylor and Francis, London, UK, 2005.

[21] W. Geebelen, D. C. Adriano, D. Van Der Lelie et al., “Selected bioavailability assays to test the efficacy of amendment-induced immobilization of lead in soils,” Plant and Soil, vol. 249, no. 1, pp. 217–228, 2003.

[22] E. Madejón, A. P. De Mora, E. Felipe, P. Burgos, and E. Cabrera, “Soil amendments reduce trace element solubility in a contaminated soil and allow regrowth of natural vegetation,” Environmental Pollution, vol. 139, no. 1, pp. 40–52, 2006.

[23] S. P. McGrath and J. Cegarra, “Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soil,” Journal of Soil Science, vol. 43, no. 2, pp. 313–321, 1992.

[24] A. K. Alva, B. Huang, and S. Paramasivam, “Soil pH affects copper fractionation and phytotoxicity,” Soil Science Society of America Journal, vol. 64, no. 3, pp. 955–962, 2000.

[25] S. Amir, M. Hafidi, G. Merlina, and J. C. Revel, “Sequential extraction of heavy metals during composting of sewage sludge,” Chemosphere, vol. 59, no. 6, pp. 801–810, 2005.

[26] S. I. Torri and R. Lavado, “Zinc distribution in soils amended with different kinds of sewage sludge,” Journal of Environmental Management, vol. 88, no. 4, pp. 1571–1579, 2008.

[27] N. T. Faithfull, Methods in Agricultural Chemicals Analysis: A Practical Handbook, CAB International Publishing, Wallingford, UK, 2004.

[28] G. Welp and G. W. Brümmer, “Adsorption and solubility of ten metals in soil samples of different composition,” Journal of Plant Nutrition and Soil Science, vol. 162, no. 2, pp. 155–161, 1999.

[29] P. C. Gomes, M. P. F. Fontes, A. G. Da Silva, E. S. De Mendonça, and A. R. Netto, “Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils,” Soil Science Society of America Journal, vol. 65, no. 4, pp. 1115–1121, 2001.

[30] N. A. Ali, M. Ater, G. I. Sunahara, and P. Y. Roubidoux, “Phytotoxicity and bioaccumulation of cooper and chromium using barley (Hordeum vulgare L.) in spiked artificial and natural forest soils,” Ecotoxicology and Environmental Safety, vol. 54, pp. 363–374, 2004.

[31] A. Lagomarsino, M. Mench, R. Marabottini et al., “Copper distribution and hydrolase activities in a contaminated soil amended with dolomitic limestone and compost,” Ecotoxicology and Environmental Safety, vol. 74, no. 7, pp. 2013–2019, 2011.

[32] R. O’Dell, W. Silk, P. Green, and V. Claassen, “Compost amendment of Cu-Zn minespoil reduces toxic bioavailable
heavy metal concentrations and promotes establishment and biomass production of Bromus carinatus (Hook and Arn.),” *Environmental Pollution*, vol. 148, no. 1, pp. 115–124, 2007.

[33] S. Dragović, N. Mihailović, and B. Gajić, “Heavy metals in soils: distribution, relationship with soil characteristics and radionuclides and multivariate assessment of contamination sources,” *Chemosphere*, vol. 72, no. 3, pp. 491–495, 2008.

[34] P. Adamo, M. Zampella, L. Gianfreda, G. Renella, F. A. Rutigliano, and F. Terribile, “Impact of river overflowing on trace element contamination of volcanic soils in south Italy: Part I. Trace element speciation in relation to soil properties,” *Environmental Pollution*, vol. 144, no. 1, pp. 308–316, 2006.

[35] F. Panfili, A. Manceau, G. Sarret et al., “The effect of phyto-stabilization on Zn speciation in a dredged contaminated sediment using scanning electron microscopy, X-ray fluorescence, EXAFS spectroscopy, and principal components analysis,” *Geochimica et Cosmochimica Acta*, vol. 69, no. 9, pp. 2265–2284, 2005.

[36] N. T. Basta and J. J. Sloan, “Application of alkaline biosolids to acid soils: changes in solubility and bioavailability of heavy metals,” *Journal of Environmental Quality*, vol. 28, pp. 633–638, 1999.

[37] S. Torri and R. Lavado, “Plant absorption of trace elements in sludge amended soils and correlation with soil chemical speciation,” *Journal of Hazardous Materials*, vol. 166, no. 2–3, pp. 1459–1465, 2009.

[38] M. P. F. Fontes and P. C. Gomes, “Simultaneous competitive adsorption of heavy metals by the mineral matrix of tropical soils,” *Applied Geochemistry*, vol. 18, no. 6, pp. 795–804, 2003.

[39] J. Kumpiene, I. Castillo Montesinos, A. Lagerkvist, and C. Maurice, “Evaluation of the critical factors controlling stability of chromium, copper, arsenic and zinc in iron-treated soil,” *Chemosphere*, vol. 67, no. 2, pp. 410–417, 2007.

[40] A. Fuentes, M. Lloréns, J. Sáez, Ma. I. Aguilar, J. F. Ortuño, and V. F. Meseguer, “Phytotoxicity and heavy metals speciation of stabilised sewage sludges,” *Journal of Hazardous Materials*, vol. 108, no. 3, pp. 161–169, 2004.

[41] M. Pueyo, J. Mateu, A. Rigol, M. Vidal, J. F. López-Sánchez, and G. N. Rao, “Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils,” *Journal of Environmental Quality*, vol. 26, no. 1, pp. 239–264, 1997.

[42] L. Q. Ma and G. N. Rao, “Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils,” *Journal of Environmental Quality*, vol. 26, no. 1, pp. 239–264, 1997.

[43] F. Panfili, A. Manceau, G. Sarret et al., “The effect of phyto-stabilization on Zn speciation in a dredged contaminated sediment using scanning electron microscopy, X-ray fluorescence, EXAFS spectroscopy, and principal components analysis,” *Geochimica et Cosmochimica Acta*, vol. 69, no. 9, pp. 2265–2284, 2005.

[44] N. T. Basta and J. J. Sloan, “Application of alkaline biosolids to acid soils: changes in solubility and bioavailability of heavy metals,” *Journal of Environmental Quality*, vol. 28, pp. 633–638, 1999.

[45] S. Torri and R. Lavado, “Plant absorption of trace elements in sludge amended soils and correlation with soil chemical speciation,” *Journal of Hazardous Materials*, vol. 166, no. 2–3, pp. 1459–1465, 2009.

[46] M. P. F. Fontes and P. C. Gomes, “Simultaneous competitive adsorption of heavy metals by the mineral matrix of tropical soils,” *Applied Geochemistry*, vol. 18, no. 6, pp. 795–804, 2003.

[47] J. Kumpiene, I. Castillo Montesinos, A. Lagerkvist, and C. Maurice, “Evaluation of the critical factors controlling stability of chromium, copper, arsenic and zinc in iron-treated soil,” *Chemosphere*, vol. 67, no. 2, pp. 410–417, 2007.

[48] A. Fuentes, M. Lloréns, J. Sáez, Ma. I. Aguilar, J. F. Ortuño, and V. F. Meseguer, “Phytotoxicity and heavy metals speciation of stabilised sewage sludges,” *Journal of Hazardous Materials*, vol. 108, no. 3, pp. 161–169, 2004.

[49] M. Pueyo, J. Mateu, A. Rigol, M. Vidal, J. F. López-Sánchez, and G. N. Rao, “Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils,” *Journal of Environmental Quality*, vol. 26, no. 1, pp. 239–264, 1997.

[50] L. Q. Ma and G. N. Rao, “Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils,” *Journal of Environmental Quality*, vol. 26, no. 1, pp. 239–264, 1997.

[51] F. Panfili, A. Manceau, G. Sarret et al., “The effect of phyto-stabilization on Zn speciation in a dredged contaminated sediment using scanning electron microscopy, X-ray fluorescence, EXAFS spectroscopy, and principal components analysis,” *Geochimica et Cosmochimica Acta*, vol. 69, no. 9, pp. 2265–2284, 2005.

[52] N. T. Basta and J. J. Sloan, “Application of alkaline biosolids to acid soils: changes in solubility and bioavailability of heavy metals,” *Journal of Environmental Quality*, vol. 28, pp. 633–638, 1999.

[53] S. Torri and R. Lavado, “Plant absorption of trace elements in sludge amended soils and correlation with soil chemical speciation,” *Journal of Hazardous Materials*, vol. 166, no. 2–3, pp. 1459–1465, 2009.

[54] M. P. F. Fontes and P. C. Gomes, “Simultaneous competitive adsorption of heavy metals by the mineral matrix of tropical soils,” *Applied Geochemistry*, vol. 18, no. 6, pp. 795–804, 2003.

[55] J. Kumpiene, I. Castillo Montesinos, A. Lagerkvist, and C. Maurice, “Evaluation of the critical factors controlling stability of chromium, copper, arsenic and zinc in iron-treated soil,” *Chemosphere*, vol. 67, no. 2, pp. 410–417, 2007.

[56] A. Fuentes, M. Lloréns, J. Sáez, Ma. I. Aguilar, J. F. Ortuño, and V. F. Meseguer, “Phytotoxicity and heavy metals speciation of stabilised sewage sludges,” *Journal of Hazardous Materials*, vol. 108, no. 3, pp. 161–169, 2004.

[57] M. Pueyo, J. Mateu, A. Rigol, M. Vidal, J. F. López-Sánchez, and G. N. Rao, “Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils,” *Journal of Environmental Quality*, vol. 26, no. 1, pp. 239–264, 1997.

[58] L. Q. Ma and G. N. Rao, “Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils,” *Journal of Environmental Quality*, vol. 26, no. 1, pp. 239–264, 1997.

[59] F. Panfili, A. Manceau, G. Sarret et al., “The effect of phyto-stabilization on Zn speciation in a dredged contaminated sediment using scanning electron microscopy, X-ray fluorescence, EXAFS spectroscopy, and principal components analysis,” *Geochimica et Cosmochimica Acta*, vol. 69, no. 9, pp. 2265–2284, 2005.
