

Research Article

Dissolution of Metals from Biosolid-Treated Soils by Organic Acid Mixtures

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Results for the solubilization of metals from biosolid- (BSL-) treated soils by simulated organic acid-based synthetic root exudates (OA mixtures) of differing composition and concentrations are presented. This study used two BSL-treated Romona soils and a BSL-free Romona soil control that were collected from experimental plots of a long-term BSL land application experiment. Results indicate that the solubility of metals in a BSL-treated soil with 0.01 and 0.1 M OA mixtures was significantly higher than that of 0.001 M concentrations. Differences in composition of OAs caused by BSL treatment and the length of growing periods did not affect the solubility of metals. There were no significant differences in organic composition and metals extracted for plants grown at 2, 4, 8, 12, and 16 weeks. The amount of metals extracted tended to decrease with the increase of the pH. Results of metal dissolution kinetics indicate two-stage metal dissolution. A rapid dissolution of metals occurred in the first 15 minutes. For Cd, Cu, Ni, and Zn, approximately 60–70% of the metals were released in the first 15 minutes while the initial releases for Cr and Pb were approximately 30% of the total. It was then followed by a slow but steady release of additional metals over 48 hours.

1. Introduction

Organic acids (OAs) provide attractive options for extracting agents not only because they are biodegradable [1, 2], but also because they are able to extract metal contaminants from soils at mildly acidic conditions (pH 3–5). OAs found in root exudates, such as citric, oxalic, tartaric, and acetic acids, are capable of forming complexes with Cu, Zn, Pb, and Co ions in solutions [3–8] and enhancing their mobilization and uptake by plants [9–12]. Römheld and Awad [13] showed that plants grown on low Fe nutrient mediums in contaminated soil had a higher uptake of Fe, Zn, Ni, and Cd (up to 200%) than control plants in adequate Fe nutrient mediums [14]. Various OAs and/or their salts were tested against two metal chelating agents (EDTA and DTPA) for their potential effects in the remediation of loam and sandy clay loam polluted by heavy metals [15, 16]. Experimental evidence shows that OAs added to humic macromolecules induced the release of adsorbed metal ions [17, 18]. In near neutral and neutral

aqueous solutions, OAs are readily dissociated. The negatively charged OA ligands are capable of forming complexes with metals (e.g., Mn, Fe, and Zn) in solutions, increasing their availability to plants [11, 19, 20].

The extent of complexation depends on the characteristics of the OAs involved (number and proximity of carboxylic groups), their concentrations, types of metal, and the pH of the soil [21]. Organic acids with only one carboxyl group, such as acetic, formic, and lactic acids, have less metal complexing ability than malic and oxalic acids, which are frequently found OAs in soils that have a high affinity for complexing metals [14, 22, 23]. The ability of OAs to complex metals is also dependent on pH [24]. For instance, the complexation of Fe by malic and oxalic acids is highly dependent on soil pH, with little or no complexation at pH > 7.0 [25]. In addition, malic and oxalic acids have the tendency to precipitate in the presence of Ca²⁺, thus reducing their potential to complex with other metals [26]. When compared with rainwater alone, OAs are able to double or even quadruple mineral dissolution

rates. The extent of the chemical reactions, however, is dependent on mineral type, pH, and OA type [22]. Jones and Kochian [23] reported that the presence of OAs increases the dissolution of Fe and Al oxyhydroxides.

OAs may be adsorbed onto the hydroxyaluminum-montmorillonite (HyA-Mt) complex. Cambier and Sposito [27] concluded that the HyA-Mt complex is stable at $4 < \text{pH} < 5.5$, and only external HyA polycations could react with citrate. Janssen et al. [28] noted that citrate did not appear to be adsorbed on the Al-OH groups of the HyA-Mt complex; instead it is adsorbed at the edge of the clay [29]. Sakurai and Huang [30] studied the effect of oxalate on the adsorption of Cd by montmorillonite (Mt) and HyA-Mt complex at pH 5. The reaction was very rapid and virtually completed within 10 minutes. The presence of oxalate markedly interfered with Cd adsorption on clays, especially on the montmorillonite. Taniguchi et al. [31] investigated the adsorption phenomena of Cd on hydroxyaluminosilicate- (HAS-) montmorillonite (Mt) and HyA-Mt complexes as influenced by oxalate and citrate. They concluded that the optimal concentrations of oxalate and citrate for Cd adsorption depended on the form of Cd ions in the solution.

Early research by Eaton [32] showed that plant roots absorbed P and Fe from “water insoluble” P and Fe containing minerals present in the growth medium. Jenny and Overstreet [33] proposed that reactions between root and solid phase minerals that were in direct contact or in close proximity would facilitate plant absorption of sparingly soluble mineral nutrients in soils. Recent studies have demonstrated that root exudates, which contain OAs, play a significant role in the solubilization of metals in soil [5, 11, 34]. In BSL, metals are present almost entirely in solid phases. Upon land application, BSL-borne metals remain largely in their original solid phases in BSL-treated soils [35]. Mobilization of metals by OAs in root exudates would be the most significant pathway through which plant absorption of metals from BSL-treated soils occurs [36]. The total amount of bioavailable metals in BSL-treated soils can be estimated by extracting the soils using OAs found in the rhizosphere of plants grown on BSL-treated medium. It follows that the rate of metal availability for plants would be in proportion to the rate of metal dissolution in the OA mixture [37].

The pH of the rhizosphere is also important in determining metal and nutrient mobilization and uptake. It also affects microbial activity in the vicinity of the root. Root induced pH change in the rhizosphere is a known phenomenon [38, 39] and has an effect on the availability or solubility of nutrients such as P, Fe, Mn, Zn, Cu, and Al [40]. Rhizosphere pH may differ from the bulk soil pH by more than 2 units [41]. Buffer capacities of soil and root activity are the main factors influencing pH at the soil-root interface [42]. Several hypotheses have been postulated to explain the different abilities of plant species in affecting rhizosphere pH: these include differences in root exudation and respiration patterns and differences in cation/anion uptake rates [43]. Since plant roots acquire most mineral nutrients and metals as ions, imbalances between the absorption of cations and anions result in roots' excretion of compensating H^+ or OH^- ions into the soil in rhizosphere, to prevent changes

TABLE 1: Chemical properties of the soil used for the experiment.

Biosolid treatment [†]	pH [‡]	Total concentration (mg kg ⁻¹)					
		Cd	Cr	Cu	Ni	Pb	Zn
Control	7.7	0.5	37	105	24	25	95
135 Mg ha ⁻¹	6.9	11	243	188	88	120	559
1,080 Mg ha ⁻¹	6.1	26	596	478	215	396	1466

[†]Obtained at Moreno Field Station of the University of California, Riverside, CA. From 1976 through 1981, composted biosolids were applied at dry weight rates of 0 (control), 22.5, and 180 Mg ha⁻¹ yr⁻¹, respectively.

[‡]1:1 w/v ratio.

in the electroneutrality of the root tissues [44]. Gollany and Schumacher [45] conducted a growth chamber study to characterize patterns of pH change within the rhizosphere of plants and the pH at different root zones was measured by a microelectrode at 1, 2, 3, and 4 mm distances from the root surface. They reported that the pH decreased to 4.82 and 4.95 in the rhizosphere around elongation and meristematic zones, respectively, compared to the control (pH = 7.6) without plants.

The objectives of this study were the following:

- (1) To use an OA mixture as a substitute for actual OAs in root exudates to solubilize metals in BSL-treated soils.
- (2) To test the solubilization of metals in BSL-treated soils by the different concentrations of the OA mixture of corn (*Zea mays* L.).

In order to meet these objectives, the researchers needed to assess OA mixture-specific metal solubility and dissolution rate constants of BSL-treated soils.

2. Materials and Methods

2.1. Chemical Properties of the Soils. Two BSL-treated Romona soils and the BSL-free Romona soil control from the field plots of a long-term BSL land application experiment were used [46]. These experiment plots were established in 1976 on a Romona sandy loam soil (fine-loamy, mixed, thermic Typic Haploxeralf) located in the Moreno Field Station of the University of California, Riverside. The Nu-earth BSL used throughout the experiment contained an average of 40, 600, 475, 250, and 3,547 mg kg⁻¹ of Cd, Cr, Cu, Ni, and Zn, respectively. From 1976 through 1981, composted BSL were applied at a rate of 0 (control), 22.5, 45, 90, and 180 Mg ha⁻¹ yr⁻¹ dry weight. The entire experimental fields were cultivated for 10 years (1982–1991) following the termination of BSL application. Soil collected in 1991 from the control, 22.5, and 180 Mg ha⁻¹ yr⁻¹ treatments was used. Soil samples were air-dried and ground to pass through a 2 mm sieve, homogenized, and stored for subsequent analysis. The chemical properties of the selected soils used in the study are presented in Table 1. For metal determination, aliquots of soil samples were digested in Teflon Parr bombs by a HNO_3 microwave digestion procedure (0.3 g soil with a mixture of 1.0 mL H_2O + 4.5 mL concentrated HNO_3 + 1.5 mL concentrated HCl, in a 120 mL Teflon digestion vessel for 20 minutes and with maximum pressure of 484 kPa) [47].

2.2. Release and Analysis of the Metals. One gram of the soils was mixed with 10 mL of OA mixtures in 50 mL Teflon test tubes. The contents were shaken and allowed to equilibrate at 298°K using a rotary mixer, SA-12 Motor Speed Control (B & B Motor and Control Corp., Long Island City, NY), which rotated the capped test tubes head to tail at approximately 1 rpm for 48 hours. The speed of rotation was maintained constant in all treatments. One mL of chloroform was added to each test tube to control microbial activity and prevent decomposition of OA mixtures during equilibration. The pH and EC of the system in the beginning and at the end of the reaction period were monitored and attempts were made to keep the pH constant. Three OA mixture concentrations 0.001, 0.01, and 0.1 M in 13.5 mM $\text{Ca}(\text{NO}_3)_2$ along with a 13.5 mM $\text{Ca}(\text{NO}_3)_2$ blank were tested. Each treatment combination was replicated two times. After equilibration, the soil suspensions were centrifuged for 20 minutes at 8,000 rpm to separate the solution and solid phases. The solution phase was passed through a 0.45 μm filter paper into 25 mL volumetric flasks. The filtrates were acidified with 0.25 mL of concentrated HNO_3 . The metal contents of the supernatants were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Atomic Absorption Spectrophotometry (AAS) [47]. The ICP-OES system was OPTIMA 3000 V (Perkin-Elmer, Norwalk, CT, USA) with AS-91 Autosampler and WinLab™ software for the optima family of ICP-OES. Another instrument utilized was the Perkin-Elmer Analyst 800 Atomic Absorption Spectrometer (Perkin-Elmer, Bodenseewerk, Germany) with AS-800 Autosampler. The same experimental setup was used for the batch metal dissolution kinetics. The metal concentrations at 0, 0.25, 0.5, 1, 2, 4, 8, 24, and 48 hours were determined for the kinetic studies.

2.3. Statistical Analysis. All experiments were repeated. Between-group differences were determined by one-way analysis of variance (ANOVA), followed by Student-Newman-Keuls test using a probability level of $P < 0.05$ in all cases. Tests were performed with SigmaStat 4.01 Software.

3. Results and Discussion

3.1. Formulation of Organic Acid Mixtures. Organic acids in rhizosphere are difficult to collect because the volume produced is limited and the components of the root exudates are readily biodegradable. To evaluate the OAs' ability in the rhizosphere to solubilize metals in the soils, a large amount of root exudates must be collected. Because of the difficulty in collecting and preserving root exudates, it is imperative that an OA-based synthetic root exudate (OA mixture) be formulated.

The OA mixture should contain the primary chemical components responsible for metal complex formation and should be in the concentration and pH ranges commonly observed in the rhizosphere. In addition, the OA mixtures should also be prepared under the same background chemical matrix of the soil solution. In this manner, the OA mixture would exhibit comparable ability of reacting with metals as the actual root exudates.

TABLE 2: Amounts of Cd extracted by organic acid (OA) mixtures of various compositions and concentrations[†].

OA concentration	OA composition [‡]	Cd concentration (mg kg^{-1})	
		Biosolid	Standard
0.1 M	2nd	2.11 ^{Ba}	1.86 ^{Ba}
	4th	2.36 ^{Aa}	2.58 ^{Aa}
	8th	1.98 ^{Ba}	1.63 ^{Ba}
	12th	1.79 ^{Ba}	1.60 ^{Ba}
	16th	1.71 ^{Ba}	1.62 ^{Ba}
0.01 M	2nd	0.39 ^{Aa}	0.31 ^{Aa}
	4th	0.41 ^{Aa}	0.43 ^{Aa}
	8th	0.44 ^{Aa}	0.35 ^{Aa}
	12th	0.47 ^{Aa}	0.37 ^{Aa}
	16th	0.51 ^{Aa}	0.43 ^{Aa}
0.001 M	2nd	0.29 ^{Aa}	0.20 ^{Aa}
	4th	0.32 ^{Aa}	0.24 ^{Aa}
	8th	0.36 ^{Aa}	0.32 ^{Aa}
	12th	0.29 ^{Aa}	0.23 ^{Aa}
	16th	0.30 ^{Aa}	0.29 ^{Aa}
13.5 mM $\text{Ca}(\text{NO}_3)_2$	Not applicable	0.10	

[†] Values represent means of four replicates. The differences of Cd concentrations among the OA compositions of growth periods were tested by one-way ANOVA. In each column of each organic concentration, values followed by the same uppercase letter were not significantly different at $P < 0.05$. The differences of the Cd concentrations between standard (STD) and biosolid (BSL) treatments were tested by Student-Newman-Keuls test. Each pair of Cd concentrations followed by the same lowercase letter was not significantly different at $P < 0.05$.

[‡] Compositions corresponding to OAs recovered from STD and BSL-treated medium of corn at 2nd, 4th, 8th, 12th, and 16th weeks of growth.

To simulate OAs in root exudates, an OA mixture of similar composition to the root exudate composition was formulated. A series of experiments were conducted to test the effect of OA compositions, the total concentration of metals, and the concentration of OAs in the dissolution of metals in the BSL-treated soils. The amount of metals extracted by the OA mixtures, representing compositions of OAs recovered from the rhizosphere of corn grown on BSL-treated medium and the standard (STD) sand medium [34], was illustrated by the Cd extractions summarized in Table 2. The differences of metals extracted due to the compositions representing OAs at 2, 4, 8, 12, and 16 weeks of plant growth were not significant at $P < 0.05$ and the differences due to OAs of STD and BSL-treated medium were not significant at $P < 0.05$. The trends were similar for other metals extracted. The data were then pooled to test the differences in metal extractions due to the concentrations of OA mixtures. They were significant at $P < 0.05$. Based on the results, the OA mixture was formulated.

3.1.1. Composition and Concentration of OAs. Although the OA compositions of the root exudates recovered from plants were grown for various lengths of time from different plant species, they did not vary significantly under our system

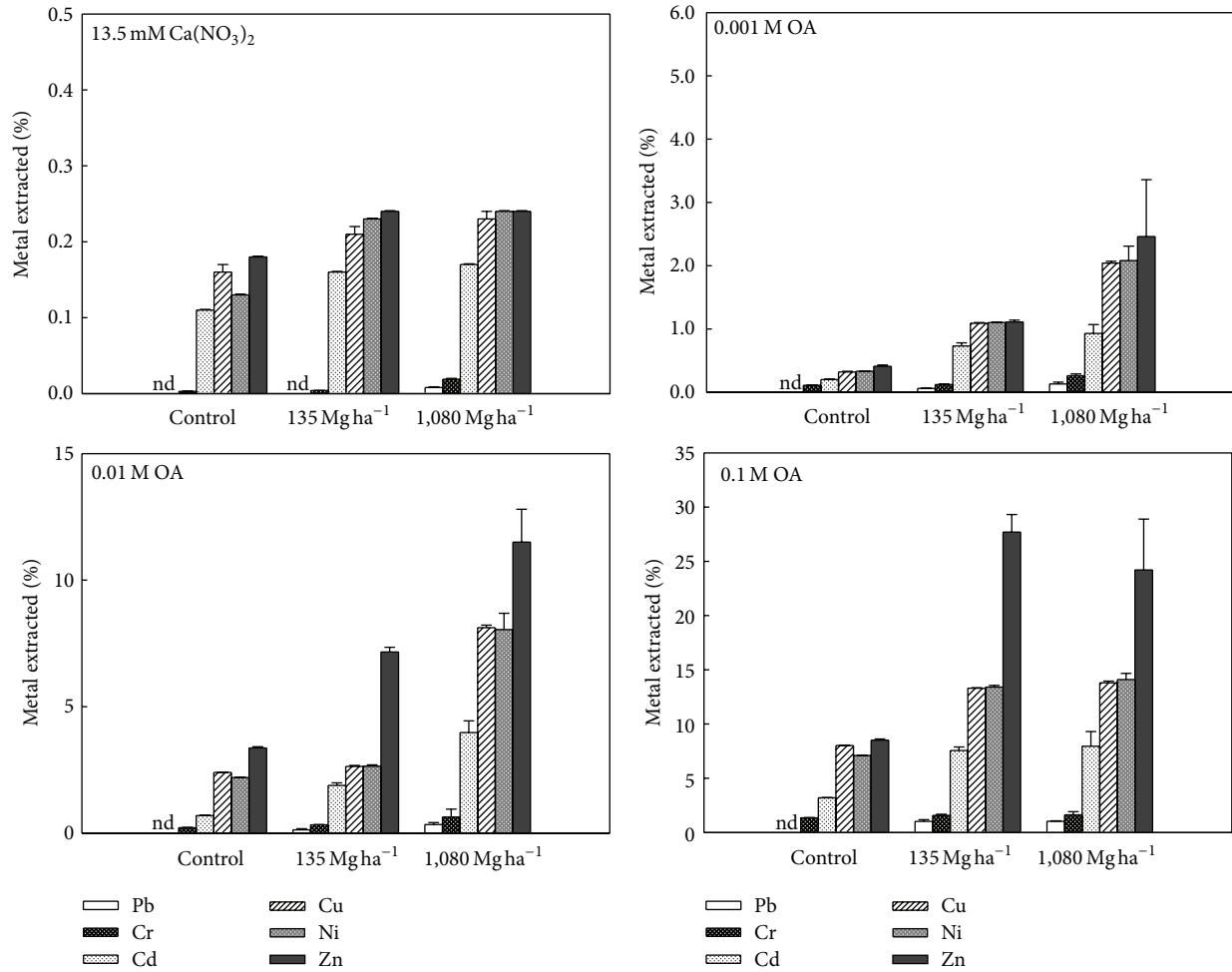


FIGURE 1: Percentages of metal extracted (means \pm SD where $n = 4$) from control and biosolid-treated Romona soil by the organic acid mixtures. Obtained at Moreno Field Station of the University of California, Riverside, CA. From 1976 through 1981, composted biosolids were applied at dry weight rates of 0 (control), 22.5, and 180 Mg ha⁻¹ yr⁻¹, respectively. Some of the observations were below detection limits (nd) of the AAS for Pb = 0.001 mg kg⁻¹.

[34]. The OA mixture composition was taken as the average composition of OAs recovered from the rhizosphere of corn grown on BSL-treated medium for 16 weeks and summarized in Table 3.

Figure 1 summarizes the amounts of metals extracted by OA mixtures at concentrations of 0.001, 0.01, and 0.1 M. The experimental results indicate that the concentrations of the OA mixtures significantly affect the amount of metals extracted. The amount of metals extracted by the OA mixtures was considerably greater than that of the neutral electrolyte solution, 13.5 mM of Ca(NO₃)₂, which was used to represent the background chemical matrix of the soil solution. Based on the moisture content of the rhizosphere and the amount of OAs recovered from the rhizosphere [34], the concentrations of OAs in the rhizosphere were estimated to be from 0.001 to 0.013 M (Table 4). As the OAs are closely associated with root exudates, their concentrations are expected to be considerably higher near the root and soil interface and could approach 0.1 M.

TABLE 3: Mole fraction of organic acids collected in root exudates of corn.

Organic acid	Molecular weight	Mole fraction ratio
Acetic	60.05	0.287
Butyric	88.11	0.209
Glutaric	132.12	0.004
Lactic	90.08	0.366
Maleic	116.07	0.042
Oxalic	90.04	0.043
Propionic	74.08	0.010
Pyruvic	88.06	0.0004
Succinic	118.09	0.006
Tartaric	150.09	0.032
Valeric	102.13	0.001

Quantitative measurements of root exudates from plant roots indicate that OA concentrations as high as 50 mM

TABLE 4: Estimated solution concentrations (16-week average) of organic acid mixtures in root exudates of corn[†].

Treatment	Estimated concentration (mM)			
	Standard (control)		Biosolid-treated	
	Mean	SD	Mean	SD
Blank	2.05	0.63	3.41	0.87
Planted	5.23	1.21	12.9	2.04

[†]All experiments performed in four replicates for each 2, 4, 8, 12, and 16 weeks. Values represent means and standard deviation of 20 replicates.

were found within 1 mm from the root surface [53], with typical concentrations in roots at 10–20 mM. For example, in corn, organic solutes present in root cells existed primarily as amino acids (10–20 mM) and sugars (90 mM) [54]. Generally, higher concentrations of OAs are expected in the rhizosphere soil compared to those in the bulk soil [34, 55]. Soil microorganisms do not utilize the carboxylic acids, which play a significant role in complexing metal ions in soils as rapidly as the carbohydrates [3].

3.1.2. pH of the Rhizosphere Soils. The rhizosphere typically extends 1–5 mm outward from the interface of the root and soil but the pH measurement is complicated. Instead of directly measuring the pH of the rhizosphere, it was deduced and estimated from data found in literature. Studies of the rhizosphere changes in pH along roots of crops and pH changes at different distances from roots are listed in Table 5.

Zhang and Pang [50] demonstrated that while pH was essentially uniform in unvegetated soil, pH was lower near the root tips than at other locations around the root in vegetated soil. The pH varied from 6.2 near the surface (0.5 cm depth) to 4.99 at 6 cm below the soil surface.

It is apparent that pH at or near the root of living plants was altered by root exudation. It varied from pH = 4–5 at the soil-root interface and gradually varied to the level comparable to the pH of bulk soils over approximately 5 mm of distance. The pH = 4.8 was chosen as the pH for the synthetic root exudates based on the results of effects of pH on the dissolution of metals in the BSL-treated soils.

3.2. Effects of pH on the Dissolution of Metals in the Biosolid-Treated Soils. The pH of the rhizosphere may vary from 4.0 to 8.0 (Table 5) and may affect the solubility of metals in the soil. The effects of pH on the dissolution of metals in BSL-treated soils by the OA mixture were determined. Based on the outcome of this experiment, the pH of the OA mixture was set at 4.8. A BSL-treated Romona soil (135 Mg ha⁻¹) was extracted by the 0.01 M OA mixture and 13.5 mM Ca(NO₃)₂ that were adjusted to pH = 4.5, 5.5, 6.5, and 7.5.

The amounts of metals extracted tended to decrease with the increase of the pH and, at the same pH level, the OA mixture typically extracted more metals than the 13.5 mM Ca(NO₃)₂ electrolyte solution (Figure 2). The extent of pH-induced changes in metal solubility was not substantial. Cadmium and zinc experienced by far the biggest decrease, from 0.04 to 0.02 and 2.3 to 1.1 mg kg⁻¹, respectively, when pH of the extracting OA mixture increased from 4.5 to 7.5. The

change in extractable Cd and Zn was larger from pH = 4.5 to 5.5 than from 6.5 to 7.5. Under the same circumstance, the Cr extracted decreased from approximately 0.1 to 0.08 mg kg⁻¹. Statistical tests indicated that metals extracted at pH = 4.5 were not significantly different from the corresponding metals extracted at pH = 5.5 (Figure 2).

In general, the holding capacity of soils for metals increases with increasing pH. Exceptions are Cr and Mo, which are commonly more mobile under alkaline conditions. Accordingly, a decrease in plant uptake of Cu, Mn, and Zn was observed when soil pH was increased [56, 57]. The pH can be issued as the main driving factor of all the factors because it can affect the surface charge of layer silicate clays, OM, and oxides of Fe and Al. In addition to the effect on the sorption of cations, which increases with increasing pH, Fernández-Ramos et al. [58] reported that the adsorption of certain trace metals onto hydrous ferric oxide depends on pH. The results correspond to our findings.

3.3. Metal Solubility by Organic Acid Mixtures. Metals in the soils were not readily extractable by the neutral electrolyte solution blank that contained 13.5 mM Ca(NO₃)₂ and, in general, less than 0.25% of any metals were solubilized (Figure 1).

For Pb, the concentrations in the extracts of blank were below limits of quantification of AAS (<0.001 mg kg⁻¹). For the control soil, the total metal concentrations and percent of metals extracted were considerably lower than those in BSL-treated soils.

In BSL-treated soils, the amount of metals extracted was proportional to the amount present in soils and the percentage of the total metals extracted from BSL-treated soils increased with the concentration of OA mixtures; however, the percentage of extraction did not appear to change significantly with the BSL loading when soils were extracted by the 0.1 M OA mixture. In general, Cd, Cu, Ni, and Zn were more readily extractable by the OA mixtures (Figure 1) than Cr and Pb. The least extractable Pb and Cr from the BSL-treated soils follow the general trend reported in the previous paper [34] because of their strong complexation with OM compounds [56] and more specifically the effective role of OM of BSL to serve as electron donors for the reduction of Cr(VI) to Cr(III) [59]. Metals extracted from BSL-treated soils were almost all from BSL. For instance, the amount of Cd extracted from control Romona soil by 13.5 mM Ca(NO₃)₂ was 0.0008 mg kg⁻¹ (Figure 1) and the amount of Cd extracted from BSL-treated soil with the same electrolyte solution blank was 0.023 mg kg⁻¹. We calculated that the amount of Cd extracted from BSL-treated soils is about 97% of the total extracted Cd.

3.4. Metal Dissolution Kinetics of Biosolid-Treated Soils by Organic Acid Mixtures. The batch equilibrium method was used to study the kinetics of metal dissolution in BSL-treated soils. The experimental procedures were similar to those previously described in the metal solubility study, with the exception that samples were equilibrated for time periods ranging from 15 minutes to 48 hours. When the BSL-treated soils (1,080 Mg ha⁻¹) were equilibrated with 0.1 M OA

TABLE 5: Reported pH ranges of rhizosphere.

Plant	Genotype	pH range	Reference
Barley	Bowman	6.2–7.6	Gollany and Schumacher [45]
	Primus II	6.0–7.8	
	Dorirumugi	4.8–7.1	Youssef and Chino [42]
Corn	Pioneer-3737	5.2–7.6	Gollany and Schumacher [45]
	Pioneer-3732	5.2–7.6	
	CM-37	6.0–7.6	
	—	4.8–6.7	Fischer et al. [48]
Clover	Trikkala	6.2–7.1	Hinsinger and Gilkes [49]
Daisy fleabane	—	5.1–6.3	Zhang and Pang [50]
Nectarine tree	Maxim	5.3–8.2	Tagliavini et al. [36]
Oat	Hyttest	6.0–7.6	Gollany and Schumacher [45]
	SD 84104	6.2–7.6	
Rape	—	5.7–6.4	Ruiz and Arvieu [25]
Rye	Standard	5.6–7.1	Hinsinger and Gilkes [49]
Sordan	S-757	6.0–7.6	Gollany and Schumacher [45]
	S-333	6.1–7.6	
Sorghum	SC-33-8-9EY	6.3–7.6	Gollany and Schumacher [45]
	SC-118-15E	6.6–7.6	
Soybean	—	5.5–7.1	Römheld and Marschner [51]
	Hawkeye	4.8–7.6	Gollany and Schumacher [45]
	PI-54169	5.8–7.6	Gollany and Schumacher [45]
	Toyosuzu	5.1–7.0	Youssef and Chino [42]
	—	4.7–7.1	Riley and Barber [52]

mixture, the amount of BSL-borne metals solubilized in the OA mixtures increased from 1.67 to 2.48, 1.46 to 5.04, 20.3 to 33.4, 16.1 to 24.1, 0.77 to 2.33, and 205 to 282 mg kg⁻¹ for Cd, Cr, Cu, Ni, Pb, and Zn, respectively, when equilibration time increased from 15 minutes to 48 hours (Tables 6–8).

The percentages of total BSL-borne metals extracted were 13.8, 1.63, 7.95, 14.1, 1.03, and 24.2% for Cd, Cr, Cu, Ni, Pb, and Zn, respectively. If OAs are responsible for converting metals in solid phases into plant available forms, the amount and rate of the metals' solubilization would be indicative of the metals' availability to plants.

The metal dissolution kinetics data was plotted as a fraction of the total dissolved metals (C_t/C_{48} , based on 48 hours' equilibration, C_{48}) that was found at time t (C_t) (Figure 3). The patterns for dissolution in the OA mixtures were essentially the same for all metals. When the BSL-treated soils were equilibrated with the 0.1 M OA mixture, there appeared to be an immediate and rapid release of metals from the soil. The amount of Cd, Cu, Ni, and Zn solubilized in the first 15 minutes ($C_{0.25}$) accounted for approximately 60–75% of the total dissolved metals. For Cr and Pb, approximately 8 hours was needed to dissolve 60–70% of the total soluble metals. After 15 minutes, the dissolution of metals slowly reached the steady state over a period of 48 hours. When the concentrations of the OA mixtures were 0.001 M and 0.01 M, the dissolution behavior of metals in BSL-treated soils

exhibited the same pattern as those of 0.1 M OA mixture. The amount of metals extracted by 0.001 M and 0.01 M OA mixtures was considerably less than the amount extracted by the 0.1 M OA mixture. The percentages of the total soluble metals that entered into the solution phase in the first 15 minutes, however, were essentially identical for 0.001, 0.01, and 0.1 M OA mixtures (Table 9).

A variety of chemical reactions occur in soils and reactions often take place simultaneously. Reaction time may vary from millisecond scale for ion exchange reactions to days (or months or years) for sorption/desorption reactions to reach equilibrium [60]. Metals present in BSL-treated soils may be present in different forms and therefore dissolve at different rates [61]. In the rhizosphere, the biosolids-borne metals are mainly present in solid forms and are not readily available to the growing plants. The dissolution by the root exudates is a significant pathway through which the plant absorbs metals from biosolid-treated soils. We hypothesized that the phytoavailable metals in biosolid-treated soils can be determined by amount of metals dissolved by root exudate derived organic acids in the rhizosphere. The metal uptake by plants is determined by the kinetics of metal released into solution by organic acids. In this manner, the phytoavailability of biosolid-borne metals may be defined in terms of capacity factor (i.e., organic acids extractable metals in soils), which describes the plant available metal concentration in

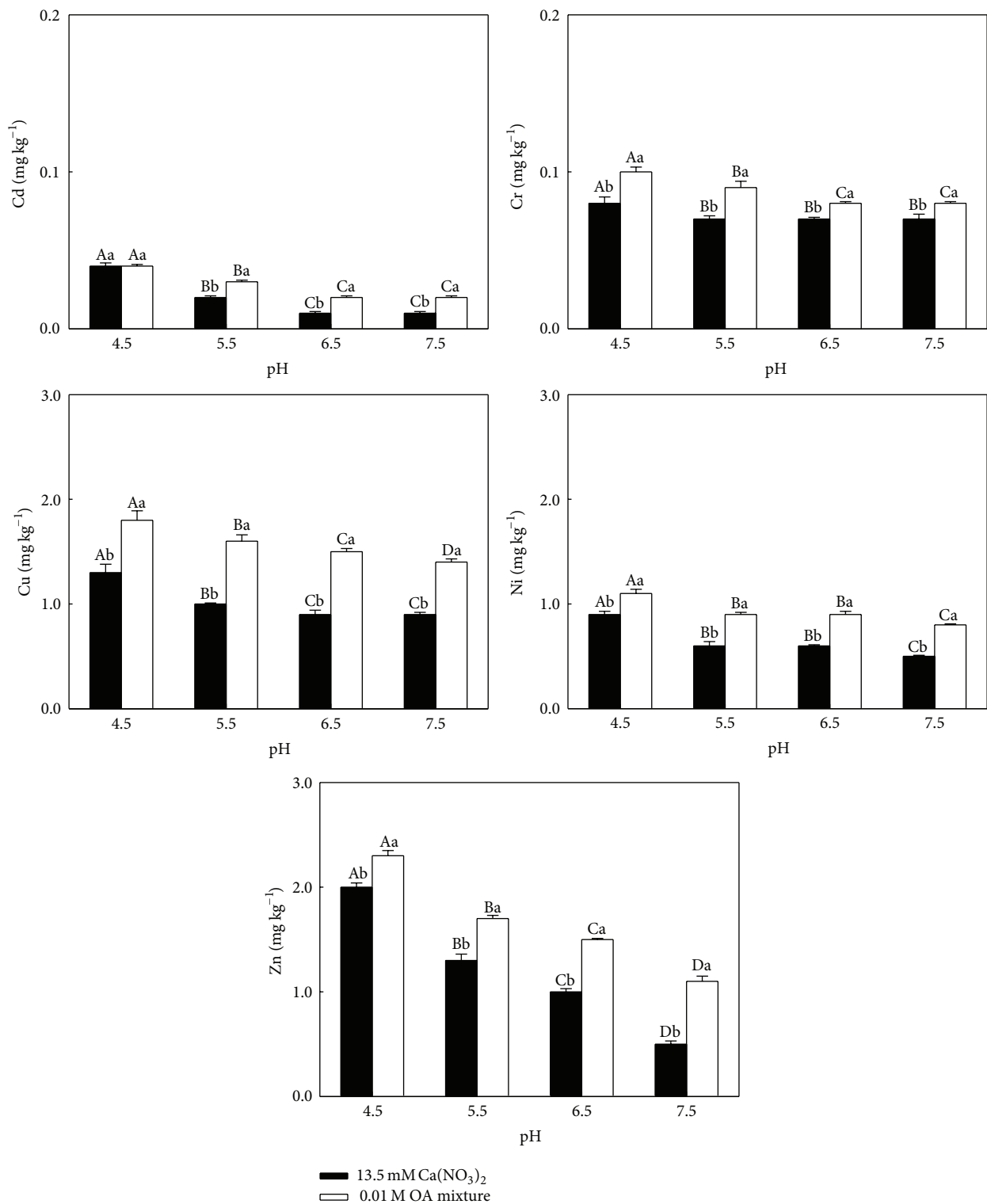


FIGURE 2: Effects of pH on the extraction of metals (four replicates) in biosolid-treated Romona soil (135 Mg ha⁻¹) by 13.5 mM Ca(NO₃)₂ electrolyte solution and 0.01 M organic acid mixtures. The differences of metal concentrations among the pH values were tested by one-way ANOVA. Values followed by the same uppercase letter were not significantly different at $P < 0.05$. The differences of the metal concentrations between 13.5 mM Ca(NO₃)₂ and 0.01 M OA mixture were tested by Student-Newman-Keuls test. Values followed by the same lowercase letter were not significantly different at $P < 0.05$.

TABLE 6: Metals release kinetics of biosolid-treated Romona soil (1,080 Mg ha⁻¹) in different concentrations of organic acid (OA) mixtures.

Element	OA concentration	Metal concentration (mg kg ⁻¹)							
		15 min	30 min	1 hr	2 hrs	4 hrs	8 hrs	24 hrs	48 hrs
Cd	0.001 M	0.31	0.32	0.33	0.35	0.37	0.40	0.46	0.47
	0.01 M	1.16	1.21	1.24	1.28	1.35	1.49	1.73	1.75
	0.1 M	1.67	1.70	1.75	1.82	1.90	2.03	2.40	2.48
Cr	0.001 M	0.34	0.40	0.44	0.49	0.57	0.73	1.09	1.12
	0.01 M	0.85	0.95	1.03	1.16	1.39	1.67	2.49	2.57
	0.1 M	1.46	1.78	1.91	2.17	2.53	3.17	4.79	5.04
Cu	0.001 M	2.41	2.48	2.63	2.78	2.88	3.14	3.81	3.89
	0.01 M	10.7	11.1	11.7	12.1	12.8	13.8	16.8	17.5
	0.1 M	20.3	21.2	22.5	23.7	25.2	26.4	32.1	33.4
Ni	0.001 M	2.53	2.64	2.83	2.94	3.13	3.28	3.72	3.79
	0.01 M	9.80	10.2	10.9	11.4	12.1	12.5	14.5	14.8
	0.1 M	16.1	16.8	18.0	18.8	19.5	20.8	23.3	24.1
Pb	0.001 M	0.13	0.14	0.15	0.18	0.22	0.29	0.42	0.46
	0.01 M	0.34	0.36	0.38	0.45	0.54	0.67	0.99	1.03
	0.1 M	0.77	0.82	0.87	1.02	1.09	1.89	2.01	2.33
Zn	0.001 M	25	26	28	29	31	32	36	38
	0.01 M	104	108	111	115	123	129	145	148
	0.1 M	205	211	220	227	235	245	275	282

TABLE 7: Metals release kinetics of biosolid-treated Romona soil (135 Mg ha⁻¹) in different concentrations of organic acid (OA) mixtures.

Element	OA concentration	Metal concentration (mg kg ⁻¹)							
		15 min	30 min	1 hr	2 hrs	4 hrs	8 hrs	24 hrs	48 hrs
Cd	0.001 M	0.055	0.059	0.063	0.066	0.068	0.073	0.089	0.091
	0.01 M	0.18	0.19	0.20	0.21	0.23	0.25	0.29	0.30
	0.1 M	0.79	0.83	0.88	0.92	1.01	1.10	1.26	1.29
Cr	0.001 M	0.07	0.08	0.09	0.10	0.13	0.16	0.22	0.23
	0.01 M	0.23	0.27	0.30	0.34	0.38	0.46	0.69	0.71
	0.1 M	0.91	1.07	1.13	1.23	1.47	1.80	2.63	2.68
Cu	0.001 M	0.86	0.88	0.92	0.97	1.05	1.15	1.38	1.42
	0.01 M	2.21	2.35	2.49	2.63	2.80	2.93	3.59	3.66
	0.1 M	7.6	7.8	8.3	8.9	9.4	10.1	12.6	12.7
Ni	0.001 M	0.53	0.55	0.59	0.62	0.66	0.68	0.79	0.81
	0.01 M	1.57	1.67	1.80	1.93	2.01	2.13	2.52	2.57
	0.1 M	6.8	7.3	7.8	8.4	8.9	9.5	11.0	11.3
Pb	0.001 M	0.021	0.023	0.025	0.030	0.035	0.044	0.063	0.065
	0.01 M	0.06	0.07	0.08	0.09	0.11	0.13	0.19	0.20
	0.1 M	0.32	0.34	0.38	0.45	0.53	0.62	0.90	0.94
Zn	0.001 M	3.96	4.19	4.35	4.48	4.69	4.91	5.60	5.66
	0.01 M	21.4	22.6	23.3	24.8	25.7	27.1	30.7	31.0
	0.1 M	100	103	108	114	117	121	134	137

biosolid-treated soil and intensity factor (i.e., the rate at which metals may be dissolved by organic acids), which indicates the rate at which metals will be absorbed by plants. The data presented in Tables 6–8 and Figure 3 may fit the two-site bicontinuum model. Under this conception, there appeared to be two dissolution reactions, a fast reaction, which quickly solubilized this component of the metals, followed by a slow reaction of the remaining components that may continue for

a long period of time. These two reactions may occur in series or in parallel. Location and chemical bonding of metals in soil and solution versus metal ratio might be the effects for two pools of metal [62]. The rapid release of metals in the first 15 minutes was fitted into a zero-order kinetics model that

$$C_t = k_0 \times t \quad \text{for } t = 0 \text{ to } t = 0.25, \quad (1)$$

TABLE 8: Metals release kinetics of control Romona soil in different concentrations of organic acid (OA) mixtures.

Element	OA concentration	Metal concentration (mg kg ⁻¹)							
		15 min	30 min	1 hr	2 hrs	4 hrs	8 hrs	24 hrs	48 hrs
Cd	0.001 M	0.0013	0.0014	0.0015	0.0015	0.0016	0.0017	0.002	0.002
	0.01 M	0.0084	0.0088	0.0091	0.0097	0.0102	0.0115	0.0137	0.014
	0.1 M	0.020	0.021	0.022	0.023	0.025	0.027	0.031	0.032
Cr	0.001 M	0.010	0.012	0.013	0.016	0.019	0.023	0.034	0.035
	0.01 M	0.015	0.018	0.020	0.023	0.028	0.035	0.052	0.053
	0.1 M	0.11	0.13	0.14	0.16	0.20	0.23	0.35	0.36
Cu	0.001 M	0.1071	0.1139	0.1207	0.1275	0.1343	0.1433	0.170	0.177
	0.01 M	0.35	0.36	0.39	0.41	0.44	0.47	0.56	0.58
	0.1 M	1.97	2.03	2.12	2.21	2.34	2.51	3.11	3.17
Ni	0.001 M	0.0603	0.063	0.0675	0.0702	0.0737	0.0773	0.0891	0.090
	0.01 M	0.39	0.42	0.47	0.48	0.51	0.53	0.63	0.64
	0.1 M	1.07	1.12	1.18	1.24	1.33	1.42	1.64	1.67
Pb	0.001 M	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]
	0.01 M	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]	n.d. [†]
	0.1 M	0.014	0.016	0.017	0.019	0.024	0.030	0.042	0.044
Zn	0.001 M	0.30	0.32	0.34	0.35	0.37	0.38	0.44	0.45
	0.01 M	1.95	2.06	2.17	2.26	2.34	2.44	2.77	2.79
	0.1 M	5.3	5.6	6.0	6.2	6.5	6.8	7.8	7.9

[†] Concentration was below detection limits of the AAS for Pb = 0.001 mg kg⁻¹.

where C_t (mg kg⁻¹) is the metal concentration at time t (hour) and k_0 (mg kg⁻¹ hr⁻¹) is the zero-order kinetics constant. The remainder portion of the metal dissolution reaction follows a first-order kinetics model that

$$C_t = (0.25 \times k_0) + \{C_s \times [1 - e^{-k_1 \times (t-0.25)}]\}; \quad \text{for } t > 0.25, \quad (2)$$

where C_s represents the ultimate metal release due to the first-order dissolution reaction (mg kg⁻¹) and k_1 is the first-order kinetics constant (hr⁻¹). The kinetics models depicting the metal dissolution reactions are summarized in Table 10. The concentrations of OA mixtures and the amount of BSL-borne metals in the soils determined the metals' dissolution and their availability to plants. For the first-order slow metal release, the rate constants for a metal (k_1) did not vary significantly. k_1 ranged from 0.07 to 0.13, 0.08 to 0.09, 0.07 to 0.09, 0.12 to 0.14, 0.08 to 0.09, and 0.1 to 0.13 for Cd, Cr, Cu, Ni, Pb, and Zn, respectively.

For the zero-order rapid metal release, the metal dissolution of the soil increased with the concentration of OA mixtures and the amount of metals dissolved by the OA mixture of a given concentration increased with the amount of BSL-borne metals in the soils. When the concentrations of OA mixtures varied from 0.001 to 0.1 M, k_0 for a given soil generally increased by 5 to 10 times. At the same OA mixture concentration, k_0 of metals varied by 20–100, 15–60, and 10–60 times for control, soil receiving 135 Mg ha⁻¹, and soil receiving 1,080 Mg ha⁻¹ of BSL, respectively.

The total metals that were extractable by the OA mixtures were calculated as the sum of metal rapidly released by the zero-order reaction ($0.25 \times k_0$) and the metal slowly released through the subsequent first-order reaction (C_s). The total

OA extractable metals would indicate the amount of metals possibly available to plants. The amount of metals that were extractable from BSL-treated soil (1,080 Mg ha⁻¹) by 0.1 M OA mixture is presented in Table 11.

Under this metal release model, plants grown on BSL-treated soils would be expected to absorb metals from the rapid release pool first. As the metal release followed a zero-order reaction, one would expect the plant uptake, and therefore tissue concentration, of metals to remain essentially the same until metals in this pool are exhausted, at which time the plant uptake of metals, and therefore the tissue concentration, is expected to decrease as metals in the slow release pool would be available to plants at a much slower rate.

The data presented in Tables 6–8 and Figure 3 also may fit the first-order kinetics model. Under this conception, the slope of the curve approached 0 as the time increased (Table 12). The trend on the cumulative metal extracted with respect to time was fitted into a first-order kinetics model and can be expressed as

$$C_t = C_0 \times (1 - e^{-k_1 \times t}), \quad (3)$$

where C_t (mg kg⁻¹) is the metal concentration at time t (hour) and k_1 (hr⁻¹) is the first-order kinetics constant and C_0 represents the ultimate metal release due to the first-order dissolution reaction (mg kg⁻¹). The concentrations of OA mixtures and the amount of BSL-borne metals in the soils determined the metals' dissolution and their availability to plants. For the first-order metal release, the rate constants for a metal (k_1) ranged from 3.88 to 6.25, 0.30 to 0.51, 3.81 to 4.88, 3.79 to 5.53, 0.24 to 0.50, and 4.85 to 6.80 for Cd, Cr, Cu, Ni,

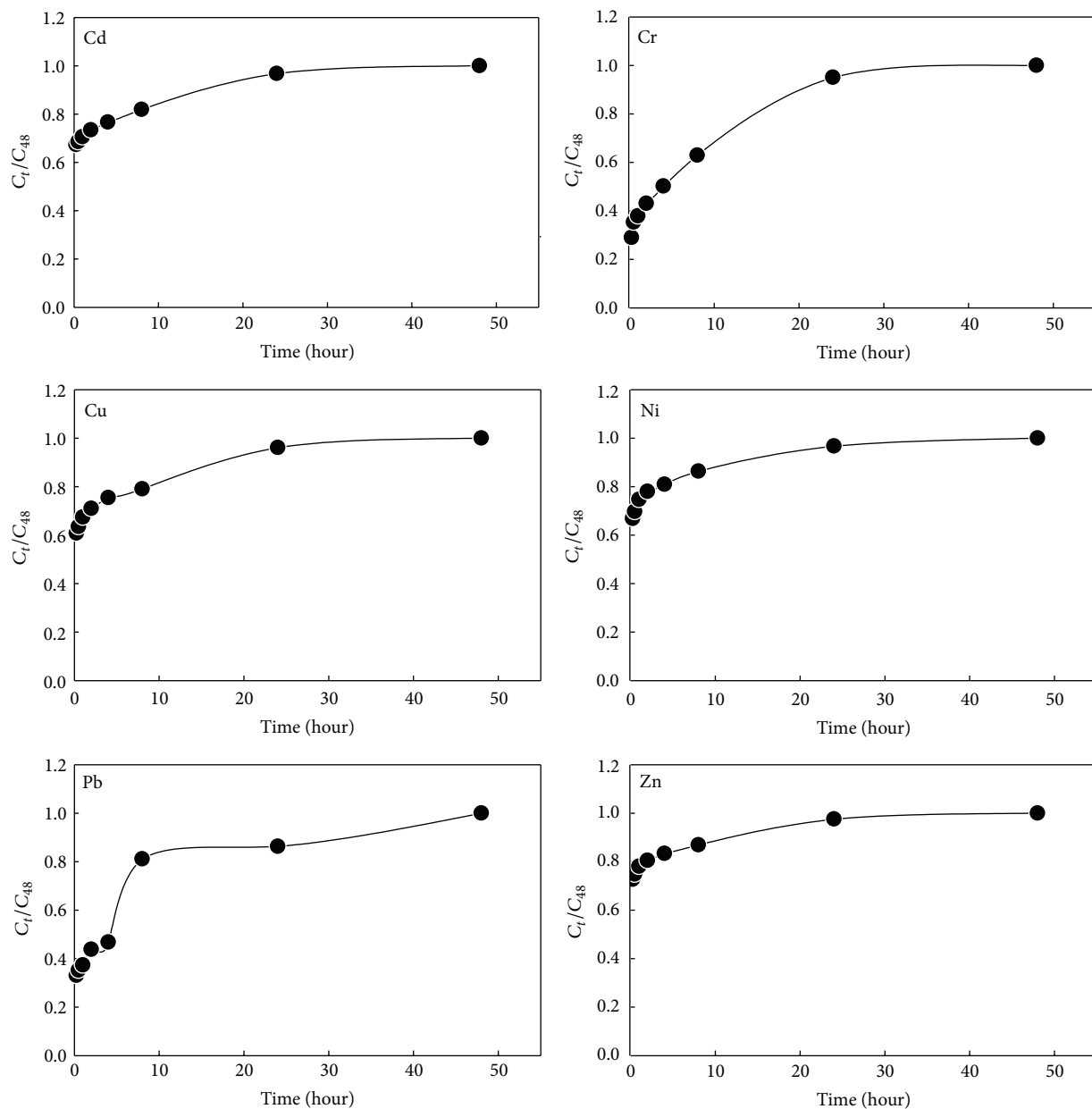


FIGURE 3: Time-dependent Cd, Cr, Cu, Ni, Pb, and Zn dissolutions of the biosolid-treated Romona soil ($1,080 \text{ Mg ha}^{-1}$) in 0.1 M organic acid mixtures (C_t denotes concentration at time t and C_{48} denotes concentration at 48 hours).

Pb, and Zn, respectively (Table 13). The total metals (C_0) that were extractable by the OA mixtures were the same as the total released amounts in Table 11. The total OA extractable metals would indicate the amount of metals possibly available to plants.

4. Conclusion

- (1) Metals present in BSL-treated soils are more extractable by an OA mixture than indigenous metals of the soil. In BSL-treated soil, more than 90% of metals extracted may be attributed to BSL-borne metals.
- (2) In general, the amount of metals extracted decreased with the increase of the pH, and at the same (4.8) pH level, the OA mixture extracted more metals than the 13.5 mM $\text{Ca}(\text{NO}_3)_2$ electrolyte solution.
- (3) In general, Cd, Cu, Ni, and Zn were more readily extractable by the OA mixtures and readily absorbed by plants grown on BSL-treated soils than Cr and Pb.
- (4) The amount of metals extracted was a function of concentration of OA mixtures. Higher concentrations of OA mixture resulted in greater extraction of metals from the BSL-treated soils.

TABLE 9: Metals of control and biosolid-treated soils solubilized by organic acid (OA) mixtures in the first 15 minutes of equilibration.

Biosolid treatment [†]	Concentration of OA mixtures	Metals dissolved in 15 minutes (% of total dissolved)					
		Cd	Cr	Cu	Ni	Pb	Zn
Control	0.001 M	63	29	61	67	n.d. [‡]	67
	0.01 M	60	28	60	61	n.d. [‡]	70
	0.1 M	63	31	62	64	32	67
135 Mg ha ⁻¹	0.001 M	60	30	61	66	32	70
	0.01 M	60	32	60	61	30	69
	0.1 M	62	34	60	60	34	73
1,080 Mg ha ⁻¹	0.001 M	66	30	62	67	28	66
	0.01 M	66	33	61	66	33	70
	0.1 M	67	29	61	67	33	73

[†]Obtained at Moreno Field Station of the University of California, Riverside, CA. From 1976 through 1981, composted biosolids were applied at dry weight rates of 0 (control), 22.5, and 180 Mg ha⁻¹ yr⁻¹, respectively.

[‡]Concentration was below detection limits of the AAS for Pb = 0.001 mg kg⁻¹.

TABLE 10: Kinetics constant for metal dissolution reaction extracted by organic acid (OA) mixtures according to (1) and (2)[†].

Biosolid treatment [†] (Mg ha ⁻¹)	Metal extracted by OAs	Zero- and first-order kinetics constant											
		Cd		Cr		Cu		Ni		Pb		Zn	
		k ₀	k ₁	k ₀	k ₁	k ₀	k ₁	k ₀	k ₁	k ₀	k ₁	k ₀	k ₁
Control	0.001 M	0.01	0.11 ^a	0.04	0.09	0.43	0.09	0.24	0.12	n.d. [§]	n.d. [§]	1.2	0.12
	0.01 M	0.03	0.10 ^a	0.06	0.09	1.40	0.09	1.56	0.14	n.d. [§]	n.d. [§]	7.8	0.13
	0.1 M	0.08	0.12 ^a	0.44	0.08	7.88	0.07	4.28	0.12	0.06	0.09	21.2	0.13
135	0.001 M	0.22	0.09 ^a	0.28	0.09	3.44	0.09	2.12	0.12	0.84	0.09	15.8	0.11
	0.01 M	0.72	0.12 ^a	0.92	0.08	8.84	0.09	6.28	0.12	0.24	0.09	85.6	0.13
	0.1 M	3.16	0.13 ^a	3.64	0.09	30.4	0.08	26.8	0.14	1.28	0.08	400	0.13
1,080	0.001 M	1.24	0.10 ^a	1.36	0.09	9.64	0.08	10.1	0.14	0.52	0.08	100	0.12
	0.01 M	4.64	0.10 ^a	3.40	0.08	42.8	0.07	39.2	0.12	1.36	0.08	416	0.12
	0.1 M	6.68	0.07 ^a	5.84	0.08	81.2	0.08	64.4	0.12	3.08	0.08	820	0.10

[†]Values represent means of two replicates. The differences of first-order kinetics constant for Cd among the treatments were tested by one-way ANOVA. In each column, values followed by the same lowercase letter were not significantly different at *P* < 0.05.

[‡]Obtained at Moreno Field Station of the University of California, Riverside, CA. From 1976 through 1981, composted biosolids were applied at dry weight rates of 0 (control), 22.5, and 180 Mg ha⁻¹ yr⁻¹, respectively.

[§]Concentration was below detection limits of the AAS for Pb = 0.001 mg kg⁻¹.

TABLE 11: Amounts of metals that were extractable from the biosolid-treated Romona soil (1,080 Mg ha⁻¹) by 0.1 M organic acid mixture.

Element	Rapid release (mg kg ⁻¹)	Slow release (mg kg ⁻¹)	Total release (mg kg ⁻¹)
Cd	1.67	0.86	2.53
Cr	1.46	3.74	5.20
Cu	20.3	13.7	34.0
Ni	16.1	8.60	24.7
Pb	0.77	1.73	2.50
Zn	205	80.0	285

TABLE 12: The slope[†] of metal extracted from the biosolid-treated Romona soil (1,080 Mg ha⁻¹) by 0.1 M organic acid mixtures according to (3).

Element	k ₁	k ₂	k ₃	k ₄	k ₅	k ₆	k ₇	k ₈
Cd	6.68	3.40	1.75	0.91	0.48	0.25	0.10	0.05
Cr	5.84	3.56	1.91	1.09	0.63	0.40	0.20	0.11
Cu	81.2	42.4	22.5	11.9	6.30	3.30	1.34	0.70
Ni	64.4	33.6	18.0	9.40	4.88	2.60	0.97	0.50
Pb	3.08	1.64	0.87	0.51	0.27	0.24	0.08	0.05
Zn	820	422	220	113	58.8	30.6	11.5	5.88

[†]Values of k₁, k₂, k₃, k₄, k₅, k₆, k₇ or k₈ indicate the slopes of metal extracted at 15 min., 30 min., 1 hr, 2 hrs., 4 hrs., 8 hrs., 24 hrs., and 48 hrs.

(5) The percentages of total BSL-borne metals extracted were 13.8, 1.63, 7.95, 14.1, 1.03, and 24.2% for Cd, Cr, Cu, Ni, Pb, and Zn, respectively. If OAs were responsible for converting metals in solid phases

into plant available forms, the amount and rate of metals' solubilization would be indicative of metals' availability to plants.

TABLE 13: First-order kinetics constant for metal dissolution reaction extracted by organic acid (OA) mixtures according to (3).

Biosolid treatment [†]	Metal extracted by OAs	First-order kinetics constant (k_1)					
		Cd	Cr	Cu	Ni	Pb	Zn
Control	0.001 M	4.71	0.34	4.11	4.87	n.d. [‡]	5.00
	0.01 M	3.99	0.30	3.90	3.93	n.d. [‡]	5.42
	0.1 M	4.30	0.37	4.49	4.46	0.36	4.92
135 Mg ha ⁻¹	0.001 M	4.13	0.38	4.05	4.65	0.38	5.63
	0.01 M	3.88	0.51	4.03	3.95	0.40	5.33
	0.1 M	3.96	0.48	3.81	3.79	0.50	6.06
1,080 Mg ha ⁻¹	0.001 M	4.93	0.32	4.30	4.81	0.24	4.85
	0.01 M	5.16	0.40	4.41	4.81	0.32	5.75
	0.1 M	6.25	0.37	4.88	5.53	0.43	6.80

[†] Obtained at Moreno Field Station of the University of California, Riverside, CA. From 1976 through 1981 composted BSL were applied at dry weight rates of 0 (control), 22.5, and 180 Mg ha⁻¹ yr⁻¹, respectively.

[‡] Concentration was below detection limits of the AAS for Pb = 0.001 mg kg⁻¹.

- (6) A rapid dissolution of metals occurred in the first 15 minutes of mixture. For Cd, Cu, Ni, and Zn, approximately 60–70% of the metals were released. For Cr and Pb, the initial releases were approximately 30% of the total.
- (7) The data of the metal dissolution kinetics in BSL-treated soils may fit either the two-site bicontinuum model in which significant amounts of the soluble metals were dissolved rapidly, following a zero-order dissolution kinetics and the remaining soluble metals released slowly over a long period of time, following a first-order dissolution kinetics, or first-order dissolution kinetics alone.

Competing Interests

The authors declare that they have no competing interests.

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