

Immobilization of copper, lead, and nickel in two arid soils amended with biosolids: effect of drinking water treatment residuals

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Abstract

Purpose This study was conducted to determine the potential of drinking water treatment residuals (DWTRs) land application in altering the distribution of Cu, Pb, and Ni among soil fractions. The main objectives of the study were to (1) assess the mobility and availability of biosolid-born Cu, Pb, and Ni in two arid zone soils differing widely in soil properties and (2) evaluate the efficiency of inexpensive DWTRs at various rates on immobilization and chemical transformation of Cu, Pb, and Ni in the biosolid-amended soils.

Materials and methods Two agricultural arid soils (calcareous and sandy) were collected and subsamples were amended with a combination of biosolids (3 %, w/w) and DWTRs (2, 4, 6, and 8 %, w/w). The amended and unamended soils were incubated for 2 months and sampled for metal bioavailability using diethylene triamine penta acetic acid (DTPA) extractant. The sequential extraction technique was performed to determine the effect of DWTRs on the distribution of Cu, Pb, and Ni among exchangeable, carbonate, oxides, organic, and residual fractions.

Results and discussion Application of DWTRs at different rates to the biosolid-amended soils greatly increased residual (RS) Cu, Pb, and Ni fractions and concurrently decreased nonresidual (NORS) fractions in both calcareous and sandy soils. The greatest reduction in NORS fractions were obtained

at the highest application rate (8 %). The NORS—Cu, Pb, and Ni fractions in biosolid-amended soils (control) decreased significantly from 51.79 to 20.93 %, from 54.5 to 39.82 %, and from 50.93 to 17.85 % respectively in calcareous soil and from 78.64 to 32.53 %, from 66 to 55.33 %, and from 55.89 to 22.63 % respectively in sandy soils. Thus, DWTRs contributed in Cu, Pb, and Ni fractions conversion from labile forms to more stable forms.

Conclusions Addition of DWTRs to biosolid-amended soils significantly reduced the availability of Cu, Pb, and Ni by chemical modification of their chemical speciation into less available forms. Our results suggest that DWTRs application could relieve the heavy metals risk of sewage sludge and spotlight the benefit of application of biosolid-amended soils with DWTRs.

Keywords DTPA extractant · Heavy metals · Sequential extraction · Water treatment residuals

1 Introduction

Biosolids are the solid residues generated during primary, secondary, or advanced treatment of domestic sanitary sewage through one or more controlled processes that reduce pathogens and minimize odors. These processes include anaerobic digestion, aerobic digestion, and lime stabilization. The US Environmental Protection Agency (USEPA) recently adopted the name “biosolids” to differentiate stabilized sewage sludge from raw sewage sludge (USEPA 2003).

Millions of tons of biosolids are generated worldwide every year. Because biosolids contain an abundant supply of nutrients and organic matter that improve soil chemical, physical, and biological properties, land application of biosolids has been proved to be quite effective as a cost-effective soil

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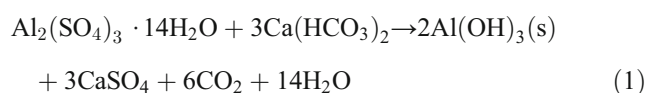
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amendment for growing agricultural crops (Logan and Harrison 1995). However, potential buildup of toxic heavy metals in biosolid-treated agricultural lands is important matters of public concern. Biosolids contain significant concentrations of heavy metals originated mainly from industrial waste water and surface water runoff. The long-term use of biosolids can cause heavy metal accumulation in the soil (Dai et al. 2006). Cabbage, amaranthus, spinach, radish, lady's finger, and forage grasses grown in sewage biosolid-amended soils showed higher concentrations of Cd, Cr, Co, Cu, Pb, Ni, and Zn as compared with those grown in unamended soil (Sekhar et al. 2002). Accumulation of these metals in the soils has toxic effects on microorganisms, plants, and ultimately on animals and human health via the food chain (Wang et al. 2005). Regulations have been issued on the land application of sewage sludge, seeking to limit the risks from pollutants (Iranpour et al. 2004; Spinosa 2004). Despite these regulations, public opposition to sewage sludge land application is growing, and wastewater treatment facilities face increasing difficulty in sewage sludge management options. This is particularly important as the amount of sewage is projected to increase significantly over the next few years due to a growing population (Brodersen et al. 2002). Thus, developing suitable treatment method for biosolids stabilization to minimize the mobility of heavy metals to overcome such problem is needed (Smolders and Degryse 2006).

Chemical immobilization is an in situ remediation method where inexpensive materials such as waste products are added to contaminated soil to reduce the mobility of heavy metals. In situ stabilization of heavy metals in the contaminated soils is considered a promising remediation path used to reduce solubility and bioavailability of the heavy metals in the soils (Chen et al. 2000). The use of drinking-water treatment residuals (DWTRs) to reduce availability of heavy metals in biosolid-amended soils has received increased attention in recent years (Sarkar et al. 2007; Mahdy et al. 2009, 2012; Fan et al. 2011; Nielsen et al. 2011; Elkhatib et al. 2013; Moharem et al. 2013). DWTRs are the byproduct of drinking water treatment, a result of the removal of suspended and dissolved mineral solids and other particulates. It is also called "alum-sludge" because alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$) is commonly used in the municipal drinking water treatment plants for water clarification. When alum is added to water (Eq. 1), it reacts with bicarbonate to form amorphous $\text{Al}(\text{OH})_3(\text{s})$:



Therefore, DWTRs normally contain sediment and organic substances removed from the raw water, along with amorphous $\text{Al}(\text{OH})_3$ (Ippolito et al. 2011). The overwhelming concern with DWTRs land application is due to the tremendous P

and heavy metals sorption on DWTR amorphous metal (hydroxides). Sarkar et al. (2007) recommended that a minimal rate of 2.5 % of Al-based DWTR could be a viable and effective in situ remediation method for low As-sorbing soils. Mahdy et al. (2012) showed that DWTRs applications significantly decreased the accumulation of Pb, Ni, Cu, and Cd in corn plants grown in biosolid-amended soils. Moharem et al. (2013) reported that the quantity of Cu sorbed on the studied soils drastically increased as a result of increasing rates of DWTRs application from 2 to 12 % (w/w). Elkhatib et al. (2013) examined the effects of DWTRs application on the characteristics of Ni retention on three alkaline soils and found that DWTRs addition has led to a significant increase in Ni sorption by the amended soils. Such increase in Ni sorption provides evidence that DWTRs has the potential for land application as a Ni sorbent in soil remediation techniques.

Although the aforementioned studies have successfully demonstrated the capability of DWTRs in reducing the bioavailability of heavy metals in contaminated soils, it is unclear whether the soil amendments influence chemical transformation and immobilization of heavy metals in biosolid-amended soils. Therefore, this study was undertaken (1) to assess the mobility and availability of biosolids born Cu, Pb, and Ni in two arid zone soils differing widely in soil properties and (2) to evaluate the efficiency of inexpensive DWTRs at various rates on immobilization and chemical transformation of Cu, Pb, and Ni in the biosolid-amended soils.

2 Materials and methods

2.1 Soils and drinking water treatment residuals

Two soil samples differed in texture and calcium carbonate content were used in this study representing arid-zone soils in Egypt. A sandy soil (Typic Quartzipsamments) from Elbostan, 80 km south west Alexandria and a calcareous soil (Typic Calciorthisds) from El-Nahda 40 km south west Alexandria. The experimental soils were collected from the top 15-cm depth at several locations in the field and subsamples of each soil type were air-dried, ground, and sieved (<2 mm) and stored in plastic bags for later use. The DWTRs were obtained from the drinking water treatment plant in Kafr El-Dawar, El-bohera, Egypt. The plant uses aluminum sulfate for flocculation. The WTR was collected fresh and transported to the laboratory, air-dried, and ground. After grinding, the aggregates were passed through sieves to collect aggregates in the <2-mm in diameter (Makris and Harris 2005). The general physical and chemical properties of soils and DWTRs were determined (Table 1), including soil pH and electrical conductivity (EC) in the saturated soil paste extract and the pH and EC of DWTRs in 1:2.5 suspension (Richards 1954), calcium carbonate content by calcimeter (Nelson 1982), and particle

Table 1 Selected chemical and physical properties of the studied soils, DWTR, and biosolids

Characteristics	Units	Calcareous ^a	Sandy	DWTR	Biosolids
pH ^b		8.33±0.08	8.26±0.06	7.45±0.11	6.72±0.09
EC	dS m ⁻¹	4.56±0.12	3.19±0.06	1.67±0.18	8.12±0.07
Clay	g kg ⁻¹	221±3.55	50±1.18	–	–
Silt	g kg ⁻¹	78±1.63	25±2.46	–	–
Sand	g kg ⁻¹	701±4.45	925±6.17	–	–
Texture		SCL	S	–	–
OM	g kg ⁻¹	1.5±0.67	0.4±0.06	57.00±1.25	492±2.87
CaCO ₃	g kg ⁻¹	22.4±0.79	3.6±0.18	3.48±0.19	–
CEC	cmol kg ⁻¹	15.0±0.41	6.0±0.69	34.78±2.06	–
Total Al	g kg ⁻¹	–	–	38.01±1.87	–
Total metal	mg kg ⁻¹				
Cu		0.950±0.12	0.218±0.22	2.87±0.13	385.93±5.65
Ni		0.159±0.09	0.393±0.14	4.63±0.23	26.83±1.34
Pb		0.905±0.11	0.712±0.13	3.06±0.12	219.24±4.87
Soluble Al	mg kg ⁻¹	–	–	1.80±0.14	–
DTPA-extractable metal	mg kg ⁻¹				
Cu		0.198±0.05	0.19±0.03	1.20±0.05	28.4±1.69
Ni		0.083±0.04	0.12±0.02	2.49±0.08	2.7±0.19
Pb		0.570±0.04	0.41±0.04	1.58±0.06	12.8±0.34
WHC	g kg ⁻¹	–	–	470±2.18	250±2.87

EC electrical conductivity (measured in soil paste), OM organic matter, CEC cation exchange capacity, SCL sandy clay loam, S sandy, WHC water holding capacity

^a Means of three samples±SD

^b pH was measured in 1:2 H₂O extract

size distribution by the hydrometer method (Day 1965). The soil organic matter (OM) content was determined by the dichromate oxidation method (Nelson and Sommers 1982). Soil cation exchange capacity (CEC) was determined by 1 M NaOAC (Rhoades 1982). Water holding capacity was determined according to Skene et al. (1995). Metal concentrations were determined according to the method described by Ure (1995). Total Al of DWTRs was determined using the acid ammonium oxalate method (Ross and Wang 1993). The available Ni, Cu, and Pb were extracted by DTPA (Lindsay and Norvell 1978) and measured by inductively coupled plasma spectrometry (Perkin Elmer Optima 2000 DV).

2.2 Biosolids

The composted biosolids were obtained from Alexandria waste water treatment plant (AWWTP-N9). The obtained biosolids were stabilized through aerobic digestion as follows: The primary sludge produced at AWWTP was mechanically dewatered by belt filter presses. Polymers (2–4 kg/ton DW) were used to produce a dry sludge cake of 580 tons/day with a solid concentration of 25–30 %. The dry sludge cake were transferred over a distance of 45 km to the central site (N9) to complete the aerobic digestion processes over a long period of 1 year to ensure low pathogen levels and high solids content.

Selected chemical properties of the biosolids were determined (Table 2). Total concentrations of heavy metals in aqua regia-digested extract (Esakku et al. 2005; Shrivastava and Banerjee 1998) were measured using inductively coupled plasma

Table 2 DTPA-extractable Cu, Pb, and Ni in the two studied soils as affected by application of DWTRs at different rates

DWTRs rate (%)	DTPA-extractable metal (mg kg ⁻¹)		
	Cu	Pb	Ni
Calcareous soil			
Control	22.75±0.45a	15.63±0.88a	7.32±1.14a
2	16.73±1.29b	5.94±1.04b	2.00±1.04b
4	14.80±1.23c	3.82±0.86c	1.68±0.87b
6	10.93±0.45d	2.81±1.3c	1.20±0.83b
8	09.31±1.38d	2.01±1.34c	0.83±0.71b
Sandy soil			
Control	34.41±0.51a	24.62±1.34a	12.81±0.51a
2	28.65±1.22b	10.34±0.51b	4.61±0.83b
4	25.98±0.71c	8.62±1.13bc	3.81±1.34b
6	19.85±1.29d	6.98±0.76c	2.87±1.04bc
8	10.81±1.22f	3.72±1.38d	1.66±0.856c

**p*<0.05—mean values (±SD, *n*=3) denoted by the same letter in columns indicate no significant difference according to Duncan's test

spectrometry (ICP). The organic matter content was estimated by the method of Walky and Black (Nelson and Sommers 1982).

2.3 Incubation experiment

Samples of 1 kg of dry soil were thoroughly mixed in plastic pots with a combination of biosolids and DWTRs. Application of biosolids (at a rate of 3 %, w/w) and DWTRs (at five rates: 0, 2, 4, 6, and 8 %, w/w) was conducted for each soil type in the laboratory. Treatment ratios and application rates were prepared based on a previous study on alkaline soils. Mahdy et al. (2009) found that the effective co-application ratio of aerobically digested biosolids to DWTRs, for increasing corn yield and minimizing the potential for bioavailable P in runoff, was approximately 1:1 at the application rate of 3 % biosolids and 4 % DWTRs in the alkaline soils. The rates used in the incubation experiment are equivalent to the field application rates of 0, 45.0, 90.0, 135.0, and 180.0 Mg ha⁻¹ for DWTRs, and 67.5 Mg ha⁻¹ for biosolids in a 15-cm soil depth, with a bulk soil density of 1.50 g cm⁻³. After mixing with biosolids and DWTRs, the soils were incubated in a moisture regime entailing periodic wetting-drying cycles. Each cycle lasted for 12 days, including 2 days of wetting (field capacity) and a subsequent 10 days of air-drying. Each treatment was replicated in three pots. Subsamples were taken from each pot for sequential fractionation analyses and DTPA extraction after 60 days. In wetting-drying cycles, pots were covered to prevent evaporation during the first 2 days of incubation at the field capacity regime and in the subsequent 10 days, the soils were allowed to air-dry at 25 °C. Before sampling for fractionation and DTPA analysis, the soil was mixed thoroughly to ensure homogeneity and representation of samples and subsamples for soil moisture content.

2.4 Fractionation of Cu, Pb, and Ni

In order to fractionate the heavy metals Cu, Pb, and Ni under study, the sequential extraction procedure developed by Tessier et al. (1979) was selected. Each of chemical fractions of heavy metal was operationally defined as follows:

1. Exchangeable: 1.0 g soil sample was extracted at room temperature for 1 h with 8 mL of 1.0 M MgCl₂ (pH 7.0) with continuous agitation.
2. Bound to carbonates: The residue obtained from step (1) was leached at room temperature with 8 mL of 1.0 M sodium acetate adjusted to pH 5.0 with acetic acid. The mixture was agitated for 5 h.
3. Bound to Fe–Mn oxides: The residue obtained from step (2) was refluxed at 100 °C with 20 mL of 0.04 M NH₂OH·HCl in 25 % (v/v) acetic acid for 6 h.
4. Bound to organic matter: To the residue obtained from step (3), 3 mL of 0.02 M HNO₃ and 5 mL of 30 %

H₂O₂ were added and pH adjusted to 2.0 with HNO₃. The mixture was refluxed at 100 °C for 2 h. A second 3-mL aliquot of 30 % H₂O₂ (pH 2 with HNO₃) was then added, and the sample was again refluxed for 3 h. After cooling, 5 mL of 3.2 M ammonium acetate in 20 % (v/v) HNO₃ was added. The sample was diluted to 100 mL and agitated continuously for 30 min. The addition of ammonium acetate is designed to prevent adsorption of extracted metals onto the oxidized sediment.

5. Residual: The residual fraction was calculated by subtracting the sum of the Cu in the four fractions from the total amount of heavy metals in contaminated soils.

Following each extraction, the samples were centrifuged at 5000×g for 10 min and the metals concentrations in supernatant were analyzed using the ICP. Three replicated samples were used in all cases, and the average was used to depict the results. All the samples were washed with deionized water prior to the next extraction step. All chemicals were of analytical grade, and all plastic and glassware were washed before use, soaked in 10 % HNO₃, and rinsed with deionized water.

In order to assess the mobile and potentially bioavailable fractions, a single extraction of heavy metals was carried out using 0.005 M diethylene triamine penta acetic acid (DTPA)–triethanolamine–calcium chloride extractant (pH adjusted to 7.3, Lindsay and Norvell 1978). This extractant has been proposed to simulate soil solution concentration and to release amounts that are well correlated with plant uptake (Karczewska et al. 1998; Mahdy et al. 2012). All the analyses were carried out in triplicates, and the concentrations of Cu, Pb, and Ni in every extract were measured by using inductively coupled plasma spectrometry (ICP).

2.5 Statistics

Data are expressed as a mean of all replicates. Significant differences among the treatment means were established using one-way analysis of variance (ANOVA) and treatment means compared by Duncan's multiple range tests at *p*<0.05 (JMP PRO, v 10. SAS Institute Inc., Cary, NC, 1989 e2010).

3 Results and discussion

3.1 Properties of the study materials

The characteristics of the soils, DWTRs, and biosolids are presented in Table 1. Both the calcareous and sandy soils used in the study were alkaline with pH difference of less than 1 unit (0.7); whereas the DWTRs and biosolids were slightly alkaline and slightly acidic, respectively. The OM and CaCO₃ contents of the calcareous soil were approximately four and six times respectively higher than those of the sandy soils. High OM

contents (5.7 %) were observed in the DWTRs, greater than OM contents in Egyptian agricultural soils. The salinity of the DWTRs was $<4 \text{ dS m}^{-1}$, and the CEC was $34.78 \text{ cmol (+)kg}^{-1}$, indicating that DWTRs could be a source of cationic nutrients. The DWTRs also have been shown, via scanning electron microscopy (SEM), to be of various shapes and sizes and are highly porous (Fig. 1). Using SEM, Yang et al. (2006) compared dewatered DWTRs to pure aluminum hydroxide and noted that the DWTRs were virtually amorphous, having no distinct shape or form, in contrast to pure aluminum hydroxide, which exhibited a regular crystalline structure.

The OM content of the biosolids was 49.2 %. The total concentrations of Cu, Pb, and Ni in the soils and DWTRs were low and the available concentrations of Cu, Pb, and Ni extracted by DTPA were very low compared with the general toxic levels of crops (Alloway 1995). The application of sewage sludge provided a source of heavy metals and enriched the soils in relatively mobile and available forms (Pengxing et al. 1997).

The application of biosolids to calcareous and sandy soils at a rate of 3 % (w/w) increased the total concentration of soil Cu, Ni, and Pb significantly (Figs. 2, 3, and 4). The total Cu and Pb concentration in both biosolid-amended soils exceeded the common concentration range of Cu (2–100 mg/kg) and Pb (10–100 mg kg⁻¹) in soils as reported by Alloway (1995). Total concentration of these elements were in decreasing order Cu>Pb>>Ni in both biosolid-amended soils. The mobility and bioavailability of metals added with sewage sludge are controlled mainly by organic matter and oxides (McBride 1995).

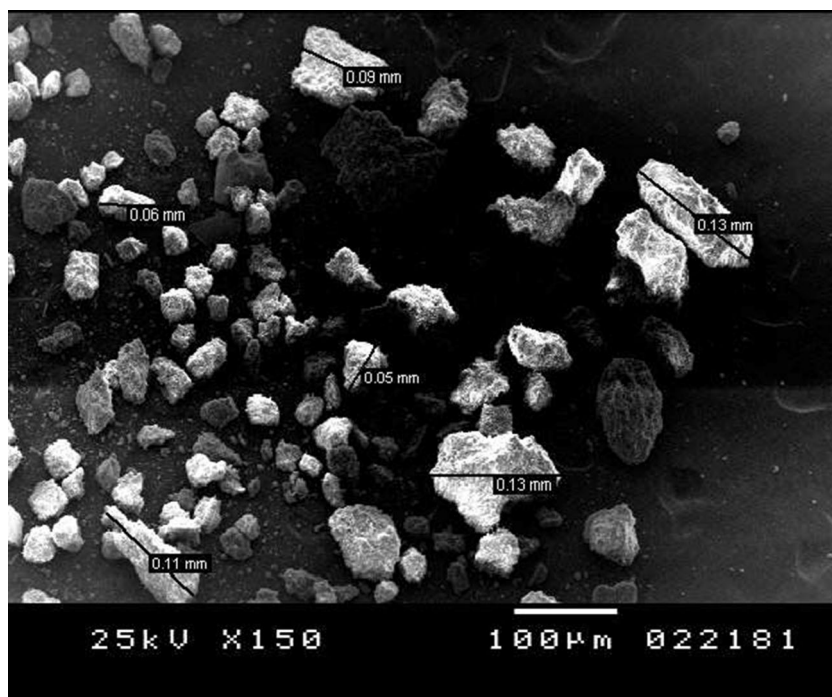
3.2 Effect of DWTRs on distribution of Cu, Pb, and Ni in the soil fractions

The sequential extraction technique was conducted on biosolid-amended soils to elucidate the chemical forms of the studied metals in various soil components as affected by different DWTR application rates (0, 2, 4, 6, and 8 % (w/w), DW). This procedure fractionates soil metal into five chemical fractions by successive extractions that follow the order of decreasing solubility (Schramel et al. 2000). Since mobility and bioavailability are related to solubility, then metal availability decreases in the sequence: exchangeable>carbonate>oxides>organic>residual. It is further assumed that metals in the nonresidual (NORS) fractions, the sum of all fractions except the residual fraction, are more mobile and bioavailable than metals associated with the residual (RS) fraction.

3.2.1 Copper

The effects of DWTRs application at various rates on Cu forms in calcareous and sandy soils amended with biosolids at a rate of 3 % (control) are shown in Fig. 2. In the control calcareous soil, Cu was mainly associated with RS phase (47.82 %) while it showed the least association with exchangeable phase (5.67 %), whereas in control sandy soil, the highest proportion of Cu was associated with organic fraction (32.67 %) and the least proportion was associated with carbonate fraction (6.47 %). The strong relationship between Cu and organic matter may explain the highest association of Cu with the organic fraction (Ponizovsky et al. 2007). The least association of Cu

Fig. 1 Scanning electron microscopy (SEM) image of DWTRs



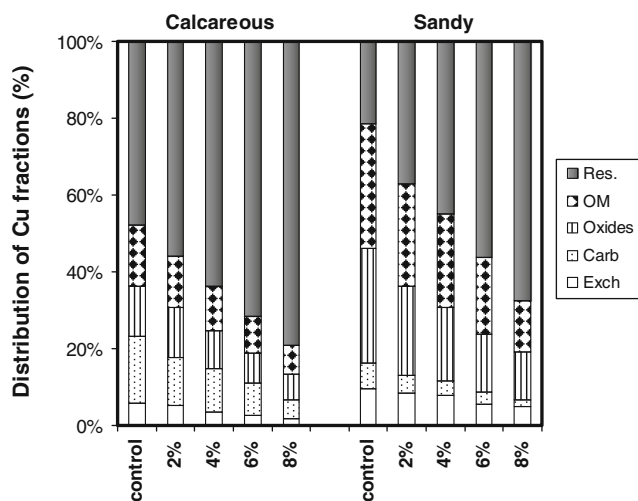


Fig. 2 Relative percentage of Cu fractions for the two studied soils treated with biosolids (3 %, w/w) and amended with DWTRs at rates of 0, 2, 4, 6, and 8 % by weight

with carbonate fraction in sandy soil could be due to low content of calcium carbonate in this soil (Table 1).

Application of DWTRs at different rates to the biosolid-amended soils greatly reduced RS-Cu fraction and concurrently increased nonresidual (NORS) fractions in both calcareous and sandy soils (Fig. 2). The greatest reduction in NORS fractions were obtained at the highest application rate (8 %). The NORS-Cu fraction in biosolid-amended soils (control) decreased from 51.79 to 20.93 % and from 78.64 to 32.53 % in sandy soils. Thus, DWTRs contributed in Cu fractions conversion from more mobile form to more stable form which was also supported by an increase in the residual Cu fractions (Fig. 2). DWTRs have a large surface area and are highly reactive, which gives them several potential applications as sorbents (Ippolito et al. 2011). In addition, DWTRs introduced a significant amount of amorphous aluminum oxide minerals of which can control metals mobility to a great

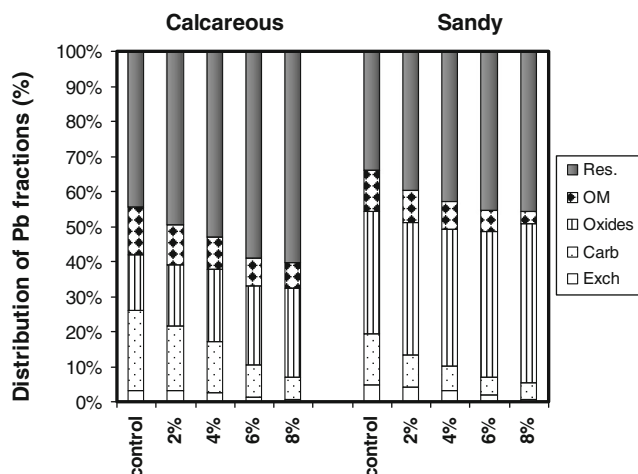


Fig. 3 Relative percentage of Pb fractions for the two studied soils treated with biosolids (3 %, w/w) and amended with DWTRs at rates of 0, 2, 4, 6, and 8 % by weight

extent by surface precipitation (Lindsay and Norvell 1978). The precipitation of newly formed Cu phases in a soil represents an important mechanism of Cu immobilization in soils. These phases may include $\text{Cu}(\text{OH})_2$, $\text{CuCO}_3/\text{Cu}_2(\text{OH})_2\text{CO}_3$, CuO , and the formation of cation–anion complexes on the surface of Fe and Al oxy-hydroxides (Aten and Gupta 1996; Dermont et al. 2008; Sun et al. 2010).

3.2.2 Lead

The geochemical distribution of Pb in fractions of biosolid-amended soils (control) is presented in Fig. 3. In calcareous control soil, the higher proportion of Pb was associated with residual fraction (44.50 %). Carbonate fraction was the next most important fraction for this soil (22.7 %), followed by oxide (15.9 %), organic (13.7 %), and exchangeable (3.2 %) fractions. In sandy control soil, the higher association of Pb was for the oxide fraction (35.1 %) while the residual fraction was the next Pb association (34.00 %), followed by carbonate (14.50 %), organic (11.60 %), and exchangeable (4.8 %) fractions. The high content of calcium carbonate in calcareous soil (Table 1) may be responsible for the high association of Pb in carbonate fraction.

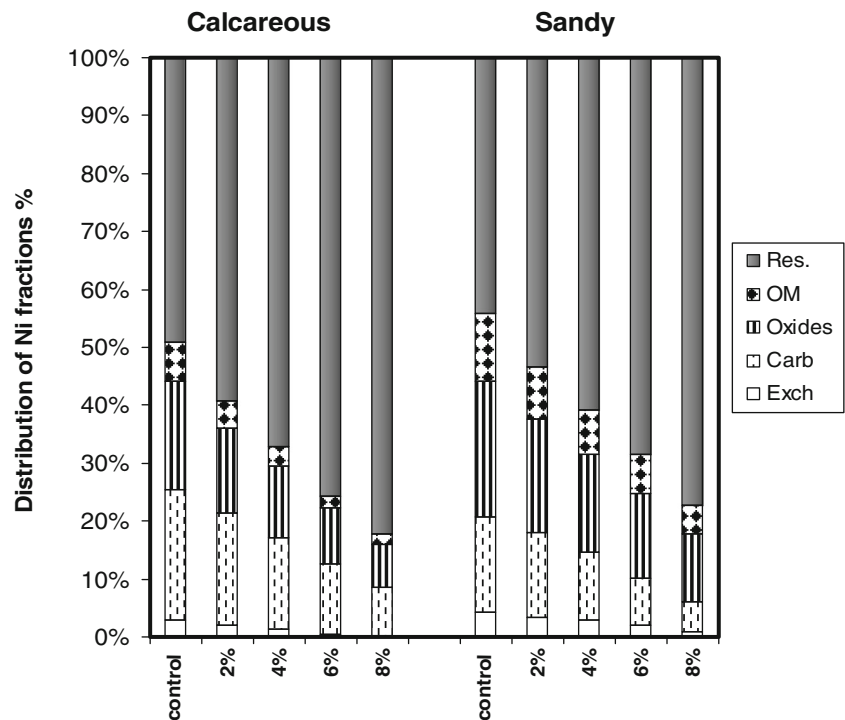
Application of DWTRs to the two soils at different rates greatly reduced exchangeable, carbonate, and organic Pb fractions and simultaneously increased oxide and residual Pb fractions in these soils (Fig. 3). Many authors demonstrated the high affinity of Pb towards oxides among other heavy metals. For instance, Benjamine and Leckie (1981) found sorption to decrease in the order $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd}$ on amorphous iron oxyhydroxide ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Biddappa et al. (1981) found the order was $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd}$ for Japanese soils dominated by volcanic parent material. Indeed, these results interpret the high percentage of oxide fraction-Pb in our study.

The association of Pb with exchangeable, carbonate, and organic fractions decreased as the application rate of DWTRs increased and the greatest reduction in NORS fractions were obtained at the highest application rate (8 %) (Fig. 3). Meanwhile, application of DWTRs at a rate of 8 % increased oxide and residual Pb fractions from 15.9 and 44.5 to 25.49 and 60.18 % in calcareous soil, respectively, and from 35.1 and 34 to 45.32 and 45.67 % in sandy soil, respectively (Fig. 3). Increasing Pb bound to oxide should exhibit low availability for plant uptake and leaching because it is immobile (Phillips and Chapple 1995). Thus, increasing the association of Pb with oxide and residual fractions could enhance Pb chemical immobilization in the studied soils.

3.2.3 Nickel

The association of Ni to various soil fractions in biosolid-amended soils (control) is presented in Fig. 4. In control calcareous soil, residual fraction was the predominant form of Ni

Fig. 4 Relative percentage of Ni fractions for the two studied soils treated with biosolids (3 %, w/w) and amended with DWTRs at rates of 0, 2, 4, 6, and 8 % by weight



representing 49.07 %. Among the NORS fractions, the carbonate fraction contained the greatest Ni (22.43 %) followed by oxide (18.82 %), organic (6.72 %), and exchangeable (2.96 %) fractions. In sandy control soil, Ni fractions were present in the following sequence: residual (44.11 %)>oxides (23.43 %)>carbonate (16.43 %)>exchangeable (4.39 %). When the two soils were amended with DWTRs, more labile Ni fractions (NORS) were strongly reduced coinciding with increase in nonlabile fraction (RS). Percentages of Ni in the NORS residual fraction decreased with every increase in DWTRs application rates (Fig. 4). At the highest application rate of 8 %, NORS fractions were reduced from 50.93 and 55.89 to 17.85 and 22.73 % for calcareous and sandy soils, respectively. These results indicate that addition of DWTRs increased RS-Ni fraction as the major binding site for Ni in the studied soils. Metals confined in the residual fractions are usually not expected to be released over short period of time under the conditions usually encountered in nature (Chlopecka et al. 1996). These results are in agreement with those of Elkhatib et al. (2013) who reported that DWTRs is an effective sorbent for Ni as sorption isotherms shift toward a higher sorption of Ni, i.e., higher affinity for Ni, with increasing DWTRs application rate. These observations support the hypothesis that the addition of DWTRs adds extra sorptive phases to soil systems and therefore alters its sorptive characteristics (Ippolito et al. 2003).

Another explanation of the increase of Ni residual fraction as a result of DWTRs application is perhaps due to Ni-LDH precipitates which may be considered an irreversible form on soils and minerals (Voegelin and Kretzschmar 2005).

Extended X-ray absorption fine structure spectroscopy studies with Ni(II) have further proved that metal sorption on clays and aluminum oxides can result in the formation of mixed-cation hydroxide phases (Scheidegger et al. 1998). The formation of Ni–Al-layered double hydroxide (LDH) phase was observed at pH values >6.25 with formation rate increasing with increasing pH (Elzinga and Sparks 2001). The general formula for the LDH materials is $(MII_{1-x}MIII_x(OH)_2)^{x+}((A^{m-})_{x/m}) \cdot nH_2O$, where M are bivalent or trivalent cations with similar radii and A are interlayer anions. Their structure is similar to that of brucite ($Mg(OH)_2$)-type octahedral layers. The cations in the layer can be changed using a wide range of main group cations (e.g., Mg, Al) or transition metal cations (e.g., Mn, Fe, Co, Ni).

3.3 Effects of DWTRs application on DTPA extractable Cu, Pb, and Ni

Soil extraction with DTPA was performed to investigate the effect of DWTRs application at different rates on mobility and bioavailability of Cu, Pb, and Ni in two biosolid-amended soils differed in physical and chemical characteristics. This extractant usually used to evaluate plant availability and mobility of heavy metals in soils amended with sewage sludge (Lebourg et al. 1996). In the current study, the average percentages of extracted metals were lower in the calcareous than in the sandy soil (Table 2), probably because the high content of soil carbonates in calcareous soils decreases the availability of metals for their effect on soil pH and their high adsorption capacity (McBride 1995).

Analysis of variance indicated that the application of DWTRs to the studied soils significantly reduced available Cu, Pb, and Ni as estimated by DTPA extractant (Table 2). For all metals and soils, the percentages of extracted metals decreased with increasing DWTR rates (Table 2). Application of DWTRs at the highest application rate of 8 % reduced DTPA extractable Cu, Pb, and Ni in calcareous soil by 59, 86, and 87 %, respectively, whereas, the decrease in the sandy soil were 68, 85, and 87 % for Cu, Pb, and Ni, respectively. The largest decreases corresponded to Ni followed by Pb and Cu. Although, Cu was the metal with the largest concentration in the biosolids, the smaller percentage of extracted Cu reflected that Cu formed more stable complexes with sludge's organic matter than Pb and Ni. These results are consistent with the results of the fractionation experiment and supported the hypothesis that DWTRs application to heavy metal-contaminated soils converted labile Cu, Pb, and Ni forms to more stable forms in the amended soils (Fan et al. 2011).

3.4 Mobility index

The potential of metal mobility was calculated as the mobility index (MI) (Salbu et al. 1998; Banat et al. 2003; Liu et al. 2007). The mobility indexes of Cu, Pb, and Ni were calculated based on the following equation:

$$MI = \sum (F_i/T_i)/n$$

Where F_i is the metal concentration in exchangeable fraction concentration of the metal, T_i is the total concentration of the metal, and n is the number of the soil samples. The high MI values have been interpreted as criterion of relatively high lability and biological availability of heavy metals in soils (Ma and Rao 1997; Ahumada et al. 1999; Narwal et al. 1999).

The mobility indexes of Cu, Pb, and Ni in biosolid-amended soils as influenced by DWTR application at different rates are shown in Fig. 5. Application of DWTRs significantly lowered the mobility of Cu, Pb, and Ni in both sandy and calcareous soils amended with biosolids, which is mainly attributed to the reduction of metal concentrations in exchangeable fraction (Figs. 2, 3, and 4). For all metals and soils, MI decreased with increasing DWTR rates (Fig. 5). Mobility indices were considerably higher (particularly for Cu) in control sandy soil than in control calcareous soil, and the order of average metals mobility in the two biosolid-amended soils was $Cu > Pb > Ni$. Overall, the mobility indices suggest that the pools of Cu, Pb, and Ni are changed with the addition of DWTRs and these metals are firmly bound with more stable fraction.

In summary, our research findings suggest that biosolids co-application with DWTRs is chemically a sound practice in terms of sorbing and retaining excess biosolid-borne heavy metals. In addition, several studies (Gallimore et al. 1999; Ippolito et al. 1999; Wagner et al. 2008; Elkhatib and Mahdy 2008; Mahdy

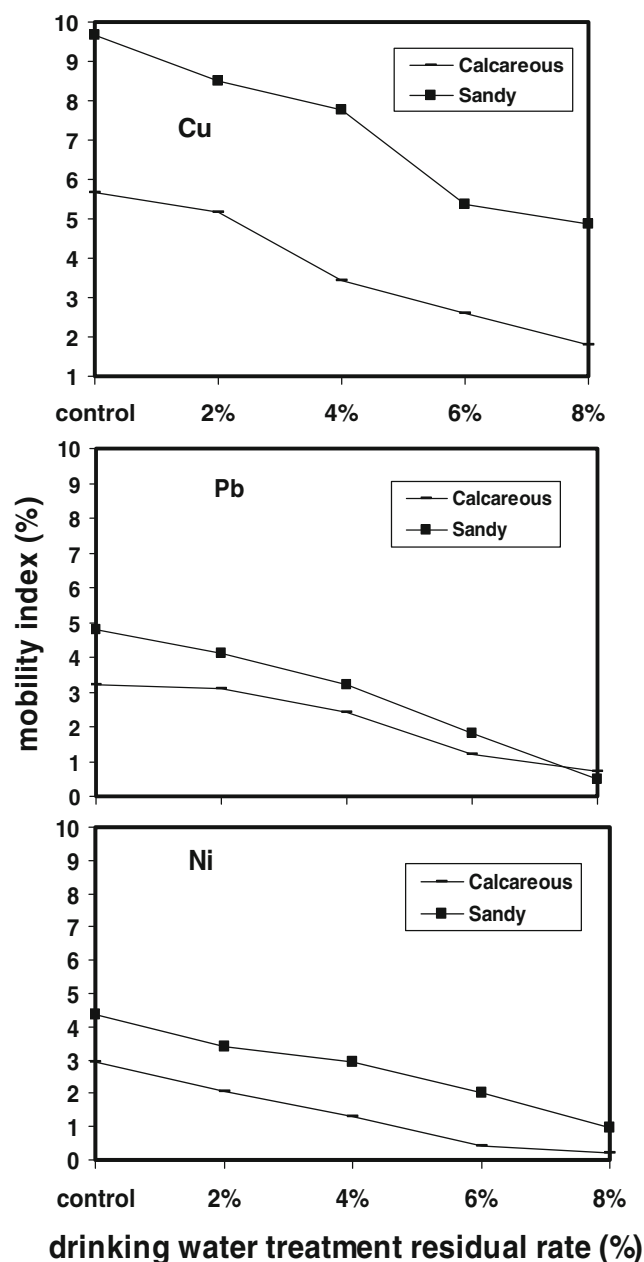


Fig. 5 Mobility index of Cu, Pb, and Ni for the two studied soils treated with biosolids (3 %, w/w) and amended with DWTRs at rates of 0, 4, 6, and 8 % by weight

et al. 2009) have demonstrated that using DWTRs as a P sorbent (either surface applied, soil-incorporated, or blending with high P-containing residuals) is an effective best management practice (BMP) to reduce P solubilities in agricultural land. These findings support the hypothesis that the DWTR phase would dominate all inorganic phases (Makris et al. 2004) and P and heavy metals sorption to amorphous Al as a result of DWTR application, will provide long-term sorption stability. A long-term (7.5 years) field study of DWTR effectiveness in reducing water extractable P in two soils with excessively high soil test P levels seems to confirm the contention (Agyin-Birikorang et al. 2007).

Thus, co-application of DWTRs with biosolids should benefit ecosystems where the potential for P and heavy metal contamination is present. However, knowing the appropriate application rate of DWTRs to biosolid-amended soil is critical because over-application can lead to excessive immobilization of soil P and induce plant P deficiency (Ippolito et al. 2011). The time, method, and rate of DWTRs—biosolids application would vary with the type of soil, the crop to be grown, the prevailing agro-climatic conditions, and also the type of DWTRs and biosolids available. Research on these aspects and long-term monitoring are needed for utilization of DWTRs—biosolids to ensure that terrestrial and aquatic ecosystem health is maintained across sites receiving DWTR-biosolid applications.

4 Conclusions

Application of water treatment residuals (DWTRs) to agricultural soils amended with biosolids was tested for its efficiency in stabilizing Cu, Pb, and Ni derived from the biosolids. Results from the sequential extraction procedure showed that DWTR application at rates of 2, 4, 6, and 8 % (w/w, DW) effectively converted large percentage of NORS fraction to the most stable form (RS). Also, DWTRs significantly reduced the DTPA-extractable Cu, Pb, and Ni from the two biosolid-amended soils, and the reduction increased with increasing DWTR application rate. Because considerable amounts of DWTRs are available free of charge from local drinking water treatment facilities, DWTRs can be regarded as an economically and eco-friendly option for Cu, Pb, and Ni amelioration in biosolid-amended soils. However, caution needs to be exercised when biosolids and DWTRs are repeatedly applied at high application rates as can cause excessive immobilization of soil P and induce plant P deficiency. More research is needed in this area to identify the soil types and initial P conditions, slopes, rainfall intensities, application methods, and DWTR and biosolid types that are most effective in reducing offsite P transport and promoting and maintaining soil fertility. In the future, long-term monitoring is still needed to evaluate the potential impacts of DWTR-biosolid land application on soil quality and the environment including surface and ground water, air, and plant/animal health as well as food quality.

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