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ARTICLE

Nano-oxides immobilize cadmium, lead, and zinc in mine spoils and contaminated soils facilitating plant growth

Srimathie P. Indraratne, Gary M. Pierzynski, Lucas R. Baker, and P.V. Vara Prasad

Abstract: Nanoparticles with high reactivity can be applied as amendments to remediate soil metal contaminations by immobilizing toxic elements. Nano-oxides of Fe have been studied but Al and Ti nano-oxides have not been tested for their remediation capacity of toxic metals. The potential of synthesized iron (Fe-O), aluminum (Al-O), and titanium (Ti-O) nano-oxides for stabilizing Cd, Pb, and Zn in mine spoil (Chat) and contaminated soil was compared using adsorption studies and a greenhouse experiment. Chat and soil were amended with nano-oxides at two rates (25 and 50 $g\cdot kg^{-1}$) and a pot experiment was conducted with sorghum (*Sorghum bicolor* L. Moench). Leachates were collected twice per week from plant emergence to harvest at maturity and metals were compared against an unamended control. Chat was contaminated with Cd, Pb, and Zn at 84, 1583, and 6154 $mg\cdot kg^{-1}$, and soil at 15, 1260, and 3082 $mg\cdot kg^{-1}$, respectively. Adsorption conformed to the Langmuir linear isotherm and adsorption maxima of metals were in the order of Al-O > Ti-O ≥ Fe-O. Nano-oxides reduced Cd concentration by 28% (Fe-O) to 87% (Ti-O) and Zn concentration by 14% (Fe-O) to 85% (Al-O) in plant tissues compared with unamended Chat. Nano-oxides significantly reduced Cd, Pb, and Zn in leachates and available Cd and Zn in Chat/soil relative to the respective unamended controls. Nano-oxides can be used to remediate heavy metal contaminated Chat and soil and facilitate plant growth under proper nutrient supplements. Nano-oxides of Al-O and Ti-O remediated metals more effectively than Fe-O.

Key words: bioavailability, immobilization, heavy metals, mine spoils, nanoscale oxides.

Résumé : On peut se servir de nanoparticules très réactives comme amendement pour atténuer la contamination du sol par les métaux, car elles immobilisent les éléments toxiques. Les nano-oxydes de fer ont déjà fait l'objet d'études, mais pas ceux d'aluminium et de titane, dont on n'a pas vérifié la capacité de neutralisation des métaux toxiques. Les auteurs ont comparé le potentiel des nano-oxydes synthétiques de fer (Fe-O), d'aluminium (Al-O) et de titane (Ti-O) pour stabiliser le cadmium, le plomb et le zinc dans les résidus miniers (conglomérat cherteux) et le sol contaminé au moyen d'essais d'adsorption et d'une expérience en serre. Dans cette optique, ils ont amendé le conglomérat cherteux et le sol avec deux taux de nano-oxydes (25 et 50 g par kilo), puis cultivé du sorgho (*Sorghum bicolor* L. Moench) en pot. Ils ont recueilli le lixiviat deux fois par semaine, de la levée à la récolte à maturité, et comparé la concentration de métaux à celle relevée dans le lixiviat d'un substrat témoin non bonifié. Le conglomérat cherteux renfermait respectivement 84, 1 583 et 6 154 mg de Cd, de Pb et de Zn par kilo, contre 15, 1 260, et 3 082 mg par kg pour le sol. L'adsorption suit l'isotherme linéaire de Langmuir et la quantité maximale de métal adsorbée respecte l'ordre Al-O > Ti-O ≥ Fe-O. Les nano-oxydes ont diminué la concentration de Cd dans les tissus végétaux de 28 % (Fe-O) à 87 % (Ti-O) et celle de Zn de 14 % (Fe-O) à 85 % (Al-O), comparativement à la concentration relevée dans le conglomérat cherteux non amendé. Les nano-oxydes diminuent significativement la teneur du lixiviat en Cd, Pb et Zn ainsi que la concentration de Cd et de Zn disponible dans le conglomérat cherteux ou le sol, comparativement à celles observées dans le substrat témoin correspondant, non bonifié. On pourrait utiliser les nano-oxydes pour atténuer la contamination du conglomérat cherteux et du sol par les métaux lourds, et favoriser la croissance des végétaux avec les oligoéléments adéquats. Les nano-oxydes Al-O et Ti-O stabilisent mieux les métaux que le Fe-O. [Traduit par la Rédaction]

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Mots-clés : biodisponibilité, immobilisation, métaux lourds, résidus miniers, nano-oxydes.

Introduction

Soil contamination with toxic elements is both a local and global concern. Globally, there are over 20 million ha of land contaminated by toxic elements with soil concentrations being higher than the geo-baseline or regulatory levels (Liu et al. 2018). Locally the Tri-State Mining Region, located in southwest Missouri, southeast Kansas, and northeast Oklahoma, USA, is a toxic metal-laden site facing major environmental challenges since it ceased operations in 1970 (Abdel-Saheb et al. 1994; Baker et al. 2011). Mine spoils, known as Chat, contaminated with Cd, Pb, and Zn due to the mining of Pb and Zn minerals, were left with a large amount of tailing piles (Pierzynski et al. 2002*a*; Johnson et al. 2016) on this site. The main impacts caused by mine tailings like Chat materials are the loss of vegetation cover and the physical, chemical, and biological degradation of soils altering ecosystems, landscape, and watercourses (Gabarrón et al. 2019). An increasing level of concern prevails over the fate of tailings especially on the consequences of contaminant release through dust, tailings, dam seepage, dam wall failure, or the direct disposal of tailings into waterways (Edraki et al. 2014). Vegetative cover establishment is one viable remediation option for such contaminated sites to reduce spreading of toxic materials (Brown et al. 2003). Hence in situ stabilization of toxic metals using effective amendments is essential in the process of preparation of Chat and contaminated soil for vegetation.

Among different technologies, in situ immobilization of metals has received a great deal of attention and turned out to be a promising solution for soil remediation (Nejad et al. 2018). Immobilizing of toxic metals can be achieved by binding toxic metals to the soil components through the addition of organic or inorganic compounds, singly or in combination (Cundy et al. 2016). Immobilization of toxic metals substantially improves soil properties and reduces trace element mobility, bioavailability, and toxicity (Hettiarachchi and Pierzynski 2004; Komarek et al. 2013). The chemical stabilization or immobilization of metals in contaminated soil has been studied extensively (Cundy et al. 2008; Komárek et al. 2013; Kumpiene et al. 2019). Inorganic and organic amendments, such as lime (Gray et al. 2006), phosphates (Hettiarachchi and Pierzynski 2004; Guo et al. 2018), iron-based amendments (Komárek et al. 2013), zeolite (Shaheen et al 2015), biochar (Indraratne et al. 2020), and livestock manure (Wan et al. 2020), have attracted attention in immobilizing toxic elements in soils owing to their cost-effectiveness and high efficacy. Hence remediation of contaminated soils using amendments to immobilize metals is a viable solution.

Natural and synthesized oxides have strong sorption and immobilization effects and have been widely used as stabilization agents to remediate metal-contaminated wastewater and soil (Komárek et al. 2007; Hua et al. 2012). Due to their small size (usually less than 100 nm), high surface area, and unique chemical characteristics, nanoparticles have been extensively studied and are being implemented with increasing frequency (Sun et al. 2006; Tosco et al. 2014). Compared with conventional in situ remediation techniques nanoremediation has emerged as a new clean-up method that is less costly, more effective, and economically sustainable (Karn et al. 2009). Though the potential and efficacy of nanotechnology are well established, there are several drawbacks related to the full-scale application such as uncertainties on mobility, reactivity, persistence of nanomaterials, and the issues related to environmental and human safety (Corsi et al. 2018). The integration of nanomaterials and bioremediation, which is termed as nanobioremediation, is one attempt of creating effective, efficient, and safe nano-products (Cecchin et al. 2017). Green synthesis is another emerging field dedicated to the development and improvement of nanoparticles production in an effective, nonhazardous, and eco-friendly manner. A green synthesized nanoscale zero-valent iron reduced 50% of environmental impact compared with conventional nano-products (Wang et al. 2019). Nanoremediation ensures a quick and efficient removal of pollutants from contaminated sites; however, proper evaluation of nanoparticles, particularly full-scale ecosystem-wide studies, needs to be conducted to prevent any potential adverse environmental impacts (Karn et al. 2009; Cecchin et al. 2017; Corsi et al. 2018).

Nanoscale materials have gained increasing interest in the area of environmental remediation because of their unique physical, chemical, and biological properties (Kostal et al. 2005; Guerra et al. 2018). Nanoscale oxides have been used for remediation of contaminated groundwater resources by converting heavy metals to less soluble substances (Tang and Lo 2013; Mohammadian et al. 2021). Toxic metals in soils were also remediated using Fe and Mn nano-oxides (Martínez-Fernández et al. 2014; Michálkova et al. 2014; Baragaño et al. 2020). Iron- and Mn-based oxides as amendments have been studied more widely than the other oxides in the contaminated soils due to their high potential to act as sorption complexes (Carbonell-Barrachina et al. 1999; Komárek et al. 2007). Arsenic and other oxyanions were the most common contaminants targeted by Fe-based amendments (Komárek et al. 2013). Iron oxides have shown high sorption capacities for cationic elements of Cd, Pb, and Zn, due to their amphoteric nature (Nielsen et al. 2016; Okkenhaug et al. 2016). Aluminum- and Ti-oxide nanoparticles can be present in many natural systems and can play a significant role in binding of heavy metals to surfaces, or by changing into more stable mineral forms, as effectively as or may be even better than Fe nano-oxides. The effectiveness of synthesized Al- and Ti-nano-oxides at different rates in immobilizing Cd, Pb, and Zn in acidic mine spoil (Chat) and contaminated soil, has not been studied to date. This research aimed to investigate the effectiveness of Fe-, Al-, and Ti-nano-oxide amendments and rates of amendments on immobilizing Cd, Pb, and Zn in mine spoil and contaminated soil by comparing adsorption capacities, leachable metals and available metals in soils, and plant tissue metal concentrations relative to unamended controls. We hypothesized that the addition of Fe-, Al- and Ti-nano-oxides at different rates would immobilize Cd, Pb, and Zn differently in the Chat and contaminated soil, reducing metal toxicities and paving way for the establishment of plant cover on contaminated sites.

Materials and Methods

Collection of Chat, soil, and nano-oxide materials

The contaminated soil used in this study was collected from a repository containing contaminated soil excavated from a residential area in Joplin, MO (USA), and from a mine of spoiled material (Chat) from the city of Galena, KS (USA). Soil and Chat were collected from the upper 20 cm, sieved through a 2 mm stainless steel screen, air-dried, and stored in plastic containers at room temperature (22–24 °C). Three nanoscale oxides, namely, iron oxide (Fe-O), aluminum oxide (Al-O), and titanium oxide (Ti-O) were used. Aluminum oxide (NanoActive Al_2O_3, 5 μm in size) and titanium oxide (NanoActive TiO_2, 5 μm in size) were purchased from NanoScale Materials Inc. (Manhattan, KS, USA) and iron oxide (Fe(II, III) oxide, 90 nm in size) purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA).

Chat and soil samples were analyzed for pH, Mehlich III-extractable P, electrical conductivity (EC), 1 mol·L^{-1} KCl-extractable NH_4^+ and NO_3^-, and bioavailable Cd, Pb, and Zn using methods described below. Soil pH was determined in a 1:1 soil-deionized water mixture with a Ross combination pH electrode (Thermo Orion, Beverly, MA, USA). Exchangeable basic cations were determined after extracting with 1 mol·L^{-1} NH_4OAc at 1:10 soil to solution ratio and the concentrations were measured by inductively coupled plasma–optical emission spectrometry (ICP–OES, Accuris 141; Fisons Instruments, Beverly, MA, USA). Electrical conductivity was measured in a saturated paste extract using an EC meter (USDA 1954). Inorganic N (NH_4^+ and NO_3^-) was extracted by shaking with 1 mol·L^{-1} KCl solution (1:10) on an Orbital shaker for 2 h and inorganic P was extracted by Mehlich-III (Mehlich 1984); samples were then analyzed colorimetrically using a flow-injection analyzer (Lachat Quikchem 8500). Nitric acid extractable total metals were determined by digesting 2 g of material (≤2 mm) with 20 mL of 4 mol·L^{-1} HNO_3 (trace metal grade) acid at 80–85 °C for 4 h (Sposito et al. 1982). Filtered digests were then analyzed for Cd, Pb, and Zn by ICP–OES. Available soil metal contents of the treated Chat and soil treatments were determined by extracting with 0.1 mol·L^{-1} $Ca(NO_3)_2$, (soil to solution ratio 1:20, 4 h shaking at 200 r·min^{-1}) and were measured by ICP–OES. Cadmium, Pb, and Zn bioavailability were also assessed with diffusive gradients in thin films (DGT) method (Sonmez and Pierzynski 2005).

Adsorption study

A monometal adsorption study was conducted for Cd, Pb, and Zn with Fe-O, Al-O, and Ti-O, separately. The adsorption study was conducted as follows: 0.1 g of Fe, Al, and Ti oxides were separately placed into acid-washed polyethylene 50 mL bottles and equilibrated with 20 mL of Cd, Pb, or Zn as nitrates for 24 h at room temperature (22–24 °C), at concentrations of 5, 10, 15, 20, 25, and 30 mg·L^{-1}, in triplicates. Separation of the solid and liquid phases was done by centrifugation at 6500 r·min^{-1} for 15 min and equilibrium metal concentrations were measured by ICP–OES. Conformity to the Freundlich-type adsorption isotherm was tested using the linear equation: $\log S = \log K_F + N \log C_{eq}$, where S is the amount of metal adsorbed by nano-oxide (mg·kg^{-1}), C_{eq} is the concentration of metal in the equilibrium solution (mg·L^{-1}), and K_F and N are empirical constants. Conformity to the Langmuir-type sorption isotherm was tested using the linear equation: $C_{eq}/S = 1/KM + C_{eq}/M$, where M is the maximum amount of metal that can be sorbed in a monolayer (mg·kg^{-1}) and K is the equilibrium constant which represents the intensity of the adsorption isotherm (L·kg^{-1}).

Greenhouse study

Chat was amended with CaO at the rate of 5.5 Mg·ha^{-1} and cattle manure compost pellets at the rate of 134 Mg·ha^{-1}, before mixing with nanoscale oxides. Chat materials were neutralized with CaO and composted to improve growth medium qualities before planting (Pierzynski et al. 2002*b*; Baker et al. 2011). Seven treatments, three nano-oxides mixed at two rates and an unamended control, with three replications were evaluated for Chat and soil separately. Treatments were control, 25 g·kg^{-1} Fe-oxide (Fe-25), 50 g·kg^{-1} Fe-oxide (Fe-50), 25 g·kg^{-1} Al-oxide (Al-25), 50 g·kg^{-1} Al-oxide (Al-50), 25 g·kg^{-1} Ti-oxide (Ti-25), and 50 g·kg^{-1} Ti-oxide (Ti-50). Nano-oxides were mixed thoroughly at the given rates with Chat or soil for the greenhouse study.

Treated materials of 1 kg were placed in pots with holes on the bottom covered with cheesecloth. A plastic container was kept under each pot to collect the leachate. Chat was washed with 1 L of deionized water before seeding to improve chemical properties of Chat, and varying amounts of metals were released from different treatments (1–138 μg of Cd, 1.6–5.2 μg of Pb, and 10–5056 μg of Zn; data not shown). Eight to 10 seeds of sorghum

(*Sorghum bicolor* L. Moench) were planted in each pot, and plants were thinned to 3 and 5 per pot in soil and Chat, respectively, due to different growth rates after a week. Pots were lightly watered daily with between 100 and 300 mL deionized water, as determined by weight to prevent free drainage. Leachates from the pots were collected twice per week starting after plant emergence and until harvesting after adding deionized water 250 mL to Chat and 450 mL to soil. Concentrations of Cd, Pb, and Zn were measured in leachates by ICP–OES. The study was conducted in a greenhouse under controlled conditions, where day and night-time temperatures were 26 and 18 °C, respectively. The length of the photoperiod was 16 h. Plants were harvested at maturity. Above-ground plant materials were thoroughly washed, first with deionized water, followed by 5 $g \cdot L^{-1}$ sodium lauryl sulfate solution (CH_3-$(CH_2)_{10}CH_2OSO_3Na$), and deionized water to remove adhered soil particles. Plant samples were oven-dried at 55 °C and weighed, and then ground to determine total metal (Cd, Pb, and Zn) and nutrients (N, P, and K). Ground subsamples (0.25 g plant material) were digested with concentrated H_2SO_4 and 30% H_2O_2 (final solid: solution ratio at 1:100) for determination of total N, P, and K in plant tissues (Thomas et al. 1967). Potassium was determined by ICP–OES, while N and P were determined colorimetrically. Subsamples (0.5 g) of plant tissue were digested with 25 mL of trace metal grade, concentrated HNO_3 acid for 4 h at 120 °C, and Cd, Pb, and Zn concentrations were determined by ICP–OES. Chat and soil were analyzed for available nutrients and metals using methods described above after harvest of plants.

Statistical analysis

Leachate metal concentration data from different treatments were statistically analyzed separately for Chat and soil to compare the effectiveness of amendments in stabilizing metals. A repeated measure analysis was conducted using the PROC MIXED procedure of SAS version 9.4 (SAS Institute Inc. 2014). The Kenward-Rogers denominator degrees of freedom method and Tukey-Kramer adjustment were used for multiple comparisons using PDIFF statement. Least squares means statement (LSMEANS) was used to access differences. A residual analysis was performed to test the normality assumption and homogeneity variances. If normality assumption and homogeneity variances are not acceptable, variance stabilization transformation (lognormal distribution) was conducted (except for soil Cd and soil Pb). Back transformations of log-transformed means were done manually (=EXP (X)). Type III test of fixed effects was employed, and means were considered significantly different at a p value of $\leq$0.05. Similarly, a separate statistical analysis was performed for Chat and soil treatments using the PROC MIXED procedure of SAS for available metals, other measured properties, and plant metals.

Table 1. Initial properties of Chat and contaminated soil used for the study.

Property	Chat	Soil
pH (1:1, distilled water)	7.03	6.38
EC ($dS \cdot m^{-1}$, saturate extract)	4.61	2.29
($NH_4 + NO_3$)-N ($mg \cdot kg^{-1}$)	45	157
Mehlich-III extractable P ($mg \cdot kg^{-1}$)	113	122
Available Ca ($mg \cdot kg^{-1}$)	3019	3937
Available Mg ($mg \cdot kg^{-1}$)	287	206
Available K ($mg \cdot kg^{-1}$)	733	260
Total Cd ($mg \cdot kg^{-1}$)	84	15
Total Pb ($mg \cdot kg^{-1}$)	1583	1260
Total Zn ($mg \cdot kg^{-1}$)	6154	3082
$Ca(NO_3)_2$ extractable Cd ($mg \cdot kg^{-1}$)	17	0.6
$Ca(NO_3)_2$ extractable Pb ($mg \cdot kg^{-1}$)	ND	ND
$Ca(NO_3)_2$ extractable Zn ($mg \cdot kg^{-1}$)	451	57
DGT extractable Cd (μg)	1.67	0.15
DGT extractable Pb (μg)	ND	ND
DGT extractable Zn (μg)	55	24

Note: DGT, diffuse gradients in thin films; EC, electrical conductivity; ND, not detectable.

Linear regression analysis was performed using SAS version 9.4 to determine the significance ($p \leq 0.05$) of the relationship of Langmuir and Freundlich isotherms, separately. Root mean square error (RMSE) and Akaike Information Criterion (AIC) were used to evaluate models while the adjusted coefficient of determination (adjusted r^2) was used for the best-fit linear theoretical isotherm selection. The best-fit model was selected between Langmuir and Freundlich isotherms with the lower RMSE/AIC value for each metal for each nano-oxide.

Results and Discussion

Basic properties of soil and Chat materials

The pH of Chat was increased to 7.03 by the addition of CaO and the initial soil pH was 6.38 (Table 1). Soluble salts measured by EC in Chat and soil were 4.61 and 2.29 $dS \cdot m^{-1}$, respectively. Available P (Mehlich-III extractable) concentrations were 113 and 122 $mg \cdot kg^{-1}$ and available N ($NH_4 + NO_3$) were 45 and 157 $mg \cdot kg^{-1}$, respectively, for Chat and soil. There were no deficiencies of Ca, Mg, or K in Chat and soil for plant growth (Table 1). Hence the initial properties of Chat amended with CaO and manure, and soil were favourable for plant growth, irrespective of their trace metal contents. Total Cd, Pb, and Zn concentrations, respectively, were 84, 1583, and 6154 $mg \cdot kg^{-1}$ for Chat, and 15, 1260, and 3082 $mg \cdot kg^{-1}$ for soil. Metal toxicity is related to bioavailability rather than the total metal concentration in soil. Available ($Ca(NO_3)_2$ extractable) Cd were 17.0 and 0.6 $mg \cdot kg^{-1}$ and Zn were 451 and 57 $mg \cdot kg^{-1}$, in Chat and soil, respectively. Similarly, phytoavailable metal concentrations evaluated by diffuse gradients in thin films (DGT) showed Cd, 1.67 and 0.15 μg, and Zn, 55 and 24 μg, respectively, for Chat and soil. Available Pb concentrations in $Ca(NO_3)_2$ extractions or DGT were below the detection

Table 2. Adsorption isotherm parameters for three nano-oxides.

	Linear Langmuir			Linear Freundlich		
	$C_{eq}/S = 1/KM + C_{eq}/M$			$\log S = \log KF + N \log C_{eq}$		
Nano-oxides	Cd	Pb	Zn	Cd	Pb	Zn
	Adjusted coefficient of determination (r^2)					
Fe-O	0.83^{***}	0.96^{***}	0.87^{***}	0.96^{***}	0.87^{***}	0.95^{***}
Al-O	0.90^{***}	0.91^{***}	0.85^{***}	0.98^{***}	0.98^{***}	0.98^{***}
Ti-O	0.94^{***}	0.93^{***}	0.95^{***}	0.98^{***}	0.99^{***}	0.99^{***}
	Root mean square error (RMSE)					
Fe-O	0.0043	3.1×10^{-5}	0.0035	0.0362	0.094	0.0412
Al-O	0.0011	8.8×10^{-6}	3.5×10^{-5}	0.0301	0.0401	0.0381
Ti-O	0.0017	1.3×10^{-5}	0.0014	0.0274	0.0311	0.0199
	M (adsorption maximum μg·g^{-1})			N parameter		
Fe-O	858c	8333b	904c	0.61b	0.57b	0.66a
Al-O	2333a	12 632a	10 000a	0.73a	0.78a	0.60a
Ti-O	1157b	1250c	1250b	0.60b	0.73a	0.54b
ANOVA		F value	p value		F value	p value
Metal (M)		42	<0.0001	M	11	0.0007
Nano-oxides (NO)		137	<0.0001	NO	10	0.0013
M × NO		12	<0.0001	M × NO	10	0.0002

Note: ANOVA, analysis of variance. Superscript *** indicate significant differences at $p \leq 0.0001$. Different lowercase letters within a column indicate significant differences at $p \leq 0.05$; $n = 18$.

limits of ICP–OES. Abdel-Saheb et al. (1994) reported available (DTPA extractable) concentrations for Cd, Pb, and Zn ranged from 0.6 to 10 mg·kg^{-1}, 7.8 to 68 mg·kg^{-1}, and 33 to 715 mg·kg^{-1}, respectively, for Chat in the tri-state mining region. Based on total and available toxic metals in Chat and soil, we cannot expect a good plant growth on these contaminated unamended Chat and soil.

Adsorption capacity of nano-oxides

Adsorption of toxic metals (Cd, Pb, and Zn) to nano-oxides (Fe-O, Al-O, and Ti-O) conformed to the linear form of the Langmuir and Freundlich equations with adjusted r^2 ranging from 0.83 to 0.99 at $p \leq 0.0001$ (Table 2). AIC criterion varied from −194 to −417 for Langmuir isotherms, while it was varied from −83 to −139 for Freundlich isotherms (data were not shown). Similarly, Langmuir linear model showed lower RMSE compared with Freundlich linear model (Table 2). Conformity to the Langmuir linear form of isotherm was superior to the linear Freundlich isotherm as indicated by lower RMSE and AIC. Dimensionless N parameter of the Freundlich equation was calculated to compare heterogeneity of the adsorbent surfaces of the three nano-oxides. As the N approaches 0, surface site heterogeneity increases, indicating that there is a broad distribution of adsorption site types (Sposito 1980; Essington 2004). Since N of nano-oxides is significantly different, the adsorption surfaces were different, Al-O showing the least heterogeneity and Fe-O showing the highest heterogeneity for Cd and Pb. The linear Langmuir isotherm was used to calculate the adsorption maximum capacity (M) of nano-oxides for Cd, Pb, and Zn. Nano-oxides can be arranged according to the highest to lowest affinity for toxic metals as Al-O > Ti-O > Fe-O (Table 2) based on M values. The order of mobility of three studied metals can be arranged as Cd > Zn > Pb. In agreement with our study, after evaluating the mobility of metals in a contaminated soil using a sequential extraction procedure, Pueyo et al. (2004) concluded Cd as the most mobile, Zn in between, and Pb the least mobile. Very high immobilization efficiencies for Pb (up to 94%) were measured for ferric oxyhydroxide powder (Kumpiene et al. 2019). Therefore, we can expect three nano-oxides to show different retention capacities for Cd, Pb, and Zn.

Metal contents in leachates of nano oxides amended treatments

Treatment (nano-oxide type and rate), time (days after planting seeds, DAP), and treatment × time interaction effects were significant for Cd, Pb, and Zn contents in Chat leachate. All three nano-oxides showed significantly lower Cd contents in Chat leachate than the respective control (unamended Chat); among nano-oxides, Al-O and Ti-O were more effective than

Fig. 1. Leachate metal contents in Chat (control) and Chat amended with nano-oxides of Fe, Al, and Ti at rates of 25 g·kg^{-1} (25) and 50 g·kg^{-1} (50), collected at 18, 21, 25, 28, 32, 35 d after plant emergence (DAP). The vertical bars indicate the standard error.

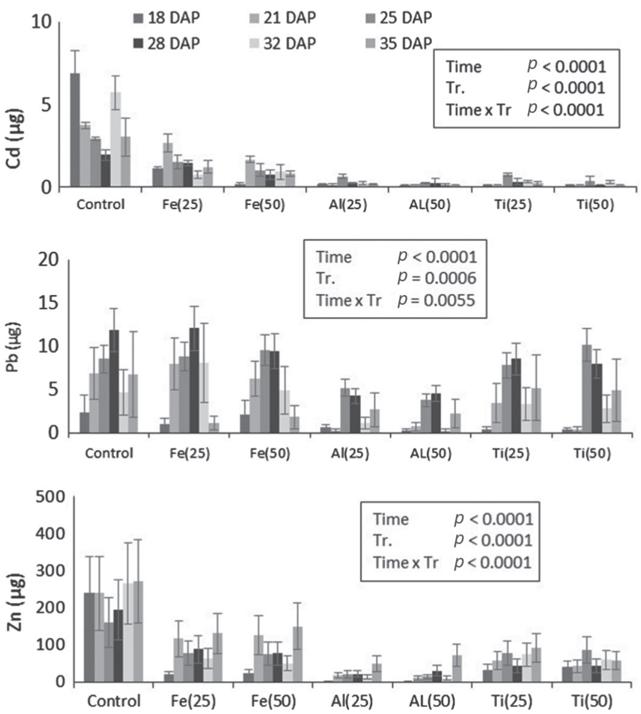
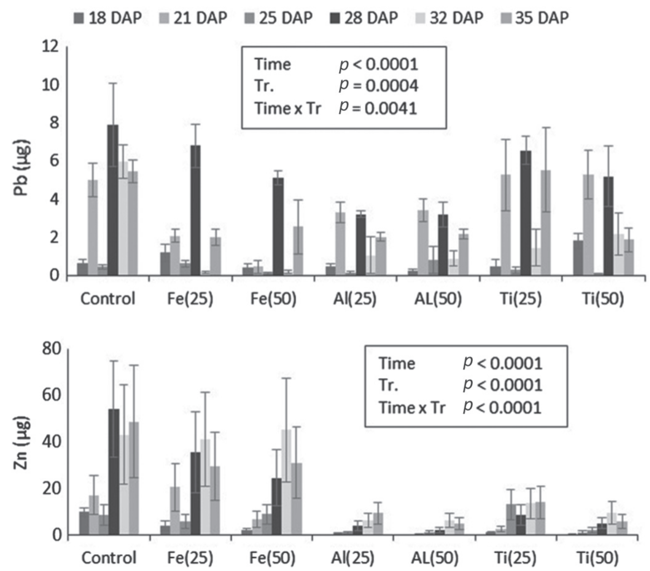


Fig. 2. Leachate metal contents in contaminated soil (control) and soil amended with nano-oxides of Fe, Al, and Ti at rates of 25 g·kg^{-1} (25) and 50 g·kg^{-1} (50), collected at 18, 21, 25, 28, 32, 35 d after plant emergence (DAP). The vertical bars indicate the standard error.



Fe-O (Fig. 1). Chat treated with Al-O significantly reduced Pb in leachate relative to the other treatments while all three nano-oxides significantly reduced Zn contents relative to the unamended control. Treatment, time, and treatment × time interaction effects were significant, for soil leachate Pb and Zn while only time effect was significant for Cd (Fig. 2). Contents of Cd, Pb, and Zn in soil leachates were much lower than the respective Chat leachates. This could be due to the lower initial contamination of metals in soil than in Chat (Table 1). Total Cd, Pb, and Zn leached from soil treatments ranged from 0.59 to 1.2 μg, 8 to 18 μg, and 15 to 213 μg, respectively, among treatments. The effectiveness of nano-oxides in reducing metals in leachates were similar for both Chat and soil, i.e., Cd and Zn by Al-O and Ti-O and Pb by Al-O. Significant reductions of metals in leachates indicated the possibility of using nano-oxides to remediate contaminated sites. Leachate results further confirm the possibility of using nano-oxides, especially Al-O and Ti-O, to reduce bioavailable forms of metals in mine spoils and contaminated soils.

Changes of properties of Chat and soil after harvesting of plants

Soil pH was not significantly different among treatments in Chat or soil after plant harvest (Table 3). Nano-oxide of Al reduced EC significantly relative to the rest of the Chat treatments, while there was no significant difference in EC among soil treatments. Electrical conductivity values decreased from the initial value in both Chat (4.6 initial to 2.4 after harvest) and soil (2.3 initial to 1.9 after harvest), as shown in Tables 1 and 3. Leaching with deionized water twice per week should have removed the excess salts from the soil and Chat. Available N forms showed no difference among treatments of Chat or soil. The most significant difference was observed with available P, with Al and Ti nano-oxide treatments having had significantly lower P than the other treatments in both Chat and soil. The critical levels of soil Olsen-P for optimal crop yield ranged from 10.9 to 21.4 mg·kg^{-1} (Bai et al. 2013). Available P concentrations in Chat treated with Al(25), Al(50), Ti(50) and soil treated with Al(50) and Ti(50), were below the critical P concentrations in soils for plant growth. The amount of inorganic P sorbed by a range of Fe- and Al-containing components were studied by McLaughlin et al. (1981), who reported that Al gel sorbed 30–70 times more P than gibbsite. The conventional method of P removal from water has involved the use of precipitation methods using hydrous oxides, more specifically ferric oxides (Hauduc et al. 2015). Maguire et al. (2001) found that biosolids treated with Fe and Al salts reduced the available P in comparison with biosolids prepared without metal salts. Since oxide minerals are important sorbents for PO_4^{3-} in soils, a negative impact can be expected on plant growth on remedial sites, if the measures were not taken to correct the P levels.

The available forms of metals ($Ca(NO_3)_2$ and DGT extractable) were significantly affected by the addition of nano-oxides, as shown by after-harvest metal values (Fig. 3).

Table 3. Properties and available nutrients in Chat and soil treatments after plant harvest.

			Available amounts (mg·kg^{-1})					
Treatments	pH (1:1)	EC (mS·cm^{-1})	NH_4^+-N	No_3^--N	P	Ca	Mg	K
Chat								
Control	7.07ab	2.4a	12a	3.5a	118a	2208b	177bc	367a
Fe(25)	7.35a	2.67a	12a	2.0a	111a	1891b	152c	279a
Fe(50)	7.39a	2.74a	12a	1.8a	106a	2225b	216bc	377a
Al(25)	7.51a	1.58bc	12a	3.3a	38b	2227b	146c	364a
Al(50)	7.43a	1.38c	12a	3.2a	10c	2538b	172bc	376a
Ti(25)	7.31a	2.51a	13a	2.5a	50b	3639a	336a	555a
Ti(50)	7.28a	2.16ab	13a	1.8a	10c	3236a	265b	430a
Soil								
Control	7.00b	1.19a	16a	63a	117a	3069c	106a	93a
Fe(25)	6.59b	0.76a	14a	30a	114a	2998c	100a	88a
Fe(50)	7.34ab	0.89a	16a	50a	107a	2989c	94a	78a
Al(25)	7.45a	0.72a	14a	45a	42c	3573b	75b	74a
Al(50)	7.59a	0.88a	14a	63a	14d	3483b	64b	67a
Ti(25)	6.88ab	1.14a	14a	50a	58b	3807b	98a	81a
Ti(50)	7.5a	1.41a	15a	107a	21d	4138a	101a	79a

Note: Al, Al nano-oxide; EC, electrical conductivity; Fe, Fe nano-oxide; Ti, Ti nano-oxide; 25 = at rate of 25 g·kg^{-1}; 50 = at rate of 50 g·kg^{-1}. Means within the column not sharing a lowercase letter differ significantly at $p \leq 0.05$.

Fig. 3. Available forms of metals ($Ca(NO_3)_2$ and DGT) in Chat (*a*, *b*, *c*, and *d*) and contaminated soil (*e*, *f*, *g*, and *h*) after plant harvest. Different letters above bars indicate a significant difference at $p \leq 0.05$. Fe, Fe nano-oxide; Al, Al nano-oxide; Ti, Ti nano-oxide; 25 = at rate of 25 g·kg^{-1}; 50 = at rate of 50 g·kg^{-1}.

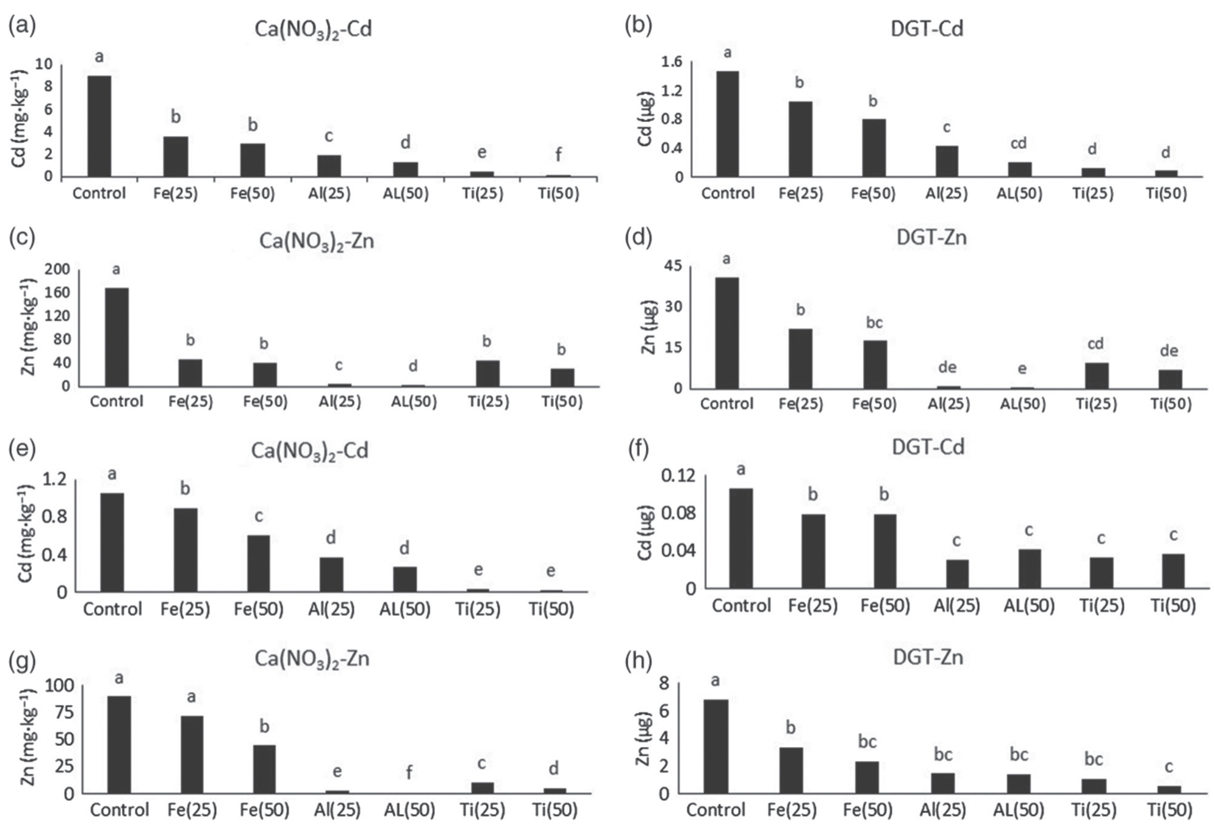
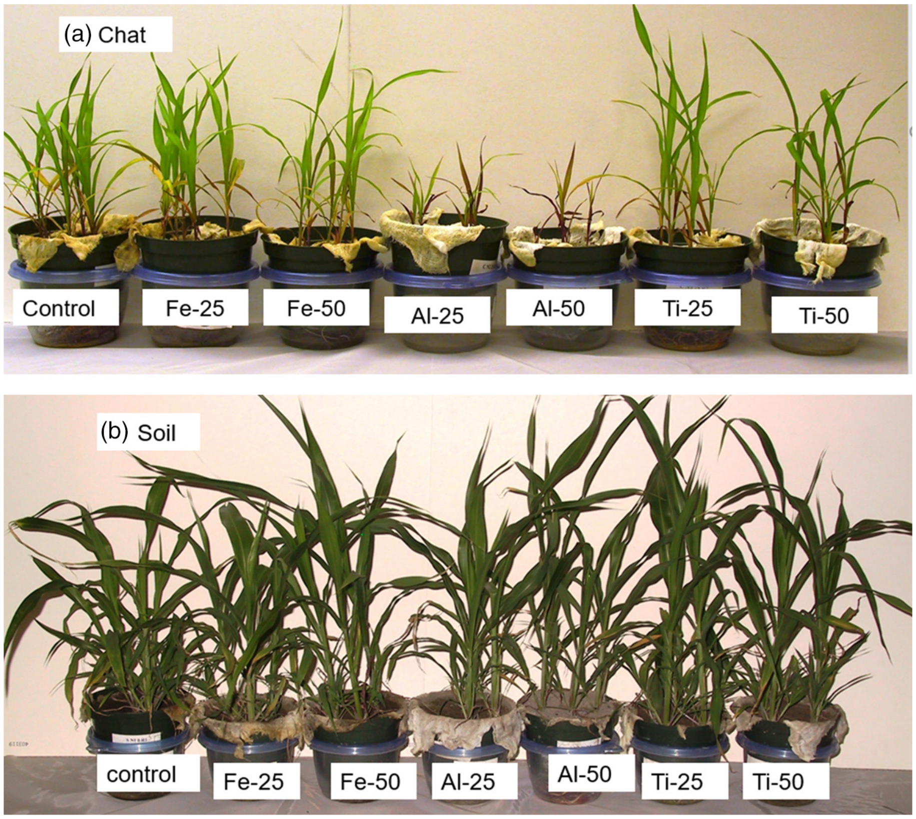


Fig. 4. Sorghum-Sudangrass performance in nano-oxide amended and unamended (*a*) Chat and (*b*) soil. Fe, Fe nano-oxide; Al, Al nano-oxide; Ti, Ti nano-oxide; control, unamended; 25 = at rate of 25 $g \cdot kg^{-1}$; 50 = at rate of 50 $g \cdot kg^{-1}$. [Color online.]



Cadmium immobilizing capacity among treatments can be arranged as Ti-O > Al-O > Fe-O > Control for Chat and soil treatments. Available Cd in soil also behaved similarly, except there was no significant difference between Fe(25) and Control treatments. Available Zn significantly decreased in all nano-oxide treated Chat and soil. Zinc immobilizing capacity of nano-oxides can be ranked as Al-O > Ti-O ≥ Fe-O > Control for Chat, and Al-O = Ti-O > Fe(50) > Fe(25) ≥ Control for soil. This further confirms the results of leachate metals; Oxides effectively reduced bioavailable forms of Cd, and Zn, Al-O and Ti-O being more effective than Fe-O. Available Pb in after harvest Chat and soils were not detectable. Iron oxides have been studied extensively and successfully used in immobilization of toxic metals in contaminated soils (Komárek et al. 2013), mainly by adsorption on the surfaces of Fe-oxides by hydroxyl groups (Manceau et al. 1992; Santona et al. 2006). Surface adsorption, surface precipitation, and co-precipitation have also been identified as metal-binding mechanisms through Fe-oxides (Lu et al. 2011). Our study confirms Al-O and Ti-O were more effective than Fe-O in immobilizing Cd and Zn in Chat and contaminated soil.

Plant performance in nano-oxide treated Chat and soil

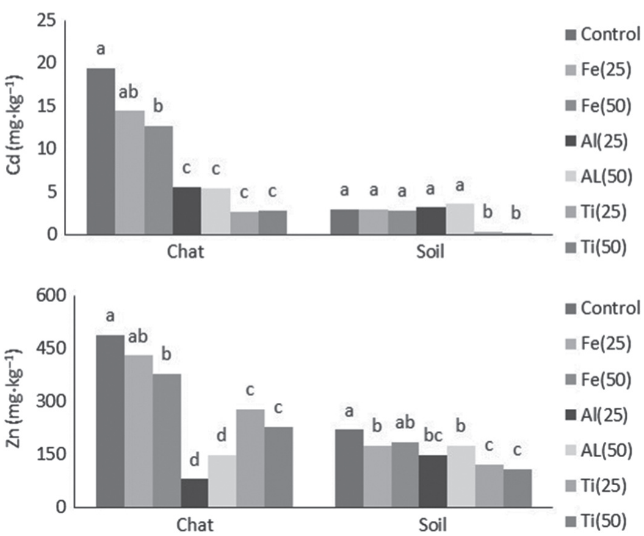
Plant growth in Al-O treatments was lower than the rest of the Chat treatments including the control. Plant growth of all treatments in contaminated soil was performed equally including unamended control (Fig. 4). As we discussed before, plant growth in nano-oxide Chat treatments was affected by fixing of P creating severe P deficiencies. The positive impact of low available metals in nano-oxide amended Chat on plant growth was masked by the P limitation. Therefore, P fertilization would play a significant role in establishing plants in these contaminated sites to harness metal remediation impact of nano-oxides. There was no significant difference among soil treatments of plant growth parameters of dry mass weights, leaf area measurements, or chlorophyll index as measured by a soil plant analysis development (SPAD) meter (Table 4). The physiological parameters of plants grown in Chat indicated poorer performance than that of plants grown in contaminated soil. Chat, which is a mine waste with some unfavourable characteristics for plant growth such as low organic matter, water holding capacity, and nutrient content and high concentrations of Cd, Pb, and Zn negatively impact plant growth. Among the Chat treatments, significantly less dry matter weight, SPAD readings (chlorophyll index), plant height, and leaf area measurements were shown in Al nano-oxide treatments (Table 4). As we highlighted above, the most probable reason for this poor growth is the low available P contents in these treatments (Table 3). Phosphorus could

Table 4. Physiological characteristics of plants grown in Chat and soil treatments.

	Chat				Soil			
Treatment	DW (g)	SPAD	Height (cm)	LA (cm^2)	DW (g)	SPAD	Height (cm)	LA (cm^2)
Control	0.70b	23.8b	5.8ab	29.2a	3.7ab	44.7b	34.7a	228a
Fe(25)	0.76ab	26.8ab	6.2a	24.4abc	4.04ab	43.5ab	37.6a	184a
Fe(50)	0.73ab	22.4b	6.2a	27.1ab	3.7ab	48.6a	36.0a	201a
Al(25)	0.21bc	7.6c	2.9b	4.4c	3.5ab	46.0ab	34.0a	175a
Al(50)	0.17c	7.6c	2.9b	3.9c	2.4b	43.3ab	37.0a	151a
Ti(25)	0.49abc	30.8a	6.4a	28.8a	3.7ab	38.1b	36.0a	203a
Ti(50)	0.26bc	31.3a	6.4a	19.8bc	4.7a	45.2ab	36.3a	150a

Note: Al, Al oxide; DW, dry weight; Fe, Fe oxide; LA, leaf area; SPAD, soil plant analysis development chlorophyll meter reading; Ti, Ti oxide; 25 = 25 $g{\cdot}kg^{-1}$; 50 = 50 $g{\cdot}kg^{-1}$. Means within the column not sharing a lowercase letter differ significantly at $p \leq 0.05$.

Fig. 5. Plant metal concentration in Chat and soil treatments. Different letters above bars indicate a significant difference at $p \leq 0.05$. Fe, Fe nano-oxide, Al, Al nano-oxide. Ti,Ti nano-oxide; 25 = at rate of 25 $g{\cdot}kg^{-1}$; 50 = at rate of 50 $g{\cdot}kg^{-1}$.



be adsorbed by oxides through the formation of Al/Fe-P complexes (Peng et al. 2021) as well as by metals, more specifically by Pb (Hettiarachchi and Pierzynski 2004). Plant P of sudangrass grown in Chat-Ti(50) was 0.9 $mg{\cdot}kg^{-1}$, and we could not determine total P in Al-O treatments due to low biomass production (data not shown). A critical P concentration in the shoots of the sorghum-sudangrass for optimum yield was reported as 1.3 $g{\cdot}kg^{-1}$ (Hardin et al. 1989). Therefore, it is necessary to monitor available P in remediated soils for favourable plant growth.

The Zn concentrations in plant tissues in Chat treatments ranged from 79 $mg{\cdot}kg^{-1}$ in the Al nano-oxide treatment to 516 $mg{\cdot}kg^{-1}$ in the control, whereas in soil treatments ranged from 107 $mg{\cdot}kg^{-1}$ in Ti-O treatments to 215 $mg{\cdot}kg^{-1}$ in the control (Fig. 5). Addition of nano-oxides of Al and Ti significantly reduced sorghum-sudangrass tissue Zn concentrations in amended Chat and soil, compared with the controls. Nano-oxides of Al and Ti significantly decreased sorghum-sudangrass tissue Cd concentrations, compared with the control in Chat. Plant tissue Cd in unamended Chat showed 20 $mg{\cdot}kg^{-1}$, whereas in Fe-O 13 $mg{\cdot}kg^{-1}$, Al-O 5 $mg{\cdot}kg^{-1}$, and Ti-O 2.8 $mg{\cdot}kg^{-1}$. Plant tissues harvested from Ti-oxide amended soil treatments showed Cd concentration <0.34 $mg{\cdot}kg^{-1}$, while all the other treatments ranged from 2.8 to 3.5 $mg{\cdot}kg^{-1}$ Cd. Normal Zn concentrations in dry matter of crops range from 25 to 150 $mg{\cdot}kg^{-1}$ while Cd levels are usually less than 1 $mg{\cdot}kg^{-1}$ (Page et al. 1981). Nano-oxides can be arranged lowest to highest Cd in plant tissues as Ti-O < Al-O < Fe-O < Control in Chat, and Ti-O < Al-O = Fe-O = Control in soil. Effectiveness of reducing Zn in plant tissues among nano-oxides was Al-O > Ti-O > Fe-O for Chat, and Ti-O > Al-O = Fe-O for soil. Concentrations of Pb in plant tissues were not detectable. Metal bioavailability, which means the availability of a metal for uptake by an organism, could be varying for different metals. While comparing the two metals Cd and Pb, Cd is readily taken up by plants, whereas Pb is not (Pierzynski et al. 2002*a*). Translocation of Pb from the soil to plant roots and through the roots to the shoots, is minimal due to chemical immobilization in soils as well as in roots (Laperche et al. 1997). Nano-oxides reduced 28% (Fe-O) to 87% (Ti-O) Cd and 14% (Fe-O) to 85% (Al-O) Zn in plant tissues compared with unamended Chat. Compared with unamended control soil, lettuce uptake of Cd, Pb, and Zn was reduced 86%, 58%, and 73%, respectively, by the addition of red-mud (Lee et al. 2009). Significant relationships were observed between Cd in plant tissue with available Cd (r = 0.87, p = 0.001), and plant-Zn with available Zn (r = 0.79, p = 0.001). No significant difference was observed between the two amendment rates, indicating 25 $g{\cdot}kg^{-1}$ was as effective as 50 $g{\cdot}kg^{-1}$. Though the results are promising, a site-specific analysis must be undertaken to assess potential applicability, the impact of the nano-oxide-metal complexes, and cost-benefit evaluations.

Conclusions

Heavy metals are environmental pollutants that threaten the health of human populations and natural ecosystems. Three nanoscale oxides at two rates were evaluated for their efficacy in reducing the bioavailability of Cd, Pb, and Zn to sorghum-sudangrass grown in Chat and contaminated soil. The results of this study show that the presence of nano-oxides immobilizes Cd, Pb, and Zn in contaminated materials significantly. In general, Cd and Zn concentrations in plant tissues of sorghum-sudangrass were reduced significantly by Al and Ti nano-oxides. All three tested nano-oxides were effective in immobilizing Cd, Pb, and Zn in Chat and soils, with Al-O and Ti-O being more effective than Fe-O. Plant growth was affected by P deficiency in Chat treatments. It is necessary to provide sufficient P to nano-oxide amended treatments, because P adsorption to oxides is very common in soils. Nano-oxides can be used successfully to remediate heavy metal contaminated Chat and soil for plant growth under proper nutrient supplements. However, sufficient care and regulatory measures for the disposal of plant materials and nano-oxide-containing materials need to be established. Additional research should be conducted to ensure nanoparticles are not hazardous to other species and to develop proper safety and disposal measures if necessary.

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