

# Stabilization of Heavy Metals in Mining Site Soil with Silica Extracted from Corn Cob

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**Abstract** Corn cob silica (CCS), produced via a modification of the sol-gel method, can reduce heavy metal availability and stabilize contaminated soil on abandoned mining sites. Adding 5 % (w/w) CCS to mining site soil increased pH from 4.0 to 7.7, and cation exchange capacity increased from 94.5 to 100.3 cmol<sup>+</sup>/kg. Sequential extraction showed that adding CCS decreased heavy metal availability in the soil. Mobility factor (MF) values indicated that CCS reduced Pb mobility more than that of Zn or Cu in all fractions. Pb concentrations in leachate from all fractions using the toxicity characteristic leaching procedure (TCLP) were greatly decreased by adding 3 % (w/w) CCS. CCS similarly reduced Zn concentrations in TCLP leachate. CCS addition did not impact Cu concentrations in leachate, likely because concentrations were much lower than those of the other metals. As was generally less mobile than the heavy metals; however, As mobility and leachability tended to increase with CCS addition because its oxyanions arsenite and arsenate have low affinity for negatively charged surfaces on the CCS. Shoot and root growth of *Spinacia oleracea* L. (spinach) was much greater in CCS-treated soil than in unamended soil.

Results demonstrate the utility of CCS to stabilize heavy metals in contaminated mining site soil, but this treatment may not be ideal for As-contaminated soils.

**Keywords** Contaminated mine soil · Heavy metals · Stabilization · Metal availability · Corn cob silica (CCS) · *Spinacia oleracea* L.

## 1 Introduction

The number of abandoned mines has rapidly increased in Korea and worldwide. Without proper management, acid drainage can become a major problem (Ko et al. 2012). Drainage from mine wastes and rocks typically contains high concentrations of dissolved Fe<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>; toxic metals such as Cu(II), Pb(II), and Cd(II); and metalloids such as As present as arsenite or arsenate (Cheng et al. 2011). The harmful effects of heavy metals in mine waste have been reported (Zhou et al. 2007). The eluted heavy metals typically combine with fine soil particles that can be subsequently released into the environment (Dalmacija et al. 2011).

Various methods have been used to treat soil polluted by mine-derived metals, including soil stabilization, soil sanitization, thermal extraction, electrokinetic remediation, and bioremediation using microorganisms or plants (Jho et al. 2011). Soil stabilization methods use adsorption and precipitation to reduce the availability and mobility of heavy metals in situ, making it a cost-effective method. Much research has been conducted on the development and use of natural and synthetic materials in search of effective stabilizers, for which zeolite, ferrihydrite, apatite, lime, silicate, and aluminate

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among others have been evaluated (Jho et al. 2011; Liu and Zhao 2013). Materials such as silica and alumina have been shown to interact with heavy metal ions such as Co, Ni, and Zn to increase cementing and improve the efficacy of solidifying or stabilizing treatments (Li et al. 2001).

Environmental applications of silica include use as a carrier, support, and adsorbent (Kibombo et al. 2011). Silica can also sequester a significant amount of carbon, thereby helping remove CO<sub>2</sub> and enhance soil quality (Mullen et al. 2010). Many studies have demonstrated silica extraction from plant materials. Kalapathy et al. (2000) reported that rice hull husk contains about 60 % silica from which they produced a xerogel containing 93 % silica. The economic benefits of using vegetal silica extracted from agricultural byproducts (such as rice hull husk and corn cob) to treat soil are considerable compared to synthetic stabilizers (Park et al. 2003). These byproducts are abundant; to obtain 100 kg of kernels of corn, as much as 18 kg of corn cob is generated (Tsai et al. 2000). This study investigates the use of corn cob silica to reduce the availability and phytotoxicity of As and heavy metals by promoting their stabilization in mining site soil.

## 2 Material and Methods

### 2.1 Preparation and Characterization of Corn Cob Silica

Corn cob silica (CCS) was produced by adapting the method of Kalapathy et al. (2000) to produce silica from rice hull ash. After ashing dried corn cobs, 10 g of ash was added to deionized water, the pH was adjusted to 3, and the solution was stirred for 2 h. The residue was collected using Whatman no. 41 filter paper and stirred in heated 1 M NaOH solution for 1 h. Additional filtration was performed using Whatman no. 41 filter paper; the residue was washed with 100 mL of 100 °C water, cooled to room temperature, and washed three times with 1 M HCl. In the original protocol, this wash is done at pH 7, but pH 10 was used here because it yielded more product, greater surface area (56.5 vs 39.9 m<sup>2</sup>/g), a greater negative charge on the surface (zeta potential of -33.6 vs -23.5 mV), and higher cation exchange capacity (CEC) (132 vs 96 cmol<sup>+</sup>/kg). These properties increase the potential for heavy metal removal compared to CCS extracted at pH 7. Silica gel precipitated within 18 h. The gel form silica was added to 100 mL of

deionized water and centrifuged at 2,500 rpm for 15 min. The supernatant was discarded, and the product washed three times with deionized water. The solution was then dried for 12 h at 80 °C. This process was repeated to produce the final xerogel form of the CCS; 2.6 g CCS was obtained from 10 g of corn cob ash.

Elemental composition of the CCS was determined by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS; JEOL JSM-6400, Tokyo, Japan) with 20 kV accelerating voltage. Surficial composition was determined using X-ray photoelectron spectroscopy (XPS) (ESCALAB 250 XPS System, Thermo Fisher Scientific, UK) conducted at 15 kV and 150 W. Mineralogical analysis was conducted by X-ray diffraction (XRD) (Philips, X'Pert-MRD, Amsterdam, Netherlands) with CuK $\alpha$  radiation. Fourier transform infrared spectroscopy (FTIR) (Perkin-Elmer, Irvine, CA, USA) was used to characterize CCS functional groups. The CCS was mixed with KBr at a ratio of 1:100 and compressed into films for the FTIR analysis.

### 2.2 Soil Characterization and Water-Soluble Pb Analysis

Soil was obtained from a gold mine waste site in Jeongeup Province, Republic of Korea. The soil was mixed, air-dried for 2 days, and passed through a 10 mesh sieve to obtain a particle size <2 mm. Concentrations of Pb, Zn, Cu, and As were 1,134, 405, 54, and 83 mg/kg, respectively. Sieved soil was digested with aqua regia (1:3 v/v concentrated HNO<sub>3</sub>/HCl). Metal and metalloid concentrations were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Teledyne-Leeman Labs, Inc., Hudson, NH, USA). Soil pH was determined with a pH meter after stirring a 1:5 (w/v) slurry of soil and deionized water for 60 min. Electrical conductivity (EC) was determined with an EC meter after stirring a similar mixture for 30 min and filtering through Whatman no. 2 filter paper. Cation exchange capacity (CEC) was determined by the ammonium saturation/displacement method (Brown and Warncke 1988). Organic matter content was determined using the method of Tyurin (1931).

To determine water-soluble Pb, 25 mL of deionized distilled water was mixed with 2 g of soil and shaken for 12 h. The mixture was then centrifuged for 15 min at 3,500 rpm, and Pb in the supernatant was quantified by ICP-AES.

### 2.3 CCS Amendment and Posttreatment Analyses

To assess the physicochemical changes in CCS-amended soil, the soil was sieved to  $<500\ \mu\text{m}$  and CCS added at 0, 1, 3, and 5 % (*w/w*). SEM was used to identify morphological changes in the soil particles after CCS treatment. X-ray fluorescence spectroscopy (XRF) (PANalytical, Axios Minerals, Almelo, Netherlands) was used to determine the elemental composition of the soil, and XRD was used for mineralogical analysis. Changes in soil pH, EC, and CEC after CCS amendment were also determined.

### 2.4 Sequential Extraction

Soil samples were separated into three fractions by dry sieving (250–500, 150–250, and  $<150\ \mu\text{m}$ ) and then amended with CCS (1, 3, and 5 % *w/w*) or were unamended. Soil (1 kg) and CCS were mixed and incubated in an open environment ( $\sim 27\text{--}30\ \text{C}$ ) for 30 days. All treatments were conducted in triplicate; controls consisted of unamended soil fractions. Water lost was replenished with 500 mL of deionized water every 3 days.

The availability of the heavy metals and As was determined by sequential extraction following the method of Tessier et al. (1979). The extractions produced five fractions: F1, the exchangeable fraction removable with 0.5 M  $\text{MgCl}_2$  (pH 7.2); F2, the fraction adsorbed or bound to carbonate removable with 1 M  $\text{CH}_3\text{COONa}$  (pH 5.0); F3, the Fe and Mn oxide-bound fraction removable with 0.04 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  containing 25 %  $\text{CH}_3\text{COOH}$ ; F4, the fraction bound to organic compounds and sulfides removable with a mixture of 0.02 M  $\text{HNO}_3$ , 30 %  $\text{H}_2\text{O}_2$  (pH 2), and 3.3 M  $\text{NH}_4\text{OAc}$  containing 20 %  $\text{HNO}_3$ ; and F5, residual heavy metals removable with a  $\text{HF}/\text{HClO}_4/\text{HNO}_3$  mixture (Agemian and Chau 1975). The Pb, Cu, Zn, and As content of each fraction was determined by ICP-AES after centrifuging at 3,500 rpm for 15 min and filtering the supernatant through a  $0.45\ \mu\text{m}$  glass fiber filter.

### 2.5 Toxicity Characteristic Leaching Procedure Test

The toxicity characteristic leaching procedure (TCLP) was performed to evaluate As and heavy metal leachability. The TCLP is designed to simulate the effect of rainwater infiltrating contaminated soil. For this test, each soil fraction (250–500, 150–250, and  $<150\ \mu\text{m}$ )

was amended with 0, 1, 3, or 5 % (*w/w*) CCS, and water was added at a water-to-soil ratio of 20:1. After incubating for 30 days at room temperature ( $27\text{--}30\ \text{C}$ ), the TCLP was conducted following USEPA Method 1311 (USEPA 1998). Leachates were filtered through  $0.45\ \mu\text{m}$  glass fiber filters and metal concentrations determined by ICP-AES.

### 2.6 Plant Growth

Spinach (*Spinacia oleracea* L.) has been used to study the toxicity of heavy metals to plants (Sinha et al. 2007) and was used here to assess growth, biomass, and chlorophyll content of plants grown in the mining site soil treated with CCS. Seeds were immersed in 70 % ethanol for 5 min, rinsed three times with sterile water, immersed in 1 %  $\text{NaOCl}$  for 30 min, washed with deionized water, and stored at  $4\ \text{C}$  for 3 days to promote uniform germination. The seeds were planted in mining site soil ( $<500\ \mu\text{m}$  particle size) amended with 5 % (*w/w*) CCS and in untreated soil (control). Planted pots were exposed to a light-emitting diode (LED) at  $25\pm 2\ \text{C}$  with an 18:6 h light-dark cycle. Experiments were conducted using a completely randomized design. After 2 weeks, stem and root lengths and weights were determined, and chlorophyll content was measured using a chlorophyll meter (SPAD 502 Plus, Minolta Corp., Ramsey, NJ, USA).

### 2.7 Statistical Analysis

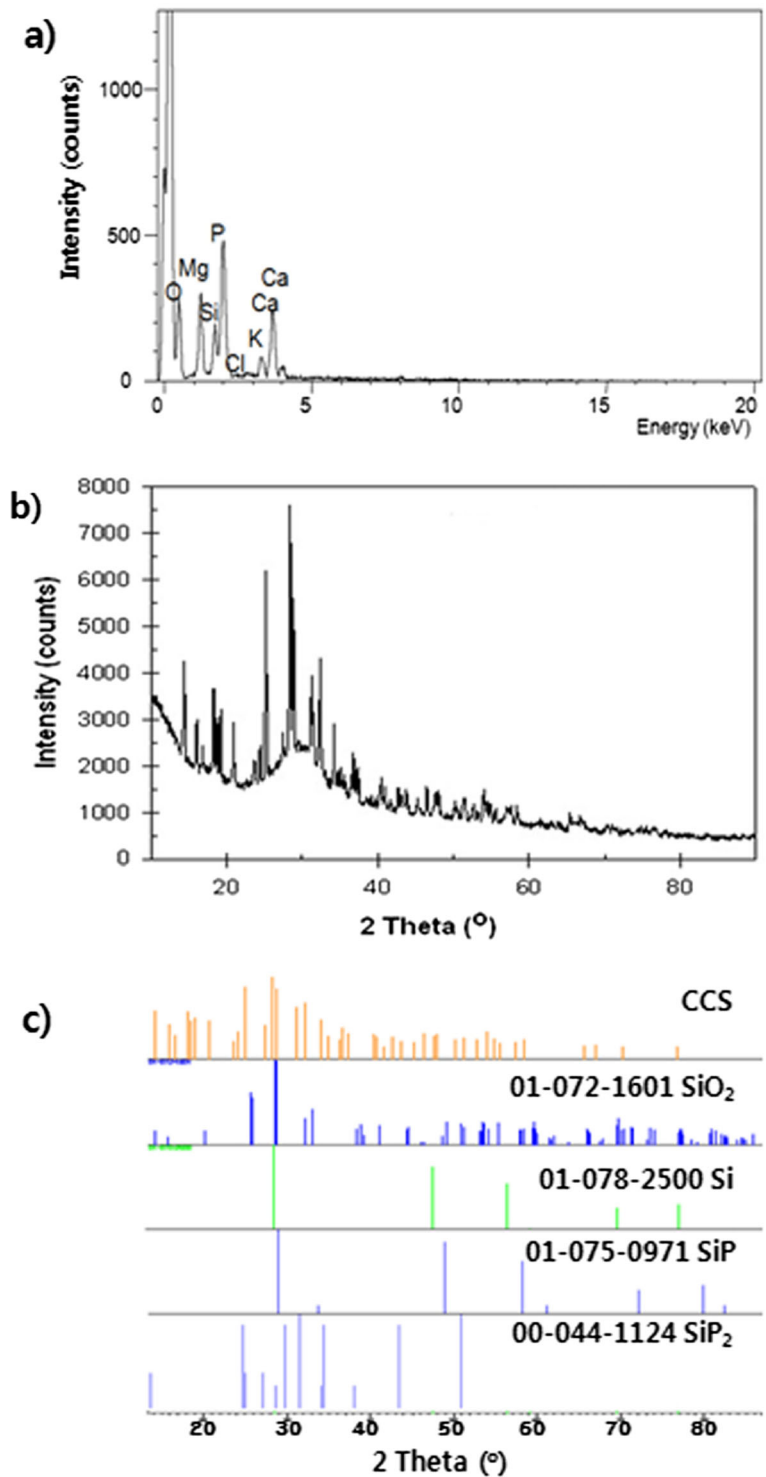
Data were analyzed using a one-way ANOVA, with  $P\leq 0.05$  considered significant (SAS 9.1, Cary, NC, USA). Duncan's multiple range test was used for mean separations.

## 3 Results and Discussion

### 3.1 CCS Characterization

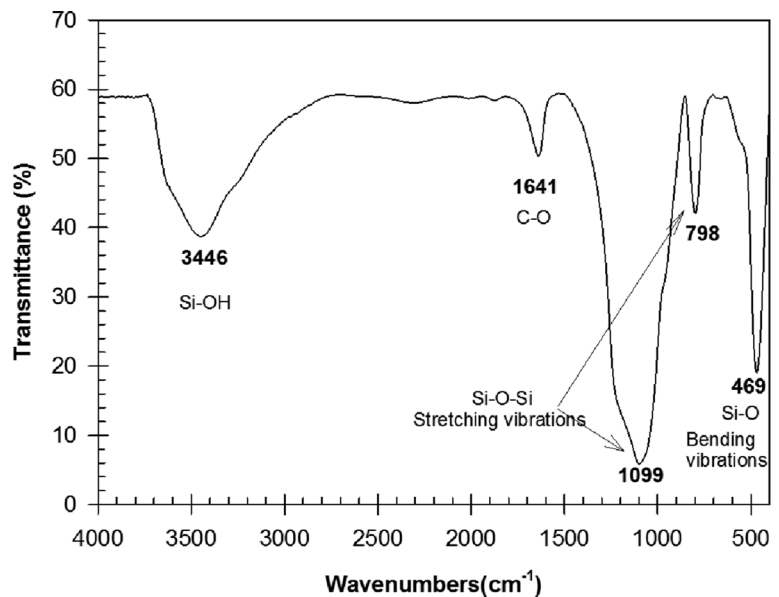
SEM-EDS analysis indicated that the prepared CCS product was primarily composed of Si, P, Mg, Ca, and O (Fig. 1a). XPS revealed a surface consisting mainly of O (55 %) and Si (28 %), with small amounts of C (8.4 %) and Na (6.3 %) that may be due to sample contamination. The XRD pattern showed sharp peaks, characteristic of a largely crystalline material (Fig. 1b). The presence of amorphous silica, silicon dioxide, and silicon phosphide was

**Fig. 1** SEM-EDS (a), XRD patterns (b), and the JCPDS database (c) of the corn cob silica



confirmed in the powder XRD database references 01-078-2500 (Si), 01-072-1601 (SiO<sub>2</sub>), 01-075-0971 (SiP), and 00-044-1124 (SiP<sub>2</sub>) (Fig. 1c). The FTIR spectrum of

the CCS is shown in Fig. 2. Broad infrared bands at 3,427 to 3,636 cm<sup>-1</sup> are from surface Si-OH groups and O-H stretching of adsorbed water. The peak at 3,446 cm<sup>-1</sup> is

**Fig. 2** FTIR spectrum of the corn cob silica

due to deformation of surface hydroxyl groups, while that at  $1,641\text{ cm}^{-1}$  is likely from C=O stretching of organic residue on the CCS surface. Peaks at  $1,099$  and  $798\text{ cm}^{-1}$  correspond to asymmetric stretching of Si-O-Si and Si-O groups, and the peak at  $469\text{ cm}^{-1}$  is due to O-Si-O bending.

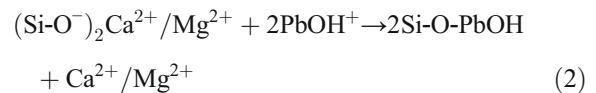
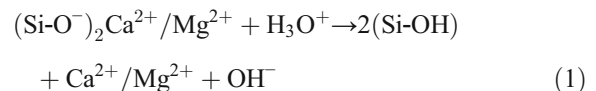
### 3.2 Soil Properties

XRF analysis of treated soil (Table 1) showed that CCS addition resulted in moderate increases in MgO and CaO. The Si added with 5 % CCS was not enough to change the average SiO<sub>2</sub> content of the soil because it is naturally high in silicates. The increase in P<sub>2</sub>O<sub>5</sub> can be attributed to P contained in the CCS ( $78.5 \pm 11.0\text{ mg PO}_4^{3-}/\text{kg}$ ).

Water-soluble Pb decreased from  $47.2 \pm 2.4$  to  $0.9 \pm 0.2\text{ mg/L}$  in particles  $<500\text{ }\mu\text{m}$  in size at 30 days after treatment with 5 % w/w CCS. The XRD pattern (Fig. 3) of highly contaminated soil treated with CCS suggests that lead silicate ( $\text{Pb}_2\text{SiO}_4 + \text{Pb}_4\text{SiO}_6$ ) is the reaction product most closely associated with a decrease in soluble Pb concentration (Moon and Dermatas 2006). Pb (and Zn) can be retained through a Si-O-Pb/Zn bond (Moulin et al. 1999) and lead silicate is very insoluble. Immobilization of Pb can be attributed to a pozzolanic reaction (Dermatas and Meng 2003), resulting in the formation of lead silicate with a concomitant decrease in calcium silicate hydrate and increase in Ca(OH)<sub>2</sub> after treatment with CCS.

Dimitrova (2002) attributed Pb(II) removal in columns packed with granular blast furnace slag to Si-OH

and Si-O<sup>-</sup> groups on the slag. The proposed mechanisms of Pb(II) removal via silica were as follows:

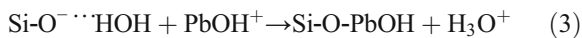
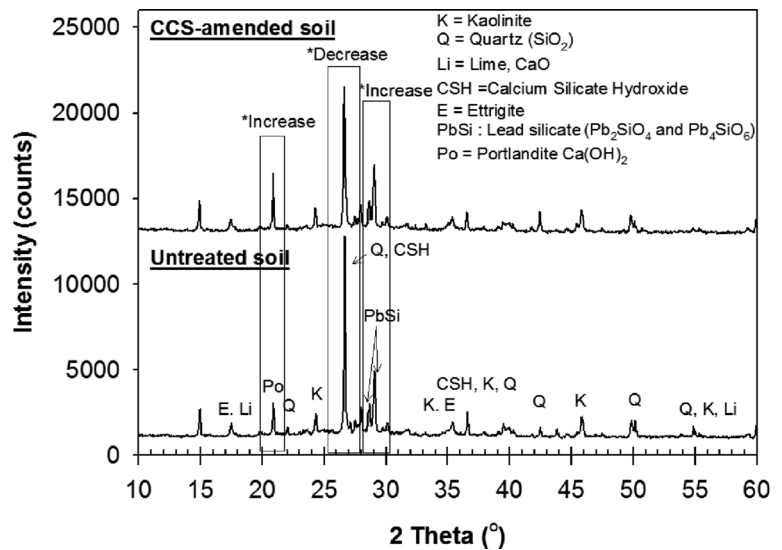
**Table 1** Composition of unamended soil and soil amended with corn cob silica as determined by X-ray fluorescence spectrometry

Component	Unamended soil (%)	Soil amended with 5 % (w/w) CCS (%)
MgO <sup>a</sup>	0.6	2.0
CaO	0.6	0.9
Al <sub>2</sub> O <sub>3</sub>	9.9	9.8
SiO <sub>2</sub>	34.3	33.3
P <sub>2</sub> O <sub>5</sub>	0.1	3.5
SO <sub>3</sub>	14.2	12.8
Fe <sub>2</sub> O <sub>3</sub>	22.9	20.7
CuO	0.8	0.7
ZnO	1.8	1.6
As <sub>2</sub> O <sub>3</sub>	0.4	0.4
PbO	8.3	7.2
LOI	3.3	2.8

LOI loss on ignition (organic carbon and carbonates)

<sup>a</sup> Measured as the oxide

**Fig. 3** XRD patterns of untreated soil and soil amended with corn cob silica after 30 days of moist curing



Physicochemical factors affecting the stability of heavy metals in soil include pH, CEC, and organic content (Naidu and Harter 1998). The properties of unamended and CCS-amended mining site soil are given in Table 2. The soil was acidic (pH 4.0), but pH increased with increasing amounts of added CCS and was highest (7.7) at 5 % w/w CCS. The pH increase likely resulted from the release of  $\text{OH}^-$  from the added silica (Eq. 1) and would reduce heavy metal solubilization and elution from soil (Mallampati et al. 2012). The increase in pH increases the availability of Al and Si to form pozzolanic reaction products (Gougar et al. 1996). In addition, phosphate-induced  $\text{Pb}^{2+}$  immobilization has been shown to reduce Pb leachability via the formation of lead phosphate compounds such as pyromorphite-like phases ( $\text{Pb}_5(\text{PO}_4)_3\text{X}$ , where X=F, Cl, or OH) (Cao et al. 2002; Scheckel and Ryan 2002).

The increase in EC with increasing amounts of added CCS was due to ions associated with silica (Table 2). Because the negative charge in silicates arises from isomorphous substitution of Si(IV) with lower valence cations, the CEC increased by about 5 % after adding CCS.

### 3.3 Binding, Availability, and Mobility of As and Heavy Metals

Metals and metalloids are present in soil as free ions, adsorbed to soil constituents and clay lattice structures; as components of colloids and compounds; or as secondary minerals such as phosphates, sulfides, or carbonates. Sequential extraction can be used to evaluate the binding of metal(loid) ions to soil constituents and as an indicator of their availability in soil solution (Usero et al. 1998). In the present study, unamended and CCS-amended soils were sequentially extracted into five fractions, and concentrations of the heavy metals and As

**Table 2** Physicochemical characteristics of mining site soil with and without added corn cob silica

	Unamended soil	Soil with added silica (% w/w)		
		1	3	5
pH	4.0±0.1	4.3±0.1	6.7±0.4	7.7±0.4
EC (μS/cm)	458.0±31.5	649.7±123.3	546.47±39.8	1,422.32±504.5
CEC (cmol+/kg)	94.5±2.3	94.8±1.8	97.1±2.1	100.3±2.5
Organic matter (%)	0.7±0.1	—	—	—

Mean±standard deviation ( $n=3$ )

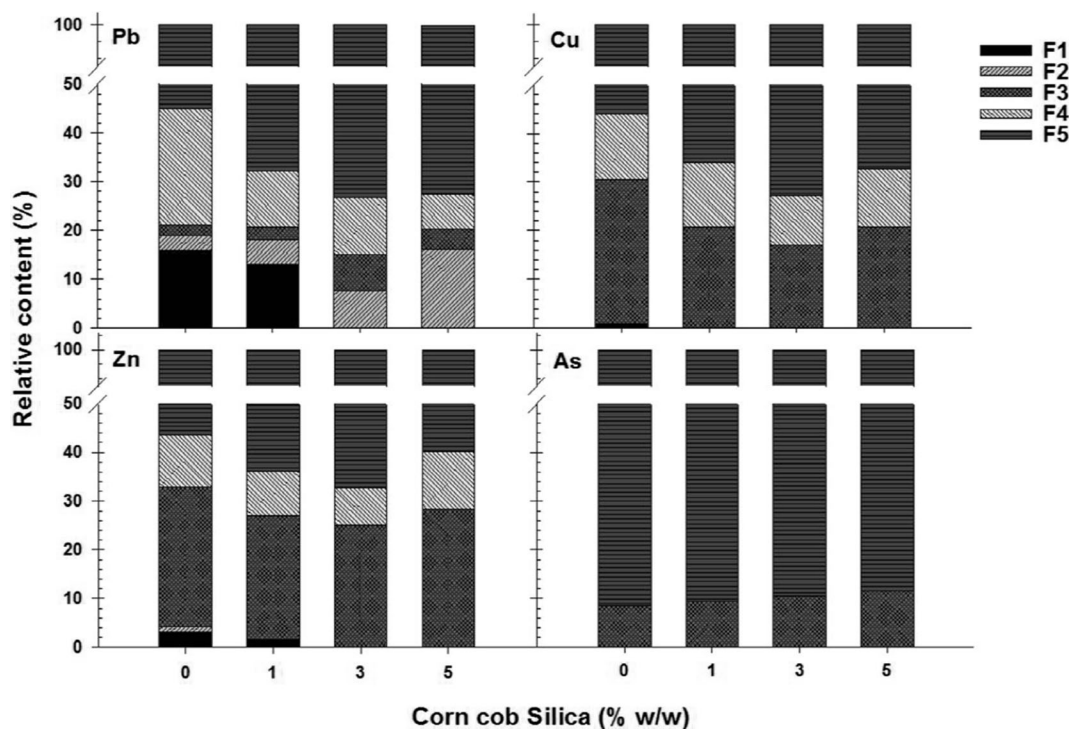


were determined (Fig. 4). About 90 % of the As associated with the 250–500  $\mu\text{m}$  particles was strongly bound (F5, residual fraction), and there was no significant change in the distribution after CCS addition, except for a slight increase in the F3 fraction (As bound to Fe and Mn oxides). Readily exchangeable Pb and Zn (F1) decreased with CCS addition, and none was detected in that fraction after adding 3 % (*w/w*) CCS, while both were increased in the residual fraction. Pb also increased in the F2 (carbonate-bound) fraction. The predominant fractions for Zn and Cu were F3 and F5, which increased with CCS addition up to 3 %. For the 150–250  $\mu\text{m}$  particles, most of the As and Zn were in the residual (F5) fraction regardless of CCS addition (Fig. 5). No exchangeable Zn or Pb (F1) was detected after adding 3 % CCS, and residual Pb and Cu (F5) increased with CCS addition. In particles <150  $\mu\text{m}$ , CCS addition decreased the exchangeable fraction (F1) of Zn and particularly Pb (Fig. 6). CCS addition increased the amounts of Zn, Pb, and Cu in the residual fraction. Metals present in the F3, F4, or F5 fractions are more strongly bound than those in F1 and F2 fractions and would be expected to exhibit low mobility (Lee

et al. 2011). It should be noted that dry sieving leaves some fine soil adhering to larger particles which was included with the larger particle size fractions.

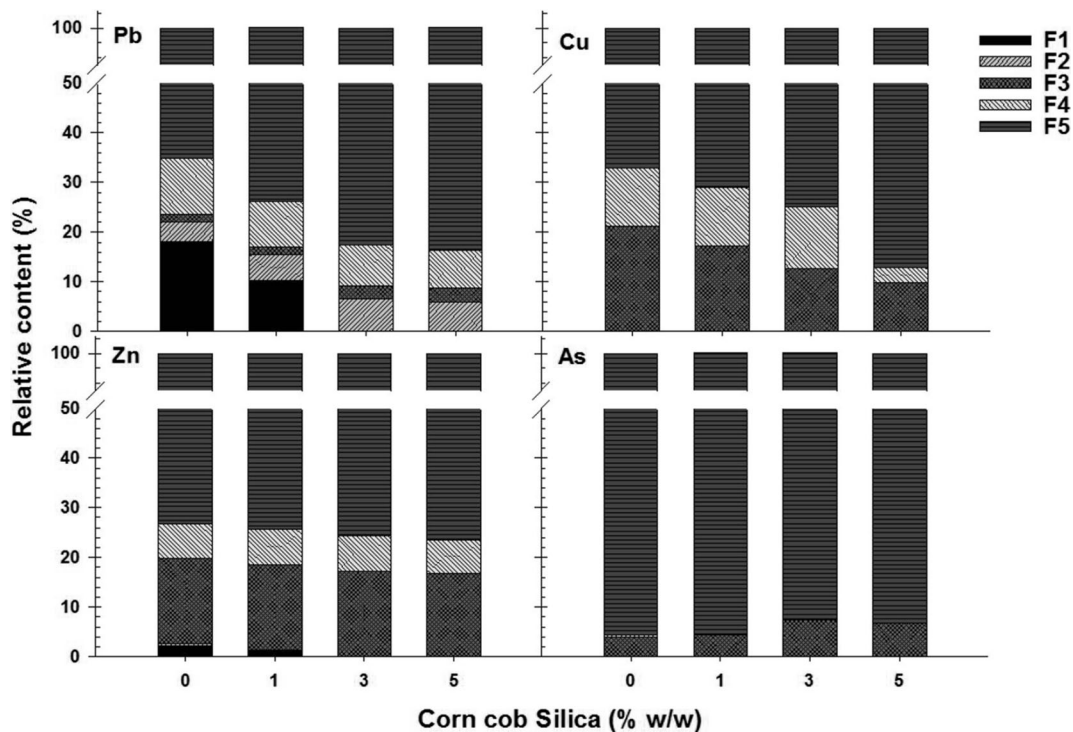
Mobility factor (MF; Narwal et al. 1999; Lee et al. 2011) values for the heavy metals and As are shown in Table 3. MF values for Cu decreased with both decreasing soil particle size and increasing amounts of added CCS, but changes in MF values for Zn were smaller. While MF values indicated greater Pb mobility in the finer fractions of unamended mine soil, the addition of CCS reduced Pb mobility to a greater extent than that of Cu or Zn in all fractions. The MF for As was generally lower than that of the other metals but tended to increase with CCS addition. Because As is typically present as the oxyanions arsenite ( $\text{AsO}_3^{3-}$ ) and arsenate ( $\text{AsO}_4^{3-}$ ), it would have low affinity for the negatively charged surfaces on CCS.

The TCLP, which simulates the result of infiltrating rainwater, was also used to assess the effectiveness of CCS as a stabilizer of the heavy metals and As in mining site soil (Fig. 7). TCLP concentrations of Pb exceeded the USEPA toxicity characteristic threshold limit value



**Fig. 4** Heavy metal and As contents of the soil 32-mesh (250–500  $\mu\text{m}$ ) fraction of unamended mining site soil and soil amended with increasing amounts of corn cob silica (F1 = exchangeable,

F2 = carbonate-bound, F3 = Fe and Mn oxide-bound, F4 = organic matter- and sulfur-bound, and F5 = residual Pb fraction)



**Fig. 5** Heavy metal and As contents of the 60-mesh (150–250  $\mu\text{m}$ ) fraction of unamended mining site soil and soil amended with increasing amounts of corn cob silica (F1 = exchangeable, F2

= carbonate-bound, F3 = Fe and Mn oxide-bound, F4 = organic matter- and sulfur-bound, and F5 = residual Pb fraction)

(TLV) for Pb (5 mg/L; USEPA 1998) for unamended soil and in soil amended with 1 % (w/w) CCS. Without CCS, TCLP leaching of Pb was greatest for the <150  $\mu\text{m}$  fraction, but Pb concentrations from all fractions were greatly decreased after adding 3 % (w/w) CCS and were below the TLV. Adding CCS similarly reduced Zn concentrations in leachate. CCS addition did not impact Cu concentrations in leachate, likely because concentrations were much lower than those of the other metals. In contrast, As concentrations in leachate increased with CCS additions >1 % (w/w) and exceeded the TLV (5 mg/L) in soil containing 5 % (w/w) CCS. These results are consistent with the observed increase in MF for As with added CCS, as determined from sequential extractions (Table 3).

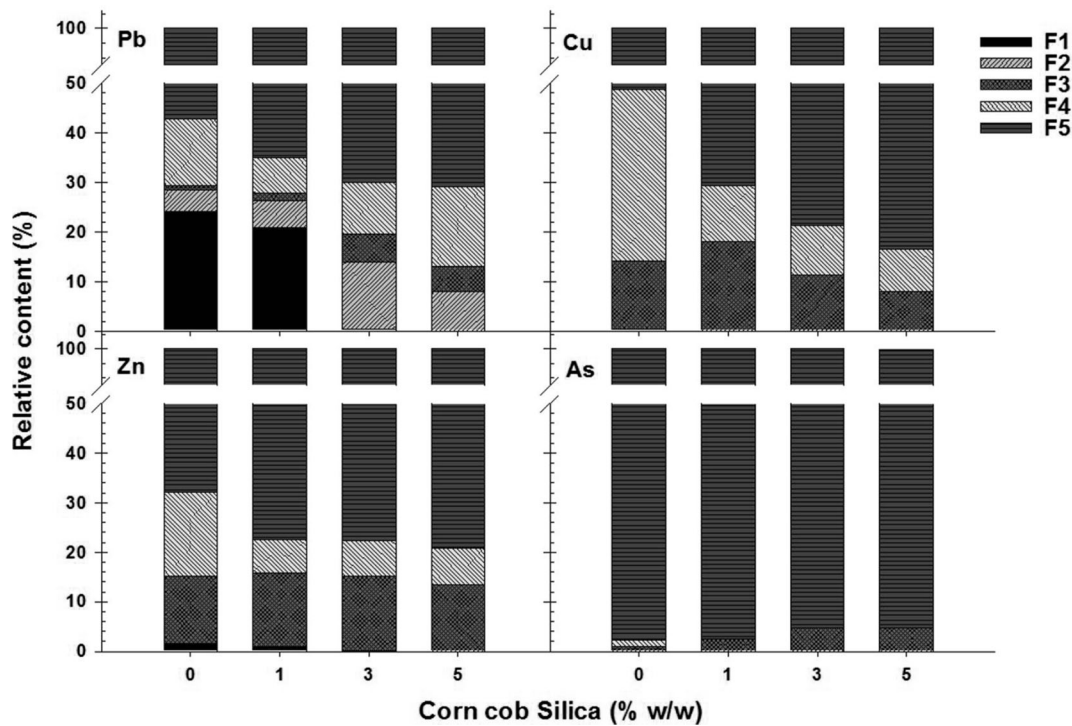
### 3.4 *S. oleracea* Growth

Heavy metal toxicity in soil is more related to concentrations of free metal ions rather than total heavy metal content (Pampura et al. 2007). Metals in the F1, F2, and F3 fractions are more mobile than metals in the F4 and

F5 fractions (Olajire et al. 2003) and can be taken up by plants (Kennedy et al. 1997). Song et al. (2009) suggested that silica deposited around plant stems and roots reduces Cd(II) toxicity by decreasing mobilization and plant uptake. In the present study, As and heavy metals reduced *S. oleracea* growth, but growth was greatly improved by adding CCS to the soil (Table 4). In soil amended with 5 % (w/w) CCS, stem and root lengths increased by 233 and 310 %, respectively, while stem and root biomass increased by 125 and 453 %, compared to those of plants grown in untreated soil. Chlorophyll content was also much higher in plants grown in CCS-treated soil (Table 4).

Adding Si to soil contaminated with heavy metals can reduce toxicity by decreasing their phytoavailability and subsequent accumulation in plants (Gu et al. 2011; Rizwan et al. 2012; Ye et al. 2012). In the present study, CCS reduced heavy metal toxicity to *S. oleracea* growing in mining site soil. The observed increase in soil pH after adding CCS promotes the adsorption of metallic cations, reducing phytoavailability. The CCS further reduces toxicity through the formation of metal-silicate precipitates, as previously reported for Si-amended soil





**Fig. 6** Heavy metal and As contents of the soil 100-mesh (<150 μm) fraction of unamended mining site soil and soil amended with increasing amounts of corn cob silica

(F1 = exchangeable, F2 = carbonate-bound, F3 = Fe and Mn oxide-bound, F4 = organic matter- and sulfur-bound, and F5 = residual Pb fraction)

(Gu et al. 2011). In addition, P contained in the CCS likely promoted plant growth. Our results with CCS are consistent with research showing that silica can mitigate toxicity in heavy metal-contaminated soil and enhance

the growth of plants such as *Oryza sativa* L., *Brassica chinensis*, *Triticum turgidum* L. cv. Claudio W., and *Kandelia obovata* (S., L.) Yong (Song et al. 2009; Gu et al. 2011; Ye et al. 2012).

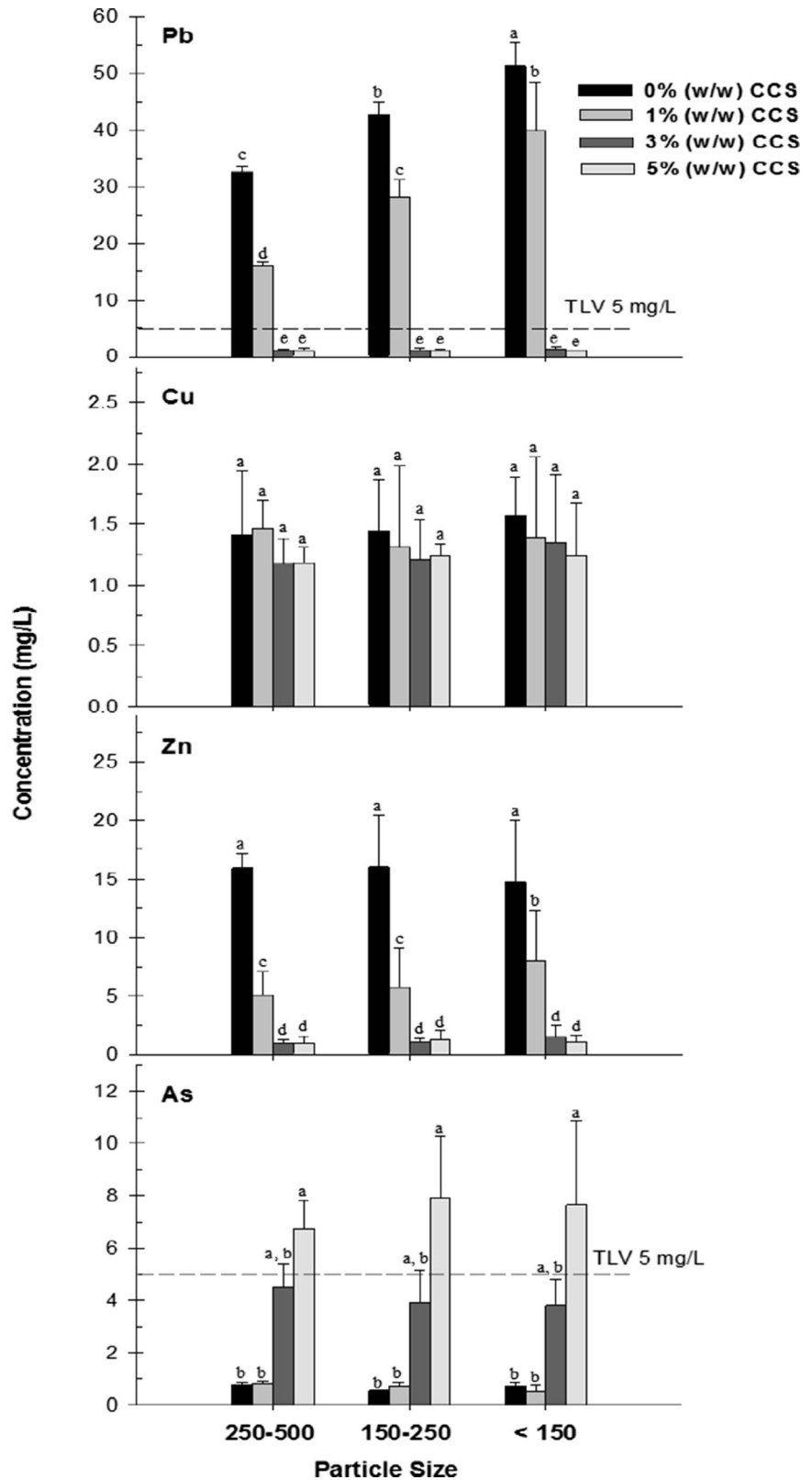
**Table 3** Mobility factors (MF) for heavy metals and As in soil fractions treated with increasing amounts of added corn cob silica

Soil fraction (particle size, μm)	Added silica (% w/w)	Mobility factor <sup>a</sup> (%)			
		Pb	Cu	Zn	As
250–500	0	18.1c	30.3a	31.7a	8.6c
	1	15.8d	20.7d	15.8de	9.4c
	3	7.3e	17.0cd	25.0d	10.6b
	5	4.1fg	15.5cde	24.1d	11.7a
150–250	0	19.7c	21.1d	19.5c	4.0d
	1	14.7d	17.2cd	19.5c	4.5e
	3	2.7g	12.8efg	17.3cd	7.4d
	5	3.0g	9.8gh	16.7cde	6.9d
<150	0	25.1a	14.1def	15.2de	1.1g
	1	22.4b	18.0cd	15.8de	2.3f
	3	6.0ef	11.4fgh	14.9de	4.7e
	5	5.1efg	8.1h	13.3e	4.7e

Means for a metal(loid) followed by the same letter(s) are not significantly different as determined by Duncan's multiple range test ( $P < 0.05$ ,  $n = 3$ )

$$^a\text{MF} = \frac{(F1 + F2)}{(F1 + F2 + F3 + F4 + F5)} \times 100$$

**Fig. 7** Toxicity characteristic leaching procedure (TCLP) leachate concentrations for heavy metals and As at 30 days after adding 0, 1, 3, or 5 % (w/w) corn cob silica to mining site soil fractions. Note differences in scaling. Error bars indicate standard deviations; values for each metal(-loid) with the same letter are not significantly different as determined by Duncan's multiple range test ( $P < 0.05$ ,  $n = 3$ ). Dashed lines indicate the USEPA threshold limit value (TLV). TLVs are not available for Cu or Zn



**Table 4** Growth and chlorophyll content of *Spinacia oleracea* L. grown in unamended mining site soil and in soil amended with 5 % (w/w) corn cob silica

Length (mm)		Weight (mg)		Chlorophyll (µg/L)
Shoot	Root	Shoot	Root	
Without added silica				
16.9±4.36a	9.36±14.5a	1.54±0.12a	0.53±0.02a	1.99±1.59a
With added silica				
39.3±6.74b	28.9±13.2b	1.93±0.18b	2.4±0.35b	6.64±1.68b

Mean±standard deviation. Means within a column followed by the same letter are not significantly different as determined by Duncan's multiple range test ( $P < 0.05$ ,  $n = 9$ )

#### 4 Conclusions

Treating heavy metal-contaminated mining site soil with CCS reduced the availability and phytotoxicity of the metals. XRD data indicated the formation of insoluble lead silicate. Adding CCS also increased soil pH, which further promoted binding of the heavy metals in the soil. CCS treatment improved the growth of spinach in contaminated soil, greatly increasing stem, root lengths, and biomass. Results demonstrate the utility of CCS to promote stabilization and to reduce the mobility and leachability of heavy metals in soil, but this treatment may not be ideal for As-contaminated soils. Additional studies on the mechanisms associated with heavy metal stabilization and long-term monitoring for changes in availability would be valuable.

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