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Immobilisation of Cu, Pb and Zn in Scrap Metal Yard Soil Using Selected Waste Materials

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Abstract Immobilisation of heavy metals in a 30-year old active scrap metal yard soil using three waste materials, namely coconut tree sawdust (CTS), sugarcane bagasse (SB) and eggshell (ES) was investigated. The contaminated soil was amended with amendments at application rates of 0 %, 1 % and 3 % (w/w). The effects of amendments on metal accumulation in water spinach (*Ipomoea aquatica*) and soil metal bioavailability were studied in a pot experiment. All amendments increased biomass yield and reduced metal accumulation in the plant shoots. The bioconcentration factor and translocation factor values of the metals were in the order of Zn > Cu > Pb. The addition of ES, an alternative source of calcium carbonate ($CaCO_3$), has significantly increased soil pH and resulted in marked reduction in soil metal bioavailability. Therefore, CTS, SB and ES are promising low-cost immobilising agents to restore metal contaminated land.

Keywords Contaminated soil · Heavy metals · Immobilisation · Waste materials · Metal uptake · Bioavailability

Rapid global industrialisation has released tremendous amount of heavy metals into the soil environment. Mining and smelting activities are the two leading sources of heavy metal contamination in soil (Zhou et al. 2014). Contribution from recycling facilities and scrap metal yards is also important in this context. For example, Jensen et al. (2009) measured 3000 mg/kg of Zn, 1000 mg/kg of Cu, 500 mg/kg of Pb and 15 mg/kg of Cd in the surface soil of Copenhagen Recycling Center, Denmark. Meanwhile, Cui et al. (2004) reported that the surface soil near a battery recycling centre in Anhui, China contained 31,000 mg/kg of Pb and 480 mg/kg of Zn. In the United States, a number of scrap metal yards have released a significant amount of heavy metals and highly toxic polychlorinated biphenyls into the soil and groundwater environment (Ferber and Grimski 2002).

Heavy metals are not biodegradable and therefore they are extremely persistent in the environment. They can be transferred from both terrestrial and aquatic resources into the food chain through uptake by plants (Kabata-Pendias 2011). Cu, Fe, Mn, Mo and Zn are classified as essential elements for plant growth, meanwhile Cd, Cr, Ni and Pb are non-essential elements and toxic even at low concentrations. High intake of Pb can cause brain disorders in children, anemia and kidney malfunction in adults (Parry 2009). Although essential elements are vital for plant metabolic health, they can be toxic at high concentrations (Kabata-Pendias 2011).

Immobilisation technique has been regarded as an eco-friendly and economically feasible remediation strategy (Yu et al. 2014). It converts contaminants from their original form to a physically and chemically more stable form, reducing the mobility, solubility, bioavailability and toxicity of heavy metals in soil (Kabata-Pendias 2011). The utilisation of waste-based materials as soil amendments has drawn several advantages such as abundant, renewable and environmental friendly.

Currently, little attention is given to the restoration effort of scrap metal yard soils. Most reports focus on remediation of soil affected by mining and smelting

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activities. In addition, little is known about exact binding mechanism(s) involved in the immobilisation process. Most researchers discussed the success of immobilisation process based on theoretical assumptions without using scientific instruments (Zhou et al. 2014; Hu et al. 2014). Therefore, energy dispersive X-ray (EDX) and fourier transform infrared (FTIR) analyses were performed to characterise soil amendments following pot experiment.

The overall aim of this study was to evaluate the effectiveness of coconut tree sawdust (CTS), sugarcane bagasse (SB) and eggshell (ES) as immobilising agents for the remediation of metal contaminated soil. Coconut tree sawdust, sugarcane bagasse and eggshell are readily available in large quantities in Malaysia. In this study, water spinach was used as an indicator to determine the efficacy of amendments to immobilise heavy metals in a scrap metal yard soil.

Materials and Methods

Soil samples (0–25 cm) were collected at 10 sampling points of a 30-year old active scrap metal yard in Selangor, Malaysia. The soil samples were transported to laboratory, air-dried, crushed and passed through a 2-mm mesh sieve. The soil pH was measured in deionised water with a soil:solution ratio of 1:2.5 using a pH meter. The electrical conductivity (EC) of soil was measured in soil and water suspension at a ratio of 1:5 (w/v) using an EC meter. The soil organic matter (OM) was determined using the Nelson-Sommers method (Nelson and Sommers 1996), while the cation exchange capacity (CEC) was determined using the ammonium-saturation and distillation method (Sumner and Miller 1996). The pipetting method described by Gee and Bauder (1986) was applied for soil textural analysis. Aqua regia extraction was used to measure the total fraction of Cu, Pb and Zn in the soil. The bioavailable fraction of metals in the soil was determined using ammonium acetate (1.0 mol/L, pH 7) at a soil:extractant ratio of 1:10.

CTS was obtained from Jati Cemerlang Sawmill, Selangor, meanwhile SB and ES were supplied by My Rasa Restaurant, Selangor. Amendments were rinsed with deionised water, dried in an oven and ground using a laboratory jar mill. Amendments were then digested separately in hot concentrated HNO_3 acid. CTS contained 9 mg/kg of Cu and 13 mg/kg of Zn, meanwhile 14 mg/kg of Cu and 22 mg/kg of Zn were measured for SB. ES contained 8 mg/kg of Cu and 35 mg/kg of Zn. Pb was not detected in CTS, SB and ES.

The amendments were added separately to the contaminated soils at three rates of application, namely control, 1 % and 3 % (w/w), in six replicates. After 2 weeks of equilibration, the water spinach seed was then sown in each pot (12.0 cm height and 14.0 cm diameter). The pots were arranged in a randomised block design. The pots were watered daily with deionised water and plants were allowed to grow under natural lighting and temperature. Mean daily temperature and humidity were monitored with a digital thermometer.

The plants were harvested at 8 weeks of growth. The plant shoots and roots were carefully cut and rinsed with deionised water to avoid contamination by soil particles. The cleaned shoots and roots were then cut into small pieces and dried in an oven. The dried plant tissues were weighed, ground using a laboratory jar mill, ashed at 450°C in a muffle furnace and digested in hot concentrated HNO_3 acid. At the end of the pot experiment, the soil pH and ammonium acetate (NH_4OAc) extractable metal content in the soil were determined, as previously described. The concentration of heavy metals in the plant digests and soil extracts were measured using a Perkin-Elmer AAnalyst 400 atomic absorption spectrometer (AAS). The estimated detection limits (mg/L) were 0.11 (Cu), 0.57 (Pb) and 0.17 (Zn), respectively, while the quantification limits (mg/L) were 1.92 (Cu), 0.45 (Pb) and 0.56 (Zn).

The ability of water spinach to accumulate metal in the shoot tissues was further evaluated using BCF. BCF refers to the ratio of metal concentration in plant shoots to metal concentration in soil (Kabata-Pendias 2011). The ability of a plant to translocate metals from the root to the shoot tissues was assessed using TF. TF is defined as the ratio of the metal concentration in shoots to metal concentration in roots (Kabata-Pendias 2011). The effects of amendment treatments on BCF and TF values of the metals are given in Table 1.

Standard reference plant materials (SRM 1573a Tomato Leaves – NIST USA and SRM 1575 Pine Needles – NBS USA) and certified reference soil material (LGC 6135 Hackney Brick Works Soil – LGC UK) were used to verify the accuracy of metal determination. Reference materials were treated and analysed using the same procedures applied for plant tissue and soil samples. The recovery rates were within 86 %–98 % for plant tissue and 88 %–103 % for soil, respectively.

Elemental analysis was performed using a Hitachi SU 8020 UHR Field Emission Scanning Electron Microscope equipped with a Horiba Energy Dispersive X-ray Spectrometer. The amendments were first coated with platinum using an Automatic Platinum Sputter Coater System (Quorum Q150RS). Infrared analysis was conducted on a Thermo Nicolet 6700 FTIR Spectrometer using KBr disc technique. The IR spectrum was recorded in the wavenumber range from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} over 30 cumulative scans.

The statistical analyses were performed using Minitab Software 17 (Minitab Inc., USA). General linear model of

Table 1 BCF and TF values for Cu, Pb and Zn following amendment treatments

Treatment	Cu	Pb	Zn
BCF values			
Control	0.185[a]	0.087[a]	1.173[a]
CTS 1 %	0.128[a]	0.065[b]	0.857[b]
CTS 3 %	0.095[b]	0.058[b,c]	0.760[b]
SB 1 %	0.077[b]	0.076[a]	0.539[c]
SB 3 %	0.065[b]	0.050[a,b]	0.464[c,d]
ES 1 %	0.040[b,c]	0.036[c]	0.403[d]
ES 3 %	0.032[c]	0.024[c]	0.355[d]
TF values			
Contol	0.170[a]	0.114[a]	2.125[a]
CTS 1 %	0.158[a]	0.073[b]	1.602[b]
CTS 3 %	0.102[b]	0.060[b,c]	1.589[b]
SB 1 %	0.097[b]	0.091[a]	1.316[c]
SB 3 %	0.081[b]	0.085[a,b]	1.294[c]
ES 1 %	0.057[b,c]	0.030[c]	1.226[d]
ES 3 %	0.040[c]	0.022[c]	1.073[d]

Different letters indicate significant statistical differences (Tukey's test at $p < 0.05$)

one-way analysis of variance (ANOVA) was used to analyse the experimental data. The least significant different (LSD) for the comparison of means was verified using Tukey's test at a significance level of $p = 0.05$, while correlation was determined by Pearson's coefficients at $p < 0.05$.

Results and Discussion

The scrap metal yard soil had a pH value of 5.62, EC of 2.41 dS/m, OM of 1.83 % and CEC of 10.07 $cmol_c$/kg. The soil contained 24.70 % of gravel, 55.84 % of sand, and 19.46 % of silt and clay. The total fraction of metals was determined as: Cu = 372, Pb = 816 and Zn = 2273 mg/kg, meanwhile the bioavailable fraction of metals was measured as: Cu = 119, Pb = 357 and Zn = 1080 mg/kg.

The water spinach seeds germinated 5 days after sowing. A significant difference in plant growth was observed at 3 weeks of the pot experiment. Soil that received amendment treatment produced plants with a healthier appearance of leaves (bigger and greener) as compared to plants grown on controls. In addition, plants grown on treated soil exhibited a better growth progress than control plants.

As expected, addition of amendments to contaminated soil increased biomass yield of water spinach. The shoot and root yields increased with the rates of amendment application. SB treatment at 3 % (w/w) has resulted in a pronounced effect, of which the shoot yield for this treatment was found to be higher than control by a factor of 3.2. The least production effect was obtained for ES 1 % (w/w), whereby the root yield for this treatment showed no great difference with root yield of control plants. The order of treatment efficiency on biomass production (total shoot and root) was SB 3 % > CTS 3 % > ES 3 % > SB 1 % > CTS 1 % > ES 1 % > control. This trend is closely related to the organic matter content in the amendments: SB (85.3 %), CTS (62.9 %) and ES (22.4 %), respectively.

The three amendments studied were beneficial as growing media through improvement of soil moisture and fertility. Amending contaminated soil with SB, CTS and ES has increased the water holding capacity of the soil by 72 %, 55 % and 29 %, respectively. The increase in biomass yield could be also related to the decrease in metal bioavailability, reducing toxicity effects to plants. The importance of increasing biomass yield as a result of adding amendments to contaminated soil was stressed by Hu et al. (2014).

The concentrations of Cu, Pb and Zn in the shoot tissues after 8 weeks of pot experiment are presented in Fig. 1. Amending contaminated soil with amendments reduced metal concentrations in the shoot tissues of water spinach. The shoot metal concentrations decreased with the rates of amendments application. Marked reductions in metal uptake were achieved following ES application at 3 % (w/w).

Amendment treatment reduced Cu, Pb and Zn uptake by water spinach. For example, the application of ES, SB and CTS at 3 % (w/w) has successfully reduced the BCF value of Zn from 1.173 (control) to 0.760, 0.464 and 0.355, respectively. Meanwhile, the TF value of Zn decreased from 2.125 (control) to 1.589, 1.294 and 1.073 following ES, SB and CTS application at 3 % (w/w). Overall, ES 3 % (w/w) treatment exhibited the best immobilisation effect in reducing Cu, Pb and Zn accumulation and translocation in the water spinach shoots.

From Table 1, it is clear that Zn was the metal most accumulated and transported from the roots to the shoots. Both Zn and Cu are essential micronutrients for plant growth. They are major components for several electron transport enzymes and involved in catalysing the redox reaction in mitochondria and chloroplasts (Yu et al. 2014). Low translocation of Pb might be due to its toxic effect to plants. Kanwal et al. (2014) discussed the toxic effects of Pb on chlorophyll synthesis, photosynthetic activity and antioxidant enzymes.

The bioavailable fraction is defined as mobile fraction of contaminants that are readily available for the uptake by plants (Kabata-Pendias 2011). The bioavailability of Cu, Pb and Zn in soil after 8 weeks of pot experiment is shown in Fig. 2. The application of amendments reduced the ammonium extractable metals in soil. For example, the bioavailability of Zn was reduced by 74.5 %, 56.2 % and

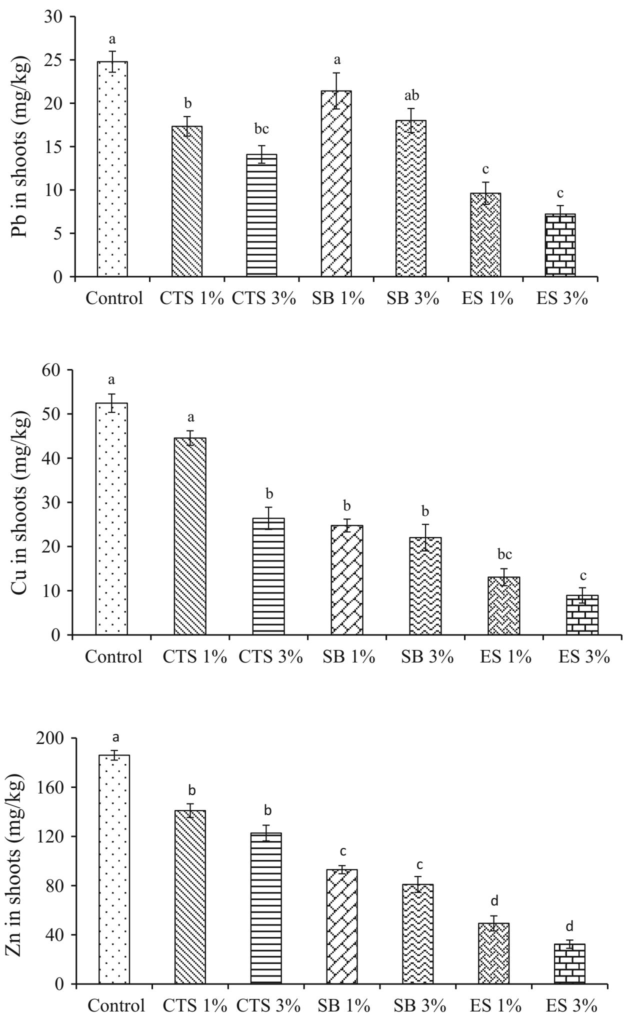

Fig. 1 Metal concentration in water spinach shoots after 8 weeks of growth. Values represent mean of 18 replicates ± standard deviation. *Different letters* indicate significant statistical differences (Tukey's test at $p < 0.05$)

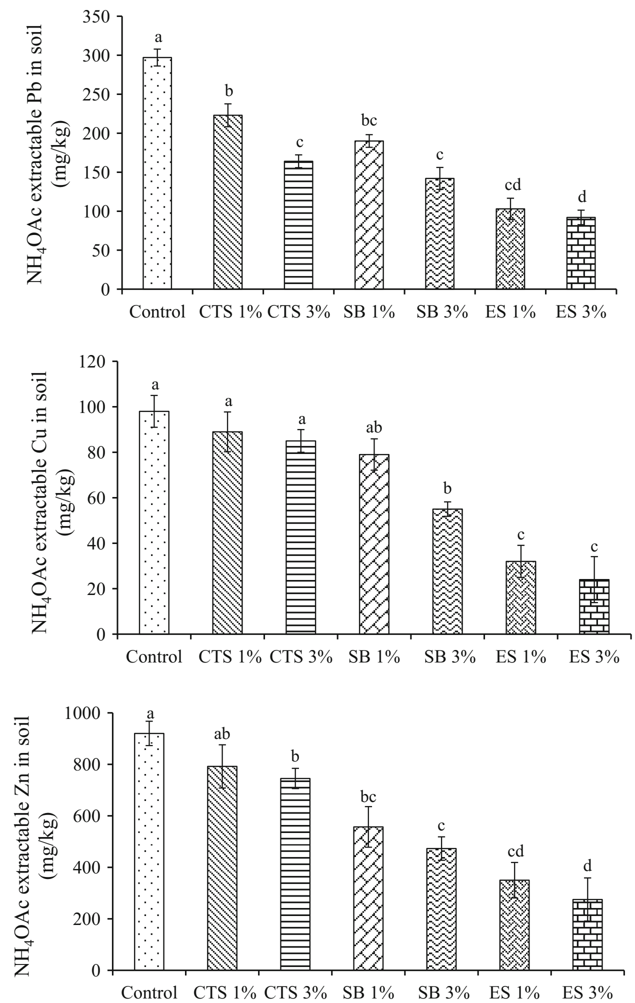

Fig. 2 Ammonium acetate extractable metals in soil after 8 weeks of pot experiment. Values represent mean of 18 replicates ± standard deviation. *Different letters* indicate significant statistical differences (Tukey's test at $p < 0.05$)

31.0 % following ES 3 %, SB 3 % and CTS 3 % (w/w) treatments, respectively.

The effectiveness of the immobilisation strategy is greatly influenced by soil pH (Zhou et al. 2014). The soil pH increased significantly from 5.62 to 8.06 and 8.22 following ES treatment at 1 % and 3 % (w/w), respectively. Addition of SB and CTS, however, increased the soil pH by 0.3–0.5 units. The findings suggest that eggshell can be used as an alternative to commercial $CaCO_3$ for lowering the bioavailability and mobility of metals in soil.

Correlations between metal concentrations in soil and metal concentrations in plant tissues were examined using two extractants, namely EDTA and ammonium acetate (data not shown). Significant correlations (Pearson's coefficients, $p < 0.05$) between metal concentrations in soil and metal concentration in plant tissues were obtained for ammonium acetate. In contrast, EDTA extraction has resulted in poor correlations. EDTA is an excellent extractant especially for metal associated with organic matter. Therefore the metals measured following EDTA extraction may not be available for uptake by plants, reducing correlations of metal concentrations in soil–plant tissues.

The EDX spectrum of eggshell after 8 weeks of pot experiment is presented in Fig. 3a, as an example. Carbon, oxygen and calcium are the major constituents in eggshell and their features can be observed at 0.277, 0.523 and 3.691 keV, respectively. The features observed at 2.05 and 9.44 keV correspond to platinum. As described earlier, the amendments were coated with platinum prior to analysis to avoid electron charging. Following pot experiment, the Zn features were observed at 1.01 and 8.37 keV confirming the ability of ES to immobilise Zn in contaminated soil.

The FTIR spectra of eggshell before and after pot experiment are shown in Fig. 3b, as an example. The

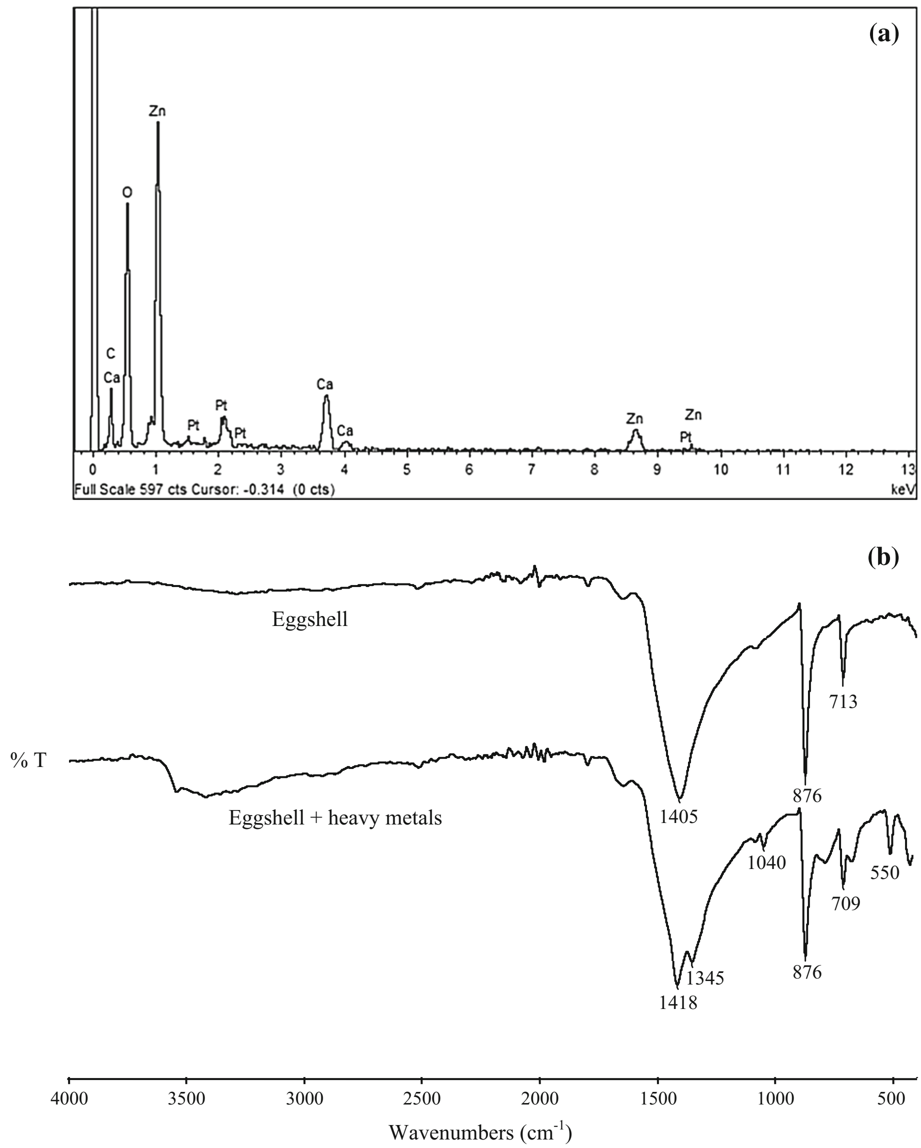

Fig. 3 EDX spectrum (**a**) and FTIR spectra (**b**) of ES before and after 8 weeks of pot experiment

absorption bands observed at 1405, 876 and 713 cm^{-1} are characteristics of carbonate (CO_3^{2-}) (Nakamoto, 2009). Following interaction with heavy metals the absorption band at 1404 cm^{-1} split to two bands, namely 1418 and 1345 cm^{-1}. In addition, the appearance of new shoulder bands at 1040, 876, 709 and 550 cm^{-1} was observed. Presumably, the formation of new absorption bands can be related to complexation between heavy metals and functional groups of amendments.

It may be concluded from the present investigation that application of ES, SB and CTS had successfully break the pollutant linkage: pollutant (heavy metal) – pathway (soil) – receptor (plant), and therefore reduced the toxicity of heavy metals and health risks to human. Results from EDX and FTIR analyses highlight the key properties of the amendments: (1) the presence of functional groups, and (2) the ability to bind heavy metals. Pot experiment however is only one aspect of such evaluation. It is imperative to assess the efficacy of amendments to immobilise heavy metals in situ. It has been hypothesised that the degradation of amendments may release previously bound metals (Kabata-Pendias 2011; Hu et al. 2014). Therefore, it is important to study the biodegradation profiles of the three waste materials studied in metal contaminated soil. We are currently investigating the efficacy of amendments to immobilise heavy metals in situ.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical Statement The authors declare that they have performed experiments that comply with the current laws of Malaysia.

References

Cui Y, Wang Q, Dong Y, Li H, Christie P (2004) Enhanced uptake of soil Pb and Zn by Indian mustard and winter wheat following combined soil application of elemental sulphur and EDTA. Plant Soil 261:181–188

Ferber U, Grimski D (2002) Brownfields and redevelopment of urban areas. Report from the Contaminated Land Rehabilitation Network for Environmental Technologies

Gee G, Bauder JW (1986) Particle size analysis. In: Klute A (ed) Methods of soil analysis. Part I. Physical and mineralogical methods. American Society of Agronomy, Madison, pp 383–411

Hu X, Yuan X, Dong L (2014) Coal fly ash and straw immobilize Cu, Cd and Zn from mining wasteland. Environ Chem Lett 12:289–295

Jensen JK, Holm PE, Nejrup J, Larsen MB, Borggaard OK (2009) The potential of willow for remediation of heavy metal polluted calcareous urban soils. Environ Pollut 157:931–937

Kabata-Pendias A (2011) Trace elements in soils and plants, 4th edn. CRC Press, Boca Raton

Kanwal U, Ali S, Shakoor MB, Farid M, Hussain S, Yasmeen T, Adrees M, Bharwana SA, Abbas F (2014) EDTA ameliorates phytoextraction of lead and plant growth by reducing morphological and biochemical injuries in *Brassica napus* L. under lead stress. Environ Sci Pollut Res 21:9899–9910

Nakamoto K (2009) Infrared and Raman spectra of inorganic and coordination compounds. Part B: applications in coordination, organometallic, and bioinorganic chemistry. Wiley, New York

Nelson DW, Sommers LE (1996) Nitrogen-total. In: Sparks DL (ed) Method of soil analysis: chemical methods. American Society of Agronomy, Madison, pp 1201–1229

Parry J (2009) Hundreds of Chinese children are left poisoned as metal smelting plants are ordered to close. BMJ 339:475

Sumner ME, Miller WP (1996) Cation exchange capacity and exchange coefficients. In: Sparks DL (ed) Method of soil analysis: chemical methods. American Society of Agronomy, Madison, pp 1031–1075

Yu XZ, Wang DQ, Zhang XH (2014) Chelator-induced phytoextraction of zinc and copper by rice seedlings. Ecotoxicol 23:749–756

Zhou H, Zhou X, Zeng M, Liao BH, Liu L, Yang WT, Wu YM, Qiu QY, Wang YJ (2014) Effects of combined amendments on heavy metal accumulation in rice (*Oryza sativa* L.) planted on contaminated paddy soil. Ecotoxicol Environ Saf 101:226–232