Immobilization of cadmium and lead in contaminated paddy field using inorganic and organic additives

Yasir Hamid1, Lin Tang1, Xiaozi Wang1, Bilal Hussain1, Muhammad Yaseen2, Muhammad Zahir Aziz2 & Xiaoe Yang1

Heavy metal contamination of agricultural soils has posed a risk to environment and human health. The present study was conducted to assess the effectiveness of soil amendments for reducing cadmium (Cd) and lead (Pb) uptake by rice (Oryza sativa L) in a contaminated field. The soil amendments used include lime, DaSan Yuan (DASY), DiKang No.1 (DEK1), biochar, Fe-biochar, Yirang, phosphorus fertilizer, (Green Stabilizing Agent) GSA-1, GSA-2, GSA-3, and GSA-4, applied at 1% rate in a field experiment. The results exposed that GSA-4 treatment showed best effects on reducing Cd and Pb phytoavailability in soil and uptake by early rice. Linear increase in pH (i.e. 5.69 to 6.75) was recorded in GSA-4 amended soil from sowing to the 3rd month of growth season. GSA-4 decreased DTPA extractable contents of cadmium (Cd) from 0.324 to 0.136 mg kg$^{-1}$ soil and lead (Pb) from 53.21 to 24.68 mg kg$^{-1}$ soil at 90 days of amendment. Treatment with GSA-4 improved rice growth (56%) and grains yield (42%). The enhancement effects on grain yield may be result from the positive effects of GSA-4 application on increasing photosynthesis (116%) and transpiration rate (152%) as compared to the control. Significant reduction in Cd and Pb uptake in shoot (42% and 44%) and in grains (77 and 88%), was observed, respectively in GSA-4 treatment as compared with the control. Moreover, negative correlation was recorded between DTPA extractable Cd/Pb and soil pH that directly depended on applied amendments. In short, use of combined amendment (GSA-4) was more effective for immobilizing heavy metals in contaminated paddy field, and secures rice safe production, as compared other tested amendment products.

Heavy metals (HMs) enter soil environment via different anthropogenic activities e.g., smelting, mining, disposing hazardous materials and fertilization1-3. Metals contamination to soil has been associated with industrial emissions and disposal of wastes in agricultural lands. Heavy metals accumulation through food chain has adverse effect on human health1-3. Among trace metals Cd and Pb are most phytotoxic that inhibits plant growth and enter food chain through plant uptake from contaminated soil4. Cadmium and Pb are categorized as most hazardous metals by United States Environmental Protection Agency (US-EPA)5. Mostly, metals are non-biodegradable, so their availability severely affects plants growth, soil quality and humans health. There is a dire need of cost effective and environmental friendly techniques to reduce metals accumulation in food chain4.

Metals availability reduction is the key for remediation of HMs contaminated soils. Different practices e.g. physical, biological and chemical and phytoremediation have been adopted to remediate metals polluted sites6 but most techniques are not efficient in terms of time and cost. In-situ remediation of HMs with different kinds of soil amendments (organic, inorganic and clay minerals) is gaining much attention in the last decade. Amendments reduce metal risk and uptake by plants and offsite contamination via leaching. However, organic amendments especially manures and biochar enhanced heavy metal immobilization by increasing soil pH, CEC and providing adsorption sites to bind metals7,8. Organic materials make soluble or insoluble complexes with heavy metals10,11.
that decreases metal uptake by plants, which ultimately reduces risk to food chain. Organic materials like green manure, animal wastes and composts can effectively remediate contaminated sites by transforming exchangeable/soluble fraction to organic bound or residual fraction, which are less available to plants12. Organic materials are also good source of essential nutrients; improve soil fertility and microbiological interactions in soil13. In-situ immobilization by clay minerals such as sepiolite and zeolite has been reported for reduced heavy metals availability14,15. Clay minerals are abundant in nature with highly negative charged layer to adsorb cations. Minerals act as sorption agents due to hydroxyl group presence and are effective in reducing heavy metal availability through adsorption or complexation16,17. This adsorption process facilitates to reduce metal leaching in soil profile18. Heavy metals bioavailability is largely pH dependent, higher in acidic conditions than alkaline, so application of liming reduced from 0.324 (control) to 0.136 mg kg−1 soil (GSA-4) and up to 0.147 mg kg−1 soil in treatment received GSA-3. In general, organic amendments can reduce Cd availability by adsorption or complexation21,22. It is obvious from the results that application of organic material does not affect total Cd content but decrease Cd availability by converting exchangeable fraction to organic matter bound fraction23. Biochar reduced metal availability by increasing surface sorption on biochar. Possible mechanisms of reduced metal phytoavailability by biochar application include precipitation of metal-organo compounds24. Lime application decreased metal mobility through attributes of precipitation and adsorption processes by changing soil pH. An increase in pH of paddy soil was observed with sepiolite application and this elevation in soil pH results in precipitation of metals as metal hydroxides and/or carbonates25. Similar reaction might occur to biochar treatment, which reduced Cd availability from 0.324 to 0.158 mg kg−1 soil. Overall reduction in Cd availability among the treatments decreased in the order of GSA-4 > GSA-3 > Biochar > GSA-2 > Lime > FE-BIOCAHR > Yirang > DASY > P fertilizer > GSA-1 > DEK1 > CK (0.136; 0.147; 0.158; 0.165; 0.173; 0.188; 0.188; 0.190; 0.195; 0.205; 0.224; 0.324 mg kg−1 soil, respectively).

A decrease in Pb availability was observed in all the treatments. After three months of amendment, biochar decreased DTPA extractable Pb from 53.2 (control) to 24.68 mg kg−1 soil in GSA-4 treatment. Treatments GSA-3 and GSA-2 resulted in reduction of DTPA extractable Pb by 25.98 and 26.12 mg kg−1 soil, respectively. Biochar has been widely used to remediate HMs contaminated soils and proposed mechanisms include ion exchange, adsorption, precipitation and co-precipitation25–27. Alkaline treatment (Liming) significantly decreased DTPA extractable Pb (26.58 mg kg−1), as compared to control, which can be attributed to pH increase28 and consequently enhanced metal precipitation29. The overall reduction in DTPA extractable Pb decreased in the following order for the different treatments: biochar > GSA-3 > GSA-2 > Lime > P fertilizer > DASY > GSA-4 > Yirang > Biochar > GSA-1 > DEK1 > CK (24.68; 25.98; 26.12; 26.58; 28.95; 29.98; 30.16; 31.38; 32.48; 32.88; 34.96; 53.21 mg kg−1 soil).

Effect of amendments on soil pH. A rapid increase in soil pH was observed in all the treatments in 15 days after amendments application except for Fe-biochar, Yirang and P fertilizer (Fig. 2). Soil liming caused consistent increase in soil pH from start to 3rd month of time interval of crop. There was significant difference in pH with lime as compared to control and other treatments. In three months, liming increased soil pH from 5.69 to 7.41. This increase in pH with liming resulted in improved nutrients availability and crop growth. Alkaline amendments are known for raising soil pH and surface negative charge, thus reducing heavy metal activity by precipitation and ion adsorption30. There was a small increase in soil pH (5.71, 5.75, 5.96), with Fe-biochar, yirang and P fertilizer at 3rd month of treatments but not significantly different from control. Application of GSA-3 and GSA-4 also raised soil pH to a noticeable level (6.86, 6.75). Addition of organic materials like manure and wood powder can change soil properties (pH, EC) that affect HMs availability due to elevated soil pH.

There was significant negative correlations between DTPA extractable Cd or Pb and soil pH at the three-month treatments (Fig. 3), with a correlation coefficients of −0.428* and −0.464*, respectively. This correlation indicated that pH is an important soil property that affects heavy metals availability in contaminated soils31,32.

Effects on metal concentration and uptake. Cadmium and Pb concentrations in plant parts such as roots, shoots, husk and grain generally decreased with application of amendments as compared to control (CK) (Fig. 4). Despite small changes in pH with Fe-biochar, Yirang and P fertilizer application, these treatments showed a reduction in plant concentrations of heavy metals. Concentration of Cd and Pb in rice roots was higher than other parts and no significant difference was observed among all the treatments. Previous studies indicated that Cd contamination effect on rice growth depends on total Cd contents, soil physico-chemical properties, rice species and water management33. Cadmium concentration in roots, shoots, husk and grains were 0.302, 0.203, 0.1439, and 0.055 mg kg−1, respectively in the composite treatment (GSA-4) where manure, lime and sepiolite were applied in combination, which is a significant decrease, as compared to control (Fig. 4). Application of biochar alone and in combination with lime, sepiolite and zeolite (GSA-2) reduced bioaccumulation of Cd in rice
grains 67% and 72%, respectively. The availability and mobility of HMs in soil is dependent on organic source, clay minerals, soil pH and Fe/Al oxides. Organic amendment provides a novel environmental friendly option in reducing trace metal accumulation in edible parts of plants. Adsorption, complexation and/or precipitation are the possible mechanisms involved in immobilization of metals by organic amendment. Organic matter has reactive groups (carboxyl and hydroxyl) that can react with soluble cadmium to form stable complexes. Overall, shoot Cd concentration was significantly decreased by the composite additives (GSA-4, GSA-2), as compared to CK (0.203; 0.223 mg kg\(^{-1}\), respectively). These composite treatments reduced shoot Cd contents by 42% and 37%. These results revealed the effectiveness of combined organic and inorganic sources in reducing Cd bioaccumulation in rice, which can be attributed to the decreased Cd availability in soil. Application of biochar alone and combined with inorganic and mineral additives (GSA-2) reduced Pb uptake by rice. Lead concentration in rice grains was significantly decreased in GSA-2, biochar and GSA-4 (90, 89 and 88%) treated plots respectively as compared to control. Addition of biochar in contaminated soil increased soil pH and reduced phytoavailability of metals. The potential role of biochar in reduced Cd uptake is more effective than other fixing agents. The reduction in Cd and Pb contents in rice may be owing to improved immobilization by biochar treatment and changes in soil HMs mobility. Combination of alkaline material and sepiolite is well reported for elevated soil pH and heavy metals reduction in different crops. This increase in pH level may result a decrease in trace metals mobility and enhanced immobilization. Alkaline treatment (lime) did not show significant difference in grains Pb contents (0.719 mg kg\(^{-1}\)) with control. Overall reduction in Pb contents of rice grains was as GSA-2 > biochar > GSA-4 > GSA-3 > Fe-biochar > GSA-1 > Yirang > DASY > P fertilizer > DEK1 > Lime > CK (90; 89; 88; 83; 82; 76; 58; 55; 44; 32; 23%). Shoot Pb contents were lessened in Yirang, Fe-biochar and DASY treated plots (54; 54 and 53%). Biochar may act as liming material with consistent increase in soil pH due to its alkaline nature. This soil pH elevation by biochar amendment endorses metals adsorption and complexation on biochar particles due to high affinity of biochar for cation exchange capacity.

![Figure 1. Effect of different amendments on available heavy metals concentration in soil under field conditions. All Amendments were applied at 1% concentration level. All values are averaged of 3 replicates (n = 3).](image-url)
Effects of soil amendments on rice grains and biomass yield. Rice grains yield and biomass was determined at harvesting from 1 square meter area of each treatment (Table 1). The application of GSA-4 significantly increased fresh weight of biomass (2.03 kg m$^{-2}$), as compared to control (1.69 kg m$^{-2}$). Combined amendment of biochar, lime, sepiolite and zeolite (GSA-2) also resulted in a significant increase in biomass fresh weight (2.01 kg m$^{-2}$) than other treatments. Biological yield was also increased up to 20300 and 20133 kg ha$^{-1}$ by the application of amendments GSA-4 and GSA-2, respectively over control (16966 kg ha$^{-1}$). As compared to control (5611 kg ha$^{-1}$), per hectare grain yield was more in GSA-3 (8037 kg ha$^{-1}$) in which a combination of organic and inorganic additives was applied. Composite treatment (GSA-4, GSA-2) also significantly improved grains yield of early rice (7913 and 7787 kg ha$^{-1}$). Animal manure and biochar are effective soil amendments that are commonly used for enhancing crop production by improving soil structure and nutrient availability$^{41-43}$. Biochar is also regarded as soil conditioner as its application increases soil fertility and plant growth by supplying retaining

Figure 2. Effect of different amendments on soil pH with advance of rice growth stages. All Amendments were applied at 1% concentration level. All values are average of 3 replicates (n = 3). Bars sharing the same letters in one treatment are statistically non-significant at 5% significance level.

Figure 3. Correlation coefficients between soil pH and available Cd and Pb concentrations after different soil amendments application for 3rd month.
nutrients and changing soil physico-chemical properties. Addition of manures increases soil organic matter contents, CEC and pH buffering capacity, and soil physical properties. Liming is helpful in increasing pH of acidic soil, thus reducing the activity of hazardous elements in soil. This decreases the activity of contaminants in soil that reduced phytotoxicity which ultimately leading to a significant increase in yield. It has been reported that mixture of lime and phosphate amendments increased rice biomass in Cd contaminated field. Liming was also testified to sustain crop yield in Cd contaminated soil. The role of natural clay minerals (sepiolite, zeolite) has already been conferred for remediation of HMs contaminated sites due to their easy availability and low cost. Application of sepiolite at 10 g kg⁻¹ soil increased crop production by 65%, as compared to control, likely due to stabilization of heavy metals in the contaminated soil.

**Effect of amendments on leaf photosynthesis of rice plants.** Composite treatments (GSA-4 and GSA-2) and application of single P fertilizer showed significant increase in photosynthetic rate (Fig. 5). Up to 116 and 112% increase in photosynthetic rate was recorded in treatments GSA-4 and GSA-2, respectively, as compared to control (CK). Similarly composite treatments GSA-2, GSA-4 and single biochar significantly increased transpiration rate over control (Fig. 5). Maximum (154%) increase in transpiration rate was observed in GSA-2 treatment where biochar was applied in composite with inorganic sources, followed by GSA-4 and biochar (152 and 143%, respectively over control). Several stress conditions were responsible for reduction in
Table 1. Effect of soil amendments on growth parameters of rice. Note: All values are averaged of 3 replicates (n = 3). Different letters indicates significantly different values at 5% significance level, PF = Phosphorus fertilizer. All treatments including control receive recommended dose of N, P and K except treatment 8 in which phosphorus was not applied.

| Treatments | Biological yield (kg ha$^{-1}$) | Grains yield (kg ha$^{-1}$) |
|------------|---------------------------------|-----------------------------|
| CK         | 16966d                          | 5611b                       |
| LIME       | 18866a-d                        | 7209ab                      |
| DASY       | 17200cd                         | 7118ab                      |
| DEKI       | 17066cd                         | 7378ab                      |
| BIOCHAR    | 18800a-d                        | 7197ab                      |
| Fe-BIOCHAR | 18700a-d                        | 7131ab                      |
| YIRANG     | 17733b-d                        | 7041ab                      |
| PF         | 19333a-d                        | 7314ab                      |
| GSA-1      | 19466a-c                        | 7491ab                      |
| GSA-2      | 20133ab                         | 7787a                       |
| GSA-3      | 19433a-c                        | 8037a                       |
| GSA-4      | 20300a                          | 7913a                       |

**Figure 5.** Effect of application of different amendments on leaf photosynthesis ($\mu$mol CO$_2$ m$^{-2}$ S$^{-1}$) and transpiration rate (mmol H$_2$O m$^{-2}$ S$^{-1}$) in rice. Bars with different letters represent significant difference among treatments. All values are average of 3 repeats (n = 3).
Heavy metals toxicity negatively affected gas exchange attributes like photosynthetic and transpiration rate in different plants and caused adverse effect on plant photosynthetic apparatus and mineral nutrient balance. Addition of amendments can improve plant growth by increasing nutrient supply and reducing metal contact with plants. An increase in physiological properties may also due to reduced uptake and accumulation of metals in plants. An increase in photosynthetic rate with biochar application was previously reported. A significant increase in photosynthetic rate and transpiration rate was noted with biochar application under stress conditions in maize and wheat.

### Methods

#### Soil amendments treatments

The field experiment was conducted in west of Zhejiang province in a contaminated red paddy soil. The soil was lightly contaminated by Cd (0.51 mg kg$^{-1}$) and Pb (106.64 mg kg$^{-1}$), which exceeded Chinese Environmental Quality Standards for Soils. Basic properties of the soil are presented in Table 2 which was analyzed with the standard methods. The experiment was started from March/2017 and ends at July/2017. Total 11 amendments product were collected from different sources, including lime, DASY, DEK1, Biochar, Fe-Biochar, Yirang, Ca-Mg-P fertilizer, GSA-1, GSA-2, GSA-3, and GSA-4 respectively. Basic physicochemical properties of the amendments are listed in Table 3. The later four amendments were newly made by our group with different organic, inorganic and minerals combination. These amendments products were applied at 1% rate with three replications for each treatment following a randomized complete block design. Plots area of each replicate was 8 m $\times$ 8 m with separate inlet and outlet for irrigation and drainage. Overall 12 treatments with one CK were applied before rice seedling transplanting and soil sampling was done before and after different treatment times. Amendments were mixed thoroughly on the upper surface of soil and then ploughed mechanically into 0–20 cm plow layer 15 days before transplanting. Basic nitrogen (N), phosphorus (P as P$\text{O}_5$), and potassium (K as K$\text{O}$) fertilizers were applied in the form of urea, diammonium phosphate and sulphate of potash, respectively at following rate in all plots (N-P$\text{O}_5$-K$\text{O}$: 145-60-165 kg ha$^{-1}$). Phosphorus fertilizer was not applied in the treatment where Ca-Mg-P fertilizer was used as amendmentfixing agent.

#### Early rice seedling

Early rice cultivar used for experiment was (Zhong zao 39) and seedlings were cultured in early April. All the cultural practices were kept the same for all treatments throughout the experiment. Harvesting was performed at maturity and 15 plants were collected randomly. Plant growth parameters were measured in field at harvesting time. Yield attributes were measured for 1 m$^2$ area in each plot. Harvested plant samples were rinsed with deionized water, oven dried and separated into roots, shoots, husk and grains for analysis.

### Table 2. Physicochemical properties of the tested soil. Sand 10%, Silt 39.70%, Clay 50.30%.

| Soil texture | Silt clay |
|--------------|-----------|
| Soil pH      | 5.69      |
| CEC (Cmolc kg$^{-1}$) | 10.40 |
| Organic carbon (g kg$^{-1}$) | 71.35 |
| Total Pb (mg kg$^{-1}$) | 106.6 |
| Total Cd (mg kg$^{-1}$) | 0.51 |

### Table 3. Physiochemical properties of tested soil amendments tested. Note: CK (control), Lime, DASY (DaSan Yuan), DEK1 (Di Kang No. 1), Yirang, GSA-1(Green Stabilizing Agent 1), GSA-2 (Green Stabilizing Agent 2), GSA-3(Green Stabilizing Agent 3), and GSA-4 (Green Stabilizing Agent 4).

| No. | Treatment name | pH  | CEC (Cmolc kg$^{-1}$) | Organic carbon (g kg$^{-1}$) | Total Pb (mg kg$^{-1}$) | Total Cd (mg kg$^{-1}$) |
|-----|----------------|-----|-----------------------|-------------------------------|------------------------|------------------------|
| 1   | Lime           | 11.34 | —                     | N/D                          | 0.692                  | 0.26                   |
| 2   | DASY           | 11.52 | 6.92                  | 25.84                         | 3.042                  | 0.24                   |
| 3   | DEK1           | 9.70  | 8.17                  | 2.27                          | 3.173                  | 1.03                   |
| 4   | Biochar        | 8.16  | 19.21                 | 403                           | 1.696                  | 0.07                   |
| 5   | Fe-Biochar     | 6.41  | 20.43                 | 297                           | 1.731                  | 0.03                   |
| 6   | Yirang         | 11.55 | —                     | 7.58                          | 2.343                  | 1.02                   |
| 7   | CaMg-P         | 7.4   | —                     | N/D                           | 3.150                  | 0.13                   |
| 8   | GSA-1          | 11.78 | 148                   | 28.12                         | 6.615                  | 0.14                   |
| 9   | GSA-2          | 11.7  | 31.40                 | 31.52                         | 2.505                  | 0.16                   |
| 10  | GSA-3          | 11.68 | —                     | 74.21                         | 4.483                  | 0.24                   |
| 11  | GSA-4          | 11.72 | —                     | 32.31                         | 4.728                  | 0.14                   |
Soil and plant analyses. Soil samples were collected from zero (transplanting) to three month at the one month interval from rice field. Randomly, five samples were collected from each plot making a composited sample. The collected soil samples were used for determining soil pH and DTPA extractable Cd and Pb. pH was determined by mixing soil with water at 1:2.5 soil:water ratio by using a pH meter (PB-10, Sartorius, Germany). DTPA extractable heavy metals (Cd and Pb) was determined by mixing 20 g of soil with 50 mL DTPA-TEA solution (0.005 M DTPA, 0.1 M TEA, and 0.01 M CaCl₂, pH = 7.3). This mixture was then shaken for 2 hrs at 25 °C on a shaker. Suspensions were then passed through 0.45-µm filter membrane and concentration of metals (Cd and Pb) was measured using ICP-MS (Agilent, 7500a, USA)55,56.

Dried plant samples were ground for heavy metals analysis57. Cadmium and Pb in roots, shoots, husk and grains were determined by digestion of 0.200 g plant sample with mixed acid solution (HClO₄ and HNO₃) at 170 °C for 4 hrs and cooled at room temperature and diluted with distilled water to make volume to 25 ml. Cadmium and Pb concentration in digested soil sample was then measured using the ICP-MS8.

Leaf photosynthesis measurement. Photosynthetic rate (Pn) and transpiration rate (Tr) were measured at day 70 of rice transplanting in field using a portable infrared gas analyzer (IRGA).

Statistical analysis. One way ANOVA was conducted to compare different treatment means using SPSS 20.0 and Origin Pro 8.0. All the results are presented as average of three replicates and standard error was estimated using Microsoft excel 2007.

Data Availability Statement The data for this manuscript is available on demand in excel sheet.

References

1. Zhu, F. et al. Influence of natural regeneration on fractal features of residue microaggregates in bauxite residue disposal areas. Land Degrad Dev 29(1), 138–149 (2018).
2. Xue, S. G. et al. Cadmium, lead, and arsenic contamination in paddy soils of a mining area and their exposure effects on human HEPG2 and keratinocyte cell-lines. Environ Res 156, 23–30 (2017).
3. Kong, X. F. et al. Development of alkaline electrochemical characteristics demonstrates soil formation in bauxite residue undergoing natural rehabilitation. Land Degrad. Dev. 29, 58–67 (2018).
4. Zhu, F. et al. Vermicompost and gypsum amendments improve aggregate formation in bauxite residue. Land Degrad Dev 28(7), 2109–2120 (2017).
5. Wu, C. et al. The effect of silicon on iron plaque formation and arsenic accumulation in rice genotypes with different radial oxygen loss (ROL). Environ. Pollut. 212, 27–33 (2016).
6. Wang, J. Ye, S., Xue, S. G., Hartley, W. & Wu, H. The physiological response of Mirabilis jalapa Linn. to lead stress and accumulation. Int. Biodeterior. Biodegrad. 128(3), 11–14 (2018).
7. Cameron, R. E. Guide to Site and Soil Description for Hazardous Waste Site Characterization, Vol. 1, EPA/600/4-91/029. Washington, DC (1992).
8. Hamid, Y. et al. Comparative efficacy of organic and inorganic amendments for cadmium and lead immobilization in contaminated soil under rice-wheat cropping system. Chemosphere 214, 259–268 (2019).
9. Khan, K. Y. et al. Effect of Biochar Amendment on Bioavailability and Accumulation of Cadmium and Trace Elements in Brassica chinensis L. (Chinese Cabbage). J Agric Sci 8(9), 23–36, ISSN 1916-9752 E-ISSN 1916-9760 (2016).
10. Cruz-Paredes, C. et al. Risk assessment of replacing conventional P fertilizers with biomass ash: residual effects on plant yield, nutrition, cadmium accumulation and mycorrhizal status. Sci. Total Environ. 575, 1168–1176 (2017).
11. Jeffer, S., Verheijen, F. G. A., van der Velde, M. & Bastos, A. C. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. AgricEcos Environ 144, 175–187 (2011).
12. Madejón, E., De Mora, A. P., Felipe, E., Burgos, P. & Cabrera, F. Soil amendments reduce trace element solubility in a contaminated soil and allow regrowth of natural vegetation. Environ. Pollut. 159, 40–52 (2006).
13. Ahmad, I., Akhtar, M. J., Zahir, Z. A. & Mitter, B. Organic amendments: effects on cereals growth and cadmium remediation. Int. J. Environ. Sci. Technol. 12, 2919–2928, https://doi.org/10.1007/s13762-014-0695-8 (2015).
14. Yan, S., Qi-Tang., W., Charles, C. C. L., Raoqn, L. & Xinxian, L. Cadmium Sorption Characteristics of Soil Amendments and its Relationship with the Cadmium Uptake by Hyperaccumulator and Normal Plants in Amended Soils. Intl. J Phytoem. 16, 496–508, https://https://doi.org/10.1080/15226514.2013.798617 (2014).
15. Ansari, M. A., Hajabbasi, M. A., Khademi, H. & Kazemian, H. Soil cadmium stabilization using an Iranian natural zeolite. Geoderma 137, 388–393 (2007).
16. Kosobucki, P., Kruk, M. & Buszewski, B. Immobilization of selected heavy metals in sewage sludge by natural zeolites. Bioresour. Technol. 99, 5972–5976 (2008).
17. Zhou, Y.-F. & Haynes, R. J. Sorption of heavy metals by inorganic and organic components of solid wastes: significance to use of wastes as low-cost adsorbents and immobilizing agents. Crit. Rev. Environ. Sci. Technol. 40, 909–977 (2010).
18. Yang, J. E., Kim, H. J., OK, Y. S., Lee, J. Y. & Park, J. Treatment of Abandoned Coal Mine Discharged Waters Using Lime Wastes. Geosci. J. 11, 111 (2007).
19. Appel, C. & Ma. L. Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils. J. Environ. Qual. 31, 581–589 (2002).
20. Lim, J. E. et al. Evaluation of the Feasibility of Oyster-Shell and Eggshell Wastes for Stabilization of Arsenic-Contaminated Soil (In Korean with English Abstract), I Korean Soc. Environ. Eng. 31, 1095 (2009).
21. Khan, M. A., Sardar, K., Anwarzeb, K. & Mheboob, A. Soil contamination with cadmium, consequences and remediation using organic amendments. Science of the Total Environment 601–602, 1591–1605 (2017).
22. Clark, G. J., Dowgough, N., Sale, P. W. G. & Tang, C. Changes in chemical and biological properties of a sodic clay subsoil with addition of organic amendments. Soil Biol. Biochem. 39, 2806–2817 (2007).
23. Mahara, Y., Kughta, T., Wagayama, R., Nakano-Ohta, T. & Nakamura, T. Effects of molecular weight of natural organic matter on cadmium mobility in soil environments and its carbon isotope characteristics. Sci. Total. Environment. 387, 220–227 (2007).
24. Bessely, L. & Marmiroli, M. The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. Environmental Pollution 159, 474–480 (2011).
25. Cao, X. D., Ma, L. N., Gao, B. & Harris, W. Dairy-manure derived biochar effectively sorbs lead and atrazine. Environ Sci Technol 43, 3285–3291 (2009a).
26. Uchimiya, M., Wartelle, L. H., Klasson, K. T., Fortier, C. A. & Lima, I. M. Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil. J Agric Food Chem 59, 2501–2510 (2011b).
56. Bao, S. D.
57. Tang, L.
54. Younis, U.
48. Zdzislaw, C., Miroslsaw, W., Wladyslaw, K. & Jadwiga, Z. Effect of organic matter and liming on the reduction of cadmium uptake in calcareous alkaline soils. Commun. Soil Sci. Plan. 106, 197–205 (1999).

Yousaf, B. et al. Investigating the potential influence of biochar and traditional organic amendments on the bioavailability and transfer of Cd in the soil–plant system. Environ Earth Sci 75, 1–10 (2016).

Hong, C. O., Lee, D. K., Chung, D. Y. & Kim, P. J. Liming effects on cadmium stabilization in upland soil affected by gold mining activity. Archives of Environmental Contamination. Toxicology 52, 496–502 (2007).

Shirvani, M., Shariatmadar, H., Kalbasi, M., Nourbakhsh, F. & Najafi, B. Sorption of cadmium on pyorgorskite, sepiolite and calcite: Equilibria and organic ligand affected kinetics. Colloids and Surfaces A: Physicochemical and Engineering Aspects 287, 182–190 (2006b).

Van Zwieten, L. et al. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. Plant Soil 327, 235–246 (2010).

Hass, A. et al. Chicken manure biochar as liming and nutrient source for acid Appalachian soil. J. Environ. Qual. 41, 1096–1106 (2012).

Ghosh, S., Wilson, B. & Ghoshal, S. Organic amendments influence soil quality and carbon sequestration in the Indo-Gangetic plains of India. AgricEcosys Environ 156, 134–141, https://doi.org/10.1016/j.agee.2012.05.009 (2012).

Liu, X. et al. Biochar's effect on crop productivity and the dependence on experimental conditions – a meta-analysis of literature data. Plant Soil 1, 583–594, https://doi.org/10.1007/s11104-013-1806-x (2013).

Atkinson, C., Fitzgerald, J. & Higgs, N. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review. Plant and Soil 337, 1–18 (2010).

Glasner, B., Lehmann, J. & Zeich, W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal: a review. Biol Fertil Soils 39(4), 219–230 (2002).

Ahmad, H. R. et al. Organic and inorganic amendments affect soil concentration and accumulation of cadmium and lead in wheat in calcareous alkaline soils. Commun. Soil Sci. Plan. 42, 111 (2011).

Trustoš, P. et al. The effect of liming on cadmium, lead, and zinc uptake reduction by spring wheat grown in contaminated soil. Plant Soil Environ. 52, 16–24 (2006).

Xiao, R. et al. Lime and Phosphate Amendment Can Significantly Reduce Uptake of Cd and Pb by Field-Grown Rice. Sustainability 9, 430, https://doi.org/10.3390/su9030430 (2017).

Zdziadsaw, C., Miroslaw, W., Wladyslaw, K. & Jadwiga, Z. Effect of organic matter and liming on the reduction of cadmium uptake from soil by triticale and spring oilseed rape. The Science of the Total Environment 281, 37–45 (2001).

Sun, Y. B. et al. Assessment of sepiolite for immobilization of cadmium-contaminated soils. Geoderma 193–194, 149–155 (2013).

Sun, Y. B. et al. In situ stabilization remediation of cadmium contaminated soils of wastewater irrigation region using sepiolite. Journal of Environmental Sci. 24, 1799–1805 (2012).

Zhu, Q. H. et al. Sepiolite is recommended for the remediation of Cd-contaminated paddy soil. Acta Agriculturae Scandinavica Section B Soil and Plant Science 60, 110–116 (2010).

Tian, T. et al. Alleviation of lead toxicity by 5-aminolevulinic acid is related to elevated growth, photosynthesis, and suppressed ultrastructural damages in oilseed rape. Biomed Res Int 2014, 1–11 (2014).

Akhtar, S. S., Andersen, M. N. & Liu, F. Residual effects of biochar on improving growth, physiology and yield of wheat under salt stress. Agri Water Manag 158, 61–68 (2015b).

Younis, U. et al. Biochar enhances the cadmium tolerance in spinach (Spinacia oleracea) through modification of Cd uptake and physiological and biochemical attributes. Environ SciPollut Res 23, 21385–21394 (2016).

Li, H. S. Principle and Technology of Plant Physiological and Biochemical Experiment. (Higher Education Press, Beijing, China, 2000).

Bao, S. D. Soil Agricultural Chemistry Analysis Method, Third edition. (China Agriculture Press, Beijing, China, 2008).

Tang, L. et al. Genotypic differences in cadmium and nitrate co-accumulation among the Chinese cabbage genotypes under field conditions. Sciortic 201, 92–100 (2016).

Acknowledgements

This research was financially supported by Zhejiang Provincial Science and Technology Bureau (#2018C02029; #2015C02011-3), Ministry of Science and Technology of China (#2016YFD0800805), and Fundamental Research Funds for the Central University.

Author Contributions

X.E.Y. designed the field experiment, and the amendment treatments Y.H., L.T., X.W. and B.H. conducted field trial Y.H. wrote the manuscript M.Z.A., M.Y. and X.E.Y. revised the manuscript.

Additional Information

Competing Interests: The authors declare no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.
