EPA Public Access

Author manuscript

Environ Sci Pollut Res Int. Author manuscript; available in PMC 2019 November 01.

About author manuscripts

Submit a manuscript

Published in final edited form as:

Environ Sci Pollut Res Int. 2018 November ; 25(31): 31396–31406. doi:10.1007/s11356-018-3126-4.

Influence of phosphate amendment and zinc foliar application on heavy metal accumulation in wheat and on soil extractability impacted by a lead-smelter near Jiyuan, China

Wei qin Xing¹, Enze Cao¹, Kirk G. Scheckel², Xiaoming Bai³, and Liping Li¹

¹School of Chemistry and the Environment, Henan University of Technology, Zhengzhou, Henan 450001, China

²U. S. Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, Ohio 45224, USA

³College of Grassland Science, Gansu Agricultural University, Lanzhou 730070, China

Abstract

Higher concentrations of Pb and Cd in wheat grains harvested in several lead smelting-polluted areas in northern China have been reported. This field experiment was conducted to investigate the effect of phosphate amendment and Zn foliar application on the accumulation of Pb and Cd in wheat grains grown in a lead-smelting impacted area in Jiyuan in northern China. The soil (total Pb and Cd are 261 and 2.65 mg kg⁻¹, respectively) was amended with superphosphate at P:Pb ratios (mol:mol) of 1.90 or 2.57 either during wheat (*Triticum aestivum* L.) planting or a split of 60% of the phosphate applied at planting, with remaining 40% applied at the jointing stage. Zn was sprayed on the canopy of the wheat plants at the jointing stage. The phosphate amendment resulted in lower DTPA (diethylene triamine pentaacetic acid)-extractable Pb (1.39–10.7% lower than the control) and Cd (0.040–7.12%) in the soil. No significant effect of split application of phosphate was found on Pb and Cd availability in soil; however, higher rates of P resulted in lower Pb and Cd availabilities in the soil. Grain Pb (5.41–21.5% lower than the control), Cd (3.62–6.76%) and Zn (4.29–9.02%) concentrations were negatively affected by the phosphate application, with higher rates of phosphate resulting in lower grain heavy metal concentrations. Foliar application had no statistically significant influence on Pb and Cd concentrations in the grain ($p > 0.05$). Although Pb and Cd concentrations in wheat grains were reduced by the phosphate application, their concentrations were still much higher than the maximum permissible concentrations for wheat in the national standards of China. The results suggest that it is feasible to reduce wheat grain concentrations of Pb and Cd in Pb smelting polluted areas in northern China by soil application of superphosphate; however, the split application of the phosphate and the foliar application of Zn compounds do not have substantial impact on reducing accumulation of Pb and Cd in the wheat grains.

Keywords

lead smelting; wheat; soil; phosphate; grain; heavy metal; split application

Introduction

Heavy metals are the most widespread pollutants in the environment, and can be readily absorbed by plants and animals, allowing entry into the food chain and exerting negative effects on human health. Nonferrous metal mining and smelting are major sources of heavy metal contamination in the environment (Ran et al. 2010; Li et al. 2011; Lu et al. 2018). During the mining and smelting process of nonferrous metals, heavy metals enter the environment through the weathering and leaching of solid wastes, emission of polluted water, or the atmospheric decomposition of particles from stacks of the smelters. China is the biggest lead (Pb) producer in the world at present. Lead mining and smelting have resulted in accumulation of lead and cadmium (Cd) in soils in many areas of some provinces, such as Henan, Hunan and Guangdong (Li et al. 2011; Qiu et al. 2016). Heavy metal pollution near smelting facilities has resulted in elevated concentrations of Pb and Cd in crop grains, bearing negative impacts on the health of local residents from the heavy metals (Bi et al. 2009; Qiu et al. 2016). Jiyuan City in Henan Province in northern China produces about 800,000 tonnes of Pb annually, which is about 10% of the world annual Pb output. High blood lead levels have been found for children living near the smelters (Qiu et al. 2015).

Immobilization of heavy metals in contaminated soils reduces their solubility and mobility resulting in an effective way to manage contaminated soils. Phosphate amendments to immobilize Pb and other heavy metals has been extensively studied (Chrysochoou et al. 2007; Baker et al. 2014; Yan et al. 2016; Obrycki et al. 2017). Phosphate amendments react with soil Pb to transform Pb into sparingly soluble Pb-phosphate minerals as an effective strategy to immobilize Pb in contaminated soils (Chrysochoou et al. 2007; Baker et al. 2014), and phosphate has been demonstrated to immobilize Cd and Zn to a lesser extent (Kirkham, 2006).

In nonferrous metal mining and smelter impacted areas, consumption of heavy metal contaminated crops is a major human exposure pathway (Bi et al. 2009; Douay et al. 2013). Thus, it is important to reduce the concentrations of heavy metals in the food sources, which involves reducing the availability of these metals in soils on which the crops grow. Thus, from a human health perspective, it is imperative to assess of the effect of metal immobilization in contaminated soils on the heavy metal accumulation and concentration in locally consumed crop grains.

Ingestion of heavy metal polluted food and water is one of the dominant pathways for accumulation in humans living near impacted areas (Chen et al. 2018). Wheat is an important global staple food crop, and is especially important for residents in northern China in their daily diet (Xing et al. 2016; Zhang et al. 2018). Comparatively, wheat can accumulate higher amounts of Cd and Pb in its grains than maize when planted in contaminated soils (Greger and Landberg, 2008; Douay et al. 2013). The maximum

permissible concentrations of Cd and Pb in wheat grain are 0.1 and 0.2 mg kg⁻¹, respectively in China. Higher levels of Cd and Pb in wheat grains have been reported in contaminated areas in northern China (Xing et al. 2016; Du et al. 2015). Du et al (2015) collected 188 wheat grain samples from an area about 1000 km² in the lead smelting polluted area in Jiyuan, Henan Province. The study indicated that the range of Cd and Pb concentrations in the wheat grains were 0.039–2.54 and 0.084–4.22 mg kg⁻¹, respectively, with mean concentrations of 0.287 and 0.640 mg kg⁻¹, respectively. Xing et al (2016) investigated an area greater distance away from the smelter in Jiyuan than in Du et al (2015)'s work, in which they found ranges of Cd and Pb concentrations in wheat grains were 0.108–0.277 and 0.0621–0.717 mg kg⁻¹, respectively.

Although immobilization of Pb and Cd with phosphate has been reported in many works, verifying effectiveness and reduction in metal mobility has predominantly been investigated with chemical analysis (leachability, sequential extraction, etc) of soil samples, or to a lesser extent with synchrotron analysis to spectroscopically measure the changes of Pb species (Chrysochoou et al. 2007; Baker et al. 2014). The effect of soil phosphate amendments on heavy metal accumulation in wheat grain has been investigated in pot experiments by some scientists. Only a few field studies have been conducted to study the effect of soil amendment on crop grain concentrations of heavy metals cultivated in contaminated soils (Rehman et al. 2015)

Most soils in northern China are calcareous. In calcareous soils, the added soluble phosphate ions may react with Ca and Mg ions resulting in less soluble phosphates and makes phosphorus fertilizer less available to plants over time (Munira et al. 2018; Zhu et al. 2018). In order to decrease the reaction between phosphate ions from fertilizer and the Ca, Mg ions in soil, it is recommended that band application is employed for P fertilizer application (Jiang et al. 2016). Phosphate and Pb ions have poor mobility in soil (Stecker et al. 2001). This is truer in calcareous contaminated soils, where the added phosphate ions from P fertilizers reacts with cations like Pb, Ca and Mg (Munira et al. 2018; Zhu et al. 2018). The concentration of Ca is often much higher than that of Pb in most soils; even contaminated soils. Therefore, if split phosphate applications are used on Pb contaminated soils, it may enhance the reaction by improving contact between Pb and phosphate and reducing the long-term conversion of P to calcium phosphates.

Cd is a common contaminant found in heavy metal contaminated soils. High concentrations of Cd in soil can result in bioaccumulation of Cd in aerial parts of crops, highlighting the flux of soil Cd into food chain transfer exposure pathway. Zinc (Zn) has similar behavior with Cd in the soil-plant system (Das et al. 1997) and can affect the absorption and accumulation of Cd from soil (Brown, 2004; Kirkham, 2006; Saifullah et al. 2016; Sarwar et al. 2010; Chen et al. 2003). Experiments have indicated that foliar application of Zn to wheat plants inhibits the accumulation of soil Cd in wheat grains (Saifullah et al. 2016; Sarwar et al. 2010; Chen et al. 2003; Sarwar et al. 2015; Qaswar et al. 2017).

This field study was conducted in a smelter impacted area in Jiyuan, China to investigate, i) the effect of whole and split application of phosphate amendments on Pb and Cd availability

in soil and the accumulation of Pb and Cd in wheat grains; and ii) the effect of foliar application of Zn to wheat plants on the accumulation of Cd in wheat grains.

Materials and methods

The contaminated field

The study was conducted in a field (ca. N35.129, E112.554) in the west suburb of Jiyuan City, Henan Province, China. The field is about 1000 m to the main stack of the Yuguang Gold and Lead Co. Ltd. The Yuguang began its production of Pb in 1950s, at present it produces about 400,000 tonnes of Pb annually, about half of the lead is smelted from lead ores, and the rest is from recycled batteries. The farm field in the vicinity of the Yuguang was contaminated with atmospheric deposition from the stack of Yuguang, no contamination from solid waste or wastewater was observed. The elevation of the field is about 250 m above sea level, the average annual temperature and precipitation of this area are 14.6 °C and 600 mm, respectively. A rotation of winter wheat-summer corn is widely practiced in this area.

The soil belongs to Ustic Cambosols according to the Chinese Soil Taxonomy standards (Chinese Soil Taxonomy Research Group, 2001). Before the experiment, three composite soil samples from 0–20 cm depth were collected from the field and the properties were analyzed according to methods in Lu (2000). The pH (water:soil=2.5:1, mL:g) was 7.92, and the electric conductivity was 0.131 mS cm⁻¹. The Olsen-P concentrations measured 5.42 mg kg⁻¹ (Murphy-Reiley Method). The available nitrogen (N) was analyzed by incubating the soil at 37 °C with NaOH and the emitted NH₃ was determined to calculate available N as 66.2 mg kg⁻¹. Soil organic matter concentration was measured as 15.1 g kg⁻¹. Total concentrations of Pb, Cd and Zn are 261, 2.65 and 130 mg kg⁻¹, respectively (HNO₃-H₂SO₄-HClO₄-HF digestion on a hot plate), and DTPA (diethylene triamine pentaacetic acid)-extractable concentrations of these three metals are 113, 1.31 and 6.20 mg kg⁻¹, respectively.

The field experiment

The field experiment was conducted during October 2013 to June 2014. There were seven treatments in this work as shown in Table 1, with 4 replicates for each treatment. The superphosphate rates of 400 and 541 g m⁻² (Table 1) correspond to P:Pb ratios (mol:mol) of 1.90 and 2.57, respectively. Before the experiment, 225 kg hm⁻² K₂SO₄ and 270 kg hm⁻² urea were applied in the soil evenly and mixed with shovels to a depth of about 20 cm. Each plot has a length of 8 m and a width of 2.5 m. The distribution of the amendment plots in the field was completely randomized. Ridges of 15 cm high and 20 cm wide were constructed between neighboring plots to minimize the influence of crossover from different plots. Granular superphosphate fertilizer (manufactured by Hubei Chufeng Chemical Engineering Co. Ltd, Zhongxiang City, Hubei Province, China) (total concentrations of P, Pb and Cd are 4.63%, 53.1 and 0.625 mg kg⁻¹, respectively) was applied manually to the surface of the plots according to the rates in Table 1, the soil and fertilizer were then mixed to 20 cm manually with shovels. The fertilizers were applied on October 3, followed by wheat (*Triticum aestivum* L. Zhengmai 9023) planting with a manual seeder on October 4. On

March 14, 300 kg hm⁻² urea was applied to all the plots, and the same superphosphate was applied (as the split application) to some of the plots as required in Table 1. For the application of urea and superphosphate, a 5 cm deep ditch was trenched about 5 cm beside the wheat plant rows and fertilizers were placed in the ditch evenly, then the ditch was covered with soil. On April 9, 0.1% ZnSO₄ solution was sprayed on the canopy of wheat plants according to the treatments in Table 1. The wheat plants were irrigated three times during its growth. Herbicide was applied in spring to control the growth of weeds.

Sample collection

On June 5, the soil and wheat plants were sampled at physiological maturity of the wheat. Two composite wheat and soil samples were collected from each plot. Three subsamples were mixed to make one composite sample. Ears of ten wheat plants were cut for each subsample at each site, then the soil where the wheat plants grew were sampled to 20 cm with a core drill. In each plot, about 1 m² wheat was harvested from two sites and the collected grains were weighed for yield estimation.

Sample analysis

The soil samples were air-dried, gently crushed to pass a 2-mm sieve and homogenized before analysis. The wheat grain samples were washed with running water three times then rinsed with deionized water for three times. The wheat samples were then dried in an oven at 75 °C, pulverized and mixed thoroughly. The wheat grain samples were digested with HNO₃-H₂O₂ on a hot plate according to Lu (2000). The soil samples were extracted with DTPA (diethylene triamine pentaacetic acid) for available Cd, Pb and Zn. The soil was extracted with 0.5 mol L⁻¹ NaHCO₃ for available P analysis (Murphy and Riley method). The concentration of heavy metals in the digestion solution or the extractants was determined with an atomic absorption spectrometer (Jena ZEE nit 700, Germany). Each sample was analyzed in triplicate. The analysis and data validation was conducted according to Lu (2000).

A standard sample of wheat grain (GBW10035, Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences) was included in the analysis of wheat grain for quality control, the recovery of Pb and Cd ranged 75.3–100.9% and 87.8–110%, respectively, with mean values of 82.9% and 96.7%.

Data processing

For each sample, the results of each analysis were expressed as the mean of three replicates, then the results of the two samples from each plot were used to calculate the result of the plot. For each treatment, the result was expressed as the mean of four plot replicates. All statistical analysis was conducted with the Statistical Package for Social Science (SPSS) 10.0, difference was reported at $p < 0.05$ according to LSD method.

Results

Wheat grain yield

Wheat grain yields (dry weight) are indicated in Fig. 1. There was no significant difference on grain yield between different treatments ($p>0.05$), suggesting that the toxicity of heavy metals and the alleviation effect of the treatments were not obvious.

Soil P availability

Significant difference was found between Olsen-P concentrations of different treatments ($p<0.05$) (Fig. 2). Phosphorus amendment increased the Olsen-P concentrations of all treatments. The differences between the control and the P-amended treatments were all significant ($p<0.05$) except that of P21. At low phosphate rate (treatments P11, P12 and P12M), the mean Olsen-P was 9.62 mg kg^{-1} , while that of high phosphate rate treatments (treatments P21, P22 and P22M) was 10.4 mg kg^{-1} . No significant difference was found between single application and split application of phosphate at both P rates ($p>0.05$), suggesting that the effect of split application on the phosphorus availability was limited.

Heavy metal availability

Concentrations of DTPA-extractable Pb, Cd and Zn of different soils were shown in Figs. 3, 4 and 5.

Phosphate amendment reduced the concentrations of DTPA-extractable Pb in all soils for 1.39–10.7%, compared with the control, however, these differences were not statistically significant ($p>0.05$). Higher P rate resulted in lower Pb availability. The average DTPA-extractable Pb concentration of treatments P11, P12 and P12M was $114 \pm 2.17 \text{ mg kg}^{-1}$, while that of P21, P22 and P22M was $107 \pm 1.81 \text{ mg kg}^{-1}$. The split application of P did not affect the Pb availability in soil ($p>0.05$).

No significant effect of phosphate amendment on Cd availability was found either. Less effect of phosphate amendment was found for Cd compared with Pb availability (Fig. 4). Compared with the control, P amendment decreased soil DTPA-extractable Cd concentrations for 0.040–7.12%, the differences were not statistically significant ($p>0.05$). The average DTPA-extractable Cd concentrations of the treatments with high P rates (P21, P22 and P22M) were $1.19 \pm 0.049 \text{ mg kg}^{-1}$, while that of the treatments with low P rates (P11, P12 and P12M) were $1.24 \pm 0.020 \text{ mg kg}^{-1}$.

Because the Zn concentration of the soil was relatively low, the DTPA-extractable Zn concentration of the soil was not high (Fig. 5). The P amendment resulted in 0.23–13.4% higher DTPA-Zn concentrations than the control, however, the difference was not statistically different ($p>0.05$).

The results of the DTPA-extractable heavy metal concentrations indicated that the P amendment slightly decreased the availability of Pb and Cd, but increased that of Zn marginally. The split application of P did not result in obvious influences on immobilization of these three metals in the soil.

Concentrations of Pb, Cd and Zn in wheat grains

The grain Pb concentration was significantly affected by the P amendment ($p<0.05$) (Fig. 6). Phosphate amendment resulted in 5.41–21.5% decrease of grain Pb concentration compared with the control, the concentrations of treatments P21 and P22 were significantly lower than the control ($p<0.05$). The results indicated that it was possible to reduce grain Pb concentrations in field conditions with P amendment in Pb smelting contaminated calcareous soils. The mean grain Pb concentration of the low (P11, P12 and P12M) and high P rates treatments (P21, P22 and P22M) were 0.468 ± 0.008 mg kg⁻¹ and 0.451 ± 0.0043 mg kg⁻¹, respectively. For the single use treatments, grain Pb concentration of the high P rate treatment (P21) was 12.6% lower than that of the low P rate treatment (P11). No significant effect of the split application of P was observed. Application of Zn resulted in higher grain Pb concentrations at both P rates (3.20 and 13.1% higher than the treatments without Zn application for low and high P rates, respectively). The effect of P amendment on wheat grain Pb concentration was in good agreement with DTPA soil Pb availability (Fig 3). The results indicated that, although the P amendment did not result in statistically significant decrease in soil Pb extractability, it did decrease the grain Pb concentrations, suggesting an influence of P amendment on soil Pb availability and Pb accumulation in grains.

Grain Cd concentrations were less affected by the treatments compared with Pb concentration (Fig. 7). Grain Cd concentrations with soil P amendment were 3.62–6.76% lower than the control, the differences were not statistically different ($p>0.05$). The split application of phosphate or the foliar application of Zn did not affect the grain Cd concentration significantly ($p>0.05$).

Fig. 8 shows the effect of treatments on grain Zn concentrations. The grain Zn of the treatments except those with Zn application were 4.29–9.02% lower than the control, while foliar Zn treatments, P12M and P22M, were 1.10% and 0.133% higher than that of the control, respectively, and some of the differences were statistically significant ($p<0.05$). Although the P amendment did not affect the soil DTPA-extractable Zn concentrations significantly ($p>0.05$), it did affect the accumulation of Zn in wheat grains negatively. The Zn foliar treatment resulted in significantly higher grain Zn concentrations than the corresponding treatment without Zn application. The Zn concentrations of P22M was 10.1% higher than that of P22, while that of P12M was 9.86% higher than that of P12. For both low and high P rates, the split application of P resulted in lower Zn concentrations in wheat grains (3.84 and 2.76% lower than the corresponding treatments with single application, respectively).

The grain heavy metal concentration results indicated that, the P amendment in soil affected the accumulation of Pb and Zn in wheat grains, but had little effect on Cd accumulation. Split application of the same amount of P fertilizer resulted in lower Zn concentrations in wheat grains, while foliar application of Zn enhanced Zn accumulation in wheat grains.

Discussion

Accumulation of heavy metals in grains of wheat growing in contaminated soils

In recent years, higher concentrations of heavy metals than the maximum permissible concentrations in wheat grains have been reported in several areas in China upon cultivation and harvesting of wheat from smelter contaminated soils (Xing et al. 2016; Du et al. 2015). Lead from both soil and atmospheric deposition contributed to Pb accumulation in wheat grains. When the level of Pb atmospheric deposition is high, Pb accumulation from leaves may become the predominant source of Pb accumulation in wheat grains (Singh et al. 2007; Douay et al. 2008; Zhao et al. 2012). Douay et al (2008) found that the closedown of a lead smelter in France resulted in sharp decrease of wheat grain Pb concentrations while Cd levels did not change much. Zhao et al (2012) also found that atmospheric deposition was the predominant source of wheat grain Pb accumulation, resulting in 90–99% of Pb in wheat grains harvested near a Pb and Zn smelter in Shaanxi Province. Before 2009, more than 100 lead smelting facilities existed in Jiyuan city, most of them had low recovery of Pb of about 80–85% from raw materials (Li et al. 2009). Stricter controls caused the closing of most lead smelting plants, with only three lead smelting plants (Yuguang, Jinli and Wanyang) existing in Jiyuan at present (Qiu et al. 2016). The remaining facilities adopted better smelting techniques and facilities with much higher Pb recovery, thus, the atmospheric deposition near the lead smelting area in Jiyuan is believed to be much lower than that before 2009. This may partly explain why the soil P amendment in our study significantly affected Pb accumulation in wheat grains (Fig. 6). Unlike Pb, accumulation of Cd in wheat grains was mainly controlled by the concentration and availability of Cd in soil. Wang et al (2012) analyzed 126 pairs of soil and wheat samples collected from the lower reach areas of the Yangtze River and found that the grain Cd concentrations correlated positively with soil Cd concentrations ($p < 0.05$). Baize et al (2009) found positive correlations between wheat grain Cd concentration and soil DTPA-Cd concentrations ($p < 0.05$). The most important factors affecting phytoavailability of Cd in soil is soil pH, where lowering of soil pH will enhance Cd availability in soil (Basta et al. 2005). Application of soluble phosphate in calcareous soil often resulted in lower soil pH (Li et al. 2012). The possible lowering of soil pH and the contribution of soil Cd to wheat grain Cd accumulation may explain why grain Cd concentration was not affected negatively by the P amendment in soil.

Influence of soil P amendment on heavy metal accumulation in wheat grains

Only a few field investigations have investigated the effect of P amendment on grain Pb accumulation. In this work, higher P rates resulted in slightly lower Pb and Cd availability in soil (Figs. 3 and 4). Phosphate was amended at 400 or 541 g m⁻² in the present work, the corresponding P:Pb ratios (mol:mol) were 1.90 and 2.57, respectively. This indicated that the P:Pb ratios employed in this work did affect the heavy metal availability in soil and their accumulation in wheat grains, although the ratios were much smaller than that used by many other scientists, especially in field works (Chrysochoou et al. 2007). The effect was in good agreement with the results of our early pot experiment, which used the P:Pb of 2:1 (mol:mol) (Li et al. 2012). Hypothetically, if the phosphate rate is elevated above rates used in this study, a better inhibition effect of phosphate on Pb and Cd accumulation in wheat grains in this area may be expected. In this work, immobilization of Cd and Zn was more

insignificant than was observed for Pb, which mainly points to the higher solubility of phosphates of Cd and Zn than that of Pb (Kumpiene et al. 2008; Zhang, 2003). However, Rehman et al (2015) found substantial effect of Cd concentration reduction in wheat grains when the soil with 3.15 mg kg^{-1} Cd was amended with high amounts mono ammonium phosphate at 0.4% or 0.8% rates.

Split application of phosphate

In order to enhance the reaction between phosphate and Pb, we investigated the effect of split application of phosphate into the contaminated soils, hypothesizing that the split application may enhance the reaction between the Pb and phosphate ions, both of which have poor mobility in soils. However, the results did not prove the hypothesis, the split application did not result in lower concentration of DTPA-extractable Cd, Pb or Zn, but it resulted in lower grain Zn concentrations at both rates (Fig. 8). In a pot experiment, Sanderson et al (2016) employed split application of phosphate in a soil with Pb concentration of $177\text{--}2545 \text{ mg kg}^{-1}$ with time interval of 7 days, the split application resulted in higher Pb availability than the single application of the same rate of phosphate. The similar or even higher Pb availability of split application than the single application may relate to the lower soil pH just after phosphate application, because of the pH buffering capacity, the acidifying effect of phosphate will be compensated as time goes on.

Effect of foliar application of Zn on Cd accumulation in wheat grains

The negative effect of foliar application of Zn on Cd accumulation in wheat grains has been confirmed in several works (Saifullah et al. 2016; Sarwar et al. 2015; Zhao et al. 2005), Saifullah et al (2016) found that application of Zn in booting stage reduced the grain Cd concentration more than other stages. Sarwar et al (2015) found the concentration of Zn affected Cd accumulation in wheat grains. In this work, the Zn was applied on April 9, which is the jointing stage in the study area, the concentration used in this work was 0.1%, both the time and the concentration were different from the optimal conditions found in other works for better inhibition of Cd accumulation in wheat grains (Saifullah et al. 2016; Sarwar et al. 2015). This may be the reason of the very limited effect of Zn application on the accumulation of Cd in wheat grains in this work.

Potential effect of P on the alleviation of heavy metal toxicity by AM fungi

Arbuscular mycorrhizal (AM) fungi is important for plants and they colonize over 80% of terrestrial plants including wheat (Chen et al, 2005; Aguilera et al, 2018; Gunathilakae et al, 2018). AM fungi play important roles in alleviating plant stresses including heavy metal contaminations and low P availability stress in soil. AM fungi can inhibit the transformation of heavy metals to plant shoots, precipitate them in soil or retain heavy metals on fungal cells, thus alleviating the toxicity of the heavy metals in soil to plants (Gunathilakae et al, 2018). Phosphorus amendment in heavy metal polluted soils is also important for reducing the phytoavailability of metals to plants, as indicated in Figs 3 and 4. However, studies indicate that AM colonization of plants is inhibited by higher phosphorus availability in soil (Gosling et al, 2013; Sarabia et al, 2017). Hence, the effect of phosphorus amendment on the accumulation of heavy metals in the wheat grain in this work (Figs. 6–8) should be a combined effect of immobilization of these metals in soil with the phosphorus amendment

and less colonization of wheat roots with AM fungi after P amendment. However, which effect is more pronounced during this process needs further investigation.

Conclusions

The amendment with phosphate in soil resulted in higher soil P availability, however, the split application did not affect soil P availability significantly. Phosphate application resulted in lower availabilities of Pb and Cd in the soil. No significant effect of split application of phosphate was found on Pb and Cd availabilities in soil, and higher rates of phosphate resulted in lower Pb and Cd availabilities in the soil. Grain Pb, Cd and Zn concentrations were negatively affected by the phosphorus application, the higher rates of phosphate resulted in lower grain heavy metal concentrations. Foliar application of Zn during wheat growth increased the grain Zn concentrations significantly, while it had no statistically significant effect on Pb and Cd concentrations in the grain. Although the Pb and Cd concentrations in wheat grains were slightly reduced by the phosphate application, their concentrations were still much higher than the maximum permissible concentrations in the national standards. The results of the field experiment suggest that it is feasible to reduce the wheat grain concentrations of Pb and Cd in calcareous areas by soil application of superphosphate, however, the split application of the phosphate and the foliar application of Zn compounds do not have substantial effect on the accumulation of Pb and Cd in the wheat grains.

Acknowledgements

This work was sponsored by The National Key Research and Development Program of China (2016YFE0106400) and National Natural Science Foundation of China (41471253). The authors also want to thank Mr. Hongyi Zhang and Huiyang Tian for their help in sample collection. Although EPA contributed to this article, the research presented was not performed by or funded by EPA and was not subject to EPA's quality system requirements. Consequently, the views, interpretations, and conclusions expressed in this article are solely those of the authors and do not necessarily reflect or represent EPA's views or policies.

References

- Aguilera P, Larsen J, Borie F, Berríos D, Tapia C, Cornejo P (2018) New evidences on the contribution of arbuscular mycorrhizal fungi inducing Al tolerance in wheat. *Rhizosphere* 5, 43–50. 10.1016/j.rhisph.2017.11.002
- Baize D, Bellanger L, Tomassone R (2009) Relationships between concentrations of trace metals in wheat grains and soil. *Agron Sustain Dev* 29: 297–312. 10.1051/agro:2008057
- Baker LR, Pierzynski GM, Hettiarachchi GM, Scheckel KG, Newville M (2014) Micro-X-ray fluorescence, micro-X-ray absorption spectroscopy, and micro-X-ray diffraction investigation of lead speciation after the addition of different phosphorus amendments to a smelter-contaminated soil. *J Environ Qual* 43:488–497. 10.2134/jeq2013.07.0281 [PubMed: 25602650]
- Basta NT, Ryan JA, Chaney RL (2005) Trace element chemistry in residual-treated soils: key concepts and metal bioavailability. *J Environ Qual* 34:49–63 10.2134/jeq2005.0049dup [PubMed: 15647534]
- Bi X, Feng X, Yang Y, Li X, Shin GPY, Li F, Qiu G, Li G, Liu T, Fu Z (2009) Allocation and source attribution of lead and cadmium in maize (*Zea mays* L.) impacted by smelting emissions. *Environ Pollut* 157:834–839. 10.1016/j.envpol.2008.11.013 [PubMed: 19100668]
- Brown S, Chaney R, Hallfrisch J, Ryan JA, Berti WR (2004) In situ soil treatments to reduce the phyto- and bioavailability of lead, zinc, and cadmium. *J Environ Qual* 33:522–531. 10.2134/jeq2004.5220 [PubMed: 15074803]

- Chen B, Zhu Y-G, Zhang X, Jakobsen I (2005) The influence of mycorrhiza on uranium and phosphorus uptake by barley plants from a field-contaminated soil. *Environ Sci & Pollut Res* 12: 325–331. 10.1065/espr2005.06.267
- Chen L, Zhou S, Shi Y, Wang C, Wu S (2018) Heavy metals in food crops, soil, and water in the Lihe River Watershed of the Taihu Region and their potential health risks when ingested. *Sci Total Environ* 615:141–149. 10.1016/j.scitotenv.2017.09.230 [PubMed: 28964989]
- Chen S, Zhu Y, Ma Y. (2006) Effects of phosphate amendments on Pb extractability and movement of phosphorus in contaminated soil. *Acta Scientiae Circumstantiae* 26:1140–1144.
- Chinese Soil Taxonomy Research Group, Institute of Soil Science, Academi Sinica. (2001) Keys to Chinese Soil Taxonomy. Press of University of Science and Technology of China, Hefei, China.
- Chrysochoou M, Dermatas D, Grubb DG. (2007) Phosphate application to firing range soils for Pb immobilization: the unclear role of phosphate. *J Hazard Mater* 144:1–14. 10.1016/j.jhazmat.2007.02.008 [PubMed: 17360110]
- Das P, Samantaray S, Rout GR (1997) Studies on cadmium toxicity in plants: a review. *Environ Pollut* 98:29–36. 10.1016/S0269-7491(97)00110-3 [PubMed: 15093342]
- Douay F, Pelfrène A, Planque J, Fourrier H, Richard A, Roussel H, Girondelot B (2013) Assessment of potential health risk for inhabitants living near a former lead smelter. Part 1: metal concentrations in soils, agricultural crops, and homegrown vegetables. *Environ Monit Assess* 185:3665–3680. 10.1007/s10661-012-2818-3 [PubMed: 22886627]
- Douay F, Roussel H, Pruvot C, Waterlot C (2008) Impact of a smelter closedown on metal contents of wheat cultivated in the neighbourhood. *Env Sci Pollut Res* 15:162–169. 10.1065/espr2006.12.366
- Du L, Feng X, Yang S, Zhang S, Zhang N, Guo Z, Li L (2015) Soil environment quality of the metal smelting area in the south foot of Taihang Mountains. *J Henan Agric Univ* 49, 254–261.
- Gosling P, Mead A, Proctor M, Hammond J, Bending G (2013) Contrasting arbuscular mycorrhizal communities colonizing different host plants show a similar response to a soil phosphorus concentration gradient. *New Phytol* 198: 546–556. 10.1111/nph.12169 [PubMed: 23421495]
- Greger M, Landberg T. (2008) Role of rhizosphere mechanisms in Cd uptake by various wheat cultivars. *Plant Soil*, 312:195–205. 10.1007/s11104-008-9725-y
- Gunathilake N, Yapa N, Hettiarachchi R (2018) Effect of arbuscular mycorrhizal fungi on the cadmium phytoremediation potential of *Eichhornia crassipes* (Mart.) solms. *Groundw Sustain Dev*. 10.1016/j.gsd.2018.03.008
- Jiang S-T, Wang H-Y, Zhou J-M, Cheg Z-M, Liu X-W. (2016) Effects of phosphorus fertilizer application methods and types on the yield and phosphorus uptake of winter wheat. *Chin J Appl Ecol* 27:1503–1510. 10.13287/j.1001-9332.201605.034
- Kirkham MB (2006) Cadmium in plants on polluted soils: Effects of soil factors, hyperaccumulation, and amendments. *Geoderma* 137:19–32. 10.1016/j.geoderma.2006.08.024
- Kumpiene J, Lagerkvist A, Maurice C (2008) Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments- A review. *Waste Manag* 28:215–225. 10.1016/j.geoderma.2006.08.024 [PubMed: 17320367]
- Li L, Xing W, Xiang G, Yang L, Zhang H, Zhang J (2012) Immobilization of Pb and Cd in a lead smelting polluted soil with different amendments. *Acta Scientiae Circumstantiae*, 32:1717–1724.
- Li Z, Feng X, Li G, Bi X, Sun G, Zhu J, Qin H, Wang J (2011) Mercury and other metal and metalloid soil contamination near a Pb/Zn smelter in east Hunan province, China. *Appl Geochem* 26:160–166. 10.1016/j.apgeochem.2010.11.014
- Lu HP, Li ZA, Gascó G, Méndez A, Shen Y, Paz-Ferreiro J (2018) Use of magnetic biochars for the immobilization of heavy metals in a multi-contaminated soil. *Sci Total Environ* 622–623:892–899. 10.1016/j.scitotenv.2017.12.056
- Lu R (2000) Methods of soil and agro-chemical analysis. China Agricultural Science and Technology Press, Beijing, China.
- Munira S, Farenhorst A, Akinremi W (2018) Phosphate and glyphosate sorption in soils following long-term phosphate applications. *Geoderma* 313: 146–153. 10.1016/j.geoderma.2017.10.030
- Obrycki JF, Scheckel KG, Basta NT (2017) Soil solution interactions may limit Pb remediation using P amendments in an urban soil. *Environ Pollut* 2017, 220: 549–556. 10.1016/j.envpol.2016.10.002 [PubMed: 27751639]

- Qaswar M, Hussain S, Rengel Z (2017) Zinc fertilisation increases grain zinc and reduces grain lead and cadmium concentrations more in zinc-biofortified than standard wheat cultivar. *Sci Total Environ* 605–606:454–460. 10.1016/j.scitotenv.2017.06.242
- Qiu K, Xing W, Scheckel KG, Chen Y, Zhao Z, Ruan X, Li L (2016) Temporal and seasonal variations of As, Cd and Pb atmospheric deposition flux in the vicinity of lead smelters in Jiyan, China. *Atmo Pollut Res* 7:170–179. 10.1016/j.apr.2015.09.003
- Rehman MZ, Khalid H, Akmal F, Ali S, Rizwan M, Qayyum MF, Iqbal M, Khalid MU, Azhar M (2017) Effect of limestone, lignite and biochar applied alone and combined on cadmium uptake in wheat and rice under rotation in an effluent irrigated field. *Environ Pollut* 227:60–568. 10.1016/j.envpol.2017.05.003
- Rehman MZ, Rizwan M, Ghafoor A, Naeem A, Ali S, Sabir M, Qayyum MF (2015) Effect of inorganic amendments for in situ stabilization of cadmium in contaminated soils and its phyto-availability to wheat and rice under rotation. *Env Sci Pollut Res* 22: 16897–16906. 10.1007/s11356-015-4883-y
- Saifullah, Javed H, Naeem A, Rengel Z, Dahlawi S (2016) Timing of foliar Zn application plays a vital role in minimizing Cd accumulation in wheat. *Env Sci Pollut Res Int* 23:16432–16439. 10.1007/s11356-016-6822-y [PubMed: 27164881]
- Saifullah, Sarwar N, Bibi S, Ahmad M, Ok YS (2014) Effectiveness of zinc application to minimize cadmium toxicity and accumulation in wheat (*Triticum aestivum* L.). *Environ Earth Sci* 71:1663–1672. 10.1007/s12665-013-2570-1
- Sanderson P, Naidu R, Bolan N (2016) The effect of environmental conditions and soil physicochemistry on phosphate stabilisation of Pb in shooting range soils. *J Environ Manag* 170: 123–130. 10.1016/j.jenvman.2016.01.017
- Sarabia M, Cornejo P, Azcón R, Carreón-Abud Y, Larsen J (2017) Mineral phosphorus fertilization modulates interactions between maize, rhizosphere yeasts and arbuscular mycorrhizal fungi. *Rhizosphere* 4:89–93. 10.1016/j.rhisph.2017.09.001
- Sarwar N, Ishaq W, Farid G, Shaheen MR, Imran M, Geng M, Hussain S (2015) Zinc-cadmium interactions: Impact on wheat physiology and mineral acquisition. *Ecotoxicol Environ Saf* 122: 528–536. 10.1016/j.ecoenv.2015.09.011 [PubMed: 26426697]
- Sarwar N, Saifullah, Malhi SS, Zia MH, Naeem A, Bibi S, Farid G (2010) Role of plant nutrients in minimizing cadmium accumulation by plant. *J Sci Food Agric* 90:925–937. 10.1002/jsfa.3916 [PubMed: 20355131]
- Singh RP, Agrawal M (2007) Effects of sewage sludge amendment on heavy metal accumulation and consequent responses of Beta vulgaris plants. *Chemosphere* 67:2229–2240. 10.1016/j.chemosphere.2006.12.019 [PubMed: 17289111]
- Stecker JA, Brown JR, Kitchen NR (2001) Residual phosphorus distribution and sorption in starter fertilizer bands applied in no-till culture. *Soil Sci Soc Am J* 65:1173–1183. 10.2136/sssaj2001.6541173x
- Wang C, Ji J, Yang Z, Chen L, Browne P, Yu R (2012) Effects of soil properties on the transfer of cadmium from soil to wheat in the Yangtze River Delta region, China—a typical industry-agriculture transition area. *Biol Trace Elem Res* 148:264–274. 10.1007/s12011-012-9367-z [PubMed: 22389245]
- Yan Y, Qi F, Seshadri B, Xu Y, Hou J, OK YS, Dong X, Li Q, Sun X, Wang L, Bolan N (2016) Utilization of phosphorus loaded alkaline residue to immobilize lead in a shooting range soil. *Chemosphere* 162:315–323. 10.1016/j.chemosphere.2016.07.068 [PubMed: 27513552]
- Zhang H (2003) *Practical Handbook of Chemistry*. Science Press, Beijing, China.
- Zhang Y, Yin C, Cao S, Cheng L, Wu G, Guo J (2018) Heavy metal accumulation and health risk assessment in soil-wheat system under different nitrogen levels. *Sci Total Environ* 622–623: 1499–1508. 10.1016/j.scitotenv.2017.09.317
- Zhao D, Wei Y, Wei S, Guo B, Cai X (2012) Isotope analysis of lead pollution sources in wheat kernel. *Transactions Chin Soc Agric Eng* 28: 258–262. 10.3969/j.issn.1002-6819.2012.08.041
- Zhao Z, Zhu Y, Cai Y (2005) Effects of zinc on cadmium uptake by spring wheat (*Triticum aestivum* L.): long-time hydroponic study and short-time ¹⁰⁹Cd tracing study. *J Zhejiang Univ-Sci A*, 6:643–648. 10.1007/BF02856167

Zhu J, Li M, Whelan M (2018) Phosphorus activators contribute to legacy phosphorus availability in agricultural soils: A review. *Sci Total Environ* 612: 522–537. <https://doi.org/10.1016/j.scitotenv.2017.08.095> [PubMed: 28865270]

EPA Author Manuscript

EPA Author Manuscript

EPA Author Manuscript

Fig. 1.

Grain yields (dry weight) of wheat growing in lead smelting contaminated soils amended with P and with or without foliar application of Zn on wheat plants. P11- P:Pb (mol:mol)=1.90, all the P was applied at planting, P12-P:Pb (mol:mol)=1.90, 60% applied at planting, the remaining 40% at jointing stage, P12M- P:Pb (mol:mol)=1.90, 60% applied at planting, the remaining 40% at jointing stage, with foliar application of Zn at jointing stage, P21- P:Pb (mol:mol)=2.57, all the P was applied at planting, P22-P:Pb (mol:mol)=2.57, 60% applied at planting, the remaining 40% at jointing stage, P22M- P:Pb (mol:mol)=2.57, 60% applied at planting, the remaining 40% at jointing stage, with foliar application of Zn at jointing stage.

Fig. 2.

Soil concentrations of Olsen-P of lead smelting contaminated soils amended with P and with or without foliar application of Zn on wheat plants. P11- P:Pb (mol:mol)=1.90, all the P was applied at planting, P12-P:Pb (mol:mol)=1.90, 60% applied at planting, the remaining 40% at jointing stage, P12M- P:Pb (mol:mol)=1.90, 60% applied at planting, the remaining 40% at jointing stage, with foliar application of Zn at jointing stage, P21- P:Pb (mol:mol)=2.57, all the P was applied at planting, P22-P:Pb (mol:mol)=2.57, 60% applied at planting, the remaining 40% at jointing stage, P22M- P:Pb (mol:mol)=2.57, 60% applied at planting, 40% at jointing stage, with foliar application of Zn at jointing stage.

Fig. 3.

Concentrations of DTPA-extractable Pb of lead smelting contaminated soils amended with P and with or without foliar application of Zn on wheat plants. P11- P:Pb (mol:mol)=1.90, all the P was applied at planting, P12-P:Pb (mol:mol)=1.90, 60% applied at planting, the remaining 40% at jointing stage, P12M- P:Pb (mol:mol)=1.90, 60% applied at planting, the remaining 40% at jointing stage, with foliar application of Zn at jointing stage, P21- P:Pb (mol:mol)=2.57, all the P was applied at planting, P22-P:Pb (mol:mol)=2.57, 60% applied at planting, the remaining 40% at jointing stage, P22M- P:Pb (mol:mol)=2.57, 60% applied at planting, the remaining 40% at jointing stage, with foliar application of Zn at jointing stage.

Fig. 4. Concentrations of DTPA-extractable Cd of lead smelting contaminated soils amended with P and with or without foliar application of Zn on wheat plants.

Fig. 5. Concentrations of DTPA-extractable Zn of lead smelting contaminated soils amended with P and with or without foliar application of Zn on wheat plants.

Fig. 6. Grain Pb concentration wheat growing in lead smelting contaminated soils amended with P and with or without foliar application of Zn on wheat plants.

Fig. 7. Grain Cd concentration of wheat growing in lead smelting contaminated soils amended with P and with or without foliar application of Zn on wheat plants.

Fig. 8.

Fig. 8 Grain Zn concentration of wheat growing in lead smelting contaminated soils amended with P and with or without foliar application of Zn on wheat plants.

Table 1

Treatments of the experiment

Code	Superphosphate		ZnSO ₄	
	Rate (g·m ⁻²)	Method of application	rate(g·m ⁻²)	Method of application
CK	0	-	-	-
P11	400	100% applied at planting	-	-
P12	400	60% applied at planting, the remaining 40% at jointing stage	-	-
P12M	400	60% applied at planting, the remaining 40% at jointing stage	0.25	100% applied at jointing stage
P21	541	100% applied at planting	-	-
P22	541	60% applied at planting, the remaining 40% at jointing stage	-	-
P22M	541	60% applied at planting, the remaining 40% at jointing stage	0.25	100% applied at jointing stage