Chemical speciation of trace metals in atmospheric deposition and impacts on soil geochemistry and vegetable bioaccumulation near a large copper smelter in China

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Key Points

- Bioavailable fractions of trace metals from recent atmospheric deposition were higher compared to metals originally present in soils.
- Recently deposited trace metals contributed 15-76% of cupper, cadmium and lead to edible parts of vegetables.
- Reducing current atmospheric deposition loads of trace metals has quick and strong effects on their accumulation in the vegetable.

Abstract: Atmospheric deposition is an important source of trace metals to surface environments, but knowledge about plant bioavailability of recently deposited metals is limited. We performed a fully factorial soil and atmosphere exposure experiment with three vegetables (radish, lettuce, and soybean), which allowed to effectively distinguish impacts of recently deposited metals (<1 year) from longer-term metal exposures in soils. Results showed that recently deposited Cu, Cd, and Pb accounted for 0.5-15.2% of total soil Cu, Cd, and Pb pools near emission source, while they contributed 15-76% of Cu, Cd, and Pb concentrations in edible parts of vegetables. The soil retention of recently deposited metals (52-73%) presented as higher mobile fractions than these previously present in soils (7-42%). These findings highlight a preferential uptake and high rates of bioaccumulation of deposited metals in vegetables and implicated that quick and potentially stronger reduction can be achieved by reducing current atmospheric source loads.

Keywords: Wet and dry deposition; Metal speciation; Soil geochemistry; Vegetable bioaccumulation

Plain Language Summary

Atmospheric deposition is a globally important source of trace metals in agricultural soils but limited attention has been given to the risk of recently deposited metals for bioaccumulation in vegetables. We performed a fully factorial soil and atmosphere exposure experiment with vegetables (radish, lettuce, and soybean) planted across three sites located along a strong gradient of atmospheric deposition, which allowed to distinguish between impacts of recently deposited metals and metals originally present in soils. The results demonstrated that recently deposited trace metals showed high bioavailability contributing preferentially to uptake in edible parts of vegetables compared to metals previously present in soils. These findings highlight a key role of atmospheric deposition for trace metals in bioaccumulation in vegetables and suggest effective measures for reducing atmospheric emissions of trace metals should been implemented to reduce environmental risks of food contamination.

1. Introduction

Soil pollution of farmland in China has caused extensive concerns in the last decades due to adverse impacts on ecosystems and human health (Hu et al., 2016; Zhao et al., 2015). A key survey by the Ministry of Ecology and Protection of the People's Republic of China conducted between 2005 and 2013 indicated that 19.4% of collected samples of agricultural soils exceeded the environmental quality standard of China, especially by exceedance of trace metals loads (cadmium, copper, lead, arsenic, mercury, chromium, etc.) causing heavy pollution. According to estimates, more than 12×10^6 t of annual crop production in China is polluted by trace metals potentially causing health risks via dietary intake, while direct inhalation and dermal contact may be of lower concern (Hu et al., 2016; Zhang et al., 2019). Identification of the sources and impacts of trace metals in agricultural systems is a first and critical step to protect agricultural production safety (Imseng et al., 2018; Salmanzadeh et al., 2017). Principle external sources of trace metals in farmland of China include agricultural irrigation, pesticide and fertilizer application, and atmospheric deposition (Ha et al., 2014; Larson, 2014; Peng et al., 2019). Previous studies were focused largely on pollution via the former two sources (Habibollahi et al., 2018; Wang et al., 2018), while effects of atmospheric deposition are less known. Atmospheric emissions of trace metals from anthropogenic activities have rapidly increased in the last decades and emissions of Cd, Cu, Pb, As, and Zn from anthropogenic sources into the atmosphere in China have reached 530 tons (Cd), 9,500 tons (Cu), 14,000 tons (Pb), 2,500 tons (As), and 22,000 tons (Zn) in 2012, respectively (Tian et al., 2015). Atmospheric deposition has been an important pathway for the transfer trace metals from point source of atmospheric emissions to surface environments (Bridgestock et al., 2017; Chien et al., 2019; Chrastny et al., 2015) and are estimated to account for more than 50% of total As, Cd, Cr, Hg, and Pb loads in agricultural soils across China (Peng et al., 2019).

Atmospheric deposition is considered to have high bioavailability in surface environments (Wang et al., 2017; Wilcke & Kaupenjohann, 1998). Research indicated that 68-74% of Cd and Zn in wet deposition are in dissolved fractions and that 25-33% of Cd and Zn in dry deposition occur in water-soluble fractions (Morselli et al., 2003). Other studies also indicated that trace metals from atmospheric deposition have high proportion of bioavailable fractions (Prieto-Parra et al., 2017; Pyeong-Koo et al., 2015) as they are preferentially retained in surface soil aggregates and found to have higher exchangeable fractions compared to metals originally present in soil aggregates (Wilcke & Kaupenjohann, 1998). Another study suggested atmospheric Cu deposition show high toxicity and inhibit phytoplankton growth in the Mediterranean Sea (Jordi et al., 2012). Combined, these studies suggest that trace metals recently deposited (<1 year of deposition) may have particularly high environmental risks and potentially high uptake and biological effects in vegetables. Differentiation of effects of recently deposited (e.g., during vegetable growing period) and original metal loads in soils available to vegetables is crucial to understand how metals accumulation may respond to changing metal deposition loads (Hintelmann et al., 2002).

Here, we present the results of a systematic experiment on bioaccumulation of trace metals from recent atmospheric deposition versus longer-term soil exposures in three vegetables (radish, lettuce, and soybean) by means of a fully factorial soil and atmosphere exposure design including seven treatment groups (2 to 3 soil exposures (S1, S2, and S3 soils) and 3 atmospheric exposures (A1, A2, and A3 sites)) conducted near a copper smelter of Guixi city, known as China's copper capital located in southeastern China (Supplementary information, Fig. S1 and Table S1). The study includes detailed analysis of soil and atmospheric deposition including chemical speciation and bioavailability estimates of trace metals.

2. Materials and methods

2.1. Experimental design

To constrain bioavailability of recently deposited trace metals in soil-vegetable system, a fully factorial soil and atmosphere exposure design with replications (n = 3) in soil profile (dimensions: 0.58 m length×0.44 m wide×0.32 m height) was conducted between July 2017 and June 2018 including seven treatment groups (Fig. S2 and Table S2). Moderately (80.02±0.88 mg/kg Cu, 0.72±0.05 mg/kg Cd, and 50.20±0.43 mg/kg Pb) and heavily (556.67±12.61 mg/kg Cu, 1.66±0.05 mg/kg Cd, and 74.13±1.77 mg/kg Pb) polluted soils (due to the long-term metal smelting emissions) from two sites (A2 and A3) were transferred to the remote site A1, while unpolluted soil (23.32±0.09 mg/kg Cu, 0.22±0.01 mg/kg Cd, and 29.61±0.19 mg/kg Pb) from site A1 was transferred to polluted sites A2 and A3. As a result, three treatment groups were placed at the control site A1, including A1-S1 (filled with soil from the control site), A1-S2 (filled with soil from the moderate deposition site A2), and A1-S3 (filled with soil from the high deposition site A3). Two treatment groups were placed at the moderate deposition site A2, including A2-S1 (filled with the soil from the control site) and A2-S2 (filled with the soil from moderate deposition site). Finally, two treatment groups were placed at the high deposition site A3, including A3-S1 (filled with the soil from the control site) and A3-S3 (filled with the soil from high deposition site). To manage the high number of treatment numbers, we selected not to expose soil from moderate deposition site A2 at the high atmospheric deposition site A3, and vice versa not to expose soil from the high deposition site A3 at the moderate atmospheric deposition site A2.

Three widely cultivated vegetables, including radish (*Raphanus sativus* L., rhizome vegetable), lettuce (*Lactuca sativa* L., leaf vegetable) and soybean (*Phaseolus vulgaris* L., fruit vegetable), were grown in each of these soil-atmosphere exposure treatments, resulting in a total of 63 plant samples (2-3 soil exposures, 3 atmospheric exposures, 3 vegetable types, 3 replications). The vegetable types were chosen because they represented different edible parts for human consumption, i.e., rhizomes for radish, leaves for lettuce, and seeds for soybean. The planting order and growing season of three vegetables were chosen according to local farming practices and described in Supplementary information (SI).

The treatment A1-S1 (soil from the control site and exposed to low atmospheric deposition) was used to estimate bioaccumulation under background conditions. The sequence of treatments A1-S1, A1-S2, and A1-S3 representing increasing soil trace metals exposed to low atmospheric deposition allowed to quantify effects of past (i.e., >1 year) atmospheric deposition impacts (Zhou et al., 2018). Differences among treatments A1-S1, A2-S1, and A3-S1 were used to quantify increasing atmospheric deposition loads of trace metals in low background soils. Finally, treatments A1-S2 and A2-S2 and treatments A1-S3 and A3-S3 were similarly designed to assess increasing atmospheric deposition effects in moderately and heavily polluted soils. Further details on the experimental design are described in SI.

2.2. Sample collection and analysis

2.2.1. Atmospheric deposition measurements and characterization of trace metal deposition chemistry, speciation, and size distribution

Atmospheric wet and dry deposition samples were collected monthly from July 2017 to June 2018 at each site using automatic wet and dry deposition sampler (APS-3A, Changsha Xianglan Scientific Instruments Co., Hunan, China). In wet deposition, hydrodynamic diameter, pH, and size distribution (> 0.45 μm for particulate, < 0.45 μm for dissolved fraction, and < 3 kDa for defined ionic fraction) of Cu, Cd, and Pb were determined (Javed et al., 2017). For dry deposition, mineral composition by X-ray diffractometer (XRD, Ultima IV, Japan) analysis and chemical fractions of Cu, Cd, and Pb (F1 exchangeable, F2 carbonate, F3 reducible, F4 organic and sulfide, and F5 residual fractions) by Tessier five-step sequential extraction were determined. In addition, the mineral composition of dust samples collected from a smelter bag filter in the Guixi copper smelter was also characterized by XRD to confirm that the likely origin of dry deposition is linked to this emission source. Further details on the samplers and sampling and analytical methods are detailed in SI.

2.2.2. Vegetable and soil sampling and trace metal characterization

Three vegetables (radish, lettuce, and soybean) were grown in sequence for the duration of 60, 45, and 75 days, respectively and harvested in early March, mid-April, and late June 2018, respectively. Contents of Cu, Cd, and Pb in vegetable tissues (rhizomes (or root) and shoot for radish and lettuce, root, stem, leaf, pod, and seed for soybean) were extracted using a 1:1 mixture of HNO_3 and H_2O_2. Surface soils were collected after final harvest in June 2018 by stratified sampling in the following depth increments: 0-2, 2-4, 4-6, 6-10, 10-15, and 15-20 cm. Concentration and speciation of Cu, Cd, and Pb in soils were characterized by Tessier five-step sequential extraction. Detailed description of sampling and analytical methods can be found in SI.

2.2.3. Bioaccumulation contribution factors

Contributions (C, %) of trace metals originally present in soils to vegetable bioaccumulation were estimated as follows:

$$C = (MC_{A1\text{-}S2} - MC_{A1\text{-}S1})/(MC_{A1\text{-}S2})$$

$$C = (MC_{A1\text{-}S3} - MC_{A1\text{-}S1})/(MC_{A1\text{-}S3}) \qquad (1)$$

where $MC_{A1\text{-}S2}$, $MC_{A1\text{-}S3}$, and $MC_{A1\text{-}S1}$ are concentrations of Cu, Cd, and Pb (mg/kg dry weight) in vegetable tissues grown in the moderate pollution soil (S2), heavy pollution soil (S3), and background soil (S1) respectively using samples placed at the control site (A1).

Contributions (C, %) of recently deposited trace metals to vegetable bioaccumulation were estimated as follows:

$$C = (MC_{A2\text{-}S1} - MC_{A1\text{-}S1})/(MC_{A2\text{-}S1})$$

$$C = (MC_{A3\text{-}S1} - MC_{A1\text{-}S1})/(MC_{A3\text{-}S1})$$

$$C = (MC_{A2\text{-}S2} - MC_{A1\text{-}S2})/(MC_{A2\text{-}S2})$$

$$C = (MC_{A3\text{-}S3} - MC_{A1\text{-}S3})/(MC_{A3\text{-}S3}) \qquad (2)$$

where $MC_{A2\text{-}S1}$, $MC_{A2\text{-}S2}$, $MC_{A1\text{-}S1}$, and $MC_{A1\text{-}S2}$ are concentrations of Cu, Cd, and Pb (mg/kg dry weight) in vegetable tissues in moderate deposition site (A2) and control site (A1) filled with the soils S1 and S2, and $MC_{A3\text{-}S1}$, $MC_{A3\text{-}S3}$, $MC_{A1\text{-}S1}$, and $MC_{A1\text{-}S3}$ represent exposures to high deposition (A3) and control (A1) sites filled with soils S1 and S3.

2.3. Statistical Analysis

Statistical analyses for all data were performed using SPSS 20.0. The differences of Cu, Cd, and Pb concentrations in soils and vegetables were analyzed among A1, A2, and A3 sites based on the one-way analysis of variance (ANOVA, Least Significant Difference test). All differences in means (n = 3) were considered significant at the $p = 0.05$ level (two-tailed).

3. Result and discussion

3.1 Cu, Cd, and Pb accumulation in vegetable and nutritional quality analysis

Cu, Cd, and Pb concentrations in soybean seed, the edible part of that vegetable, grown in control soils were 20.21±0.99, 0.38±0.02, and 0.32±0.01 mg/kg when exposed to high atmospheric deposition (A3-S1) and significantly higher ($p < 0.05$) compared to low atmospheric exposures (A1-S1: 15.41±1.14, 0.26±0.01, and 0.18±0.01 mg/kg) (Fig. 1). Similarly, Cu, Cd, and Pb concentrations in radish rhizomes (the edible part) grown in control soils (A1-S1) of 3.97±0.25, 0.52±0.03, and 0.38±0.01 mg/kg were significantly increased under high atmospheric deposition (A3-S1, 7.36±0.38, 1.21±0.12, and 0.83±0.03 mg/kg) (Fig. S3). For lettuce, Cu, Cd, and Pb concentrations of shoots grown in control soils (A1-S1, 8.15±0.40, 3.78±0.28, and 1.37±0.03 mg/kg) significantly increased to 33.96±1.96, 8.25±0.26, and 3.75±0.11 mg/kg (A3-S1) when exposed to high atmospheric deposition (Fig. S4). Meanwhile, trace metals concentrations of other, non-edible root and shoot tissues of the three vegetables grown in control and strongly polluted soils exposed to the high deposition (A3) were also statistically significantly increased compared to those exposed at the control site (A1) (Fig. 1, Fig. S3, and Fig. S4). Similarly, plant Cu, Cd, and Pb concentrations in control and moderately polluted soils were significantly and slightly increased when exposed to moderate deposition (A2) compared to the control site (A1) (Fig. 1, Fig. S3, and Fig. S4). For instance, Cu, Cd, and Pb concentrations of lettuce shoot in moderately polluted soil exposed to moderate deposition (A2) were 19.75±0.65, 16.92±0.57, and 3.43±0.12 mg/kg (A2-S2), which were significantly higher compared to low atmospheric exposures (A1-S2: 15.76±0.91, 14.66±0.44, and 2.81±0.09 mg/kg), respectively (Fig. S4). These results showed that trace metals accumulation in vegetable plant are significantly and slightly increased under both high and moderate atmospheric deposition loads.

Trace metals concentrations of vegetable plants strongly responded to longer-term soil pollution levels (S1, S2, and S3) as well. For instance, Cu, Cd, and Pb concentrations of soybean seeds from control soils (A1-S1: 15.41±1.14, 0.26±0.01, and 0.18±0.01 mg/kg) significantly increased to 19.06±1.03, 0.68±0.02, and 0.25±0.01 mg/kg in moderately polluted soil (A1-S2) and 24.36±2.18, 0.99±0.02, and 0.29±0.01 mg/kg in heavily polluted soil (A1-S3) (Fig. 1). Similarly, trace metals concentrations of other tissues in the three vegetables grown in polluted soils (S2 and S3) also were statistically significantly increased ($p < 0.05$) compared to those in control soil (S1) (Fig. 1, Fig. S3, and Fig. S4). Different soil exposures S1 through S3 are indicative of effect of past (i.e., >1 year) atmospheric deposition impacts similar to observed increases in previous studies for Pb in vegetables and maize from long-term atmospheric deposition inputs near nonferrous metal smelters (Bi et al., 2009; Li et al., 2012).

By comparing concentration increase in tissues of moderate and high atmospheric exposures compared to control locations, we calculated the percentage contribution of recently (<1 year) atmospheric deposition according to the Eq. (2). Contributions induced by atmospheric deposition to Cu, Cd, and Pb in soybean seed ranged from 2-14% and 15-42% in plants exposed to moderate (A2) and high (A3) atmospheric deposition sites, respectively (Table S3). For radish, Cu, Cd, and Pb from atmospheric deposition in rhizomes, representing the edible part, ranged from 5-12% and 16-57% under moderate and high atmospheric deposition exposure sites, respectively (Table S4). For lettuce, Cu, Cd, and Pb from atmospheric deposition in shoots as the edible parts ranged from 13-35% and 18-76% under moderate and high atmospheric deposition exposure sites, respectively (Table S5). Similarly, by comparing concentration increases in tissues due to soil exposures at the control site, we calculated the percentage contribution of earlier (i.e., >1 year) atmospheric deposition to trace metals concentrations according to the Eq. (1). Contributions by soil exposures to Cu, Cd, and Pb in soybean seed ranged from 19-62% and 29-74% in plants exposed to moderately (S2) and heavily (S3) polluted soils, respectively (Table S6). Similar results were also observed in radish rhizome and lettuce shoot (Table S6). These results indicate that trace metal accumulation in various vegetables and tissues exposed to recent atmospheric deposition was enhanced compared to original root-to-shoot transfer of trace metals from soils.

We also observed that contributions under high atmospheric deposition loads (A3-S1) were always higher in lettuce shoots compared to that of soybean seeds and radish rhizomes. For example, Cu contributions from recent deposition averaged 76% in lettuce shoots compared to 24% in soybean seeds and 46% in radish rhizomes. Similar effects were observed for Pb and Cd (Table S3, S4, and S5). These patterns may be related to different transfer pathways of trace metals to various tissues (Shahid et al., 2016): for example, atmospheric deposition can be absorbed by direct foliar uptake or indirectly through soil-root uptake after deposition (Schreck et al., 2014). Still, we propose that trace metals in radish rhizomes largely accumulate from soil-root transfer pathway, similar to a previous study that concluded that < 1% of foliar uptake can be translocated to root tissues (Shahid et al., 2016). For lettuce shoot and soybean seeds, the two uptake pathways may occur simultaneously. Indeed, significant differences in Cu, Cd and Pb concentrations were observed between washed and unwashed leaves and pods of soybean (see description of experimental design in Text S5) suggesting that airborne trace metals can be directly taken up and fixed in leaves and pods (Fig. 1) and then be partially transported from the leaves to seeds via phloem stream along with photosynthates (Shahid et al., 2016). Higher trace metals concentrations of lettuce and soybean roots exposed at high deposition site also indicate a pathway of atmosphere-soil-root transfer similar to that in radish rhizome whereby metals in root are transported to the aerial parts via xylem transport. Unfortunately, the present study cannot accurately distinguish the effect of the two transfer pathways because pathways likely occur simultaneously.

It is noteworthy that recently deposited Cu, Cd, and Pb at the high deposition site (A3-S1) accounted for 1-15% of total trace metal pools in soils but 24-76% in edible vegetation parts. In heavily polluted soils (A3-S3), recent deposition accounted for soil pool sizes of 0.5-2.1% while in edible plants recent atmospheric deposition accounted for 15-54% of loads. While recently deposited metals contributed much lower proportions (< 1%) to soils under moderate deposition in treatments A2-S1 and A2-S2, contribution to edible plants from recent deposition were between 2 and 35%. These results highlight a high bioaccumulation potential of recently deposited trace metals in vegetables roots, leaves, and seeds. This is an important finding and reasons for high bioaccumulation are discussed in sections 3.2 and 3.3.

3.2 Cu, Cd, and Pb in soils

Total Cu and Cd concentrations in surface horizons (0-2 or 2-4 and 4-6 cm) exposed at deposition sites A2 and A3 after one year were significantly increased compared to corresponding soils exposed at the control site A1 (Fig. 2A-F). Similarly, Pb concentrations in topsoil (0-4 cm) exposed at sites A2 and A3 were slightly (but not statistically significant) increased compared to soil exposed at A1 (Fig. 2G-I). Obviously, original soil metal concentrations differed significantly between soils collected from the three sites (mean values of 0.22-1.66 mg/kg for Cd and 23.32-556.67 mg/kg for Cu, Table S1). Combined, soils showed statistically significant concentration differences in surface soil metal concentrations after one year from lowest to highest exposure sites, with a mean increase of mean 0.19 mg/kg for Cd and mean 34.73 mg/kg for Cu (Fig. 2 and Table S7). The results suggest that while farmland soils experience substantial long-term atmospheric deposition with highest pollution loads found nearby the large smelter, relatively short exposures (1 year) to high atmospheric deposition results in further trace metal concentration enhancements in surface soils. At the same time, total Cu, Cd, and Pb concentrations in deeper soils (6-20 cm profile) were not affected ($p > 0.05$) by different atmospheric deposition exposures (Fig. 2) indicating that recently deposited trace metals were largely retained in surface soil. Reason for efficient surface accumulation of trace metals include physical retention, adsorption and complexing effects from clay minerals, iron oxides and organic matter in the upper soil layers (Stolpe et al., 2013; Werkenthin et al., 2014).

Environmental risk of trace metals in soils strongly depended on chemical speciation, especially on exchangeable fractions (Liu et al., 2017; Uzu et al., 2009). Sequential extraction results in our study show that the concentrations and percentages of exchangeable Cu and Cd in the surface horizons exposed to moderate and high atmospheric deposition sites (A2 and A3) after one year were increased 110 to 610% (in concentrations) and 0.9 to 10.6 % (as percentage exchangeable, respectively; Table S7 and Fig. S5). For instance, exchangeable Cu and Cd (9.2±0.3 and 0.13±0.01 mg/kg) in the surface (0-2 cm profile) of background soils exposed to 1 year of high atmospheric deposition (A3-S1) was 6.1 and 2.2 times higher than exposed at the background site (A1-S1: 1.5±0.1 and 0.06±0.00 mg/kg). In addition, percentages of exchangeable fractions also increased, e.g., accounting for 17% and 29% for Cu and Cd at high atmospheric exposures in control soils (A3-S1, 0-2 cm profile) compared to background atmospheric exposures (A1-S1: 6% and 19%, respectively), under simultaneously decreased percentages of immobile Cu and Cd (Fig. S5). These results indicate that recently deposited trace metals in topsoil are present in highly bioavailable fractions exceeding availability of trace metals previously present in soils. This notion partly explains the finding of high bioaccumulation of recently deposited trace metals reported in vegetable in the section above (e.g. see Fig. 1).

3.3 Atmospheric Cu, Cd, and Pb deposition

Atmospheric deposition fluxes of Cu, Cd, and Pb, separated into wet and dry deposition components over the one year period of measurements (July 2017 to June 2018) at the three gradient sites (A1, A2, and A3) are shown in Fig. 3A. Deposition fluxes show strong gradients in deposition loads with distance from the smelter: highest annual bulk deposition (combined wet and dry deposition) of Cu, Cd, and Pb were 1091.8, 8.6, and 87.5 mg/m^2 in A3, which was about 9, 4, and 3 times higher than deposition measured at site A2 (117.2, 2.4, and 29.2 mg/m^2) and about 67, 9, and 13 times higher than at the control site A1 (16.4, 0.9, and 6.8 mg/m^2), respectively.

Chemical fractionation of wet deposition can reveal additional information about biological activities (Lee et al., 2015; Liu et al., 2017). Our results showed that most Cu, Cd, and Pb (85-97%) in wet deposition across the three study sites (Fig. 3B) was in dissolved and colloid fractions (< 0.45 μm). In addition, the ionic fraction (associated with < 3 kDa size particles) of Cu, Cd, and Pb accounted for 70-85% of total wet deposition. We propose that very low pH observed in wet deposition (3.07-6.30) (Table S8) promote particle dispersion and increases solubility of trace metals. Indeed, results of hydrodynamic diameter analysis (Table S8) showed that the main particles in wet deposition were in the nanometer scale (2.99-88.07 nm), which was consistent with or smaller than the previous report for metal particles sizes (50 nm -1 um) in cloud droplets (Li et al., 2013). The fractionation of trace metals in atmospheric deposition is important as metals in small size particles are more easily absorbed and bioaccumulated in crop (Ma et al., 2010; Peng et al., 2018).

We compared the mineralogical compositions of dry deposition across the three study sites with dust collected from the Cu smelter and found that they showed strong similarities. We show XRD fitting curves for site A3 and dust in Fig. 3D as an example. All samples were mainly composed of quartz, feldspar, calcite, and hydromica (Fig. 3D), suggesting that atmospheric deposition in the study area was related to emissions from the Cu smelter. Sequential extraction experiments of dry deposition (Fig. 3C) showed that Cu was primarily bound to organics and sulfides (Fraction F4: 57-71%) and in reducible fraction (F3: 13-22%), which is in agreement with the mineralogical composition of dust from the smelter and in deposition sample analysis that shows Cu sulfides and oxides (Cu_2S, Fe_5CuO_8, and Cu_2O) (Fig. 3D). Pb in dry deposition of the three study sites was dominantly bound to reducible fraction (fraction F3: 43-46%) and was followed by organics and sulfides (F4: 17-23%) (Fig.

3C). Additionally, a smaller fraction of Cu and Pb occurred in the exchangeable form (F1: Cu 8-10% and Pb 10-15%) indicating that dry deposited Cu and Pb in our study may be potentially less mobile. Compared to Cu and Pb, the exchangeable (F1) and carbonate fractions (F2) of Cd were highest (16-22% and 9-11%) indicating relatively high bioactivity of Cd (Liu et al., 2017). As mentioned, as the study area showed strong acid deposition and soils were strongly acidified (soil pH of 4.28-5.27) (Table S1), we suggest that the sum of a wet deposition (< 0.45 μm) plus dry deposition fractions F1 + F2 may serve as a measure of bioavailable fractions in our study. Following this approach, bioavailable fractions of Cu, Cd, and Pb from atmospheric deposition were in the range of 52-65% for Cu, 68-73% for Cd, and 53-58% for Pb of total deposition. Using the speciation in soils, the bioavailability of trace metals from measured atmospheric deposition exceeded the bioavailability in soils, which we determined to be 8-19% for Cu, 36-42% for Cd, and 7-14% for Pb (Table S7). The results indicate recently deposited trace metals to have much higher bioavailability compared to previous deposition or natural background of trace metals observed in soils. This notion further explains our finding: recently deposited trace metals have high bioavailability contributing preferentially to uptake in edible parts of vegetables compared to trace metals previously present in soils.

4 Environmental implications

Current remediation strategies of reducing trace metals in polluted cropland soils in China are mainly driven by immobilization of amendments in-situ, yet their effects are not particularly high (10%-50%) (Ali et al., 2020; Gong et al., 2020; Huang et al., 2020; Liu et al., 2020) and immobilization efficiencies decrease over time (Cui et al., 2016). The major implication of this study is that quick and potentially stronger reduction trace metal accumulation (2%-76%) in edible parts of vegetables can be achieved by reducing current atmospheric source loads. Therefore, eliminating and reducing current atmospheric deposition loads of trace metals should be considered as an environmental risk management strategy to reduce vegetable trace metal pollution.

Notes

The authors declare no competing financial interest.

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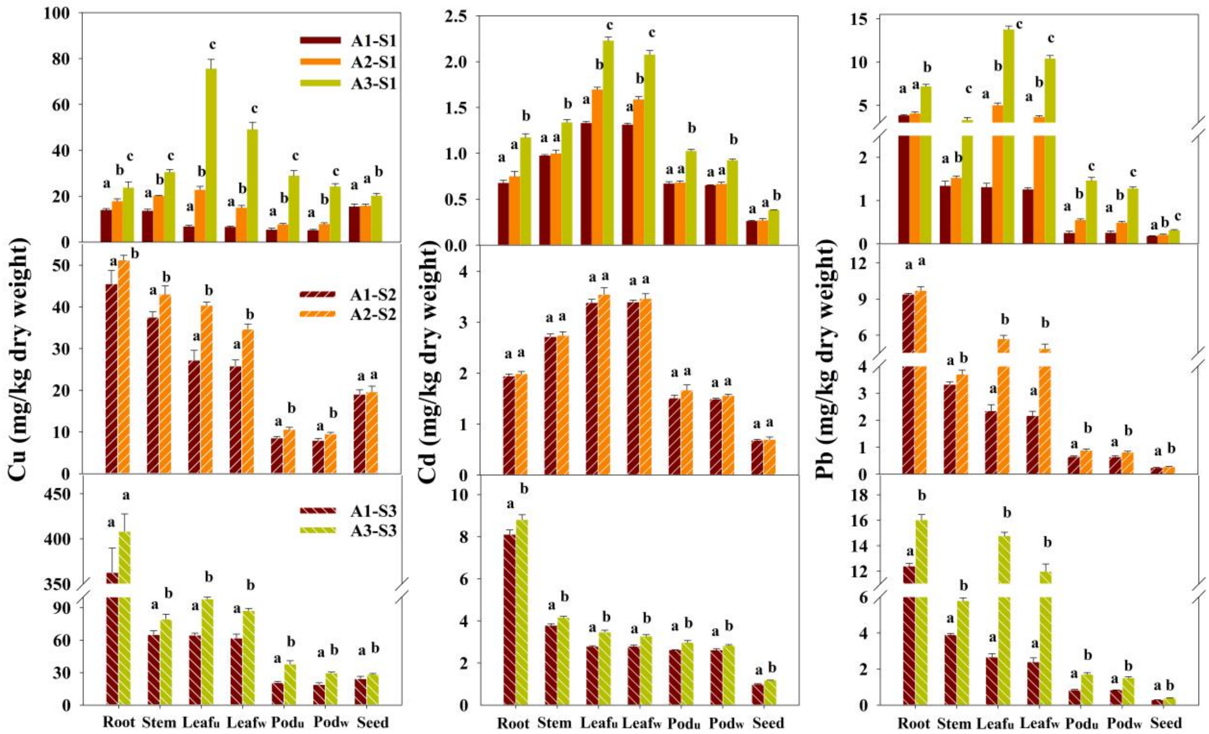

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514 **Fig. 1.** Concentrations of Cu, Cd, and Pb in root, stem, $leaf_u$ (without washing), $leaf_w$

515 (washing), pod_u (without washing), pod_w (washing), and seed of soybean. Different letters

516 indicate values significantly different among three deposition sites ($p < 0.05$).

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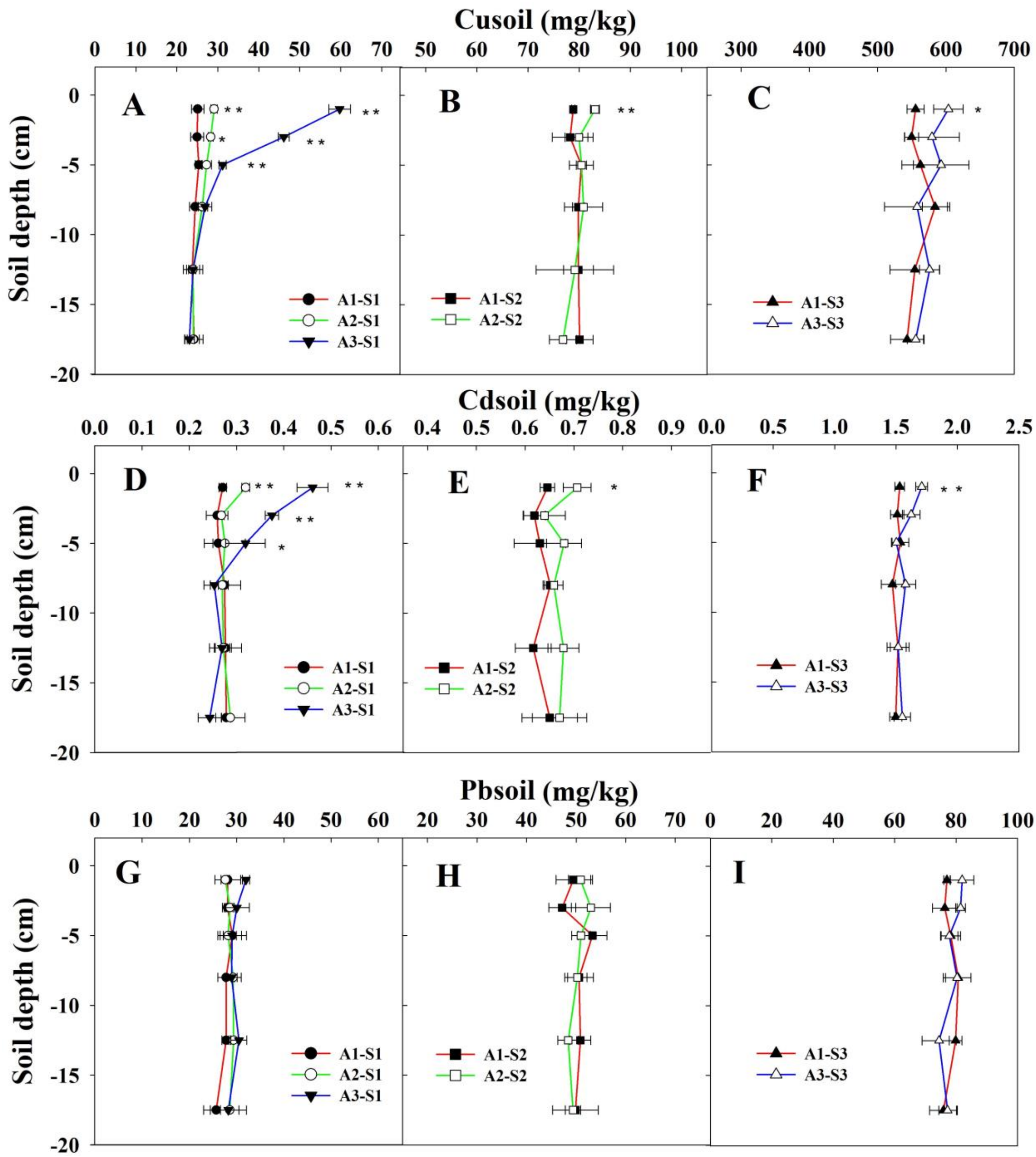

Fig. 2. Cu, Cd, and Pb concentrations in soils (0-20 cm profile). One asterisk and two asterisks indicate values significantly different between the deposition sites (A2 and A3) and control site (A1) ($p < 0.05$ and $p < 0.01$).

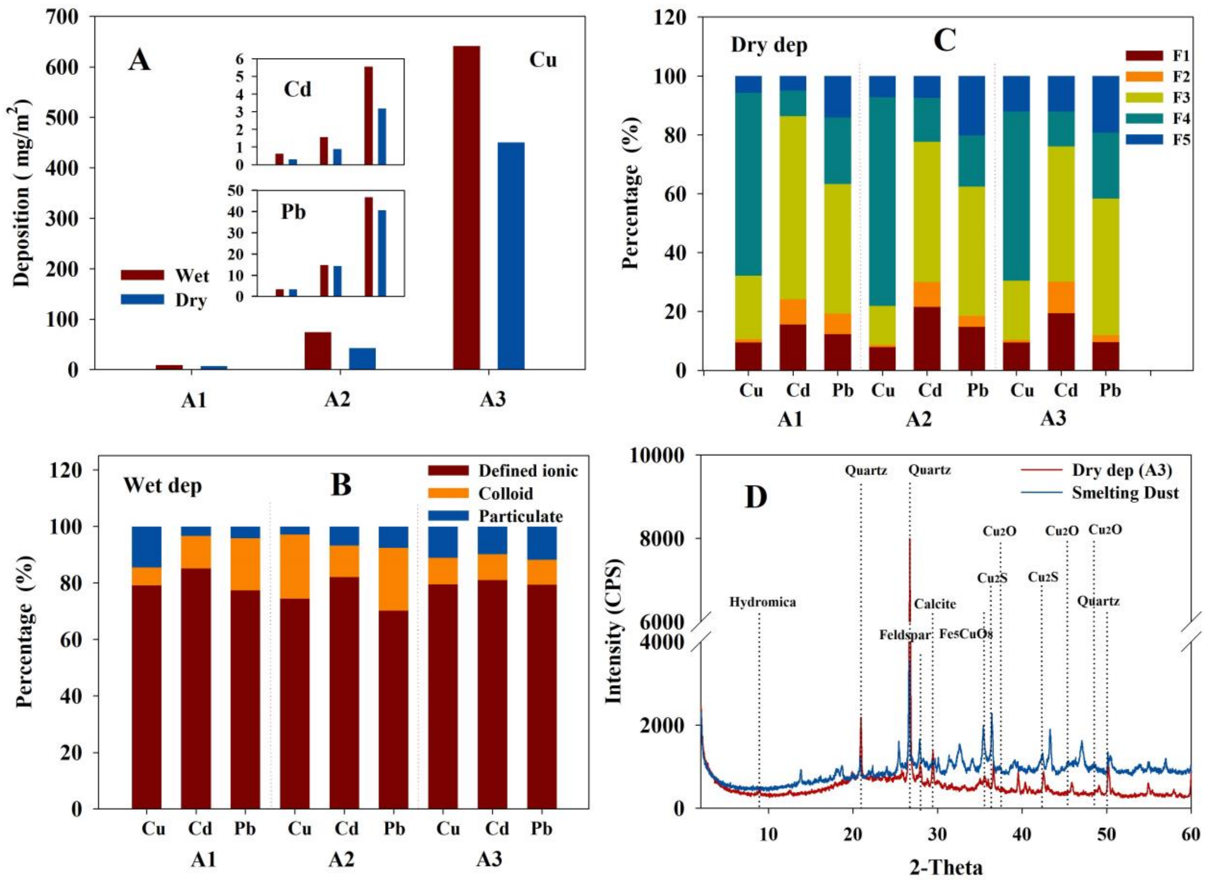

Fig. 3. Atmospheric wet and dry deposition flux (mg/m^2) of Cu, Cd, and Pb in July 2017 to June 2018 (A). The percentage of Cu, Cd, and Pb in size range of wet deposition and the chemical partitioning of dry deposition are given (B and C). The mineral composition of dry deposition and the dust from smelting are also given (D).