The bioavailability and contribution of the newly deposited heavy metals (copper and lead) from atmosphere to rice (*Oryza sativa* L.)

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GRAPHICAL ABSTRACT
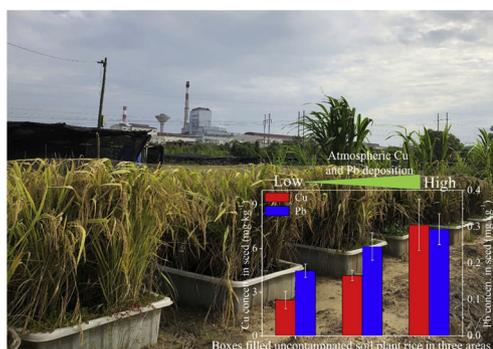
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ABSTRACT

Despite the global importance of atmospheric heavy metal input into agricultural soils, research has primarily focused on the amount of the depositions with limited attention given to the risk of the newly deposited heavy metals. To understand the remobilization of the newly deposited copper (Cu) and lead (Pb) from the atmosphere and explore the metals' mobility and bioavailability to rice (*Oryza sativa* L.), a soil transplant experiment was conducted in three areas along a gradient of atmospheric depositions. Approximately 61% of the Cu and 76% of the Pb depositions tended to be present in potentially mobile fractions. The soil retention of newly deposited Cu and Pb presented as higher mobile fractions than these in the original soil. The newly deposited Cu and Pb in soils only accounted for 0.34–8.7% and 0.07-0.29% of the total soil Cu and Pb pools, but they contributed 30–84% and 6–41% in rice tissues, respectively. A major implication of these findings is that once the heavy metal is deposited, it may be reactivated in soils and transported to aerial parts or foliar uptake into plant tissues, emphasizing the important role of the newly deposited Cu and Pb in contributing to the edible parts of crops.

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1. Introduction

Consumption of fossil energy and mineral resource has emitted large amounts of heavy metals into the atmosphere, which are then deposited to the surface environment; these effects are recognized as major global soil ecological and public health concerns (Gonzalez et al., 2016; Liu et al., 2018; Zhou et al., 2019a; Rosca et al., 2019). In the 1980s, mean annual global emission rates from anthropogenic sources to atmosphere were estimated to be copper (Cu) at 35,370 t, lead (Pb) at 332,350 t, cadmium (Cd) at 7570 t, zinc (Zn) at 131,880 t, and mercury (Hg) at 3560 t (Nriagu and Pacyna, 1988). With the rapid development of the worldwide economy, atmospheric emissions of heavy metals continue to surge (Tian et al., 2015). Nonferrous metal smelting, coal-fired industrial boilers and ferrous metal smelting were the major sources of heavy metal emissions (Tian et al., 2015; Zhou et al., 2018). Compared to natural emissions of heavy metals, the anthropogenic emission accounted for relatively larger proportions (Nriagu and Pacyna, 1988; Pacyna, 1986).

Atmospheric heavy metal depositions are important sources of those metals found in the surface environment of the earth, playing an important role in the global biogeochemical cycle of heavy metals (Jeremiason et al., 2018; Singh et al., 2017; Zhou et al., 2019b). Once deposited, owing to their persistence and the accumulation capacity of organism and natural surfaces, heavy metals can bio-accumulate and then enter food chains, resulting in potential eco-toxicological risks (Ali et al., 2019; Rota et al., 2018). Unexpectedly, atmospheric deposition is the major pathway of most of the heavy metal entry into natural waters on a global scale, representing over 72% for Pb and vanadium (V), 30% for mercury (Hg), and 20% for cadmium (Cd) (Nriagu and Pacyna, 1988). Meanwhile, atmospheric deposition is the principal route of heavy metal accumulation in agricultural soil; for instance, in the past 10 years, atmospheric deposition was responsible for 50–93% of the total arsenic, Cd, chromium, Hg, nickel, and Pb inputs on the national scale of China (Peng et al., 2019), and for over 82% of the Cu, Pb and Ni input fluxes in northern France agro-systems (Azimi et al., 2004). In some surrounding areas of industrial cities or nonferrous metal smelters, the amount of heavy metals inputted into agro-systems by atmospheric deposition is tens or hundreds of times greater than those arriving through irrigation and fertilization (Qiu et al., 2016; Yi et al., 2018). In areas with high heavy metal loadings, the biogeochemical evolution of heavy metals in the soil environment may be inextricably linked with the geochemical evolution of these metals from atmospheric depositions and they may also, to some extent, be restricted by the process of depositions.

Studies showed that most of the deposited heavy metals present as the water-soluble fraction in wet deposition, which is more bioavailable (Weerasundara et al., 2017; Tao et al., 2014). For dry depositions, the chemical sequential extraction method showed that Pb was predominantly present in the carbonate-bound and reducible fractions, and Cu was significantly associated with the organic fraction in Asian dust (Lee et al., 2015); however, once the external pH or redox conditions were changed, these fractions would probably be activated (Williams et al., 2014). (Wilcke and Kaupenjohann (1998)) showed that deposited metals are mainly absorbed into the aggregate surface rather than in the core, and higher ratios of the total metal concentrations are measured in exchangeable fractions in the aggregate surface. Another study also suggests that newly deposited Hg is more readily transformed to a more toxic form (methylmercury) and then bio-accumulated in rice than the original Hg in soil (Meng et al., 2011).

These results indicate that heavy metals from atmospheric deposition has a high potential risk of mobilization; however, the bioavailability and bioaccumulation effect of the newly deposited heavy metals in an agricultural ecosystem is unknown. Additionally, rice is a major staple food and important source of calories and nutritive elements for more than half of the world's human population. To date, how the heavy metal fractions deposited from the atmosphere influence the soil metal fractions and their bioaccumulation in rice has not been studied. The aims of this study are to (1) verify the high mobility of the Cu and Pb from the atmospheric deposition; (2) study the bioavailability of the newly deposited Cu and Pb in soils; and (3) quality the bioaccumulation effect of the newly deposited Cu and Pb on rice. A soil transplant experiment was conducted to explore the hypothesis that mobility and bioavailability of the newly deposited Cu and Pb to rice are higher compared to the original soil Cu and Pb.

2. Materials and methods

2.1. Experimental design

To investigate the remobilization of newly deposited Cu and Pb, a soil transplant experiment was carefully designed around the largest Cu smelter in China. The production capacity of the smelter was about 7.5×10^5 tons of Cu in 2007. Some other accessory products were also produced simultaneously, such as 1.65×10^5 tons of H_2SO_4, 1.4×10^3 tons of As_2O_3, 1.3×10 tons of gold, and 3.5×10^2 tons of silver per year (Xiao et al., 2011), and detailed in the Text S1 in Supporting Information (SI). Three areas were selected according to the different Cu and Pb deposition fluxes, which included a high flux area located about 1 km away (HS), a moderate flux area located about 6 km away (MS) and a background area (BS) located about 36 km away from the smelter (Fig. S1). The three areas were in the southeast of smelter, which has the largest frequency of wind direction (13.3%) around the smelter (Fig. S2). The polluted soils in HS and MS were transplanted to the BS and the unpolluted soil in the BS was transplanted to HS and MS, respectively, forming seven test-soil groups in total (Fig. 1). Three replicates were conducted for each group. Briefly, three experimental groups were set up in the background area receiving no Cu and Pb deposition; these were BS−A (filled background paddy soil), BS−B (filled paddy soil from moderate deposition) and BS−C (filled paddy soil from high deposition), respectively. Two experimental groups were set in the moderate deposition area; these were MS−A (filled paddy soil from background) and MS−B (filled paddy soil from moderate
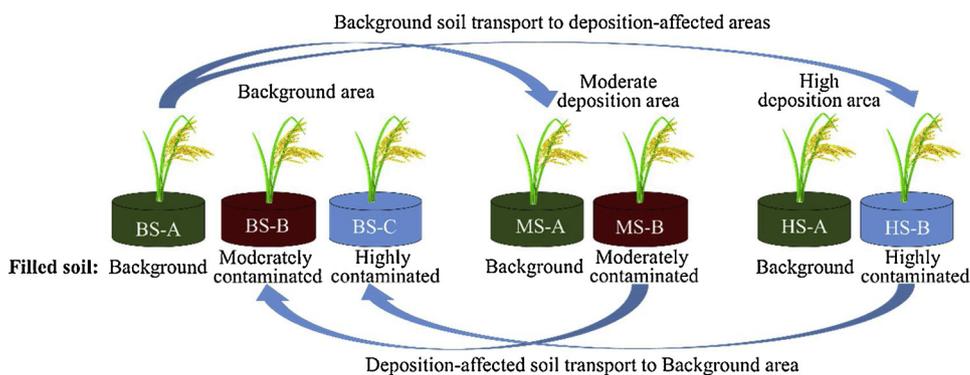

Background soil transport to deposition-affected areas

Deposition-affected soil transport to Background area

Fig. 1. The soil transplant experiment in three areas with different atmospheric depositions. BS-A, MS-A and HS-A are the pots filled with background soil and exposed to the background, moderate and high atmospheric depositions; BS-B and MS-B are the pots filled with moderately contaminated soil and exposed to the low, moderate atmospheric depositions; BS-C and HS-B are the pots filled with highly contaminated soil and exposed to the low, high atmospheric depositions.

deposition). Similarly, two experimental groups were set in the high deposition area; these were HS−A (filled paddy soil from background) and HS−B (filled paddy soil from high deposition). The experimental design is detailed further in the Text S2. Using this method, the soil transplant experiment can effectively distinguish the newly deposited soil Cu and Pb from atmosphere and soil Cu and Pb with an extended residence time (the original soil Cu and Pb). To investigate the bioavailability of newly deposited and original Cu and Pb for rice, a rice cultivar (Wuyouhuazhan) was cultivated in the tested soils. Additionally, to investigate the rice plant growth impact on the atmospheric deposition to soils, a control pot for each of the experimental group without any plant cultivation was also set.

All the pots (size: 0.8 m (wide) × 1.2 m (length) × 0.4 m (height)) were irrigated with the local drinking water containing low concentrations of Cu and Pb (under the detection limit), if there was not enough rainfall to maintain the water levels. In each pot, about 360-kg soil was filled. The method of rice cultivation and the physic-chemical properties of the test soil properties are shown in Table S1. In the current study, the comparisons was conducted among the same soil exposed to different atmospheric depositions, so the different soil parameters of the three study sites would not influence the experimental design.

2.2. Sample collection and preparation

The atmospheric dry and wet deposition samples were collected monthly from July to October 2017 by automatic precipitation/dustfall sampler in the three areas. All the deposition samples were stored in Teflon bottles which were pre-cleaned rigorously by dipping in 10% HNO_3 for more than 24 h, rinsing with ultrapure deionized water, and then being stored in a fridge under 4 ℃ until analysis.

Three sampling rounds of growth for 60, 75, 90, 105 days were conducted during the rice growing season. For each experimental pot, two whole rice plants were collected during each sampling event and the root, stalk, leaf and rice grain were divided. The soil profile in each plot after rice harvest (by 105 d) was collected from the top horizon to a depth of 20 cm with 6 intervals (0 − 2, 2 − 4, 4 − 6, 6 − 10, 10 − 15, 15 − 20 cm). The detailed sampling procedures were showed in the Text S3.

2.3. Analytical methods

Samples of soil and dry deposition were digested with mixed HNO_3, HF and $HClO_4$, and rice tissue samples were digested with mixed HNO_3 and $HClO_4$. For the rainfall samples (atmospheric wet deposition), the hydration particle sizes of dissolved Cu and Pb, including < 3 kDa, > 3 kDa and < 0.45 μm, and > 0.45 μm, were measured by dynamic light scattering (Nano Brook 90 Plus PALS, USA). The extraction of Cu and Pb fractions in samples of atmospheric dry deposition (0.2 g) and fresh profile soils (1 g) were based on the method of Tessier five-step sequential extraction (F1: exchangeable, F2: carbonate-bound, F3: Fe-Mn oxides-bound, F4: organic material-bound, and F5: residual fractions) (Tessier et al., 1979). The metal concentrations in the digested solutions were measured using inductively coupled plasma mass spectrometry. A detailed description of analytical methods were showed in the Text S4. The redox potential (Eh), pH, available soil phosphorus, total soil phosphorus, cation exchange capacity (CEC) and soil organic matter (SOM) content were also measured in the topsoil (0 − 2 cm) and middle soil (6 − 10 cm) of the profile and detailed in the Text S4.

2.4. Contribution calculation

The contribution (C, %) from the newly deposited Cu and Pb to the rice tissues was estimated according to the following equations:

$$C = (MC_{d, i} - MC_{b, i})/MC_{d, i} \times 100\%$$

where MC_d is the heavy metal concentration of rice tissues in high or moderate flux areas; MC_b is the heavy metal concentration of rice tissues from the pot filled with the same soils in background areas; i is the heavy metal variety (e.g. Cu or Pb).

2.5. Statistical analysis

The mean Cu and Pb concentrations in soil fractions, rice grain, husk, root, leaf and straw were compared between BS, MS and HS using one-way analyses of variance (ANOVAs). All differences in means were significant at the p = 0.05 level (two-tailed), and all means are reported with ± standard deviation from the mean. Statistical analyses were performed with SPSS (SPSS Inc. 16.0) software.

3. Results and discussion

3.1. Deposition and fraction of Cu and Pb in atmospheric deposition

The dry and wet atmospheric Cu and Pb depositions from July to October in the three areas are shown in Fig. S3 and S4. The atmospheric depositions of Cu and Pb differed significantly with distance from the smelter. Atmospheric depositions (dry + wet) of Cu and Pb were approximately 567 and 23 mg m^{-2} in the HS, which were 7.8 and 2.5 times higher than those in the MS (73 and 9.0 mg m^{-2}) and 40 and 9.8 times higher than those in the BS (14 and 2.3 mg m^{-2}), respectively. The annual Cu and Pb depositions in the HS (our unpublished data, Cu and Pb: 767, 76 μg m^{-2} yr^{-1}) were 8 and 3.5 times higher than in a lead-zinc mining area (Zhang et al., 2010) and the Pb deposition was 1.5-fold that in the surrounding area of a Pb smelter (Temmerman et al., 2015). The results suggest that much higher Cu and Pb levels are loaded in our study area, which can effectively help to distinguish those in soils from new atmospheric deposition. Additionally, on average, half of the total Cu and Pb depositions were dissolved in rainfall and presented as wet deposition (Fig. S3 and S4). Previous studies have indicated that heavy metals are more bioavailable in their water-soluble forms rather than the water-insoluble forms presented as dry depositions (Fernández-Olmo et al., 2014; Tate and Bates, 1984). Therefore, the deposited heavy metals may cause serious ecological risks.

It is important to focus on heavy metal fractions in the atmospheric deposition. For example, the metals of small size present in the fraction will be more likely to enter food chains, thus making them a greater hazard to human health than metals of large size in the fraction in wet samples (Tate and Bates, 1984). A previous study used oral doses to research the oral bioavailability of 1, 2 and 5 kDa polyethylene glycol-coated 5 nm gold nanoparticles and found that the concentrations in blood was significantly greater for the 1 kDa gold nanoparticles than particles coated with 2 or 5 gold nanoparticles (Alalaiwe et al., 2017). The size composition of the wet samples of atmospheric deposition is presented in Fig. 2a. More than 89% of Cu and 84% of Pb depositions were present in ionic and colloid fractions with the diameter less than 0.45 μm. Additionally, colloidal fraction (< 3 kDa) in total aqueous phase for the concerned metals Cu and Pb averaged 84% and 75% of the total wet depositions, respectively. Furthermore, the result of dynamic light scattering suggested the main particles in the wet samples presented in a range of 2.80 − 79.05 nm on the nanometer scale (Table S2). These results suggest that most of the heavy metals from wet deposition have the potential for mobilization and bioavailability.

The major mineralogical composition of dry deposition and dust from the pulse bag filter was not significantly different from that of deposition sites. The XRD patterns showed that the deposition and dust contained quartz, feldspar and hydromica (Fig. S5). Additionally, dust from the pulse bag filter contained relatively high amounts of Cu_2S, Cu_2O and Fe_5CuO_8. This result suggests that dry deposition is generally derived from the metallurgical emissions and hosted mineral phases.
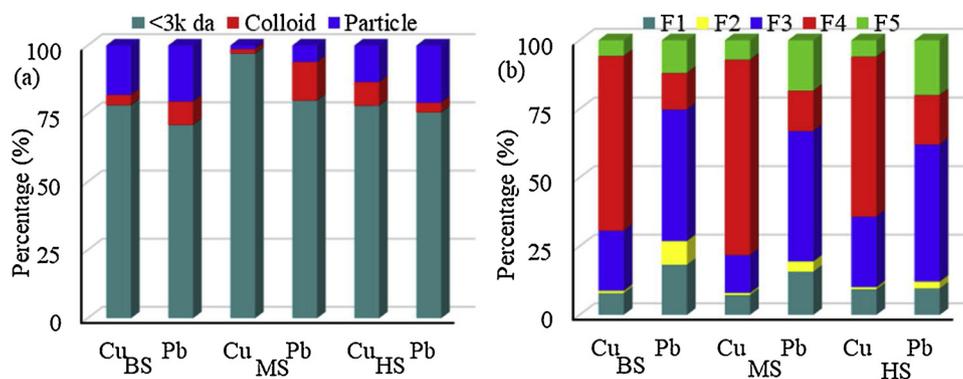
Fig. 2. The percentage of Cu and Pb in size range of wet deposition (a) and in different fractions (F1 exchangeable, F2 carbonate, F3 reducible, F4 organic and sulfide, and F5 residual fractions) of dry deposition (b) during the study period (July − October).

Copper was dominantly bound to the F4, which indicated that the organic matter or sulfide minerals can act as important scavengers of Cu, with the role of the F3 (carbonate-bound fraction) of subsequent importance as a carrier of Cu (Fig. 2b), consistent with the XRD patterns. This result suggests that Cu can be classified as a potentially less mobile element (Lee et al., 2013), which can leach into the environment under strong oxidizing/reducing conditions. In the three areas tested, the Pb in the dry samples was of high mobility: F3 accounted for 48 − 50% of the total Pb, with F1 (10 − 18%), F5 (12 − 20%) and F4 (13 − 18%) being the next most important, whereas a very small amount of Pb was bound to F2 (Fig. 2b). This result is consistent with previous findings for dry deposition in South Korea, where Pb is likely to be co-precipitated with carbonate and adsorbed by Fe/Mn-hydroxide (Lee et al., 2015). The result indicates that Pb in dry deposition can be easily released in lower pH levels (acid soil) and slightly reducing conditions (e.g. a flooding paddy) due to ion exchange, dissolution of carbonates and Fe/Mn hydroxides (Table S3).

The mobility and bioavailability of heavy metal in soil and water decreases approximately with the order of the colloid size and extraction sequence (F1 to F5) (Tessier et al., 1979; Li et al., 2018; Zhou et al., 2015a). The paddy soil was flooded during the rice cultivation and soil acidification was increased by acid deposition in south China (Zhou et al., 2015b). Considering the sum of F1 + F2 + F3 (dry deposition) + a wet deposition of < 0.45 μm, the percentage of mobility and bioavailability of Cu and Pb in the total depositions averaged 61% and 76% in the study areas, indicating the deposited Cu and Pb were highly mobile and can be harmful to the environment. Hence, considering the ecological effect of newly deposited heavy metals with metal and soil-crop interactions would provide an appropriate evaluation of the risks arising from atmospheric depositions.

3.2. Fractions of Cu and Pb in soils exposed to atmospheric deposition

Total Cu and Pb concentrations in surface horizons (0 − 4 cm) exposed to HS and MS were significantly increased compared to the corresponding soil exposed to the BS ($p < 0.05$) (Fig. 3), which were originated from the atmospheric depositions due to limited other sources. The Cu and Pb concentrations dropped strongly from the surface (0 − 4 cm) to lower horizons (from 6 − 20 cm) and those in the lower horizons in the pots filled with the same soils showed no variation among the three areas, suggesting that the new Cu and Pb mainly accumulated in the surface soils. The reason for this result could be that the deposited Cu and Pb were immobilized through complexing with clay minerals and the affinity of binding groups like thiol (Liu et al., 2019; Zhang et al., 2019). Compared to the control pot with non-plant cultivation, the total Cu and Pb concentrations were slightly higher but not significantly different compared to the corresponding pot filled with the same soils (Fig. S6), which may be due to the interception of rice plant.

Soil total heavy metal concentrations can tell us the degree of soil pollution, while soil metal fractions can provide the environmental risk of metals in the soil (Zhou et al., 2015a). In the fresh soil samples, Cu and Pb fractions in the surface soils (0 − 4 cm for Cu and 0 − 2 cm for Pb) showed that the concentrations and percentages of the exchangeable fraction (F1) exposed to HS and MS were significantly elevated compared to the corresponding soil exposed to the BS (Fig. 3 and S7). For example, the Cu concentrations of F1 in 0 − 2 cm of MS-A (1.2 ± 0.2 mg·kg^{-1}) and HS-A (4.1 ± 0.4 mg·kg^{-1}) were 5.5 and 19 times higher than in the BS-A pot (0.21 ± 0.04 mg kg^{-1}), while the corresponding Pb concentrations of F1 in MS-A and in HS-A were approximately 1.53 and 1.57 times higher than in the BS-A pot. The increased Cu and Pb in surface horizons also significantly increased the percentages of exchangeable fractions (Cu and Pb) in the MS-A pot (6.9% and 7.1%) and HS-A pot (8.9% and 6.5%) compared to those in the BS-A pot (1.6% and 4.8%) (Fig. S7). Additionally, exchangeable Cu and Pb fractions of surface soil in the MS-B and HS-B pots were significantly increased compared to the soil transported to BS (BS-B and BS-C) ($p < 0.05$).

Although the metal fractions in the Fe-Mn oxides-bound fraction (F3) and organic material-bound fraction (F4) are unavailable to rice (Yu et al., 2016a), they have potential mobility and bioavailability. In the current study, compared to the corresponding soils in the background site, the both Cu concentration and percentage of F3 and F4 also significantly increased in the surface soil exposed to both sites influenced by atmospheric deposition ($p < 0.01$). The F1, F3 and F4 fractions of both Cu and Pb significantly decreased, while the residual fractions (F5) significantly increased. This result was consistent with our hypothesis that the soils with newly deposited Cu and Pb from the atmosphere are more mobile compared to those in the original soil. It should be noted that the pH in wet deposition over four months in the HS and MS was significantly lower than that in the BS, which may facilitate the heavy metal activation (Table S4); however, acid deposition did not influence the soil pH values during the rice growing seasons (Table S3). The reason may be that the soils have strong buffering capacity and the pH cannot be changed in a short time (Yu et al., 2016b; Li et al., 2017).

The result that soil Cu and Pb from atmospheric deposition was more mobile is consistent with the fractions of deposited Cu and Pb from atmosphere, with high percentages of mobility and bioavailability as stated above. The reason may be that the newly deposited heavy metals tended to be accumulated in the soil aggregate surface and the original heavy metals were mainly accumulated in the core, and higher proportions of the total metal concentrations were in the mobile metal fractions in the aggregate surface than in the core fractions (Wilcke and Kaupenjohann, 1998). Hence, a criterion that considers the bioavailability of the newly deposited and the original Cu and Pb in the soil would be fundamental to the appropriate assessment of risks from both areas.
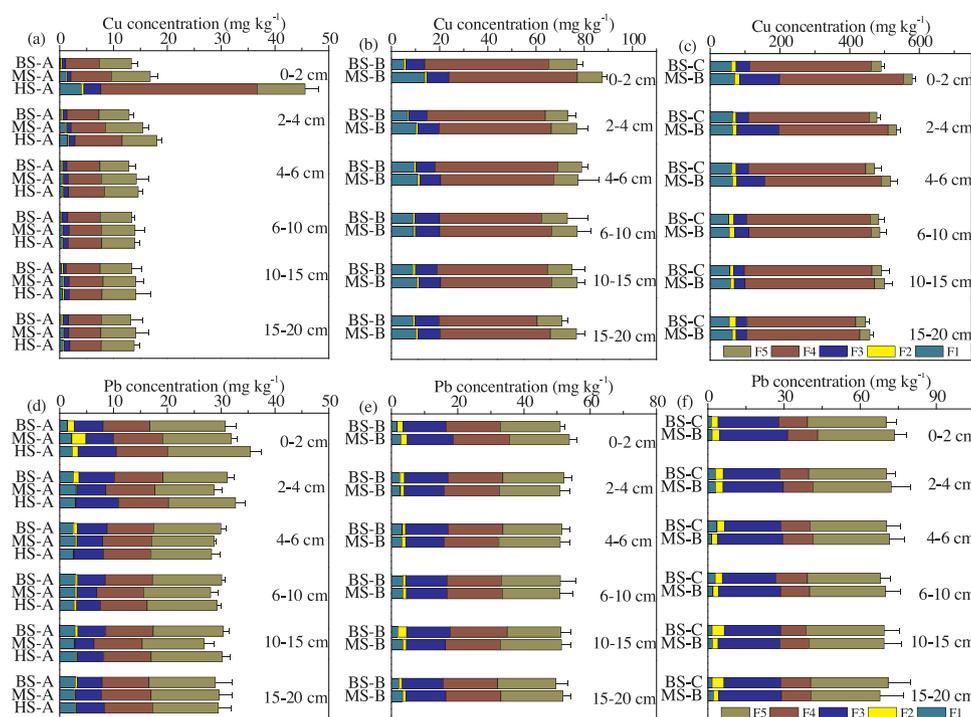
Fig. 3. Concentration (F1 exchangeable, F2 carbonate, F3 reducible, F4 organic and sulfide, and F5 residual fractions) of Cu (a–c) and Pb (d–f) in soil profile exposed atmospheric deposition in the gradient areas of atmospheric deposition. Data are shown as mean ± SD (n = 3).

Some studies imply that soil Eh could affect the availability of metals in paddy soils (Pan et al., 2016; Zou et al., 2018). In the rice harvest stage (105 d), the Eh varied from −25 to −124 mV under flooded conditions. The soils were highly reduced under flooded conditions suggesting that the soils were anaerobic. Atmospheric depositions significantly increased Eh in the topsoil (0 − 2 cm) but not the lower horizons (6 − 10 cm) between that in the HS and the BS (Table S5). Higher Eh conditions seemed to favor Cu and Pb mobility, because oxidation of S^{2-} to SO_4^{2-} is likely to occur in the higher Eh, which can promote the precipitation of S^{2-} with heavy metals (e.g. CuS and PbS) to mobile fractions in soils (Hockmann et al., 2014; Viana et al., 2019; Fulda et al., 2013). These results of previous studies were consistent with the current study, which showed both higher F1 fraction and Eh values in the topsoil of HS compare to the corresponding pot filled with the same soils in BS, while no variations of Cu and Pb fraction in the lower horizons due to similar Eh values (Fig. 3 and Table S5).

Additionally, soil P contents could reduce the availability of Pb and Cu in the soils due to forming Cu- and Pb-precipitates as insoluble phosphate forms (Netherway et al., 2019; Gao et al., 2019). In the current study, available and total P were higher in HS soil due to the previous application of alkaline materials containing P to stabilize heavy metal as a farmland remediation, and followed by MS and BS. The same trend was showed in the order of average percentages of F1 in the three soils, which showed lowest in the HS soil (3.4%) and followed by MS soil (5.1%) and (8.5%), suggesting that soil P could immobilization of soil heavy metals. Additionally, the CEC and SOM showed the inverted order of F1 percentage in the three soils, because higher CEC and SOM could exchange the exchangeable Cu and Pb in soil and resulted in immobilization of soil Cu and Pb (Abdelwaheb et al., 2019; Kandic et al., 2019). However, the transplanted soil (e.g. BS-A, MS-A and HS-A) in the three areas showed no significant variations of available P, total P, CEC and SOM, suggesting that atmospheric depositions did not significantly change the soil properties and the higher fractions of bioavailable factions in surface soils in HS and MS were originated from the bioavailable heavy metal of atmospheric depositions.

3.3. Copper and Pb in tissues of rice plants during the rice growing season

Excessive bioavailability of Cu and Pb in soil can lead to biological toxicity, e.g. disturbances of photosynthesis, destroying cell structures and inhibiting protein synthesis, resulting in reduced plant biomass and poor quality products (Liu et al., 2019; Xie et al., 2018). The biomass of rice plant tissues significantly decreased when exposed to HS in the current study (Table S6). Variations in Cu and Pb concentrations in tissues of rice collected from the experimental areas are shown in Fig. S8 and S9 and the corresponding Cu and Pb mass in rice plants are shown in Fig. 4 and 5. Before the rice seedlings were transplanted to the pots, the Cu and Pb concentrations were the same; however, the mean concentration of Cu and Pb in roots in the background soil from MS-A and HS-A exposed to moderate and high deposition were significantly higher than in the rice root from BS-A during the rice growing season (p < 0.01).

The contribution values (C, %) to the rice root were 31% and 23% for MS−A and 74% and 46% for HS−A (Table 1). Similarly, shoot Cu and Pb in moderately and seriously contaminated soils collected from MS and HS were also significantly reduced (p < 0.05) when the soil was transported to BS (BS-B and BS-C), compared to those in MS-B and HS-B. The corresponding contribution values of Cu and Pb from the newly deposited atmospheric metals were up to 30% and 19% for MS-B and 31% and 31% for HS-B, respectively. Generally, before heavy metals uptake by root, the part of metal dissolved in the soil solution is first adsorbed onto the root surfaces, and then bound to polysaccharides of the rhizodermal cell surface or carboxyl groups of mucilage uronic acid (Seregin and Ivanov, 2001). The significantly increased root metal concentrations in MS and HS would be due to the higher metal concentrations in soil solution that resulted from the higher fractions of bioavailable metal in atmospheric depositions. After adsorption on roots surface, heavy metals penetrate the roots passively and diffuse via translocating water streams. The increased heavy metals in roots would also attribute the Cu and Pb in rice shoots. The Cu concentration and mass in the roots reduced at the stage of rice seed formation (Supplementary Fig. S8a and 4a). This result could be attributed to Cu
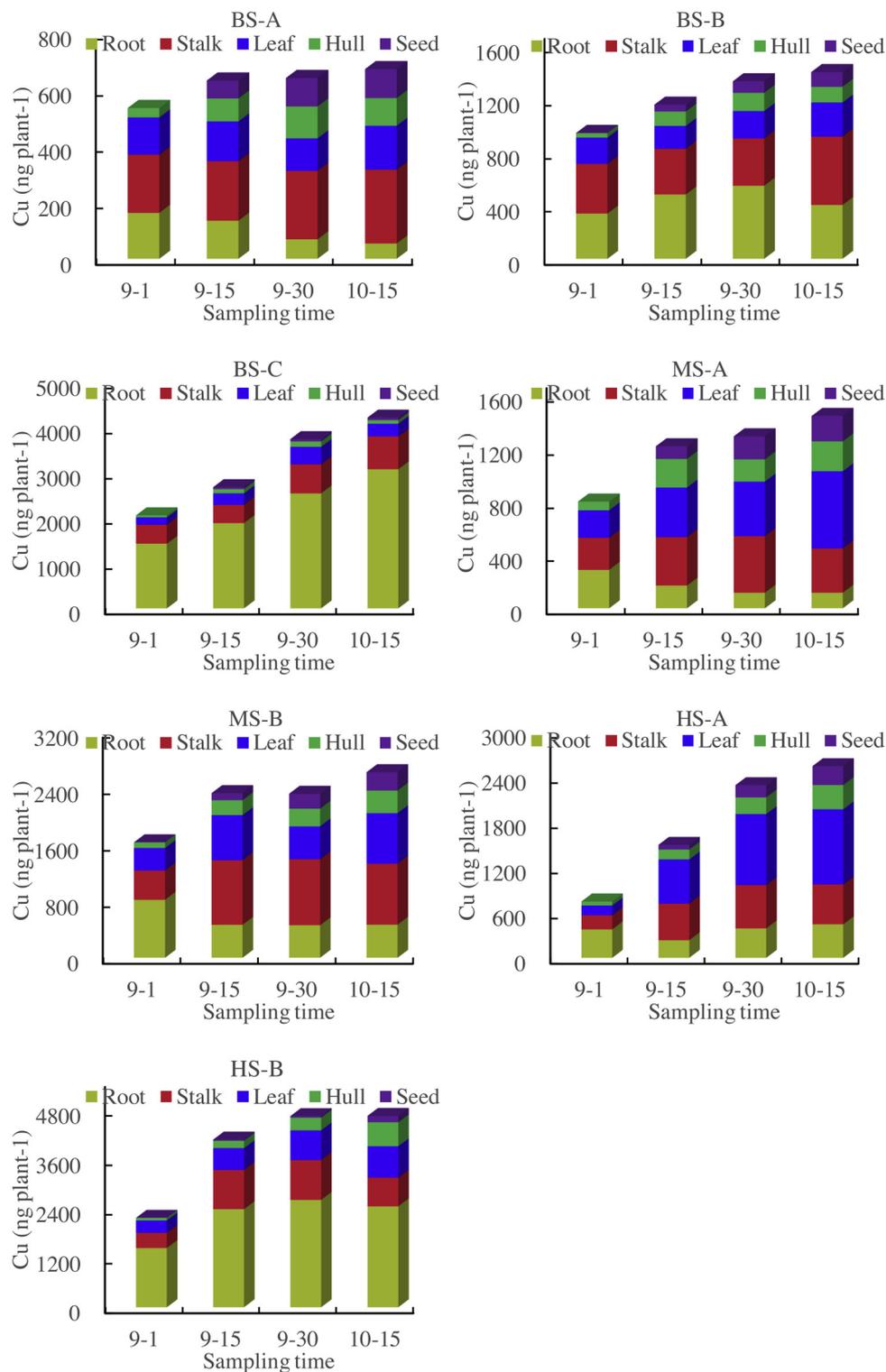
Fig. 4. Copper mass in tissues of rice plants collected from the background area (BS-A, BS-B, BS-C), moderate deposition area (MS-A, MS-B) and high deposition area (HS-A, HS-B) during the rice growing season.

translocation from roots to seeds (Li et al., 2009; Peng et al., 2018). Unlike Cu, the Pb concentration and mass in the roots significantly decreased $0 - 15$ days before harvest (Supplementary Fig. 9a and 5a), the reason being that the Pb in the roots translocated to the shoot and enhanced shoot Pb mass during this period; this result is consistent with a previous study of (Ashraf et al. (2017)).

During the rice growing period, the mean Cu and Pb concentrations in leaves and stalks were significantly elevated in background soils exposed to moderate (MS-A) and high deposition (HS-A) compared to those from BS-A ($p < 0.05$, Fig. S8b-c and S9b-c). The mean contribution values of stalk Cu and Pb from atmospheric deposition were 31% and 5% for MS-A, and 66% and 18% for HS-A, and the contribution values of leaf Cu and Pb were 63% and 24% for MS-B, and 84% and 41% for HS-B (Table 1). The much higher contribution values of Cu than Pb not only arose from the higher mobility and bioavailability of Cu in soils, but also as Cu as an essential element for plant growth,
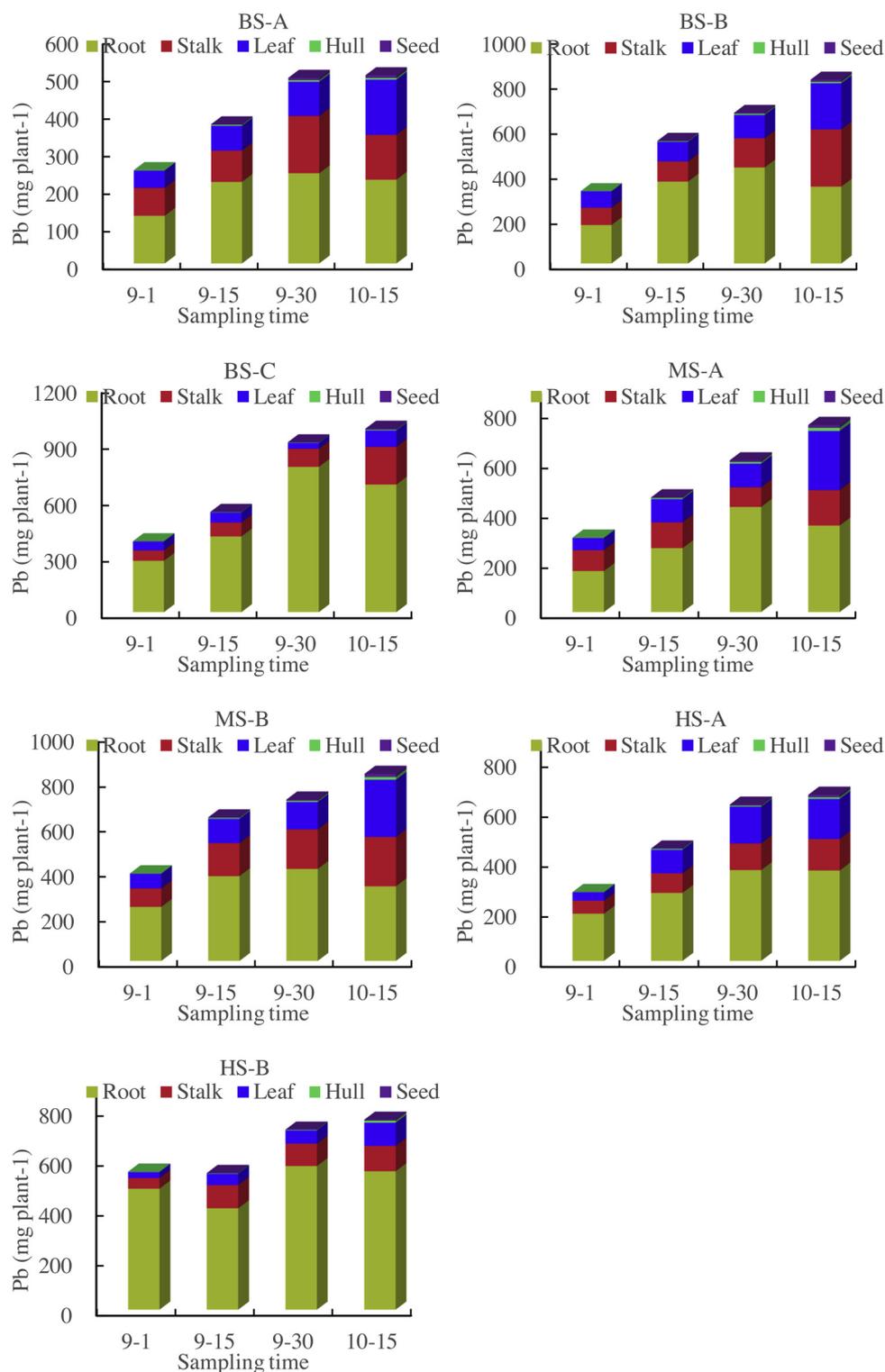
Fig. 5. Lead mass in tissues of rice plants collected from the background area (BS-A, BS-B, BS-C), moderate deposition area (MS-A, MS-B) and high deposition area (HS-A, HS-B) during the rice growing season.

making it more easily bio-accumulated (Sun et al., 2017). In contrast, Pb has a low translocation rate so could not readily cross the root iron plaque and bio-accumulate in the shoots of rice plants (Lai et al., 2018). The Cu concentrations in rice stalks and leaves in most groups reached their highest levels at 30 days before harvest and then decreased, finally stabilizing at the ripening stage. Meanwhile, Pb concentrations significantly increased at the beginning of seed formation (Sep 1 to 15) and then decreased, increasing again at the ripening stage. These results

may be related to the essential element Cu being translocated to the seed and the non-essential element Pb being immobilized in the leaf and stalk (Xie et al., 2018; Li et al., 2009; Zhao et al., 2018).

For all seven groups, brown rice recorded the lowest concentration of Cu and Pb compared to the other tissues (Fig. S8 and S9), which is in consistent with previous studies (Xie et al., 2018; Li et al., 2009; Ashraf et al., 2017; Sun et al., 2017). In the ripening stage (Oct 15), the mean concentration of Cu and Pb concentrations in brown rice in background

Table 1
The contribution values (%) of atmosheric deposition to the rice tissues during the rice growing season.

| Date	Treatment	Cu					Pb				
		Root	Stalk	Leaf	Hull	Seed	Root	Stalk	Leaf	Hull	Seed
9-1	MS-A	36 ± 3.5	11 ± 1.1	37 ± 2.4	52 ± 1.9		11 ± 1.9	7.1 ± 0.23	6.8 ± 0.98	9.4 ± 0.58	
	MS-B	50 ± 5.6	7.9 ± 0.87	49 ± 0.81	55 ± 0.95		13 ± 2.5	4.9 ± 0.39	8.5 ± 1.0	16 ± 1.8	
	HS-A	57 ± 5.8	46 ± 66.7	49 ± 3.7	57 ± 5.1		32 ± 3.0	30 ± 1.6	32 ± 1.9	4.1 ± 0.32	
	HS-B	2.6 ± 0.23	35 ± 0.38	77 ± 9.6	40 ± 3.9		45 ± 6.0	25 ± 2.2	15 ± 0.18	8.5 ± 1.0	
9-15	MS-A	7.2 ± 0.98	33 ± 5.3	60 ± 10	45 ± 5.9	11 ± 2.1	0.13 ± 0.10	7.0 ± 0.98	25 ± 1.34	25 ± 4.25	1.5 ± 0.15
	MS-B	12 ± 3.4	39 ± 5.7	69 ± 6.0	42 ± 6.9	13 ± 2.9	18 ± 5.9	2.0 ± 0.34	6.0 ± 1.0	28 ± 4.8	0.74 ± 0.13
	HS-A	61 ± 5.8	68 ± 4.8	80 ± 4.0	43 ± 5.2	32 ± 1.9	47 ± 3.1	20 ± 2.2	41 ± 2.8	27 ± 1.8	22 ± 2.0
	HS-B	46 ± 4.9	63 ± 8.2	67 ± 4.9	89 ± 14	41 ± 6.9	32 ± 3.9	35 ± 4.9	20 ± 2.2	25 ± 1.9	7.6 ± 0.98
9-30	MS-A	40 ± 4.9	35 ± 3.9	70 ± 11	12 ± 1.9	39 ± 4.9	42 ± 2.9	2.4 ± 3.4	6.0 ± 1.0	14 ± 1.5	0.73 ± 0.21
	MS-B	1.6 ± 0.15	58 ± 13	56 ± 5.9	28 ± 4.2	48 ± 2.3	14 ± 3.6	18 ± 1.9	14 ± 2.1	1.1 ± 0.13	4.9 ± 0.67
	HS-A	89 ± 4.6	73 ± 5.2	92 ± 5.8	62 ± 5.2	64 ± 5.9	48 ± 2.8	9.3 ± 1.2	62 ± 8.6	13 ± 2.4	15 ± 2.1
	HS-B	39 ± 4.2	53 ± 3.4	61 ± 5.7	77 ± 5.8	45 ± 3.1	19 ± 1.8	24 ± 2.3	58 ± 4.3	35 ± 2.9	4.7 ± 0.15
10-15	MS-A	54 ± 3.7	46 ± 3.9	74 ± 4.8	51 ± 4.3	41 ± 3.9	31 ± 2.6	4.9 ± 0.47	36 ± 1.9	57 ± 2.3	27 ± 3.9
	MS-B	46 ± 4.8	54 ± 6.2	72 ± 4.8	57 ± 6.8	48 ± 3.9	35 ± 4.8	11 ± 1.9	37 ± 4.7	39 ± 5.1	15 ± 1.9
	HS-A	89 ± 12	72 ± 11	87 ± 9.1	85 ± 5.7	68 ± 3.9	50 ± 4.3	11 ± 1.4	20 ± 4.9	66 ± 6.1	39 ± 3.8
	HS-B	18 ± 1.8	19 ± 1.3	62 ± 6.9	85 ± 4.7	77 ± 4.9	32 ± 2.9	1.8 ± 0.32	0.32 ± 0.11	50 ± 2.9	6.3 ± 1.0
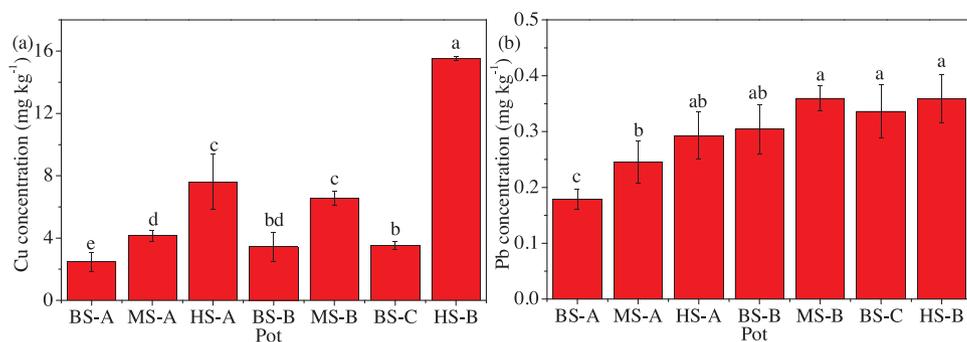
Fig. 6. Concentration of Cu (a) and Pb (b) (dry weight with standard deviations) in brown rice at the ripping stage collected from seven experiment groups in the three areas. BS−A, MS−A, HS−A, BS−B, MS-BBS-C and HS−B are corresponded to those in the Fig. 1.

soil from MS-A (Cu: 4.1 ± 0.4 mg kg^{-1}, Pb: 0.25 ± 0.04 mg kg^{-1}) and HS-A (7.6 ± 1.8 mg kg^{-1}, Pb: 0.29 ± 0.04 mg kg^{-1}) exposed to moderate and high deposition were significantly higher than in the brown rice from BS-A (2.5 ± 0.6 mg kg^{-1}, Pb: 0.18 ± 0.02 mg kg^{-1}) during the rice growing season (p < 0.01) (Fig. 6). The mean contribution values of Cu and Pb from atmospheric deposition were 40% and 27% for MS-A, 68% and 39% for HS-A, 48% and 15% for MS-B, and 77% and 6% for HS-B (Table 1). Generally, the grain concentrations of 10 and 0.2 mg kg^{-1} for Cu and Pb is defined as the maximum allowable limit recommended by the Ministry of Public Health of China, respectively. Lead in ripe brown rice obtained from soil transplant experiments (BS-B, BS-C, MS-A, MS-B, HS-A and HS-B) and Cu from the HS-B exceeded the allowable limits, posing a risk of potential adverse health effects for local residents (Fig. 6).

Copper and Pb can be accumulated in plant leaf via both root transfer and translocation (Xie et al., 2018; Li et al., 2009), and foliar uptake and adsorption after atmospheric deposition on the foliar surfaces (Abtahi et al., 2017; Shahid et al., 2017). Similar to the current research, foliar uptake of metals from atmospheric particulate matter (PM) depositions can greatly enhance metal levels in crops, particularly when farms or gardens are near smelters or urban areas (Uzu et al., 2010; Mombo et al., 2016; Al Jassir et al., 2005; Singh and Pandey, 2012). Foliar surface uptake of metals occurs through stomata, cuticular cracks, lenticels, ectodesmata and aqueous pores (Gajbhiye et al., 2016; Fernández and Brown, 2013). Actually, absorption of foliar-deposited heavy metals takes place mainly through ectodesmata, which are non-plasmatic channels positioned mainly between subsidiary cells and guard cells in the cuticular membrane or epidermal cell wall (Shahid et al., 2017). A previous study suggested that fine PM can penetrate inside the leaves, while large PM are stuck on the surface wax. Additionally, soluble compounds interact directly with the cuticle,

which is a waxy layer and confers a hydrophobic feature to the surface of plants (Birbaum et al., 2010). As we stated about, more than 89% of Cu and 84% of Pb wet depositions were present in ionic/colloid fractions in the current study, which were more easily enter inside the leaf tissues. After penetration through leaves, the translocation of metals within plants occurs via penetration through the cuticle and phloem vascular system in the same way as photosynthates (Chamel et al., 1991). This translocation inside plants varies with the chemical property of metals. Lead as an immobile metal, may precipitate as the phosphate (Ziegler, 1975) and showed resemblances to calcium in this regard. A study showed that very little transportation of foliar applied Pb into the seeds and pods of the *Phaseolus vulgaris* (Dollard, 1986). Thus, it is believed that Pb accumulation by foliar transfer is of similar importance to the root transfer only for exposed leaf, because Pb concentrations in roots, fruits, pods and other aerial tissues appeared to be generally negligible after foliar translocation (Harrison and Chirgawi, 1989). Therefore, we suspect that the increased Pb concentrations in the brown rice was mainly from the root uptake duo to immobilization of Pb in leaf. Unlike Pb, an increase in fruit yield and both leaf and fruit Cu concentration in tomato has been reported under foliar Cu application (Perez-Labrada et al., 2019). The reason may be that Cu can move inside plants with the bulk flow of metabolites and may form chelates or complexes with organic compounds present in the phloem, inhibiting their precipitation (Kandic et al., 2019).

Although the newly deposited Cu for the MS-A and HS-A only accounted 1.2% and 8.7% of the total soil Cu pools, Cu measured in rice tissues that came from the newly deposited Cu were 31–63% and 66–84%, respectively. Similarly, the newly deposited Pb accounted for 0.11% and 0.29% of the total soil Pb pools and the contribution values were 5–27% and 18–46% for the MS-A and HS-A, respectively. Even with lower proportions of the newly deposited Cu (0.34% and 0.39%)

and Pb (0.07% and 0.12%) in deposition areas (MS-B and HS-B), the contribution values were 30–84% and 6–41%, respectively. These results verified our hypothesis that newly deposited Cu and Pb in soil from the atmosphere is more bioavailable to rice than these in the original soils. Previous research also showed that newly deposited Hg was more readily transformed to more toxic methylmercury and accumulated in rice than that with an extended residence time in soil (Meng et al., 2011). The current study only could calculate the total Cu and Pb bioaccumulation effects in rice (root transfer and foliar uptake) and but cannot accurately distinguish the two pathways, because the two kinds of uptake pathways can occur simultaneously near atmospheric deposition-affected areas.

4. Conclusions and environmental implications

Using the soil transplant experiment in three areas with different atmospheric metal depositions, we can effectively distinguish newly deposited Cu and Pb from the atmosphere from the original Cu and Pb in soil. The potential mobilization of Cu and Pb from atmospheric deposition results from their bioavailability from the soil to the rice plant. Small ratios of the total soil heavy metal pool from atmospheric deposition contributed much higher ratios to rice in the areas influenced by atmospheric deposition. The major implication of the current study is that soil in the area is not polluted, but atmospheric metal deposition may result in the local crop exceeding the allowable limit; in other words, when a crop exceeding the allowable heavy metal limit is produced in unpolluted soil, the criminal may be the newly deposited heavy metals that contribute a high proportion of heavy metals making up the edible part of the plants. Additionally, in contaminated soil under moderate and high depositions, atmospheric deposition contributed a relatively higher proportion of heavy metals to the crop. Newly deposited heavy metals may pose a risk to the quality of agricultural products, at least in areas where substantial atmospheric heavy metal deposition is occurring. Therefore, reducing atmospheric heavy metal input to agriculture soil can effectively decrease the metal concentrations in crops.

Acknowledgments

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2019.121285.

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