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Dynamic Behaviors of Newly Deposited Atmospheric Heavy Metals in the Soil-Pak Choi System

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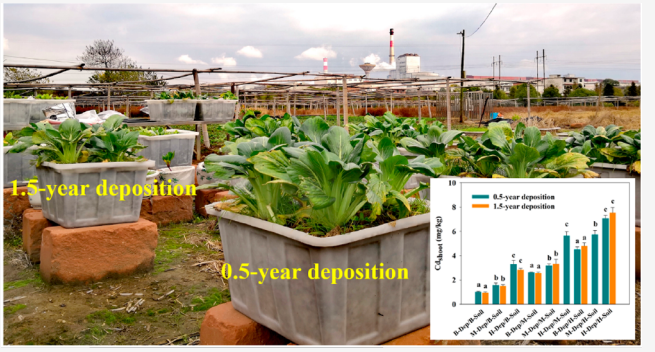
ABSTRACT: Dynamic behaviors of the newly deposited atmospheric heavy metals in the soil-pak choi (*Brassica chinensis* L.) system are investigated by a fully factorial atmospheric exposure experiment using soils exposed to 0.5-year and 1.5-year atmospheric depositions. The results showed approximately 17−87%, 19−64%, and 43−84% of the Cu, Cd, and Pb in pak choi edible parts were contributed from the new depositions, respectively. For the newly deposited metals, foliar uptake was the key pathway of shoot bioaccumulation rather than from root uptake of the deposited metals in soils, resulting in no significant soil contribution differences between pak chois growing in 0.5-year and 1.5-year exposed soils. Indeed, highly bioavailable metals in atmospheric deposition significantly increased the soil plant-bioavailable Cu, Cd, and Pb fractions; however, soil aging resulted in similar percentages of the plant-bioavailable fractions in 0.5-year and 1.5-year exposed soils, which indicated the bioavailability of metals deposited into soils rapidly decreased with aging. The soil aging process of the deposited metals was well fitted with the first-order exponential decay model, and soil organic matter and clay were the major driving factors. Our findings highlight high plant bioaccumulation rates and the rapid soil aging process of newly deposited metals during the plant growth period.



KEYWORDS: *atmospheric deposition, atmospheric exposure, foliar uptake, metal bioavailability, soil aging process*

1. INTRODUCTION

In the last decades, numerous human activities from nonferrous mining and smelting, industrial coal-fired boilers, ferrous metal smelting, etc. have emitted large amounts of toxic heavy metals into the atmospheric environment.[1,2] In 2005, the anthropogenic atmospheric emissions of mercury (Hg), lead (Pb), and cadmium (Cd) in Europe were estimated at about 200 t, 1,100 t, and 500 t, respectively.[3] Compared to those in Europe, the anthropogenic emissions in Asia were much higher due to rapid industrialization with the fossil fuels consumption. Tian et al.[2] reviewed atmospheric heavy metals in China and showed that the anthropogenic emissions of Hg, Pb, Cd, arsenic (As), copper (Cu), and nickel (Ni) to the atmosphere had reached 700 t, 14,000 t, 500 t, 2,500 t, 9,500 t, and 3,400 t in 2012, respectively, resulting in mean atmospheric As, Cd, and Ni concentrations being 7.3, 2.6, and 1.2 times the recommended limits by the WHO, respectively.[4] These metals through atmospheric deposition could migrate to the surface environment[5] and become an important input source of heavy metals in agricultural soils.[6−9] For example, at the beginning of this century, Nicholson et al.[10] showed atmospheric deposition was the main source of most metals in agricultural soils in England and Wales, ranging from 25% to 85% of the total inputs. Furthermore, in the past 10 years, heavy metals from atmospheric deposition were estimated to be responsible for up to 50−93% of total inputted Cd, As, Pb, Hg, and chromium (Cr) loads in agricultural soils across China.[6]

Heavy metals from atmospheric deposition usually have a relatively high mobility and are an important external source of bioavailable heavy metals in the agricultural environment.[11,12] Over 90% of Cd in wet deposition in Central Europe occurred in soluble form (<0.45 um), and approximately 25−29% and 9−12% of Cd and Pb in bulk deposition in southern China were in an exchangeable fraction.[13,14] Additionally, the proportion of fine particles (including PM2.5 and PM1) emitted to the atmosphere has been increased because of the effective technology of dust removal in industry in the past decade.[1,15] Heavy metals bound to fine particles are generally more bioavailable for microbial transformation and plant uptake.[16,17] Previous studies found that the new Hg deposited into soils was more easily methylated and then bioaccumulated

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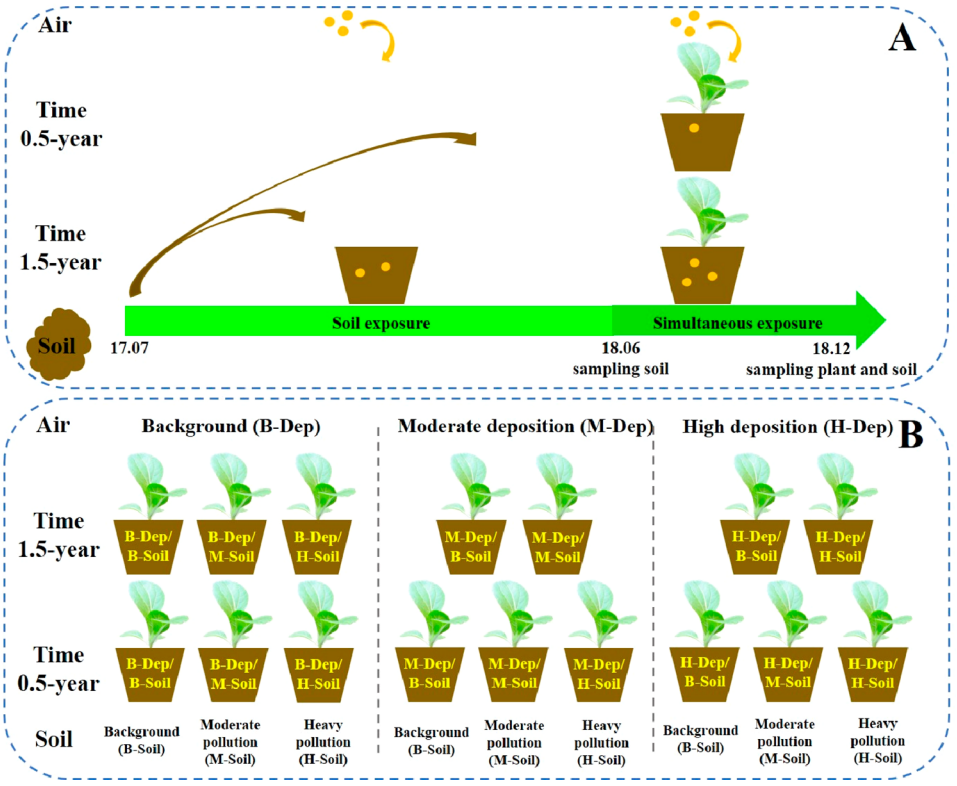

Figure 1. Design of a fully factorial field atmospheric exposure experiment using soils exposed to a 0.5-year deposition and a 1.5-year deposition (A) with pak choi including 16 treatment groups (B).

in rice than original Hg in soils,[18,19] and atmospherically deposited Cd and Pb were more bioavailable and readily taken up by bush beans and lettuce.[11,20] Additionally, numerous studies have found that foliar can directly take up fine particles from atmospheric deposition on the leaf surface.[21,22] Cuticle internalization and stomatal infiltration may be the main ways for foliar absorption of the particulate form of the deposited heavy metals.[21] For the dissolved forms of the deposited metals, the hydrophilic diffusion via aqueous pores and stomates may be the main way of foliar absorption.[15] After foliar absorption, heavy metals can be transported inside vegetable plants via the phloem vascular system to different vegetable organs (flower and even fruit).[23,24] These studies potentially suggest that the newly deposited atmospheric heavy metals may have a high bioaccumulation effect on vegetables. However, the bioaccumulation of the newly deposited metals via root and foliar uptake still has not been quantified, and the corresponding key bioaccumulation pathways of the newly deposited metals to vegetable edible parts still need further research.[11] In addition, limited research has studied the dynamic behavior of heavy metals from newly atmospheric deposition in soils and crops.[25] The water-soluble heavy metal fractions from atmospheric deposition may gradually decrease with aging in the soil environment,[26] as they can be readily converted to a less labile fraction via microporous diffusion, cavity entrapment, and surface coprecipitation in solid phase,[27,28] or on the contrary, heavy metals bound to a sulfide fraction inputted to soil by dry deposition can be further active with the dissolution of particulate matter by the soil environment (e.g., reduced pH and dynamic oxidation−reduction potential).[26,29] Therefore, elucidating aging effects of atmospheric metals deposited to soil in the nature process is more crucial to accurately evaluating their bioavailability in the soil-vegetable system.

In this paper, a fully factorial field soil and atmospheric exposure experiment was designed in three sites along a gradient of atmospheric deposition. Using the field experiment, the uptake pathway and bioaccumulation contributions of atmospherically deposited metals in the soil-pak choi (*Brassica chinensis* L.) system were analyzed, and the impacts of atmospheric deposition on soil metal chemical fractions, the aging rate of the deposited metals, and the key soil factors controlling aging process were elucidated. In addition, a greenhouse experiment simulating soil and foliar exposed to atmospheric deposition was also carefully designed to further investigate bioaccumulation pathways of atmospheric heavy metals in pak choi plants.

2. MATERIALS AND METHODS

2.1. Fully Factorial Field Exposure Experiment. A fully factorial field atmospheric exposure experiment using soils exposed to 0.5-year and 1.5-year atmospheric depositions was conducted nearby the largest Cu smelter in China, located in Guixi City. We selected three sites with atmospheric heavy metal deposition gradients, including B-Dep, a background site with low deposition; M-Dep, a moderate atmospheric deposition site; and H-Dep, a high atmospheric deposition site. The detailed information on study sites (including geographical location, meteorological and environmental pollution information) was shown in the Supporting Information (Text S1 and Figure S1). The field exposure experiment with pak choi in the three study sites was performed by pot treatment in 1.5 years from July 2017 to December 2018 (Figure 1). For the 1.5-year soils exposed to

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atmospheric deposition: in the first year (July 2017), background, moderately, and heavily polluted soils (B-Soil, M-Soil, and H-Soil) from three sites (B-Dep, M-Dep, and H-Dep) were transplanted to the background site B-Dep; the background soil (B-Soil) and moderately polluted soil (M-Soil) from B-Dep and M-Dep were transplanted to the polluted site M-Dep; and the background soil (B-Soil) and heavily polluted soil (H-Soil) from B-Dep and H-Dep were transplanted to the polluted site H-Dep, forming seven treatments. Note that the soils in the M-Dep and H-Dep sites were not reciprocally transplanted in the first year, because we thought that both soils were polluted soils which cannot distinguish well the newly deposited heavy metals and original soil heavy metals. For the 0.5-year soils exposed to atmospheric deposition: in the second year (July 2018), same as the first year, one more soil transplant experiment was conducted in the three study sites; besides, moderately polluted soil (M-Soil) from M-Dep was transplanted to H-Dep, and heavily polluted soil (H-Soil) from H-Dep was transplanted to M-Dep, forming nine treatments, and the additional two treatments were used to verify our original thought. The factorial field experiment design was detailed further in Text S3. Totally, 16 treatments were conducted for a 1.5-year deposition and a 0.5-year deposition in experimental triplicate (Figure 1 and Table S2).

A widely cultivated pak choi (*Brassica chinensis* L.) was grown in each of these soils and atmospheric exposure pot treatments in mid-November 2018. All pots filled with monoliths of soils (dimensions: 0.58 m length × 0.44 m wide × 0.30 m height) were mounted on the stone mounds (about 0.5 m height), which may ensure the top edge of the pot more than 0.8 m above the surrounding ground and minimize contamination from soil particles by splashing during heavy rainfall.[30] Totally, 48 pots were used in this study, containing about 92−98 kg of soils per pot with bulk density of 1.2−1.3 g/cm^3.

The treatments B-Dep/B-Soil, M-Dep/B-Soil, and H-Dep/B-Soil representing increasing atmospheric deposition loads of heavy metals in the unpolluted background soil (B-Soil) are used to quantify current atmospheric deposited metals to pak choi bioaccumulation. Treatments B-Dep/M-Soil, M-Dep/M-Soil, and H-Dep/M-Soil and treatments B-Dep/H-Soil, M-Dep/H-Soil, and H-Dep/H-Soil were similarly designed to assess both soil and atmospheric exposures on the heavy metal bioaccumulation from the originally polluted soils and newly deposited metals from the atmosphere. Our factorial soil and atmospheric exposure experiments can effectively distinguish the bioavailability and contribution of the newly deposited and original metals (including parent rock matrix, input by human activity, and earlier deposited atmospheric heavy metals) in soils, which has been verified by the previous studies.[18,31] In addition, the heavy metal translocation factor (TF) from pak choi roots to shoots in H-Dep, M-Dep, and B-Dep treatments was used to analyze the main bioaccumulation pathway (root or foliar uptake) of the newly deposited metals to pak choi edible parts (see section 2.4).[32] Finally, seven treatments for a 1.5-year deposition and nine treatments for a 0.5-year deposition were designed to understand the dynamic behavior of heavy metals from new atmospheric deposition in the soil-pak choi system (see section 2.4).

2.2. Greenhouse Experiment Design of Root and Foliar Exposure. Additional experiments of simulated soil and foliar exposed to atmospheric deposition were conducted in the greenhouse, which could distinguish foliar uptake or root uptake from atmospherically deposited heavy metals. Therefore, the greenhouse experiment can further investigate bioaccumulation pathways of atmospheric metals in pak choi plants. The experiment included four treatments: ck (control), two soil exposures (dry deposition and wet deposition), and one foliar exposure (dry deposition). The exposure dosage represented an approximately 0.5-year atmospheric Cu deposition load. Dust samples collected from a pulse dust catcher in the Guixi copper smelter were applied to simulate dry deposition that was added to soil and pak choi leaf. The collected dust samples showed some of the same major mineralogical compositions measured in dry deposition in the field based on X-ray diffractometer (XRD) results (Figure S2A); meanwhile, chemical fractions of heavy metals, especially for the weak acid extractable fraction (F1), also showed a strong similarity between the dust and dry deposition (Figure S2B). Atmospheric precipitation collected from the high deposition site (H-Dep) was applied to simulate atmospheric wet deposition, which was irrigated throughout the pak choi growing season. One pak choi seedling was planted in each pot, and three replicates were performed for each of the four treatments. The greenhouse experiment was detailed further in Text S4.

2.3. Sample Collection and Analysis. Atmospheric deposition samples were collected monthly from July 2017 to December 2018 at each site by an automatic wet and dry deposition sampler (APS-3A, Xianglan Scientific Instruments Co., China). Soil profile samples in seven treatments (the first year) of the field experiment were sampled at the end of June 2018. In addition, soil profiles and pak choi samples in the 16 treatments of the field experiment were also sampled at the end of December 2018 (Figure 1). In order to further investigate the dynamic behavior of deposited metals, two additional sets of soil profiles were collected in the third year (June and December 2019) (Figure S3). The sampled pak chois were separated into shoots and roots and then carefully washed by running tap water for 30 s and double deionized water for 1 min to remove the adhering soil and dust present on the tissue surface not tightly bound.[15] Partial shoot samples of the field experiment after washing were stored in glutaraldehyde (2.5%), and then the deposited particles on leaf surfaces were characterized by ESEM (environmental scanning electron microscopy, XL-30 ESEM, Philips) coupled with energy dispersive X-ray spectrometry (EDS).[16] Other separated plants were dried in the oven at 105 °C for 30 min and then dried at 60 °C to a constant weight. Then, the dried plants were ground and sieved to <0.15 mm for further analysis. The soil profiles were collected by stratified sampling in the following depth increments: 0−2, 2−4, 4−6, 6−10, 10−15, and 15−20 cm.

For the greenhouse experiment, the pak chois were sampled after a 45-d cultivation. Plants were separated into shoots and roots. Besides water washing, more washing procedures (using 10 mM HNO_3 and 10 mM L-cysteine)[33] were conducted to eliminate metals present on the tissue surface as much as possible, especially for foliar exposure. Then, the other preprocessing was the same as the field experiment.

For wet deposition, pH soluble and insoluble metal (Cu, Cd, and Pb) fractions (>0.45 μm for insoluble and <0.45 μm for soluble) were determined. For dry deposition and soil samples, total heavy metals were digested with three acids (concentrated HNO_3, HF, and $HClO_4$), and chemical fractions of heavy metals were analyzed by a BCR four-step sequential

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extraction (F1 weak acid extractable, F2 reducible, F3 oxidizable, and F4 residual fractions).[34] Plant samples were digested with concentrated HNO_3 and H_2O_2. The detailed information on the sampler, sampling, and analytical methods was described in Texts S5 and S6.

2.4. Bioaccumulation Contribution Rate. The contribution (C_{air}, %) of the newly deposited heavy metals to the pak choi accumulation in the field factorial experiment was calculated by

$$C_{air} = \frac{(MC_{deposition} \times DW_{deposition} - MC_{background} \times DW_{background})}{MC_{deposition} \times DW_{deposition}} \times 100\% \quad (1)$$

where $MC_{deposition}$ and $MC_{background}$ are Cu, Cd, and Pb concentrations in pak choi tissues exposed to high and moderate atmospheric deposition (H-Dep and M-Dep) and background site (B-Dep) filled with the same soils (B-Soil or M-Soil or H-Soil) during the same deposition time, and $DW_{deposition}$ and $DW_{background}$ are the corresponding dry weight of pak choi tissues (mass in grams dry weight).

The heavy metal translocation factor (TF) value from roots (MC_{root}) to shoots (MC_{shoot}) in the field experiment was calculated by

$$TF = \frac{MC_{shoot}}{MC_{root}} \quad (2)$$

Atmospheric metals could be absorbed by leaf vegetables through direct foliar uptake after deposition on leaves or through root uptake after deposition into soils.[17,18] In this study, if TF values (root to shoot) of atmospheric metals deposition into soils were the same as those values of metals in original soils (in B-Dep/B-Soil, B-Dep/M-Soil, or B-Dep/H-Soil) and direct foliar uptake of the deposited metals was almost not translocated to root tissues (<1%) (validated by the greenhouse experiment in section 3.1), the relative contribution proportion of the direct foliar uptake (C_{foliar}) and soil-root transfer (C_{root}) of atmospherically deposited metals to the pak choi edible part (shoot) in the field experiment was calculated by

$$C_{foliar} = \frac{\left(1 - \frac{TF_{background}}{TF_{deposition}}\right)}{C_{air/shoot}} \times 100\%$$

$$C_{root} = (1 - C_{foliar}) \times 100\% \quad (3)$$

where $TF_{deposition}$ and $TF_{background}$ are heavy metal translocation factor (TF) values for pak choi tissues exposed to high and moderate atmospheric deposition (H-Dep and M-Dep) and background site (B-Dep) filled with the same soils (B-Soil or M-Soil or H-Soil) during the same deposition time, and $C_{air/shoot}$ is the contribution of atmospheric deposited metals to the pak choi shoot accumulation in the treatment group consistent with $TF_{deposition}$.

However, the translocation behavior of Cd and Cu from atmospheric new deposition and the original soils may be not exactly the same;[35−37] thus, the relative contribution proportion of the direct foliar uptake (C_{foliar}) and soil-root transfer (C_{root}) calculated by eq 3[32] was only an approximate estimation. Eq 3 was detailed further in Text S7. In order to verify the estimation result by eq 3, the relative contribution proportion of C_{foliar} and C_{root} was also evaluated by the greenhouse experiment to further investigate the bioaccumulation pathway

$$C_{foliar} = \frac{(MC_{exp/foliar} \times DW_{exp/foliar} - MC_{ck} \times DW_{ck})}{(MC_{exp/foliar} \times DW_{exp/foliar} + MC_{exp/soil} \times DW_{exp/soil} - 2 \times MC_{ck} \times DW_{ck})} \times 100\%$$

$$C_{root} = (1 - C_{foliar}) \times 100\% \quad (4)$$

where $MC_{exp/folair}$ and $MC_{exp/soil}$ represent the Cu, Cd, and Pb concentrations in the pak choi tissues of foliar and root exposure, respectively, ck is the control group, and DW is the dry weight of pak choi tissue (mass in grams dry weight).

2.5. Dynamic Behavior of Atmospheric Deposited Metals. The changes of heavy metal speciation and distribution in soil profile and the accumulated contribution of atmospheric deposited metals to the pak choi with different deposition periods (0.5 and 1.5-year deposition) in the field experiment were used to assess dynamic behavior of atmospheric deposited metals in the soil-pak choi system. The percentage changes of the soil bioavailable-metal fraction (i.e., the weak acid extractable fraction (F1)) from atmospheric deposition (in the first year, July 2017 to June 2018) with the passage of time were considered as the target to assess the aging process.[38,39] The aging times include 0 d, 7 d, 180 d, 360 d, and 540 d. More specifically, as a continuous process of atmospheric deposition, chemical speciation of metals deposited into soil after 0 d aging was in direct correspondence with those of atmospheric deposition, where the soluble heavy metals in wet deposition and the bioavailable fraction of metals in dry deposition were expediently considered as bioavailable fractions. Then, the differences of bioavailable-fraction concentrations in the same soils (the first year, to June 2018) exposed to the atmospheric deposited sites (M-Dep and H-Dep) and background site (B-Dep) were expediently considered as bioavailable-metal fractions deposited into soil after short-term 7 d aging, which were measured in the previous study.[11] Further, the differences of the bioavailable-fraction concentrations in the same soils and sites exposed to 0.5- and 1.5-year depositions (to December 2018) were expediently considered as bioavailable fractions deposited into soil (the first-year deposition) after 180 d of aging. Meanwhile, the differences of the bioavailable-fraction concentrations in soils exposed to 1- and 2-year depositions (to June 2019) and 1.5- and 2.5-year depositions (to December 2019) were also measured and considered as bioavailable fractions deposited into soil (the first-year deposition) after 360 and 540 d of aging, respectively (Figure S3). A widely used kinetic equation—the first order exponential decay model,[40,41] was applied to fit the data (the percentage of bioavailable fraction) of the aging process and calculated by the following

$$PE_t = PE_e + (a \times e^{-kt}) \quad (5)$$

where PE_e (%) and PE_t (%) are the percentages of the bioavailable fraction of atmospheric metals deposited into soil

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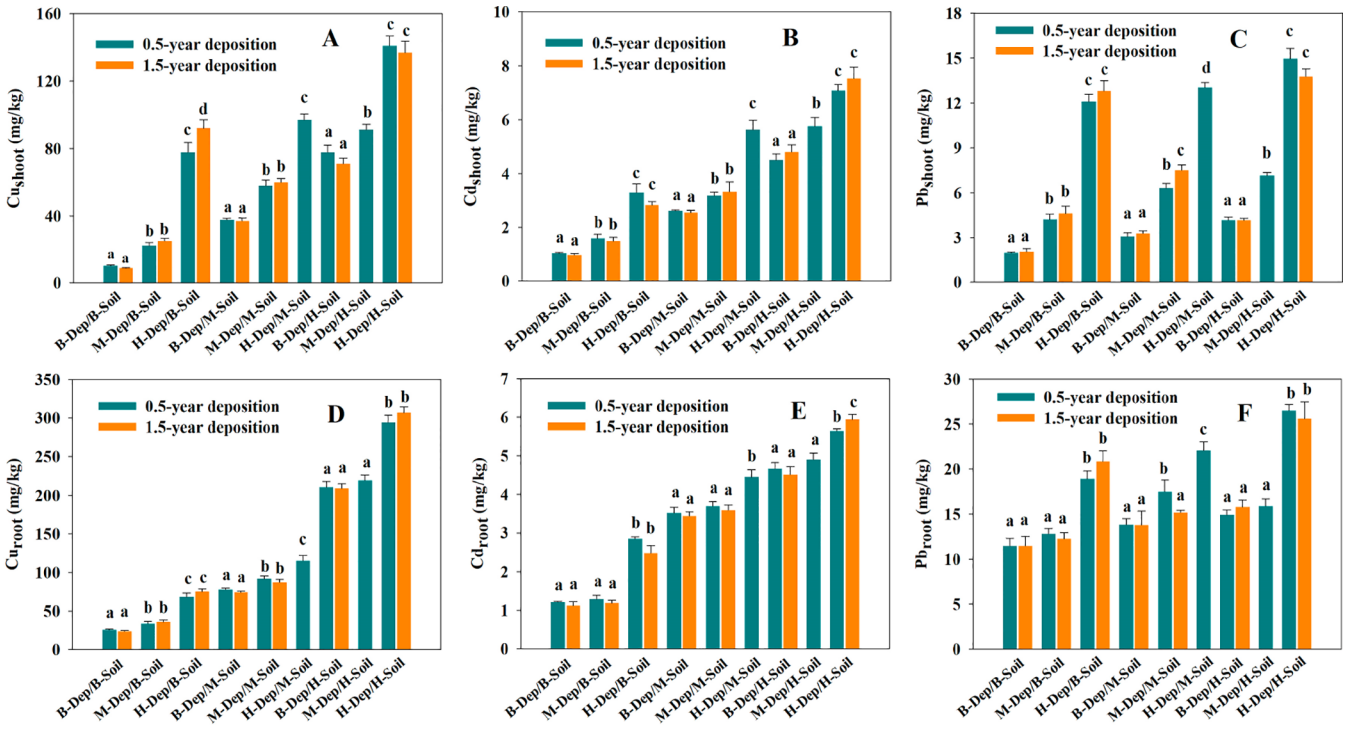

Figure 2. Concentrations of Cu, Cd, and Pb in pak choi shoots and roots along an atmospheric deposition gradient in three sites using soils exposed to a 0.5-year deposition and a 1.5-year deposition. Different lowercase letters indicate significant differences among three deposition sites and between two deposition periods ($p < 0.05$). Data are shown as mean ± SD ($n = 3$).

Table 1. Contribution (%) of Atmospheric Cu, Cd, and Pb Deposition to Pak Choi Tissues in Soils Exposed to a 0.5-Year Deposition and a 1.5-Year Deposition[a]

		Cu		Cd		Pb	
deposition period	group	root	shoot	root	shoot	root	shoot
0.5-year	M-Dep/B-Soil	26.5 ± 0.9	55.0 ± 1.6	8.5 ± 0.5	34.8 ± 2.2	12.3 ± 0.6	53.4 ± 1.3
	M-Dep/M-Soil	18.8 ± 1.6	36.0 ± 1.5	8.0 ± 0.4	19.4 ± 1.4	23.6 ± 0.5	52.6 ± 1.7
	M-Dep/H-Soil	8.3 ± 0.2	17.4 ± 0.9	9.3 ± 0.3	23.9 ± 1.1	10.6 ± 0.6	43.4 ± 1.4
	H-Dep/B-Soil	62.2 ± 1.6	87.0 ± 0.4	55.5 ± 0.8	68.8 ± 1.9	39.4 ± 1.2	83.7 ± 0.3
	H-Dep/M-Soil	31.9 ± 1.3	60.9 ± 0.8	20.0 ± 1.0	53.2 ± 2.0	37.4 ± 1.0	76.4 ± 1.4
	H-Dep/H-Soil	28.4 ± 0.1	44.6 ± 1.1	17.3 ± 1.8	35.6 ± 0.9	43.2 ± 0.7	71.7 ± 0.4
1.5-year	M-Dep/B-Soil	35.8 ± 1.5	65.7 ± 1.3	8.1 ± 0.1	36.7 ± 1.8	9.0 ± 0.4	56.1 ± 2.1
	M-Dep/M-Soil	17.5 ± 2.0	38.9 ± 0.8	7.9 ± 0.4	23.5 ± 0.6	9.2 ± 0.2	56.6 ± 0.4
	H-Dep/B-Soil	67.5 ± 0.9	90.5 ± 0.4	53.7 ± 0.5	66.1 ± 0.4	43.2 ± 0.7	84.0 ± 0.9
	H-Dep/H-Soil	31.8 ± 1.4	47.5 ± 0.1	24.2 ± 1.9	35.7 ± 1.4	38.7 ± 1.1	69.4 ± 0.2

[a]Data are shown as mean ± SD ($n = 3$).

at equilibrium and time t, respectively, k is the apparent rate constant (or attenuation factor), and a is the model parameter.

3. RESULTS AND DISCUSSION

3.1. Heavy Metal Accumulation Behavior in Pak Choi Plants. The Cu, Cd, and Pb concentrations in pak choi shoots, the edible part of the vegetable, grown in background soil in the field experiment were significantly increased ($p < 0.05$) when exposed to moderate and high atmospheric deposition compared to the background of both soils exposed to a 0.5-year deposition and a 1.5-year deposition (Figure 2A-C). For instance, Cu, Cd, and Pb concentrations in shoots of background soil exposed to a 0.5-year deposition were significantly increased by 123%, 56%, and 114% in the moderate deposition site (M-Dep/B-Soil) and 676%, 224%, and 512% in the high deposition site (H-Dep/B-Soil), while those exposed to a 1.5-year deposition were significantly increased by 188%, 56%, and 127% (M-Dep/B-Soil) and 962%, 196%, and 529% (H-Dep/B-Soil), respectively. Similarly, Cu, Cd, and Pb concentrations in pak choi shoots in moderately and heavily polluted soil exposure to a 0.5-year deposition and a 1.5-year deposition were both significantly increased ($p < 0.05$) when exposed in moderate and high deposition sites (M-Dep and H-Dep) compared to exposure in the background site (B-Dep) (Figure 2). For pak choi roots, Cu, Cd, and Pb concentrations were also increased when exposed to moderate and high atmospheric deposition compared to background deposition (Figure 2D-F). The Cu, Cd, and Pb concentrations of pak choi roots in heavily polluted soil exposure to heavy deposition (0.5-year deposition) were significantly increased by 40%, 21%, and 78% (H-Dep/H-Soil), while those exposed to a 1.5-year deposition were significantly increased by 46%, 31%, and 62% (H-Dep/H-Soil) compared

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to those soils in the background site, respectively. These results indicated the elevated accumulation of heavy metals in pak choi tissues under high atmospheric deposition loads. It was noteworthy that Cu, Cd, and Pb concentrations of pak choi tissues grown in soils exposed to 0.5-year deposition and 1.5-year deposition treatments had no significant differences whether they were grown in background or polluted soils in all three sites (Figure 2). These results indicated atmospheric deposition during the plant growth period was the key heavy metal source in vegetables in areas with deposition loads.

The contribution of the deposited heavy metals to the pak choi accumulation in the field experiment was calculated according to eq 1. For 0.5-year exposed soils, the contributions from atmospheric Cu, Cd, and Pb deposition (C_{air}, %) ranged from 17% to 55% and 36% to 87% for plant shoots when exposed to moderate (M-Dep) and high (H-Dep) atmospheric deposition sites, respectively (Table 1). Similarly, for 1.5-year exposed soils, the atmospheric Cu, Cd, and Pb deposition contributed 24%−66% and 36−91% to plant shoots under the exposures of moderate (M-Dep) and high (H-Dep) atmospheric deposition. For roots, the contributions to Cu, Cd, and Pb bioaccumulations were also similar and ranged from 8% to 62% and 8% to 68% for both 0.5- and 1.5-year exposed soils under atmospheric deposition (M-Dep and H-Dep), respectively (Table 1). These results suggested that the relatively higher percentages of heavy metals in pak choi tissues were from the newly deposited heavy metals during the plant growth period. Our results were also consistent with the previous study, which showed the excessive 50% Pb accumulation in Chinese cabbage resulted from airborne Pb.[12] Further, it was noteworthy that Cu, Cd, and Pb from 0.5-year and 1.5-year depositions at the high deposition site (H-Dep) in this study only accounted for 0.3%−16% and 0.8%−32% of total heavy metal pools in soils (B-Soil, M-Soil and H-Soil) but over proportionally contributed to 36%−87% and 36%−91% in edible pak choi shoots, respectively. Even at the moderate deposition site (M-Dep), the deposited metals contributed much lower proportions (0.1%−7% for a 0.5-year deposition and 0.2%−12% for a 1.5-year deposition) to soils, while atmospheric deposition accounted for 17%−55% and 24%−66% of loads in pak choi shoots. Our results highlight a high bioaccumulation potential of atmospheric deposition heavy metals during the plant growth period, which over proportionally contributed to plant bioaccumulations. Several recent research studies using the stable isotope technique traced the source and bioaccumulation of heavy metals in soil-plant systems.[35,36,42] For instance, the contribution of atmospheric deposition to rice grains was quantified as 18−64% for Cd and 28−41% for Pb via the isotope tracer.[42] Thus, the further exact identifying atmospheric deposited metal contribution using isotope tracing is necessary and also will be conducted in the study area, which will be helpful to make further guidelines for industrial emission control.

The high bioaccumulation in the study would be related to transfer behavior of the deposited metals in the soil-pak choi system, as atmospheric metals could be absorbed by pak choi through direct foliar uptake after deposition on leaves or through root uptake after deposition into soils.[17,18] For instance, the increased Cu, Cd, and Pb accumulation in pak choi roots exposed to high atmospheric deposition (H-Dep) (Figure 2) in the field experiment indicated the pathway of atmosphere-soil-root transfer, due to direct foliar uptake of the deposited metals almost cannot be translocated to root tissues (discussed below and shown in Figure S4B), while metals in roots can be transferred to the aerial parts via xylem transport.[21] However, the higher translocation factor (TF) values (calculated by eq 2) in the field experiment were observed from roots to shoots with the increased heavy metal deposition loads among three sites (Figure S5), which indicated the pathway of direct foliar atmospheric uptake.[43] The relative contribution of the direct foliar uptake (C_{foliar}) and soil-root transfer (C_{root}) of atmospheric deposition metals to pak choi edible parts (shoots) in the field experiment were approximatively calculated by eq 3. For Cu and Pb, C_{foliar} was the main uptake pathway, accounting for 50%−84% and 70%−99% of metals in pak choi shoots. For Cd, C_{foliar} was also the key uptake pathway and accounted for 38%−88% of the loads (Table S4). Further, a greenhouse experiment was conducted to further assess bioaccumulation pathways of atmospheric heavy metals in pak choi plants. Results showed significantly higher Cu, Cd, and Pb concentrations in pak choi shoots in foliar exposure treatment compared to soil exposure treatments with the addition of equal amounts of atmospheric metal deposition (Figure S4A). It should be noted that heavy metals in pak choi shoots in foliar exposure treatment were almost not translocated to root tissues (Figure S4B), verifying the assumption of eq 3. Furthermore, the relative contribution proportion (calculated by eq 4) from the direct foliar uptake (C_{foliar}) of atmospheric deposition metals in pak choi shoots in the greenhouse experiment was also much higher (90−96% for Cu, 64−80% for Cd, and 92−95% for Pb) compared to those from soil-root transfer (C_{root}) (4−10% for Cu, 20−36% for Cd, and 5−8% for Pb) (Table S5). These results validated our estimation results by eq 3 in the field experiment and also further highlighted the key role of foliar uptake for atmospheric deposition metals of bioaccumulation in pak choi edible parts.

Leaf-deposited atmospheric heavy metals can be absorbed through aqueous pores, cuticular cracks, and stomata,[15] and the soluble metals from precipitation or metals resulting from the dissolution of dry deposited particles can diffuse through aqueous pores, stomata, and anticlinal cell walls of cuticles, following the hydrophilic pathway.[15,21] Additionally, some fine particles with heavy metals in the micron or nanoscale sizes were observed either on the leaf surface or inside the stomata of pak choi leaves by ESEM-EDS in the field experiment of this study (Figure S6), suggesting that dry deposition can enter the leaves by stomata due to the sufficient large width and length of the stomatal apertures (apertures: 4−10 μm), which was also demonstrated in previous research.[12] After penetration through leaves, heavy metals can be partially transported from the exposed leaves to other tissues, such as flower and even fruit via the phloem stream along with photosynthates.[23,24] Therefore, foliar uptake is especially important for shoot bioaccumulation of atmospheric deposited heavy metals in pak choi plants under high atmospheric deposition loads. This was also consistent with higher bioavailability of the newly deposited heavy metals during the plant growth period (see section 3.3). As mentioned above, the concentrations of heavy metals in both pak choi shoots and roots and the bioaccumulation contributions from atmospheric deposition between the two exposed soil treatments (0.5-year and 1.5-year depositions) were not significantly different, indicating the aging process of metals deposited into soils occurred and the bioavailability of those was reduced with the passage of time (see section 3.2).

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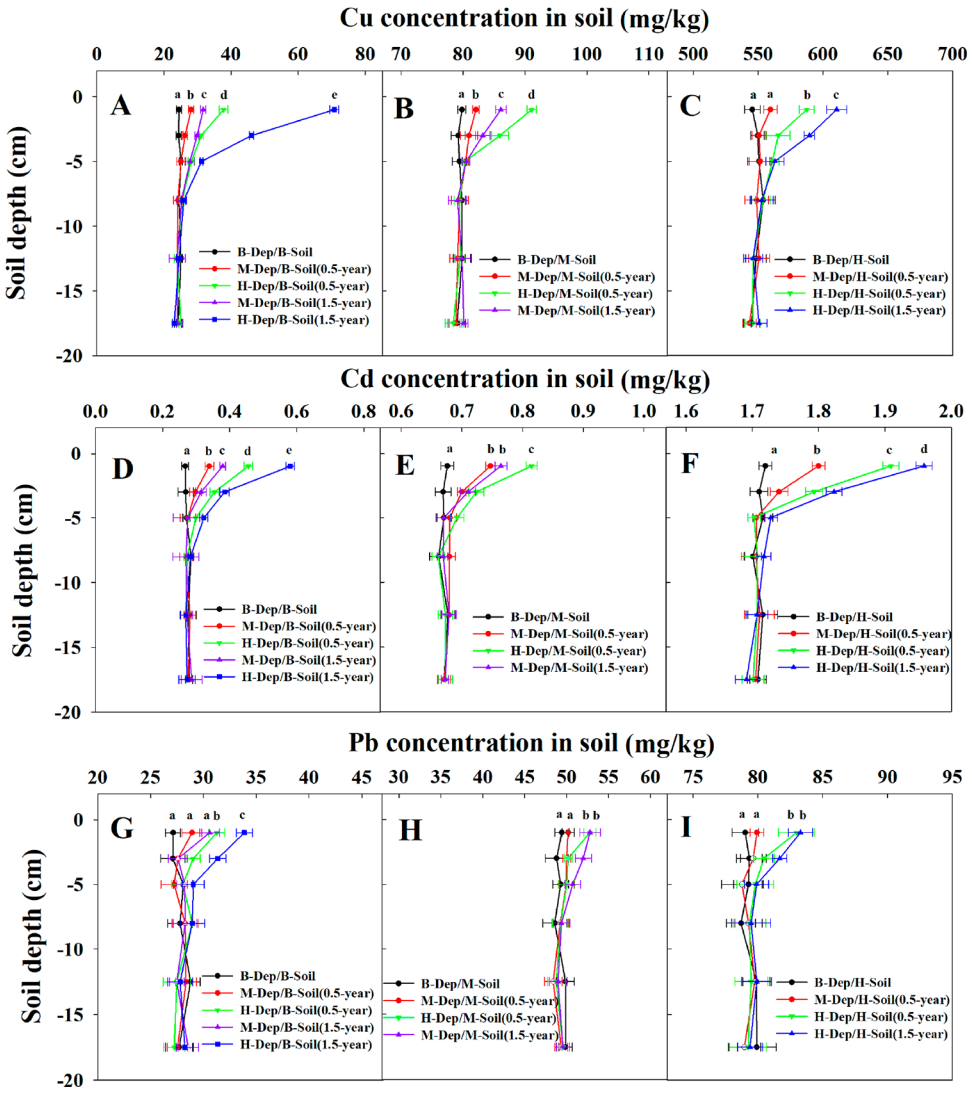

Figure 3. Total Cu, Cd, and Pb concentrations in soils (0−20 cm profile) along an atmospheric deposition gradient in three sites using soils exposed to a 0.5-year deposition and a 1.5-year deposition. For topsoil (0−2 cm), different lowercase letters indicate significant differences among three deposition sites and between two deposition periods ($p < 0.05$). Data are shown as mean ± SD ($n = 3$).

3.2. Heavy Metal Distribution and Chemical Fractions of the Soil Profile. Total Cu, Cd, and Pb concentrations in the topsoil profile (0−2 cm) exposed in the moderate deposition site (M-Dep) and the high deposition site (H-Dep) after 0.5 or 1.5 years in the field experiment were both significantly increased ($p < 0.05$) compared to corresponding soils exposed at the background site (B-Dep) (except Pb concentrations exposed to M-Dep) (Figure 3). Meanwhile, there was an obvious or partial increase of total Cu, Cd, and Pb concentrations in all the topsoil (background and polluted soils) with the increase in exposure time (from 0.5 year to 1.5 year) in high-deposition and moderate-deposition sites compared to those in the background site (Figure 3). Additionally, total Cu, Cd, and Pb concentrations in the soil profile exposed to atmospheric deposition were significantly decreased in depth (2−6 cm), while in deeper soils (6−20 cm), Cu, Cd, and Pb concentrations were not significantly different in the same soils but were exposed in different sites and with different exposure duration. These results suggest the deposited metals during the relatively short period (1.5 year) were mostly accumulated in the topsoil, which may be due to physical retardation of particulate bound metals and chemical adsorption to minerals and humus in topsoil.[44,45]

Total soil heavy metal concentrations could indicate the degree of heavy metal pollution, whereas the environmental risk of heavy metals in soil may be more attributed to chemical forms, especially on the weak acid extractable fraction. Sequential extraction results in the field experiment of our study showed that the concentrations and percentages of the weak acid extractable Cu, Cd, and Pb (0−2 cm profile) exposed to high deposition after 0.5 or 1.5 years were all increased compared to corresponding soils exposed at the background site B-Dep (Figures S7−S10). Meanwhile, the concentrations of the extractable Cu, Cd, and Pb in background topsoil (0−2 cm) were significantly increased ($p < 0.05$) when exposed in the high deposition site (H-Dep) with the exposure time (from 0.5 year to 1.5 year) (Figure S11). The results showed the weak acid extractable Cu, Cd, and Pb concentrations in H-Dep/B-Soil topsoil were 6.69 ± 0.43, 0.242 ± 0.008, and 2.40 ± 0.04 mg/kg by a 0.5-year deposition and then increased up to 13.1 ± 0.6, 0.294 ± 0.010, and 2.67 ± 0.09 mg/kg by a 1.5-year deposition, respectively.

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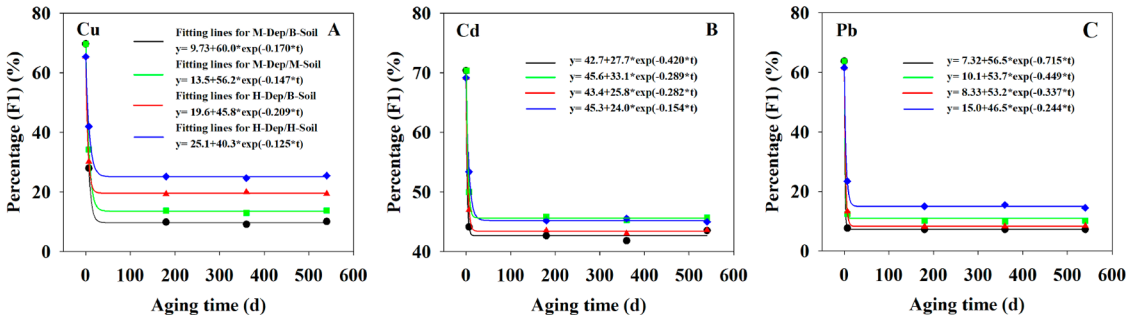

Figure 4. Percentages of the bioavailable fraction (F1) of metals of atmospheric deposition into soils with the aging time (0 d, 7 d, 180 d, 360 and 540 d). Data are shown as mean (n = 3), and lines are the fitted attenuation curves.

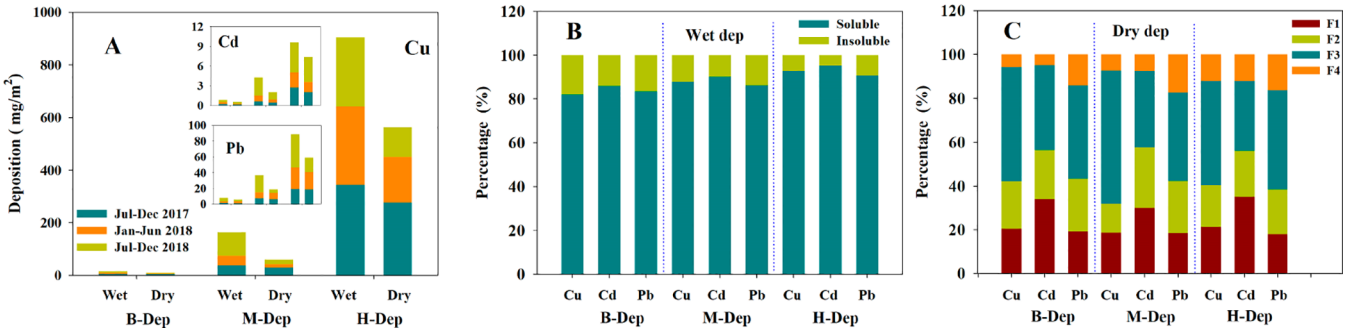

Figure 5. Atmospheric wet and dry Cu, Cd, and Pb deposition (mg/m^2) from July 2017 to December 2018 in three study sites (B-Dep, M-Dep, and H-Dep) (A). The percentage of soluble and insoluble metals in wet deposition (B) and the chemical partitioning of metals in dry deposition (C) are also given.

These results indicated soil heavy metals from an atmospheric new deposition were presented in high mobile forms compared to those in original soils. It should be noted that the acid deposition in the high and moderate sites (Table S6) would influence the soil heavy metal mobilization, but due to the shorter study cycle (1.5-year), the impact of soil acidification was weak based on the result of soil pH exposed to atmospheric deposition in this study (Table S7). Additionally, the concentrations and percentages of the weak acid extractable Cu, Cd, and Pb in the soil profile exposed to atmospheric deposition were significantly decreased with depths (2−6 cm) (Figures S7−S9), while in more deeper soils (6−20 cm), chemical fractions of heavy metals were not significantly influenced by atmospheric deposition and shown to be similar in the same soils among three sites with gradient atmospheric deposition (B-Dep, M-Dep, and H-Dep) (Figures S7−S9).

It was noteworthy that the extractable Cu, Cd, and Pb concentrations in polluted topsoil (0−2 cm) in deposition sites (M-Dep and H-Dep) between 0.5-year deposition and 1.5-year deposition exposure treatments were not statistically different (Figure S11). Meanwhile, we also found the percentages of the weak acid extractable fractions in topsoil (B-Soil, M-Soil and H-Soil) exposed to atmospheric deposition with the experiment period increments (from 0.5 to 1.5 year) were also not statistically increased (Figure S10). These results indicated the weak acid extractable fractions of metals previously deposited into soils were decreased and simultaneously immobilized with time (Figures S7−S9). This phenomenon may be due to the aging effect of acid extractable heavy metals readily converted to a less labile fraction with the passage of time.[26,46,47]

The changes of percentages (%) of the bioavailable fraction (for the weak acid extractable fraction) of metals of atmospheric deposition (the first year, July 2017 to June 2018) into soils with the passage of time were used to assess the aging process (0 d, 7 d, 180 d, 360 d (the date of soil metals shown in Figure S12), and 540 d (the date of soil metals shown in Figure S13)) (Figure 4). The date of the aging process was well fitted by the first order exponential decay model (r^2 = 0.999, p < 0.01) (Table S8). The bioavailable fraction deposited into soils was quickly and sharply decreased during the first 10 d with precipitation/nucleation processes and occlusion processes by organic matter. Then, the bioavailable fraction of metals was slowly decreased with micropore diffusion processes,[48] and the aging process was basically finished at 60 d (accounting for 98% of the decrease in bioavailable metals) (Figure 4). This result was also consistent with previous research, which showed the aging process of the spiked soluble Cu and Cd salts and CuO nanoparticles was basically finished at 30−90 days.[46,49−51] Further, the apparent rate constants (k, attenuation factor) of the aging process were always highest in the background soil (B-Soil) compared to those in polluted soils (M-Soil and H-Soil) when exposed to moderate or high atmospheric deposition (Table S8). The difference in the soil aging rates may be affected by soil properties.[27,47,48] Correlation coefficients between soil properties (Table S1) and aging rates (k) were shown in Table S9. For Cu and Pb, aging rates (k) were significantly positively correlated with soil organic matter (OM) (p < 0.05). For Cd, besides OM, aging rates (k) were also significantly positively correlated with soil clay (p < 0.05). Therefore, the occlusion effects from OM and adsorption effects from clay would promote the rapid aging of heavy metals of atmospheric deposition into acid soils (Table S1) in the present study.[48] Further, atmospheric deposited metals were bound preferentially to soil aggregate

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surfaces under short-term natural aging, while with the passage of time, these metals were increasingly migrated to soil aggregate cores by micropore diffusion processes.[47,52] This notion partly explains our above finding: the reduced bioavailability of heavy metals deposited into soils with the passage of time shown in vegetables (e.g., see Figure 2). However, due to the continuous process of atmospheric deposition and temporal heterogeneity, it is still necessary to further study the dynamic behavior of the bioavailability of atmospheric deposited metals.

3.3. Characteristics of Atmospheric Cu, Cd, and Pb Deposition. Atmospheric deposition fluxes of Cu, Cd, and Pb (separated into wet and dry deposition) over one and a half years (from July 2017 to December 2018) at three study sites were shown in Figure 5A and indicated a strongly spatial heterogeneity. Deposition fluxes showed an obvious gradient pattern along with the distance from the copper smelter. Total Cu, Cd, and Pb deposition from July to December 2018 at the H-Dep site was estimated to be 4, 2, and 2 times higher than deposition measured at site M-Dep and about 46, 15, and 9 times higher than at the B-Dep background site, respectively. Annual deposition fluxes of heavy metals in the H-Dep site were also much higher than those in other countries and regions,[14,53,54] and the sum of atmospheric deposited metals minus the vegetable uptake contents in the study cycle was basically equal to the increased soil metal pools (section 3.2) exposed to atmospheric deposition (Table S10). Large gradients among the three sites in this study can effectively distinguish the newly deposited heavy metals from those originally presented in the soils.

Chemical heavy metal fractions in atmospheric deposition at three study sites were shown in Figure 5B−C. For wet deposition, 82−95% of Cu, Cd, and Pb was presented in soluble fractions (<0.45 μm). The percentages of soluble Cu, Cd, and Pb in atmospheric wet deposition among three study sites were partly different, which were much higher at the H-Dep (91−95%) site compared to those in sites M-Dep (86−90%) and B-Dep (82−85%), respectively. The lower pH (3.1−4.5) observed in wet deposition at the H-Dep site (Table S6) due to the emission of acid sulfur-containing particles from the smelter (Text S1) may increase the solubility of heavy metals.[29] These results indicated the relatively high bioavailability of heavy metals in wet deposition in the present study, especially the high H-Dep deposition site nearby the smelter. For dry deposition, the deposited Cu and Pb were dominantly bound to oxidizable fractions (F3), which accounted for 47−61% and 40−45%, respectively (Figure 5C). Relatively high fractions of Cu and Pb also occurred in the weak acid extractable form (F1, 18−21%), indicating the potentially biological activity of Cu and Pb in dry deposition. Comparatively, much higher percentages of the weak acid extractable fraction were observed for Cd (F1, 30−35%) (Figure 5C). If the soluble heavy metals in wet deposition and the weak acid extractable form of metals in dry deposition were considered as bioavailable fractions, the bioavailable fractions of Cu, Cd, and Pb accounted for 58−70%, 66−71%, and 57−64% of total deposition, which exceeded the bioavailability in original soils (9−21% for Cu, 40−45% for Cd, and 7−14% for Pb), respectively (Figure S10). Therefore, these results indicated that atmospherically deposited heavy metals during the study period have higher bioavailability compared to those in original soils from the previous deposition or geogenic source, etc., which also offered some support for our above finding that the bioavailability of atmospheric metals deposited into soils was reduced with the soil aging process.

3.4. Environmental Implications. High proportions (17−87%) of heavy metals in pak choi edible parts were contributed from the newly atmospheric deposition. For the newly deposited metals, foliar uptake of atmospheric metals during plant growth period was the key pathway of shoot bioaccumulation (accounting for 38−99%), rather than from root uptake of the deposited metals in soils. Furthermore, the rapid soil aging process reduced the bioavailability of atmospheric metals deposited into soils. These results give slight insight into reducing current atmospheric loads of heavy metals in the study area by controlling pollution emissions may have an instant impact for the bioaccumulation in vegetables. In addition, from the perspective of foliar uptake, more in-depth investigation into the deposited metal localization using an isotope tracer technique and the absorption mechanism (e.g., transporter proteins) at the molecular level will be helpful to realize effective prevention and control of heavy metal accumulation in vegetables from the source of atmospheric deposition.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c04062.

Texts 1−7, Tables S1−S11, Figures S1−S13, details of study sites, soil properties, experiment design, sample preparation and analytical methods, biomass of pak choi tissues, contribution values of foliar and root uptake of deposited metals to pak choi shoots, kinetic equations of aging process, correlation between soil properties and aging process, mass balance between atmospheric deposition metals and increased soil metals; XRD spectra of dry deposition and dust, ESEM-EDS analyses of particles in pak choi leaves, TF of pak choi roots to shoots, metal fraction in soils of field experiment, and metal concentrations of pak choi tissues in greenhouse experiment (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Srivastava, D.; Xu, J.; Vu, T. V.; Liu, D.; Li, L.; Fu, P.; Hou, S.; Moreno Palmerola, N.; Shi, Z.; Harrison, R. M. Insight into PM2.5 sources by applying positive matrix factorization (PMF) at urban and rural sites of Beijing. *Atmos. Chem. Phys.* **2021**, *21* (19), 14703−14724.

(2) Tian, H. Z.; Zhu, C. Y.; Gao, J. J.; Cheng, K.; Hao, J. M.; Wang, K.; Hua, S. B.; Wang, Y.; Zhou, J. R. Quantitative assessment of atmospheric emissions of toxic heavy metals from anthropogenic sources in China: historical trend, spatial distribution, uncertainties, and control policies. *Atmos. Chem. Phys.* **2015**, *15* (17), 10127−10147.

(3) Pacyna, J. M.; Pacyna, E. G.; Aas, W. Changes of emissions and atmospheric deposition of mercury, lead, and cadmium. *Atmos. Environ.* **2009**, *43* (1), 117−127.

(4) Duan, J.; Tan, J. Atmospheric heavy metals and arsenic in China: situation, sources and control policies. *Atmos. Environ.* **2013**, *74*, 93−101.

(5) Li, C.; Shen, J.; Zhang, J.; Lei, P.; Kong, Y.; Zhang, J.; Tang, W.; Chen, T.; Xiang, X.; Wang, S.; Zhang, W.; Zhong, H. The silver linings of mercury: Reconsideration of its impacts on living organisms from a multi-timescale perspective. *Environ. Int.* **2021**, *155*, 106670.

(6) Peng, H.; Chen, Y.; Weng, L.; Ma, J.; Ma, Y.; Li, Y.; Islam, M. S. Comparisons of heavy metal input inventory in agricultural soils in North and South China: A review. *Sci. Total Environ.* **2019**, *660*, 776−786.

(7) Fu, Y.; Li, F.; Guo, S.; Zhao, M. Cadmium concentration and its typical input and output fluxes in agricultural soil downstream of a heavy metal sewage irrigation area. *J. Hazard. Mater.* **2021**, *412*, 125203.

(8) de Vries, W.; McLaughlin, M. J. Modeling the cadmium balance in Australian agricultural systems in view of potential impacts on food and water quality. *Sci. Total Environ.* **2013**, *461*, 240−257.

(9) Belon, E.; Boisson, M.; Deportes, I. Z.; Eglin, T. K.; Feix, I.; Bispo, A. O.; Galsomies, L.; Leblond, S.; Guellier, C. R. An inventory of trace elements inputs to French agricultural soils. *Sci. Total Environ.* **2012**, *439*, 87−95.

(10) Nicholson, F. A.; Smith, S. R.; Alloway, B. J.; Carlton-Smith, C.; Chambers, B. J. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci. Total Environ.* **2003**, *311* (1−3), 205−219.

(11) Liu, H.; Zhou, J.; Li, M.; Obrist, D.; Wang, X.; Zhou, J. Chemical speciation of trace metals in atmospheric deposition and impacts on soil geochemistry and vegetable bioaccumulation near a large copper smelter in China. *J. Hazard. Mater.* **2021**, *413*, 125346.

(12) Gao, P.; Xue, P.; Dong, J.; Zhang, X.; Sun, H.; Geng, L.; Luo, S.; Zhao, J.; Liu, W. Contribution of PM2.5-Pb in atmospheric fallout to Pb accumulation in Chinese cabbage leaves via stomata. *J. Hazard. Mater.* **2021**, *407*, 124356.

(13) Bohdalkova, L.; Novak, M.; Krachler, M.; Mikova, J.; Chrastny, V.; Veselovsky, F.; Voldrichova, P.; Pacherova, P.; Komarek, A.; Prechova, E. Cadmium contents of vertically and horizontally deposited winter precipitation in Central Europe: spatial distribution and long-term trends. *Environ. Pollut.* **2020**, *265*, 114949.

(14) Feng, W.; Guo, Z.; Xiao, X.; Peng, C.; Shi, L.; Ran, H.; Xu, W. Atmospheric deposition as a source of cadmium and lead to soil-rice system and associated risk assessment. *Ecotoxicol. Environ. Saf.* **2019**, *180*, 160−167.

(15) Uzu, G.; Sobanska, S.; Sarret, G.; Munoz, M.; Dumat, C. Foliar lead uptake by lettuce exposed to atmospheric fallouts. *Environ. Sci. Technol.* **2010**, *44* (3), 1036−1042.

(16) Xiong, T.; Dumat, C.; Dappe, V.; Vezin, H.; Schreck, E.; Shahid, M.; Pierart, A.; Sobanska, S. Copper oxide nanoparticle foliar uptake, phytotoxicity, and consequences for sustainable urban agriculture. *Environ. Sci. Technol.* **2017**, *51* (9), 5242−5251.

(17) Ma, C.; Liu, F.; Xie, P.; Zhang, K.; Yang, J.; Zhao, J.; Zhang, H. Mechanism of Pb absorption in wheat grains. *J. Hazard. Mater.* **2021**, *415*, 125618.

(18) Meng, B.; Feng, X.; Qiu, G.; Liang, P.; Li, P.; Chen, C.; Shang, L. The process of methylmercury accumulation in rice (Oryza sativa L.). *Environ. Sci. Technol.* **2011**, *45* (7), 2711−2717.

(19) Ao, M.; Xu, X.; Wu, Y.; Zhang, C.; Meng, B.; Shang, L.; Liang, L.; Qiu, R.; Wang, S.; Qian, X.; Zhao, L.; Qiu, G. Newly deposited atmospheric mercury in a simulated rice ecosystem in an active mercury mining region: High loading, accumulation, and availability. *Chemosphere* **2020**, *238*, 124630.

(20) De Temmerman, L.; Waegeneers, N.; Ruttens, A.; Vandermeiren, K. Accumulation of atmospheric deposition of As, Cd and Pb by bush bean plants. *Environ. Pollut.* **2015**, *199*, 83−88.

(21) Shahid, M.; Dumat, C.; Khalid, S.; Schreck, E.; Xiong, T.; Niazi, N. K. Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake. *J. Hazard. Mater.* **2017**, *325*, 36−58.

(22) Luo, X.; Bing, H.; Luo, Z.; Wang, Y.; Jin, L. Impacts of atmospheric particulate matter pollution on environmental biogeochemistry of trace metals in soil-plant system: A review. *Environ. Pollut.* **2019**, *255* (1), 113138.

(23) Li, M.; Liu, H.; Dang, F.; Hintelmann, H.; Yin, B.; Zhou, D. Alteration of crop yield and quality of three vegetables upon exposure to silver nanoparticles in sludge-amended soil. *ACS Sustain. Chem. Eng.* **2020**, *8* (6), 2472−2480.

(24) Dang, F.; Chen, Y.; Huang, Y.; Hintelmann, H.; Si, Y.; Zhou, D. Discerning the sources of silver nanoparticle in a terrestrial food chain by stable isotope tracer technique. *Environ. Sci. Technol.* **2019**, *53* (7), 3802−3810.

(25) Hintelmann, H.; Harris, R.; Heyes, A.; Hurley, J. P.; Kelly, C. A.; Krabbenhoft, D. P.; Lindberg, S.; Rudd, J. W. M.; Scott, K. J.; St Louis, V. L. Reactivity and mobility of new and old mercury deposition in a Boreal forest ecosystem during the first year of the METAALICUS study. *Environ. Sci. Technol.* **2002**, *36* (23), 5034−5040.

(26) Schreck, E.; Foucault, Y.; Geret, F.; Pradere, P.; Dumat, C. Influence of soil ageing on bioavailability and ecotoxicity of lead carried by process waste metallic ultrafine particles. *Chemosphere* **2011**, *85* (10), 1555−1562.

(27) Ma, Y. B.; Lombi, E.; Nolan, A. L.; McLaughlin, M. J. Short-term natural attenuation of copper in soils: Effects of time, temperature, and soil characteristics. *Environ. Toxicol. Chem.* **2006**, *25* (3), 652−658.
(28) Liu, H.; Li, M.; Zhou, J.; Zhou, D.; Wang, Y. Effects of soil properties and aging process on the acute toxicity of cadmium to earthworm Eisenia fetida. *Environ. Sci. Pollut. Res.* **2018**, *25*, 3708−3717.
(29) Li, W.; Wang, Y.; Collett, J. L., Jr.; Chen, J.; Zhang, X.; Wang, Z.; Wang, W. Microscopic evaluation of trace metals in cloud droplets in an acid precipitation region. *Environ. Sci. Technol.* **2013**, *47* (9), 4172−4180.
(30) Weerasundara, L.; Amarasekara, R. W. K.; Magana-Arachchi, D. N.; Ziyath, A. M.; Karunaratne, D. G. G. P.; Goonetilleke, A.; Vithanage, M. Microorganisms and heavy metals associated with atmospheric deposition in a congested urban environment of a developing country: Sri Lanka. *Sci. Total Environ.* **2017**, *584*, 803−812.
(31) Liu, H.; Zhou, J.; Li, M.; Hu, Y.; Liu, X.; Zhou, J. Study of the bioavailability of heavy metals from atmospheric deposition on the soil-pakchoi (Brassica chinensis L.) system. *J. Hazard. Mater.* **2019**, *362*, 9−16.
(32) Wang, C.; Jin, H.; Zhong, C.; Wang, J.; Sun, M.; Xie, M. Estimating the contribution of atmosphere on heavy metals accumulation in the aboveground wheat tissues induced by anthropogenic forcing. *Environ. Res.* **2020**, *189*, 109955.
(33) Li, C.; Dang, F.; Li, M.; Zhu, M.; Zhong, H.; Hintelmann, H.; Zhou, D. Effects of exposure pathways on the accumulation and phytotoxicity of silver nanoparticles in soybean and rice. *Nanotoxicology* **2017**, *11* (5), 699−709.
(34) Mittermueller, M.; Saatz, J.; Daus, B. A sequential extraction procedure to evaluate the mobilization behavior of rare earth elements in soils and tailings materials. *Chemosphere* **2016**, *147*, 155−162.
(35) Zhou, J.; Li, Z.; Liu, M.; Yu, H.-M.; Wu, L.; Huang, F.; Luo, Y.; Christie, P. Cadmium isotopic fractionation in the soil-plant system during repeated phytoextraction with a cadmium hyperaccumulating plant species. *Environ. Sci. Technol.* **2020**, *54* (21), 13598−13609.
(36) Wiggenhauser, M.; Bigalke, M.; Imseng, M.; Muller, M.; Keller, A.; Murphy, K.; Kreissig, K.; Rehkamper, M.; Wilcke, W.; Frossard, E. Cadmium isotope fractionation in soil-wheat systems. *Environ. Sci. Technol.* **2016**, *50* (17), 9223−9231.
(37) Weinstein, C.; Moynier, F.; Wang, K.; Paniello, R.; Foriel, J.; Catalano, J.; Pichat, S. Isotopic fractionation of Cu in plants. *Chem. Geol.* **2011**, *286* (3−4), 266−271.
(38) Dong, Q.; Liu, Y.; Liu, G.; Guo, Y.; Yang, Q.; Shi, J.; Hu, L.; Liang, Y.; Yin, Y.; Cai, Y.; Jiang, G. Enriched isotope tracing to reveal the fractionation and lability of legacy and newly introduced cadmium under different amendments. *J. Hazard. Mater.* **2021**, *403*, 123975.
(39) Chadwick, S. P.; Babiarz, C. L.; Hurley, J. P.; Armstrong, D. E. Importance of hypolimnetic cycling in aging of "new" mercury in a northern temperate lake. *Sci. Total Environ.* **2013**, *448*, 176−188.
(40) Tao, Y.; Xue, B.; Yao, S.; Deng, J.; Gui, Z. Triolein embedded cellulose acetate membrane as a tool to evaluate sequestration of PAHs in lake sediment core at large temporal scale. *Environ. Sci. Technol.* **2012**, *46* (7), 3851−3858.
(41) Huang, B.; Li, Z.; Huang, J.; Chen, G.; Nie, X.; Ma, W.; Yao, H.; Zhen, J.; Zeng, G. Aging effect on the leaching behavior of heavy metals (Cu, Zn, and Cd) in red paddy soil. *Environ. Sci. Pollut. Res.* **2015**, *22* (15), 11467−11477.
(42) Zhu, Z.; Xu, Z.; Peng, J.; Fei, J.; Yu, P.; Wang, M.; Tan, Y.; Huang, Y.; Zhran, M.; Fahmy, A. The contribution of atmospheric deposition of cadmium and lead to their accumulation in rice grains. *Plant Soil* **2022**, DOI: 10.1007/s11104-022-05429-x.
(43) Zhang, H.; Zhang, Y.; Wang, Z.; Ding, M.; Jiang, Y.; Xie, Z. Traffic-related metal(loid) status and uptake by dominant plants growing naturally in roadside soils in the Tibetan plateau, China. *Sci. Total Environ.* **2016**, *573*, 915−923.
(44) Werkenthin, M.; Kluge, B.; Wessolek, G. Metals in European roadside soils and soil solution - a review. *Environ. Pollut.* **2014**, *189*, 98−110.
(45) Wang, X.; Du, Y.; Li, F.; Fang, L.; Pang, T.; Wu, W.; Liu, C.; Chen, L. Unique feature of Fe-OM complexes for limiting Cd accumulation in grains by target-regulating gene expression in rice tissues. *J. Hazard. Mater.* **2022**, *424*, 127361.
(46) Wang, Q. Y.; Sun, J. Y.; Yu, H. W.; Yang, X. T.; Hu, N. W. Laboratory versus field soil aging: impacts on cadmium distribution, release, and bioavailability. *Sci. Total Environ.* **2021**, *779* (20), 146442.
(47) Ma, Y.; Lombi, E.; McLaughlin, M. J.; Oliver, I. W.; Nolan, A. L.; Oorts, K.; Smolders, E. Aging of nickel added to soils as predicted by soil pH and time. *Chemosphere* **2013**, *92* (8), 962−968.
(48) Zeng, S.; Li, J.; Wei, D.; Ma, Y. A new model integrating short- and long-term aging of copper added to soils. *PLoS One* **2017**, *12* (8), e0182944.
(49) Qiu, H.; Smolders, E. Nanospecific phytotoxicity of CuO nanoparticles in soils disappeared when bioavailability factors were considered. *Environ. Sci. Technol.* **2017**, *51* (20), 11976−11985.
(50) McShane, H. V. A.; Sunahara, G. I.; Whalen, J. K.; Hendershot, W. H. Differences in soil solution chemistry between soils amended with nanosized CuO or Cu reference materials: implications for nanotoxicity tests. *Environ. Sci. Technol.* **2014**, *48* (14), 8135−8142.
(51) Ma, Y.; Lombi, E.; Oliver, I. W.; Nolan, A. L.; McLaughlin, M. J. Long-term aging of copper added to soils. *Environ. Sci. Technol.* **2006**, *40* (20), 6310−6317.
(52) Wilcke, W.; Kaupenjohann, M. Heavy metal distribution between soil aggregate core and surface fractions along gradients of deposition from the atmosphere. *Geoderma* **1998**, *83* (1−2), 55−66.
(53) Zhang, X.; Geng, L.; Gao, P.; Dong, J.; Zhou, C.; Li, H.; Chen, M.; Xue, P.; Liu, W. Bioimaging of Pb by LA-ICP-MS and Pb isotopic compositions reveal distributions and origins of Pb in wheat grain. *Sci. Total Environ.* **2022**, *802*, 149729.
(54) Fernández-Olmo, I.; Puente, M.; Montecalvo, L.; Irabien, A. Source contribution to the bulk atmospheric deposition of minor and trace elements in a Northern Spanish coastal urban area. *Atmos. Res.* **2014**, *145−146*, 80−91.

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