Supporting information of

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

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Summary

25 SI pages containing 5 texts, 5 figures and 8 tables

Text S1

Study site

The study was conducted nearby the largest Cu smelter in China located in Guixi city of Jiangxi province in southeastern China (Supplementary information, Fig. S1). The climate is typical subtropical humid with an annually average temperature of 18 ^{o}C, average annual rainfall of 1905 mm and prevailing northeastern winds. The production capacity of the smelter was about 7.2×10^{5} tons of Cu in 2018. 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 (Au), and 3.5×10^{2} tons of silver (Ag) per year (Xiao et al., 2011). Due to a large amount of metal smelting, the surrounding farmland has been heavily polluted, resulting in trace metals concentrations in crops exceeding the acceptable level (Xu et al., 2017a). Annual atmospheric deposition fluxes of trace metals around the smelter between July 2012 to June 2016 were 767.0 $mg\cdot m^{-2}\cdot a^{-1}$, 6.6 $mg\cdot m^{-2}\cdot a^{-1}$, and 70.0 $mg\cdot m^{-2}\cdot a^{-1}$ for Cu, Cd, and Pb, respectively (Zhou et al., 2018).

Three study sites (A1, A2, and A3) along an expected gradient of atmospheric deposition near the smelter were selected, including: a high atmospheric deposition site (A3) located about 1 km downwind from the smelter; a moderate atmospheric deposition site (A2) located about 6 km away following the same direction as site A3; and a control site with low deposition (A1) located about 34 km away, also following the same direction as sites A2 and A3 (Supplementary information, Fig. S1).

Text S2

Soil properties and measuring method

Soils properties used to grow vegetables were showed in Table S1. In short, soils (S1, S2, and S3) were hydragric anthrosols, acidic (pH_{CaCl_2}=4.3-5.3), and moderately fertile (OM=27-41 g/kg, CEC=7.4-8.8 cmol/kg), with available nitrogen of 113-185 mg/kg, available phosphorus of 34-58 mg/kg, and available potassium of 67-76 mg/kg). Soils S2 taken from the atmospheric exposure site A2 were moderately polluted (80.02±0.88 mg/kg Cu, 0.72±0.05 mg/kg Cd and 50.20±0.43 mg/kg Pb) while soils S3 from site A3 were heavily polluted (556.67±12.61 mg/kg Cu, 1.66±0.05 mg/kg Cd, and 74.13±1.77 mg/kg Pb) due to the long-term metal smelting emissions. Soil S1 from the control site (A1) was not or only minimally affected by smelting emissions (23.32±0.09 mg/kg Cu, 0.22±0.01 mg/kg Cd, and 29.61±0.19 mg/kg Pb) and lower than the regulatory limit for soil pollution of agricultural land by the China Ministry of Ecology and Environment (GB 15618-2018, 50 mg/kg for Cu, 0.3 mg/kg for Cd, and 70 mg/kg for Pb). While in general soil physicochemical properties of soils from the three study sites were similar (Table S1), soil pH and available P were higher in soils S3 due to previous applications of alkaline materials containing phosphorus to stabilize trace metals as a farmland remediation technique (Xu et al., 2017b).

Soil pH was measured in 0.01M $CaCl_2$ (1 : 2.5 soil : solution ratio). OM was measured by the Walkley and Black method (Potassium dichromate oxidation-ferrous sulphate titrimetry). Soil texture (percent sand, silt, and clay) was analyzed by Laser particle size analyzer (Beckman LS 13320, America). Cation exchange capacity (CEC) was measured by the ammonium acetate centrifugal exchange method. Available N was measured by the alkaline hydrolysis diffusion method. Available P was measured by Mo-Sb colorimetry. Available K was measured by ammonium acetate extraction-flame spectrophotometry. The values of trace metals in soils were determined by the inductively coupled plasma mass spectrometry (Agilent 7800 ICP-MS, America) with mixed-acid digestion (HNO_3-$HClO_4$-HF). Blanks and the certified soil reference material (GBW07406, the National Research Center for Standard Materials of China) were used for controlling the quality of our analysis and the recovery rates were 96-105%.

Text S3

Method of the fully factorial exposure experiment

In order to distinguish the recently trace metals by atmospheric deposition (<1 year) and the original trace metals (including parent rock matrix and earlier deposited atmospheric trace metals), a fully factorial soil and atmosphere exposure design with replications (n = 3) including seven treatment groups was conducted between July 2017 and June 2018. The polluted soils in moderate and high sites of atmospheric deposition were transferred to a control site and the unpolluted soil in control site was transferred to moderate and high deposition sites. In brief, the first treatment pot was a control site-box (A1-S1), located at A1 site, and filled with topsoil collected from A1 paddy field with the low levels of trace metals (23.32±0.09 mg/kg Cu, 0.22±0.01 mg/kg Cd, and 29.61±0.19 mg/kg Pb). This box received a comparatively low trace metals input by atmospheric deposition. The second treatment pot was also a control site-box (A1-S2), located at A1 site, but filled with A2 paddy field topsoil (S2) with the moderately polluted levels of trace metals (80.02±0.88 mg/kg Cu, 0.72±0.05 mg/kg Cd, and 50.20±0.43 mg/kg Pb). The third pot was a control site-box (A1-S3), located at A1 site, and filled with topsoil collected from A3 paddy field (S3) with the heavily polluted levels of trace metals (556.67±12.61 mg/kg Cu, 1.66±0.05 mg/kg Cd, and 74.13±1.77 mg/kg Pb). The pots of A1-S1, A1-S2 and A1-S3 received a low trace metals input by atmospheric deposition throughout the cultivation duration. The fourth pot was a moderate deposition site-box (A2-S1), located at A2 site receiving the moderate metals input by atmospheric deposition, but filled with the paddy field with the low levels of trace metals from A1 site. The fifth pot was also a moderate deposition site-box (A2-S2), located at A2 site receiving the same deposition input as A2-S1, and filled with the moderately polluted paddy soil from A2 site itself. The sixth pot was a high deposition site-box (A3-S1), located at A3 site, but filled with A1 paddy field topsoil with the low levels of trace metals. The box received a high trace metals input by atmospheric deposition. The seventh box was also a high deposition site-box (A3-S3), located at A3 site, and filled with the heavily polluted paddy soil from A3 site itself. To manage the high number of treatment numbers, we selected not to expose soil from moderate deposition site A2 at the high atmospheric deposition site A3, and vice versa not to expose soil from the high deposition site A3 at the moderate atmospheric deposition site A2. All boxes filled with soil profiles (dimensions: 0.58 m length×0.44 m wide×0.32 m height) were mounted on the stone mounds about 0.5 m above the surrounding ground in order to avoid any contamination from soil particles by splashing during heavy rainfall. These boxes were also filled with 10 mm thickness acid washed quartz and 40 mesh nylon mesh in the bottom with hole (3 cm in diameter) in order to discharge excess water in the rainy season.

Three wide cultivation vegetables in study area, including radish (*Raphanus sativus* L., rhizome vegetable), lettuce (*Lactuca sativa* L., leaf vegetable) and soybean (*Phaseolus vulgaris* L., fruit vegetable) were grown in each of these combined soil-atmosphere exposure categories, resulting in a total of 63 plant samples for the study (2-3 soil exposures, 3 atmospheric exposures, 3 vegetable types, 3 replications). The vegetable types were chosen because they represented different edible parts for human consumption, such as rhizomes for radish, leaves for lettuce and seeds for soybean. The planting order and growing season of the three vegetables were chosen according to local farming practices. Germinated radish seeds were firstly cultivated in the experimental with a density of 4 seedlings each pot in early January 2018. The radish was exposed for 60 d and then the lettuce seedlings (mean 8 g for fresh biomass, with the germinated seeds firstly cultivated in uncontaminated soils for one month) were continuously transplanted into plots in early March 2018. The lettuce was exposed for 45 d, after which the germinated soybean seeds were continuously transplanted into plots in mid-April 2018 and the mature soybean was harvested in late June 2018. Vegetables were watered by the qualified tap water containing the low concentrations of trace metals (Cu < 0.1 μg/L, Cd < 0.01 μg/L, and Pb < 0.01 μg/L) during the entire experiment. The effect of trace metals in the irrigation water was negligible compared with atmospheric deposition trace metals.

The objective of A1-S1 (filled with soil from the control site) exposed to low atmospheric deposition was to estimate bioaccumulation of trace metals in three vegetables from background soils (not/minimally affected by recent or earlier atmospheric deposition). Further, the key difference among A1-S3, A1-S2, and A1-S3 was the pollution level of trace metals in soils. The objective of three groups was to estimate bioaccumulation of trace metals in three vegetables from soils exposures, which would be indicative of the effect of past (i.e., >1 year) atmospheric deposition impacts (Zhou et al., 2018). Moreover, the key difference among A1-S1, A2-S1, and A3-S1 was the deposition flux. The objective of three groups was to understand whether the recently deposited trace metals are readily absorbed and accumulated in vegetable. Meanwhile, the objective of group A1-S2 and A2-S2 was to understand the process of trace metals accumulation from the moderately polluted soil and air. In addition, the objective of group A1-S3 and A3-S3 was to understand the contribution of trace metals accumulation in vegetable from the heavily polluted soil and air. The bioavailability of the recently deposited Cu, Cd, and Pb and those in original soil for vegetable can be well distinguished using such experimental design method. The bioaccumulation effect from the recently deposited trace metals on different edible types of vegetables also can be well investigated by this experiment.

Text S4

Method of sampling and analytical deposition

The atmospheric deposition samples during the period July 2017 to June 2018 were collected each month by automatic wet and dry deposition sampler (APS-3A, Changsha Xianglan Scientific Instruments Co., Hunan, China) situated on the rooftops of buildings at each site to minimize local soil contamination. The collector was equipped with one moisture sensor to collect dry and wet deposition separately. The moisture sensor would activate the electric pathway allowing automatic transfer of the dustproof cover from wet deposition polyethylene bottle to dry deposition polyethylene bottle during the rain event. The sampler was washed every month by 2% HNO_3 solution and 0.2% benzalkonium chloride (Osvan) for sterilization (Osada et al., 2014). For wet deposition, the sample was not collected in October 2017 due to absent rain; for dry deposition each month, a plastic brush was carefully used to collect deposition particles, and then they were stored in polypropylene centrifuge tube at 4 ^{o}C (Corning, USA) and brought into laboratory for subsequent analyses. The operating principle of collector in detail can be obtained from the previous study (Wang et al., 2012).

In wet deposition, the rain samples of each month were divided into two equal parts, and one was used to determine pH and hydrodynamic diameter by Dynamic light scattering (DLS, NanoBrook 90Plus PALS, America). The other part was used to measure size distribution of Cu, Cd, and Pb, whereby size distribution included separation into particulate (> 0.45 μm, unfiltered samples), dissolved (corresponding colloid fraction, < 0.45 μm, filtered by 0.45 μm filter) (PES, MEMBRANA, Germany), and defined ionic fraction (i.e., ionic metals and those adsorbed onto small molecular weight colloid, < 3 kDa, filtered by 3 kDa filter) (Amicon Ultra-15, Millipore, USA) (Javed et al., 2017). All rain samples analyzed for species of trace metals (Cu, Cd, and Pb) were extracted using nitric acid (5%, *v/v*) facilitated by heating under 80 ℃ according to the modified method of USEPA 200.8 and determined by ICP-MS (Agilent 7800, America) (Wang et al., 2017).

For dry deposition, samples were air-dried, grinded and sieved to < 0.15 mm. One of the halves samples each month were used to conduct the characterization of mineral composition by X-ray diffractometer XRD (Ultima IV, Japan) analysis. Dust samples from pulse bag filter from the Guixi copper smelter were also collected and sieved to < 0.15 mm to assist in the characterization of trace metal hosting mineral phases by XRD considering that the low trace metal content in atmospheric deposition cannot meet the

XRD identification limit, which can be also used for verifying the likely origin of atmospheric deposition and links to this assumed emission source. The other halves were used to conduct Tessier five-step sequential extraction (F1 exchangeable, F2 carbonate, F3 reducible, F4 organic and sulfide, and F5 residual fractions) determining the partitioning of trace metals (Cu, Cd, and Pb) by ICP-MS (Agilent 7800, America) (Lee et al., 2015). Blanks and the certified soil reference material (GBW07442, the National Research Center for Standard Materials of China) were used for controlling the quality of our analysis and the recovery rates were 97-103%. These characteristics were conducive to analyze the mobility and bioavailability of atmospheric deposition trace metals.

Text S5

Method of sampling and analytical vegetable and soil

The three vegetables (radish, lettuce, and soybean) grown in sequence for the duration of 60, 45, and 75 days, respectively were harvested in early March, mid-April, and late June 2018, respectively. Sampling radish and lettuce were dissected into shoot and rhizome (or root) washed by running tap water and then deionized water (Uzu et al., 2010), and the root, stem, and seed of soybean were also washed by the same operation as above. Additionally, the leaf and pod (excluding seed) of soybean were both splitted in two sub samples and one was washed as above and the other halve was unwashed and cleaned carefully with a brush to compare and study the effect of the direct foliar absorption of atmospheric deposition pollutants on trace metals accumulation in vegetables (De Temmerman et al., 2015). The fresh weight and dry weight of vegetable tissues were weighed separately, and then samples were dried at 105 ℃ for 30 min and 80 ℃ to a constant weight, grinded, sieved to < 0.15 mm and Cu, Cd, and Pb of vegetable samples were extracted in a 1:1 mixture of HNO_3 and H_2O_2 at 90 ℃ for 4 h. Meanwhile, the corresponding surface soils after harvest of the soybean in late June 2018 were collected by stratified sampling (0-2, 2-4, 4-6, 6-10, 10-15, and 15-20 cm, three samples constituting one pooled sample per layer per pot) and stored in liquid nitrogen. Tessier five-step sequential extraction (F1 exchangeable, F2 carbonate, F3 reducible, F4 organic and sulfide, and F5 residual fractions) was performed using 1.0 g sub-samples of soils within polypropylene centrifuge tubes to determine the partitioning of Cu, Cd, and Pb in soils.

Soil and plant extracted samples were determined by ICP-MS (Agilent 7800, America) for Cu, Cd, and Pb. Blanks and the certified soil and spinach reference material (GBW07442 and 10015, the National Research Center for Standard Materials of China) were used for controlling the quality of our analysis and the recovery rates were 96-102%.

Table S1

Soil properties of all three study sites. Data are shown as mean ± SD (n = 3).

Soil ID	S1	S2	S3
Soil type	Hydragric anthrosols	Hydragric anthrosols	Hydragric anthrosols
Latitude	116°56′20″ E	117°10′8″ E	117°12′32″ E
Longitude	28°12′29″ N	28°17′42″ N	28°19′44″ N
pH	4.28±0.03	4.45±0.01	5.27±0.02
OM (g/kg)	40.62±0.91	27.13±0.62	32.05±0.81
CEC (cmol/kg)	8.81±0.01	8.32±0.08	7.35±0.03
Clay %	27.45±0.07	22.80±0.14	15.50±0.09
Silt %	48.35±0.21	40.7±0.01	23.70±0.14
Sand %	23.60±0.12	36.13±0.08	57.15±0.23
Available N (mg/kg)	184.69±1.59	146.81±1.79	113.41±2.85
Available P (mg/kg)	34.11±0.58	43.55±1.02	58.09±0.26
Available K (mg/kg)	74.10±2.40	67.18±0.88	75.75±2.33
Cd (mg/kg)	0.22±0.01	0.72±0.05	1.66±0.05
Cu (mg/kg)	23.32±0.09	80.02±0.88	556.67±12.61
As (mg/kg)	5.58±0.13	11.24±0.42	50.17±0.59
Pb (mg/kg)	29.61±0.19	50.20±0.43	74.13±1.77
Cr (mg/kg)	63.76±0.85	52.45±0.70	38.28±1.11
Zn (mg/kg)	52.41±0.48	80.27±0.68	77.55±2.15
Ni (mg/kg)	16.53±0.23	16.07±0.23	12.78±0.40

Table S2

Descriptive design of a fully factorial soil and atmosphere exposure experiment including seven treatment groups.

Soil substrate/Atmospheric exposure	A1: Low atmospheric deposition (control)	A2: Moderate atmospheric deposition	A3: High atmospheric deposition
S1: Background soil (control)	A1-S1	A2-S1	A3-S1
S2: Moderate soil pollution	A1-S2	A2-S2	---
S3: Heavy soil pollution	A1-S3	---	A3-S3

Table S3

The contribution range (%) of recently atmospheric deposition to Cu, Cd, and Pb of soybean tissues.

Group	Cu					Cd					Pb				
	root	stem	leaf	pod	seed	root	stem	leaf	pod	seed	root	stem	leaf	pod	seed
A2-S1	21.6	32.6	56.8	35.1	2.6	9.5	2.3	17.3	2.2	3.2	5.5	12.2	65.7	47.7	14.2
A2-S2	11.1	12.8	25.6	15.9	3.0	2.4	1.0	2.0	4.4	2.2	3.3	10.2	55.7	21.0	11.3
A3-S1	41.2	55.4	86.8	78.9	23.8	42.2	27.1	36.7	29.4	31.3	46.5	59.7	87.9	79.9	42.4
A3-S3	11.2	18.1	29.1	35.6	14.6	8.0	9.2	15.0	8.0	15.8	22.7	32.6	80.1	44.8	27.3

Table S4

The contribution range (%) of recently atmospheric deposition to Cu, Cd, and Pb of radish tissues.

Group	Cu		Cd		Pb	
	rhizome	shoot	rhizome	shoot	rhizome	shoot
A2-S1	8.6	37.2	12.1	29.1	5.8	35.1
A2-S2	4.7	14.6	2.5	8.2	8.0	21.9
A3-S1	46.1	78.8	56.6	57.2	54.8	67.4
A3-S3	16.2	29.1	31.5	27.3	39.3	53.8

Table S5

The contribution range (%) of recently atmospheric deposition to Cu, Cd, and Pb of lettuce tissues.

Group	Cu		Cd		Pb	
	root	shoot	root	shoot	root	shoot
A2-S1	8.5	30.1	9.2	35.4	10.2	25.2
A2-S2	5.0	20.2	0.3	13.4	2.2	18.0
A3-S1	54.2	76.0	22.3	58.4	37.5	63.6
A3-S3	23.7	48.6	13.8	32.6	28.7	44.5

Table S6

The contribution range (%) of trace metals originally present in soils to vegetable bioaccumulation.

Vegetable	Soil substrate	Cu	Cd	Pb
soybean	moderate pollution S2	19.2	61.8	28.0
	heavy pollution S3	36.7	73.7	37.9
radish	moderate pollution S2	66.0	60.6	47.5
	heavy pollution S3	80.3	67.4	64.8
lettuce	moderate pollution S2	48.3	74.3	51.3
	heavy pollution S3	68.6	81.5	57.4

Table S7 The partitioning (F1 exchangeable, F2 carbonate, F3 reducible, F4 organic and sulfide, and F5 residual fractions) of Cu, Cd, and Pb (mg/kg) in soils (0-2 and 2-4 cm profile) exposed to atmospheric deposition over one year. Data are shown as mean ± SD (n = 3).

Metal	Group	F1		F2		F3		F4		F5	
		0-2cm	2-4 cm	0-2 cm	2-4 cm	0-2 cm	2-4 cm	0-2 cm	2-4 cm	0-2 cm	2-4 cm
Cu	A1-S1	1.5±0.1 [a]	1.6±0.1 [a]	0.5±0.0 [a]	0.5±0.0 [a]	1.5±0.1 [a]	1.4±0.1 [a]	13.1±0.2 [a]	12.7±0.8 [a]	8.1±0.5 [a]	7.9±0.4 [a]
	A2-S1	2.4±0.2 [b]	2.3±0.1 [b]	1.0±0.1[b]	0.9±0.1[b]	1.9±0.1[b]	1.8±0.1[b]	15.1±0.7 [b]	14.3±1.0 [a]	8.3±0.5 [a]	8.1±0.5 [a]
	A3-S1	9.2±0.3[c]	5.7±0.2 [c]	5.0±0.1[c]	2.9±0.0 [c]	5.1±0.1 [c]	4.2±0.2 [c]	25.7±1.5 [c]	21.2±1.1[c]	10.2±0.5 [b]	9.3±0.4 [a]
	A1-S2	7.0±0.2 [a]	5.1±0.2 [a]	2.1±0.1 [a]	1.9±0.1 [a]	5.2±0.2 [a]	5.2±0.2 [a]	40±2 [a]	38±2 [a]	24±2 [a]	24±3 [a]
	A2-S2	8.5±0.3 [b]	5.1±0.3 [b]	2.4±0.2 [a]	2.0±0.1 [a]	5.6±0.3 [a]	5.3±0.2 [a]	41±3 [a]	40±3 [a]	24±1 [a]	23±2 [a]
	A1-S3	83±3 [a]	87±6 [a]	20±1 [a]	18±1 [a]	140±12 [a]	141±11 [a]	238±12 [a]	235±9 [a]	57±5 [a]	55±6 [a]
	A3-S3	93±4 [b]	92±7 [a]	23±1 [a]	19±1 [a]	150±13 [a]	147±16 [a]	255±15 [a]	248±5 [a]	60±8 [a]	58±7 [a]
Cd	A1-S1	0.06±0.00 [a]	0.06±0.00 [a]	0.07±0.00 [a]	0.07±0.00 [a]	0.07±0.00 [a]	0.07±0.00 [a]	0.06±0.00 [a]	0.05±0.00 [a]	0.05±0.00 [a]	0.05±0.00 [a]
	A2-S1	0.08±0.00 [b]	0.06±0.00 [a]	0.08±0.01 [a]	0.07±0.00 [a]	0.07±0.00 [a]	0.07±0.00 [a]	0.06±0.00 [a]	0.05±0.00 [a]	0.05±0.00 [a]	0.05±0.00 [a]
	A3-S1	0.13±0.01 [b]	0.09±0.00 [b]	0.09±0.00 [b]	0.08±0.00 [a]	0.09±0.01[b]	0.07±0.00 [a]	0.08±0.01 [a]	0.07±0.01 [b]	0.06±0.00 [b]	0.05±0.00 [a]
	A1-S2	0.20±0.01 [a]	0.19±0.01 [a]	0.09±0.01 [a]	0.09±0.01 [a]	0.11±0.00 [a]	0.11±0.00 [a]	0.14±0.00 [a]	0.14±0.01 [a]	0.10±0.01 [a]	0.10±0.01 [a]
	A2-S2	0.25±0.01 [b]	0.20±0.01 [a]	0.10±0.01 [a]	0.09±0.01 [a]	0.12±0.01 [a]	0.11±0.00 [a]	0.15±0.01 [a]	0.14±0.00 [a]	0.10±0.00 [a]	0.11±0.01 [a]
	A1-S3	0.64±0.03[a]	0.60±0.02 [a]	0.17±0.02 [a]	0.16±0.01 [a]	0.27±0.02 [a]	0.27±0.03 [a]	0.51±0.02 [a]	0.51±0.02 [a]	0.432±0.03 [a]	0.43±0.02 [a]
	A3-S3	0.73±0.02 [b]	0.65±0.03 [a]	0.22±0.03[a]	0.20±0.02 [a]	0.30±0.03 [a]	0.28±0.02 [a]	0.54±0.03 [a]	0.51±0.02 [a]	0.43±0.04 [a]	0.43±0.05 [a]
Pb	A1-S1	1.02±0.05 [a]	1.03±0.07 [a]	1.45±0.09 [a]	1.34±0.10 [a]	6.44±0.19 [a]	6.38±0.20 [a]	7.20±0.13 [a]	7.43±0.15 [a]	18.7±0.7 [a]	18.6±0.9 [a]
	A2-S1	1.04±0.02 [a]	1.03±0.07 [a]	1.45±0.05 [a]	1.33±0.10 a	6.38±0.10 [a]	6.41±0.22 [a]	7.20±0.30 [a]	7.40±0.42 [a]	18.6±0.8 [a]	18.6±1.4 [a]
	A3-S1	1.20±0.15 [a]	1.14±0.12 [a]	1.46±0.20 [a]	1.37±0.15 [a]	6.83±0.24 [a]	6.77±0.30 [a]	7.21±0.21 [a]	7.93±0.61 [a]	18.4±1.1 [a]	18.8±0.8 [a]
	A1-S2	3.08±0.20 [a]	2.88±0.10 [a]	2.04±0.10 [a]	2.02±0.10 a	13.5±2.3 [a]	12.0±1.3 [a]	9.20±0.13 [a]	9.08±0.33 [a]	22.2±1.7 [a]	21.2±2.7 [a]
	A2-S2	3.15±0.31 [a]	2.95±0.20 [a]	2.14±0.10 [a]	2.07±0.10 a	14.0±1.8 [a]	12.1±2.5 [a]	9.30±0.32 [a]	9.14±0.42 [a]	22.8±2.1 [a]	22.0±1.5 [a]
	A1-S3	4.81±0.42 [a]	4.58±0.17 [a]	5.48±0.55 [a]	5.55±0.53 [a]	21.5±2.3 [a]	22.4±0.8 [a]	12.5±0.9 [a]	12.5±0.4 [a]	29.8±2.7 [a]	29.5±1.6 [a]
	A3-S3	4.95±0.72 [a]	4.89±0.37 [a]	6.35±0.90 [a]	6.23±0.56 [a]	21.7±1.3 [a]	22.9±1.7 [a]	12.7±0.4 [a]	11.8±0.8 [a]	30.7±2.1 [a]	29.6±1.7 [a]

Table S8

Hydrodynamic diameter distributions of fine particles (intensity) and pH in wet deposition over one year (July 2017 to June 2018). The precipitation is absent in October 2017. Data are shown as mean ± SD (n = 6).

Month	A1			A2			A3		
	Size (nm)	PDI*	pH	Size (nm)	PDI*	pH	Size (nm)	PDI*	pH
17-07	3.19±0.16	0.26±0.05	5.21±0.04	13.56±4.06	0.34±0.02	4.46±0.05	5.30±1.06	0.29±0.06	3.41±0.04
17-08	10.23±2.75	0.38±0.04	4.86±0.06	37.73±7.50	0.36±0.01	4.35±0.04	39.50±5.82	0.32±0.01	3.53±0.05
17-09	3.85±0.18	0.46±0.11	4.73±0.05	52.93±2.37	0.30±0.01	4.44±0.02	26.77±4.03	0.26±0.04	3.79±0.03
17-10	---	---	---	---	---	---	---	---	---
17-11	79.05±7.73	0.47±0.06	6.11±0.05	2.80±0.20	0.52±0.02	4.99±0.04	12.26±2.05	0.35±0.03	3.07±0.05
17-12	2.99±1.05	0.47±0.05	5.34±0.03	3.08±1.09	0.37±0.02	4.64±0.03	6.06±0.47	0.50±0.04	4.50±0.04
18-01	3.82±0.19	0.48±0.03	6.30±0.04	31.3±4.7	0.35±0.05	4.39±0.03	88.07±8.80	0.33±0.03	3.77±0.05
18-02	9.56±0.25	0.31±0.01	5.94±0.02	18.49±2.13	0.40±0.03	4.56±0.02	8.48±1.05	0.46±0.05	3.43±0.04
18-03	22.06±3.74	0.53±0.05	6.12±0.03	30.94±5.19	0.36±0.05	4.63±0.04	15.07±2.10	0.32±0.08	3.24±0.02
18-04	15.35±0.96	0.38±0.02	5.53±0.04	10.69±3.03	0.29±0.02	4.32±0.03	21.09±4.11	0.44±0.03	3.09±0.03
18-05	9.84±0.62	0.22±0.02	4.98±0.03	7.74±1.08	0.41±0.03	4.52±0.05	12.82±2.18	0.26±0.05	3.51±0.02
18-06	19.41±1.14	0.32±0.03	5.13±0.02	11.01±2.08	0.27±0.02	4.43±0.02	4.19±0.86	0.30±0.06	3.63±0.05

* PDI (particle dispersion index).

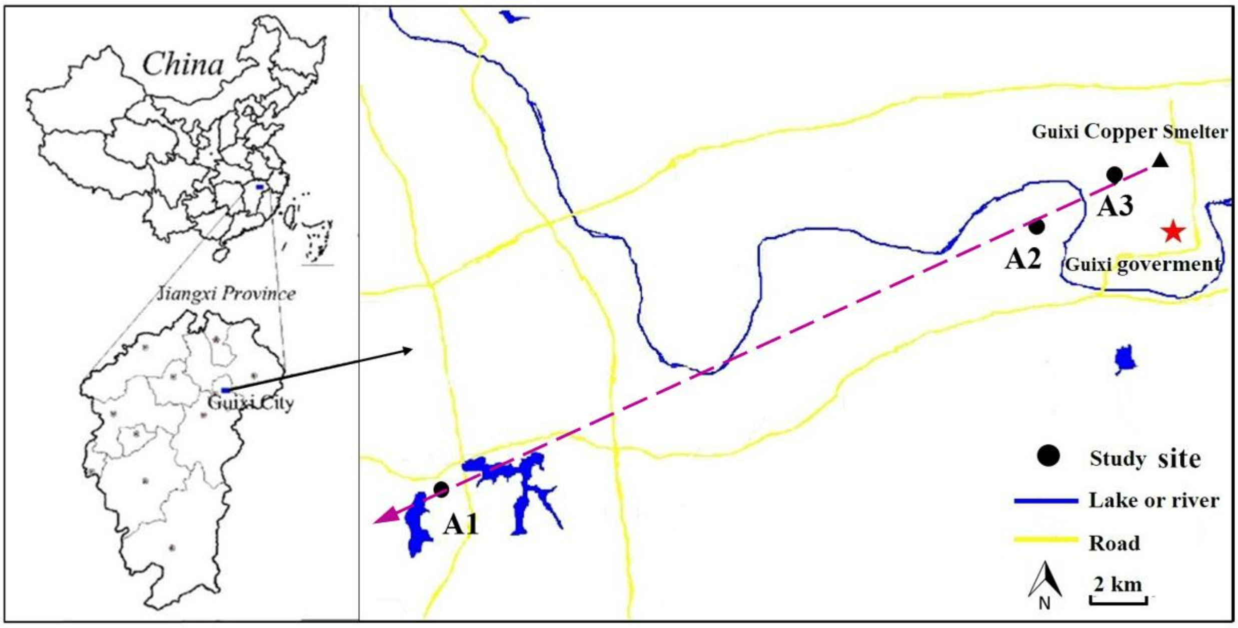

Fig. S1. Locations of the study sites.

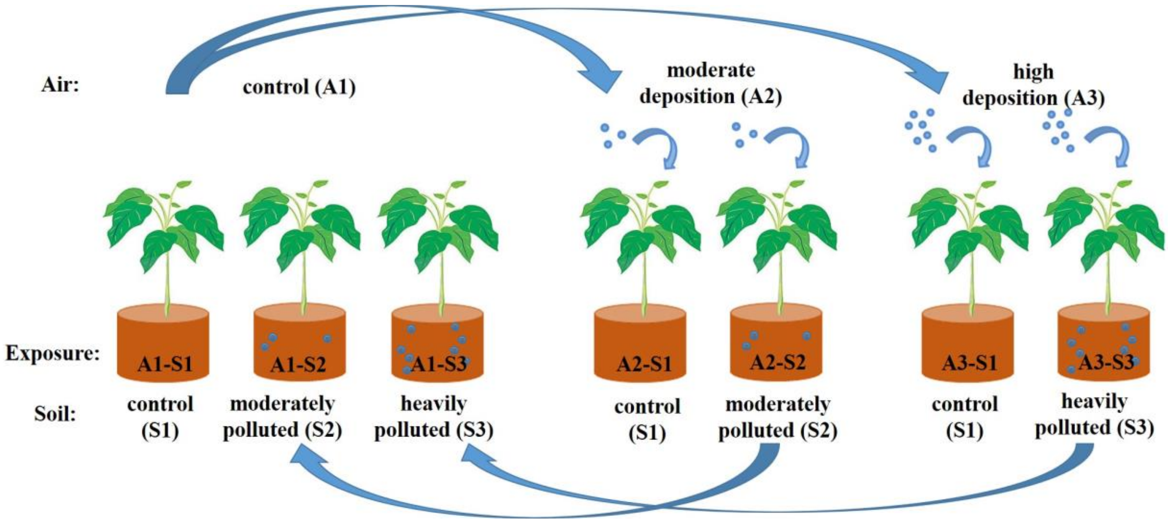

Fig. S2. Design of a fully factorial soil and atmospheric exposure experiment with vegetable including seven treatment groups.

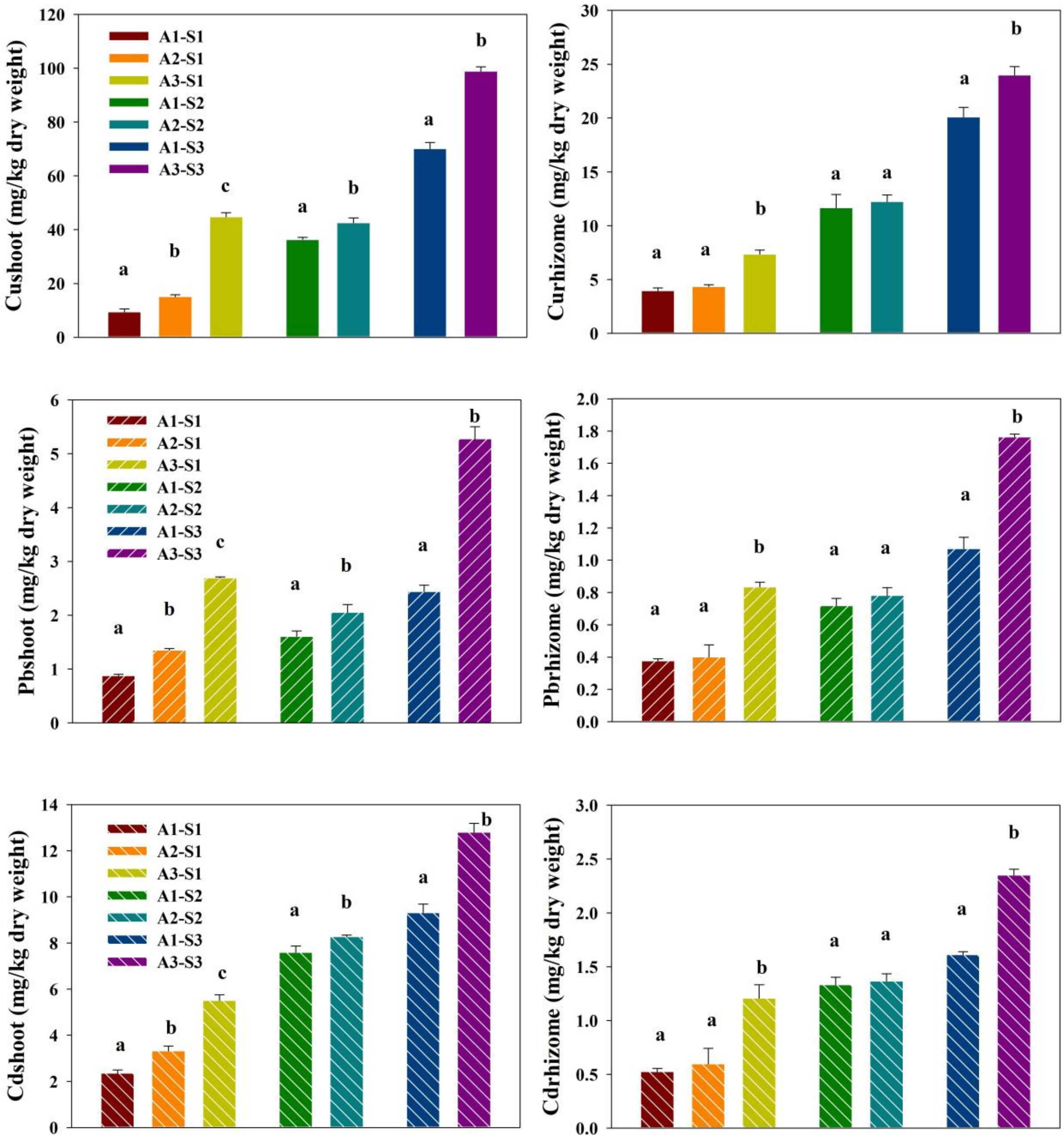

Fig. S3. Total Cu, Pb, and Cd concentrations of radish shoots and rhizomes collected from seven experiment groups in three study sites. Different letters indicate values significantly different among three deposition sites ($p < 0.05$). Data are shown as mean ± SD (n = 3).

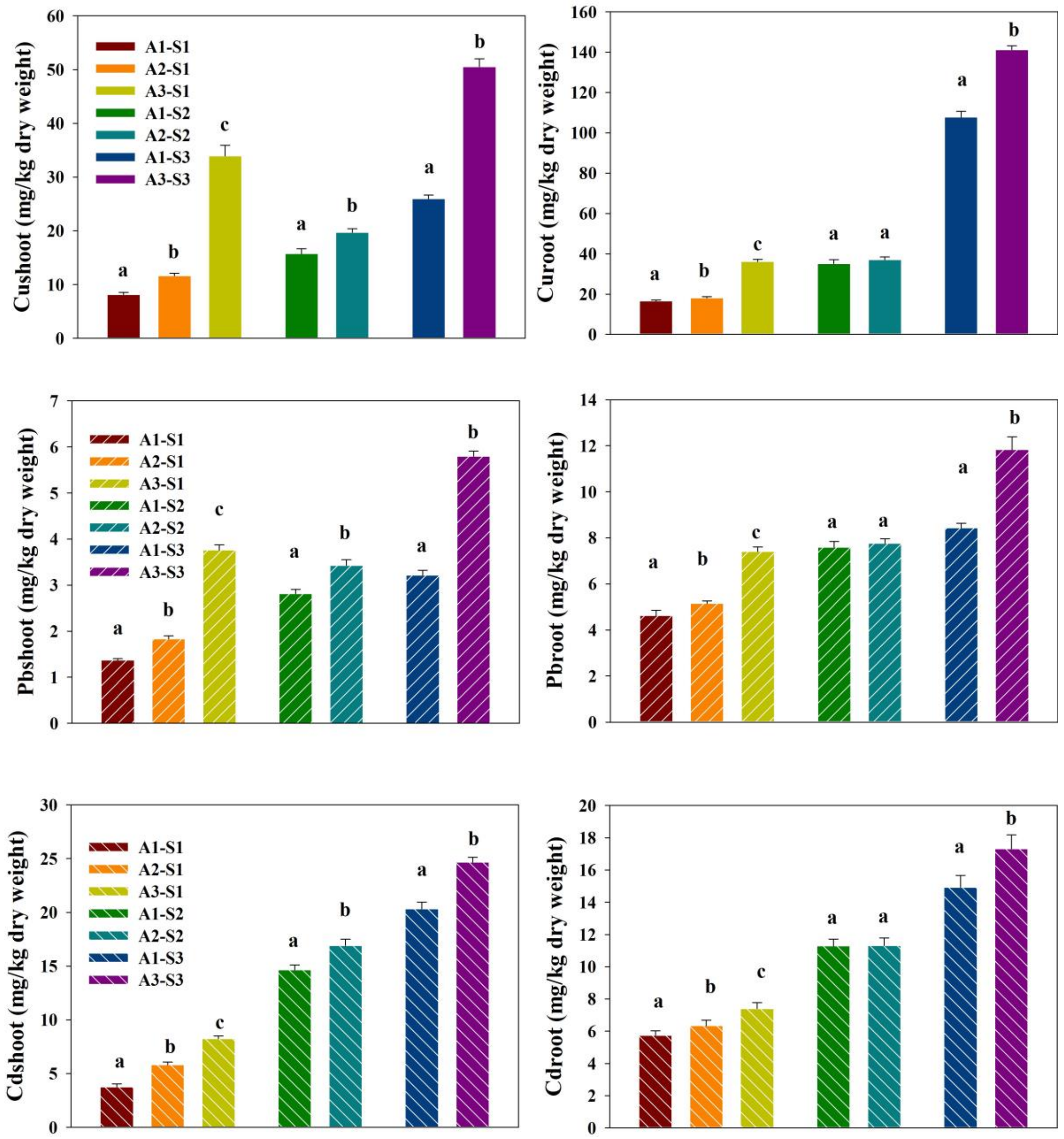

Fig. S4. Total Cu, Pb, and Cd concentrations of lettuce shoots and roots collected from seven experiment groups in three study sites. Different letters indicate values significantly different among three deposition sites ($p < 0.05$). Data are shown as mean ± SD (n = 3).

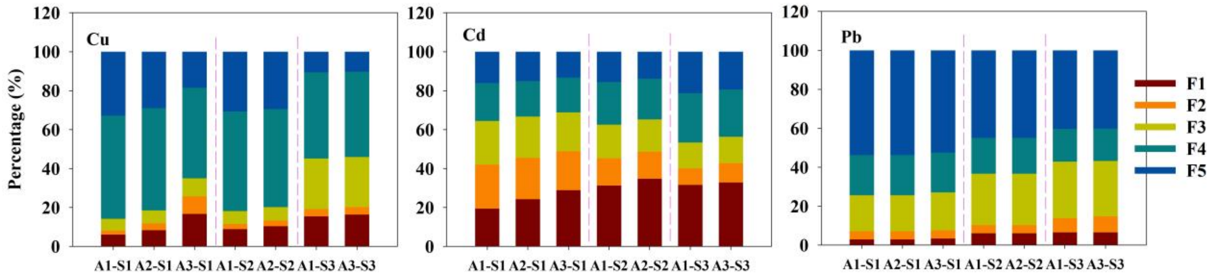

Fig. S5. The percentage of Cu, Cd, and Pb in soils (0-2 cm profile) exposed to atmospheric deposition over one year. Data are shown as mean (n = 3).

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