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Atmospheric deposition of arsenic, cadmium, copper, lead, and zinc near an operating and an abandoned lead smelter

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Abstract

Atmospheric deposition samples were collected over 15 mo at several locations near an operating smelter and an abandoned Pb smelter to investigate the contribution of Pb smelting to depositional fluxes and potential local air quality degradation. Samples were analyzed for As, Cd, Cu, Pb, and Zn and subjected to scanning electron microscopy (SEM)–energy dispersive spectroscopy (EDS). Concentrations of Cd and Pb at both sites were greater than at the control site ($p < .05$), and significant correlations existed between Cd and Pb concentrations at both sites ($p < .05$). Monthly depositional flux variations at both sites were similar, with greater deposition during cold and dry periods. Heavy metal(loid)s deposition during these periods was correlated with wind speed. Greater Cd depositional flux differences were found between the smelter and control sites compared with other elements. The SEM images suggested that some particles at the operating smelter site were from Pb smelting material. However, most particles at both sites had no characteristics of smelting, suggesting reactions occurred between the smelter-emitted particles and soil components. The EDS results indicated that atmospheric deposition from both sites had lower Pb concentrations than smelting material or ash. The main atmospheric deposition source at the operating and abandoned sites was likely from the resuspension of heavy metal(loid)-enriched soil particles. Greater risk of air pollution from historical Pb smelting facilities exists years after closing down. Reducing soil wind erosional losses may help reduce heavy metal(loid)s dispersion across environments.

1 | INTRODUCTION

Nonferrous metal mining and smelting are main sources of environmental heavy metal(loid)s pollution (Ettler, Rohovec, Navrátil, & Mihaljević, 2007; Kang et al., 2019; Li,

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Ma, Van Der Kuijp, Yuan, & Huang, 2014; Zhang et al., 2012). Because of the co-existence of different heavy metal(loid)s in smelting ores, nonferrous metal mining and smelting often result in environmental contamination of multiple elements and commonly include cadmium (Cd), lead (Pb), and zinc (Zn) (Cheng, Zhao, Wang, & Qiu, 2014; Douay et al., 2013; Ohmsen, 2001; Zhang et al., 2012). In the past, Pb smelting depended heavily on sintering techniques using simple facilities that had low ore metal recovery; this smelting technique contributed greatly to environmental heavy metal(loid)s pollution via particulate deposition. Historical, atmospherically deposited heavy metal(loid)s-containing particulate matter has been proven to enhance soil metal concentrations in smelter vicinities (Douay et al., 2013; Lee, Kang, Yu, & Kwon, 2020; Xing, Zheng, Scheckel, Luo, & Li, 2019a).

Lead smelting techniques have improved in recent years, and thus ore recovery has improved. However, due to past environmental pollution and the concern regarding heavy metal(loid)s pollution effects on local soils, crops, and residents, some nonferrous metal smelters have been closed (Douay, Roussel, Pruvot, & Waterlot, 2008; Gelly et al., 2019; Lee et al., 2020; Van Pelt et al., 2020). Regardless of site closures or improved smelting techniques at existing facilities, areas near former/current smelters continue to contain elevated soil heavy metal(loid)s concentrations. Within these contaminated areas may lie an environmental health issue simply due to heavy metal(loid)s-contaminated soil resuspension and subsequent deposition.

Environmental heavy metal(loid)s deposition has negatively affected soil health (Ettler, 2016; Li et al., 2020). After smelter stack particulate matters are deposited on the soil surface, they may undergo movement phenomena or chemical reactions. Particulate matter may be atmospherically resuspended or weathered, sorbed onto soil particles, partly dissolved with soluble ions precipitated as mineral phases, chelated, or absorbed by plant roots (Ettler et al., 2016; Ghayoraneh & Qishlaqi, 2017; Lee et al., 2020; Van Pelt et al., 2020). Evidence also suggests that Pb species in particulate matter, when in contact with soil, can result in elevated organic Pb phases that increase Pb inhalation bioaccessibility (Xing, Zhao, Scheckel, Zheng, & Li, 2019b). Land use also affects depositional heavy metal(loid)s behavior. In many conventional farmland soils, surface-deposited particulate matter is tilled into and mixed with soil from deeper depths, reducing overall soil surface metal concentrations. However, in either no-till or in non-farmland soil surfaces, the lack of plowing maintains elevated soil surface metal concentrations as well as original particulate mineral characteristics (Ettler et al., 2016; Kang et al., 2019). Resuspended particulates from the ground/soil surface, in conjunction with smelter stack-emitted particulates, likely exert a negative effect on air quality and may negatively affect human health near Pb smelter locations.

Although numerous studies have been conducted on the atmospheric quality near operating smelters (Ettler, 2016; Hernández-Pellón & Fernández-Olmo, 2019; Lee et al., 2020; Qiu et al., 2016), one may question whether, years after a nonferrous smelter is closed down, soil surface-deposited heavy metal(loid)s can be atmospherically resuspended and compromise local air quality. The answer to this question is critical to environmental quality and human health exposure (Ettler, 2016; Feng et al., 2019; Hernández-Pellón & Fernández-Olmo, 2019; Qiu et al., 2016; Van Pelt et al., 2020) of residents in and near contaminated areas.

A research project was conducted in and near a city in the Henan Province, China, near an operating Pb smelter and an abandoned Pb smelter to investigate atmospheric depositional fluxes of arsenic (As), Cd, copper (Cu), Pb, and Zn. Depositional materials collected over time were also subjected to scanning electron microscopy–energy dispersal X-ray spectroscopy (SEM-EDS) to ascertain morphological and additional chemical composition information. Heavy metal(loid)s concentrations and the particulate matter depositional flux over time (Feng et al., 2019) may help elucidate whether surface-deposited heavy metal(loid)s from the abandoned and the operating Pb smelters contribute to particulate heavy metal(loid)s in local air.

2 | MATERIALS AND METHODS

2.1 | Study area

The study area was located near a historic/current Pb smelting city in Henan Province in northern China (Figure 1). The area is about 140–250 m asl and has a warm temperate continental monsoon climate, with annual mean temperature and precipitation of 14.6 °C and 650 mm, respectively. Approximately 55% of the precipitation occurs during July–September; winters and springs are dry. Prevailing winds in the area come mostly from the east-northeast. The majority of farmland within the study area is in a winter wheat (*Triticum aestivum* L.)–corn (*Zea mays* L.) rotation.

The study area has several large manufacturing facilities that produce steel, coal, and nonferrous metals. Most facilities lie to the west and northwest of an urban area, with some facilities having been in operation for more than 50 yr. Heavy metal(loid)s pollution of soils and crops and particulate matter near these facilities have been reported (Guo, Lei, Chen, & Yang, 2018; Qiu et al., 2016; Xing et al., 2019a; Xing, Zhang, Scheckel, & Li, 2016).

Atmospheric deposition samples were collected from three sampling sites named YG (E112.55189, N35.13417), JLG (E112.43736, N35.17953), and DZ (E112.42413, N34.94679). The YG site has ~1,500 residents and is in a flat area about 500 m west of an operating Pb smelter near the city in Henan Province, China (Figure 1). The Pb smelter produces about 400,000 t of Pb annually and has been operating at this location for more than 30 yr. The JLG site is located ~12.5 km to the northwest of the YG site in an 80-m wide mountain valley, about 70 m from an abandoned Pb smelter. The smelter processed Pb ore for about 12 yr and had an annual Pb output of ~4,000 t before closing in 2010. Smelting residues and facilities have been removed from the site. No obvious pollution source near the JLG site has been found. Small areas of farmlands existed on the flat areas in the valley. Twelve households lie within 80 m of the sampling site. The DZ site is located in a mountainous area to the southwest of the city and to the south of the YG (~25 km) and the JLG (~26 km) sites. The valley floor is ~150 m wide. The mountains in this region are 20–30 m higher than the valley bottom, with slopes of ~10–20°. Most of the mountain slopes are used for crops, and about 30 households lie near the sampling site. The DZ site is far away from any populated areas, busy highways, and large industrial facilities and therefore was chosen as the control site.

2.2 | Sample collection

Bulk atmospheric deposition samples were collected once a month from October 2017 to December 2019. The samples were collected according to the National Standard GB15265-94 (Ministry of Environment Protection, 1994), except that glycol was not added to avoid its interference in sample digestion. Polyethylene cylinders (diameter, 15.3 cm; height, 40 cm) were used for atmospheric deposition collection. At the beginning of each month, clean cylinders were installed at each site. At the end of the month the cylinders were collected and returned to the laboratory, and new sample cylinders were installed for the subsequent month's sampling. On-site cylinders were mounted on flat roofs of local residence buildings at each sampling site at about 5 m above the ground. Four, three, and three replicate cylinders were set up at the YG, JLG, and DZ sites each month, respectively, at locations where residents were willing to participate. Before being installed on roofs, the cylinders were soaked in 5% HNO_3 for more than 2 h, triple-washed with deionized (DI) water, and air-dried. After sampling, the cylinders were sealed with plastic wrap and returned to the laboratory for analysis.

Lead ore and smelter bottom ash samples were collected from a local Pb smelting plant. This was performed for comparison to atmospheric samples collected at the three sites.

2.3 | Sample analysis

Plant leaves or insects found in the cylinders were carefully removed and rinsed with DI water. Rinse water was returned into the cylinders to recover adhered particulates or ions. The cylinder contents were emptied into 1,000ml glass beakers, the cylinder was carefully washed with DI water three times to recover all ions and particles and placed into the beaker, and the contents in the beaker were evaporated to about 30–50ml by heating on a hot plate. The contents of the beaker were transferred to a pre-weighed porcelain crucible, heated on a hot plate, and evaporated to dryness. The weight of the sample was then measured.

All samples collected were split into triplicates and digested in a MARS-6 microwave digestion system (CEM) using USEPA method 3051A (USEPA, 2007). After digestion, the solution was cooled to room temperature, and the digestion tube was placed into an EHD-24 digestion instrument (Donghang) set at 160 °C to evaporate the sample until 1 ml remained. The digestion solutions were diluted with DI water to 50 ml and filtered for analysis.

Digestate Cd, Cu, Pb, and Zn concentrations were determined using a TAS-990 flame atomic absorption spectrophotometer (PGeneral), and As concentrations were determined using an AF-7550 atomic fluorescence spectrophotometer (EWAI). The instrument detection limits for As, Cd, Cu, Pb, and Zn were 0.05 $\mu\text{g L}^{-1}$ and 0.01, 0.08, 0.01, and 0.006 mg L^{-1} , respectively.

2.4 | SEM-EDS analysis

Additional bulk samples were collected in January 2019 for morphology and elemental composition analysis using scanning electron microscopy (SEM) in conjunction with energy dispersive X-ray spectroscopy (EDS) using a FEI Quanta 250 (Thermo Fisher). Secondary electron images were taken at an accelerating voltage of 3 keV and at magnification between

1,000 and 10,000 $\times$. For each sample, EDS data were collected at three representative areas (10 $\mu\text{m} \times 10 \mu\text{m}$).

2.5 | Meteorological data collection and processing

Daily precipitation and daily mean wind speed data during October 2017–December 2018 were downloaded from National Meteorological Information Center of China. However, because no study area meteorological data were available, we used data from an observatory about 52–75 km from these three sites; this location had similar topographical conditions to the study area. Monthly total precipitation and monthly mean wind speed were determined.

2.6 | Quality control and quality assurance

All glassware was soaked in 5% nitric acid solution for more than 2 h before use and then triple rinsed with DI water. Along with the triplicate samples, analytical blanks and a standard reference soil (GBW07405) were included in the digestion of each sample batch. The recovery rates of As, Cd, Cu, Pb, and Zn in the reference soil were 89.1–101.4% (mean 93.2%), 87.2–114.6% (99.6%), 87.6–118.8% (101.3%), 102.9–118.6% (109.2%), and 85.9–105.2% (98.3%), respectively.

2.7 | Data analysis

Deposition flux is the mass of deposition in a certain area over a given period. The deposition area was the area of the cylinder opening. The heavy metal(loid)s mass was calculated by multiplying the metal(loid)s concentration by the deposition mass. The EDS results of each sample were averaged, and the mean values are presented.

Data were analyzed using SPSS version 25.0. Analysis of variance of element concentrations across sites at each period, or across sites overall, was conducted with significance tested at a $p < .05$. When ANOVA significance was present across sites, a Tukey's honestly significant difference pairwise comparisons test was used to determine differences between sampling points. Pearson correlations (two-tailed) were conducted between different elements of samples from the same site.

3 | RESULTS AND DISCUSSION

3.1 | Atmospheric heavy metal(loid)s deposition concentrations

The mean concentrations of all five elements from these three sites followed the order YG > JLG > DZ (Table 1), suggesting that both the operating and the abandoned Pb smelting facilities contributed to heavy metal(loid)s accumulation via atmospheric deposition. The concentrations of all elements at the DZ site (considered a control site in this study) were ~3–2,500 times greater than the background soil elemental concentrations (Cheng et al., 2014) and were much greater than the heavy metal(loid)s concentrations from other studies (Jia et al., 2020; Liu et al., 2019). Given the distance of DZ from any industrial pollution source (~25 km), element accumulation at this site was likely due to atmospheric resuspension and transportation/deposition of relatively small particles. Further research is required to determine the heavy metal(loid)s sources at the DZ site.

Significant differences were observed between the DZ and JLG sites for Cd and Pb concentrations but not for As, Cu, and Zn (Table 1). These findings suggest that Pb smelting mainly contributed to the accumulation of Cd and Pb in the environment, as found by others (Cheng et al., 2014; Douay et al., 2013; Li, Lin, Cheng, Duan, & Lei, 2015; Xing et al., 2019a). A decade after decommissioning the smelting facility, effects on atmospheric heavy metal(loid)s deposition still appear to be a concern. Significantly greater concentrations of all five elements existed at the YG site as compared to the other two sites, as illustrated by the mean elemental concentrations as well as element ratios between the sites (Table 1). The greater YG elemental concentrations are likely attributed to (a) the greater Pb smelting duration at the YG versus the JLG site, (b) the sheer Pb smelting scale differences between the two sites (i.e., the YG site has simply processed more ore than the JLG site and thus the YG site likely has received more heavy metal(loid)s pollution than the JLG site), and (c) the JLG site has been closed since 2010, although smelting continues at the YG site. Thus, emissions likely continue from the YG site up to the point of sampling in the current study.

Pearson correlation results indicated significant, positive relationships between almost all elements at the YG and JLG sites yet only between several elements at the DZ site (Table 2). Statistically significant correlations between Cd, Pb, and Zn are generally regarded as a characteristic result from Pb smelting activities (Cheng et al., 2014; Ghayoraneh & Qishlaqi, 2017; Stafilov et al., 2010; Xing et al., 2019a).

3.2 | Atmospheric depositional flux

The atmospheric depositional fluxes of all five elements at the three sites are illustrated in Figure 2. The mean deposition fluxes ranked YG > JLG > DZ, with mean deposition flux ratios between those of the YG and DZ sites for As, Cd, Cu, Pb, and Zn equal to 4.94, 12.17, 7.52, 4.13, and 6.46, respectively, and those between the JLG and DZ sites equal to 2.21, 3.08, 2.26, 1.66, and 2.60, respectively. These ratios suggest that Cd had the greatest degree of accumulation among the five elements at the YG and JLG sites. This result is in agreement with past findings in this general vicinity (Cheng et al., 2014; Xing et al., 2019a). In most months, the deposition fluxes of these five elements at the YG site were significantly greater than those of the JLG and DZ sites ($p < .05$); in some months, significant depositional flux differences were found between the DZ and the JLG sites ($p < .05$). The greater As, Cd, Cu, Pb, and Zn depositional fluxes at the YG site, and to a lesser extent at the JLG site, as compared to the DZ site suggest that both the operating and closed Pb smelters have resulted in elevated atmospheric deposition of these elements in the surrounding areas, although the effect of the closed smelter site is much less than that of the operating smelter site.

For the YG site, maximum elemental depositional fluxes occurred generally early in the year (Figure 2); the JLG site followed a similar pattern for As, Cu, and Zn. Less depositional variability was observed at the DZ site, although Pb deposition appeared to peak roughly between May and October. The monthly depositional fluxes at these three sites could imply that elemental deposition at the YG and JLG sites was partly affected by similar meteorological factors, including monthly rainfall distribution, humidity, wind speed, soil moisture conditions, and vegetation cover. Colder seasons occur with less rainfall in the

study area (Figure 3), which, along with lower degrees of soil surface vegetative cover (e.g., shortened height of winter wheat), suggests that soil particles are more easily resuspended into the atmosphere by wind. Particulate deposition during yearly cold periods has been shown by others (Qiu et al., 2016; Xing et al., 2019a, 2019b).

In support of the contention that wind causes particle resuspension, linear correlations between particulate depositional fluxes and either monthly precipitation or average monthly wind speed was performed. Results indicated that mean monthly wind speed contributed more than monthly precipitation to depositional metal fluxes for the JLG and YG sites (Table 3). However, monthly precipitation contributed to Cd and Pb deposition fluxes at the DZ site, suggesting the source of Cd and Pb at this site is different from the JLG and YG sites (Table 3).

Elemental deposition from the current study was compared with reported literature values (Supplemental Table S1). Arsenic, Cd, and Cu depositional fluxes at the YG site were greater than at most locations yet were comparable to those of heavily polluted areas, such as Zhuzhou, China (Li et al., 2017); Puchuncaví-Ventanas, Chile (Rueda-Holgado, Calvo-Blázquez, Cereceda-Balic, & Pinilla-Gil, 2016); and Guixi, China (Zhou et al., 2018). The YG Zn depositional flux was also comparable to literature results (Feng et al., 2019; Hernández-Pellón & Fernández-Olmo, 2019; Pan & Wang, 2015; Rueda-Holgado et al., 2016; Sánchez Bisquert, Matías Peñas Castejón, & García Fernández, 2017; Ye et al., 2018). However, the YG Pb depositional flux typically was greater than reported literature values, except for that of Zhuzhou, China (Li et al., 2017).

Cadmium and Pb deposition fluxes at the JLG site were greater than previously reported values (Supplemental Table S1), indicating that this decommissioned site likely still contributes to Cd and Pb pollution in the area. Based on data collected in this study, means to control particulate resuspension via wind erosion might be warranted. The DZ control site had greater Cd and Pb depositional fluxes than most of results found in the literature (Supplemental Table S1), although no industrial emission source is near this site. Increased DZ fluxes are unexplainable but may be partly attributed to long-distance transport of particulate matter from other sources, local household emissions, or area traffic.

3.3 | Morphology and composition of the deposition by SEM-EDS

Figure 4 presents SEM images of the particles collected at the three sites and those of Pb smelting material and bottom ash from a Pb smelter in the study area. Most of the particles from the YG site have irregular shapes, ranging from ~2 to ~40 µm (Figure 4a,b). There are several blocky/angular-shaped particles in Figure 4a, and their shape and size are similar to particles found in Pb smelting material (Figure 4e) (also as found by Ettler et al. [2016]); these blocky/angular-shaped particles at the YG site may be from Pb smelting material. The potential galena composition in the YG samples may be from smelting ores spilled on the ground during raw material transportation or from wind erosion of raw material piles at the facility, as noticed during sample collection. The greater Pb ($p < .05$) and S concentrations in the YG samples than in the JLG and DZ samples (EDS results; Supplemental Table S2) support this contention because PbS is the main component of the Pb smelting material (see Results of Lead Smelting Material Samples in Supplemental Table S2). There are several

spherical particles in the bottom ash sample, with particle diameters between 3 and 4 μm (Figure 4f). However, most of the particles are about 1 to 2 μm , with non-smooth, ridge-like, and bar-like protrusions. These shapes are typically the result of rapid cooling processes (Kutchko & Kim, 2006). For the Pb smelting process, particles from the emission stack should be spherical (Ettler et al., 2016). However, no spherical particles or particles with similar shape in the bottom ash in Figure 4f were found in the YG samples. Furthermore, the Pb concentrations of the bottom ash were 77–81% (Supplemental Table S2), which were much greater than the Pb concentrations in the YG samples (2.10–9.53%; Supplemental Table S2).

The above SEM-EDS results suggest that particulate deposition at the YG site may not be solely from Pb smelter emissions and quite possibly could be from the resuspension of the Pb-enriched soil particles. The differences between particle shapes at the YG site and the typical spherical shape from high-temperature processes suggest that Pb smelting particulate emissions have experienced aggregation, dissolution, and other physicochemical reactions with a soil matrix and have lost their original shapes after relatively prolonged soil deposition (Rieuwerts, Farago, Cikrt, & Bencko, 2000). This hypothesis is supported by the fact that, in recent years, Pb smelting techniques have been improved to the point where particulate Pb emissions have been greatly reduced (Guo, Liu, & Xie, 2017; Zhang & Zeng, 2018). It is quite likely that the elevated Pb depositional concentrations at the YG site are mainly the results of historical Pb smelting deposition and smelting material.

The particles from the JLG and the DZ sites had similar shapes and sizes (Figure 4). Most of the irregularly shaped particles were between 15 and 50 μm ; some of the particles were aggregates of smaller particles. Judging by particle shapes, these particles are not the result of industrial processes but rather may simply be soil particles. Based on EDS results, the JLG samples had relatively lower concentrations of Pb and S and higher concentrations of Si and O than the YG samples (Supplemental Table S2), suggesting more (alumino)silicates in the JLG and the DZ samples. The DZ samples had even lower Pb and S concentrations than those from the JLG site.

Due to the lack of information regarding the closed JLG smelter site, it is difficult to make a quantitative connection between the present heavy metal(loid)s deposition data with the former smelter production parameters. However, the historical Pb smelting effect on heavy metal(loid)s accumulation in the particulates at JLG can be confirmed by (a) the significantly greater Cd and Pb concentrations in the atmospheric deposition than at the DZ site ($p < .05$) (Table 1); (b) the significant correlation between Cd and Pb concentrations, which is regarded as typical for pollution from Pb smelting ($p < .05$) (Cheng et al., 2014; Douay et al., 2013; Li et al., 2015; Xing et al., 2019a); and (c) the significantly greater heavy metal(loid)s deposition fluxes at the JLG site than the DZ site in certain months ($p < .05$) (Figure 2). Heavy metal(loid)s deposition fluxes (Figure 2) near the JLG Pb smelter site clearly indicate an air pollution risk. This implies that, for closed Pb smelters, attention should be paid not only to the unsafe soil heavy metal(loid)s concentrations but perhaps more important to the soil heavy metal(loid)s negative effect on air quality and human health.

The risk of soil heavy metal(loid)s movement into humans via ingestion likely can be greatly reduced simply by not eating plants harvested from contaminated soils. However, heavy metal(loid)s inhalation or dermal absorption may prove more difficult to overcome (Sánchez Bisquert et al., 2017; Xing et al., 2019b). Based on results from the current work, contaminated soil heavy metal(loid)s resuspension will likely exist for a relatively long period of time (e.g., data presented in Table 1 and Figure 2). Thus, reducing this latter human health risk may entail reducing or eliminating soil resuspension into the atmosphere. Mixing topsoil with underlying cleaner soil, providing amendments to reduce heavy metal(loid)s bioavailability, movement, or resuspension, increasing year-round vegetative cover, or other measures to reduce contaminated soil movement should be considered.

4 | CONCLUSIONS

Atmospheric deposition at both an operating and an abandoned Pb smelter site were likely due to resuspended particles from the ground or soil surface, with those resuspended particles enriched with heavy metal(loid)s from Pb smelting activities. Both the operating and abandoned Pb smelter facilities contributed to elevated atmospheric depositional Pb and Cd concentrations. This conclusion was supported by correlations between Pb and Cd concentrations in atmospheric depositional samples and similar monthly depositional flux variations near these two sites. Meteorological factors, and especially wind events, likely increased monthly deposition fluxes during colder and drier seasons (January–April). Finding means by which ground/soil surface particulate resuspension can be decreased is imperative to reduce further environmental degradation and to protect human health.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations:

DI	deionized
EDS	energy dispersive spectroscopy
SEM	scanning electron microscopy
SEM-EDS	scanning electron microscopy–energy dispersal X-ray spectroscopy

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Core ideas

- Atmospheric deposition was investigated near a closed and an operating smelter.
- Heavy metal(loid)s depositional characteristics were similar at both sites.
- Depositional metal(loid)s were mainly resuspended historical deposition.
- Health risk of resuspended particles existed years after smelter closedown.

FIGURE 1.

The three sampling sites (YG, JLG, and DZ) in Jiyuan, Henan Province, China, as indicated in the large map. The small map shows the location of Jiyuan

FIGURE 2.

(a) Arsenic, (b) Cd, (c) Cu, (d) Pb, and (e) Zn atmospheric depositional flux at the DZ, JLG, and YG sites in Henan, China, over 15 continuous months. *Statistically significant differences ($p < .05$) for depositional fluxes between various sites. Colored values at the right side of each line are the mean depositional fluxes during the entire sampling period at each site, with different letters to the right of these values indicating statistically significant differences between different sites ($p < .05$). The DZ site was regarded as a control site due to its relative distance from industrial pollution sources (~25 km). The JLG site was about 70 m to an abandoned Pb smelter, and the YG site was about 500 m to a large operating Pb smelter

FIGURE 3.
Monthly precipitation and mean wind speed in the general study area

FIGURE 4. Scanning electron microscopy images of atmospheric depositional materials from the (a, b) YG, (c) JLG, and (d) DZ sites in Jiyuan, Henan Province, China. (e) Lead smelting ore. (f) Bottom ash from a Pb smelter

TABLE 1

Mean atmospheric heavy metal(loid)s deposition concentrations at three sites (YG, JLG and DZ), depositional ratios between sites, and background soil concentrations (Cheng et al., 2014) in Henan Province, China

Site	As	Cd	Cu	Pb	Zn
	mg kg ⁻¹				
Mean YG	209 (99)a	180 (62)a	526 (233)a	5,440 (1420)a	1,700 (539)a
Mean JLG	108 (73)b	51 (22)b	188 (101)b	2,310 (527)b	812 (555)b
Mean DZ	46 (20)b	16 (7)c	72 (27)b	1,280 (487)c	296 (111)b
Mean YG/mean DZ	4.52	11.27	7.33	4.24	5.75
Mean JLG/mean DZ	2.33	3.16	2.62	1.80	2.74
Background soil	9.4	0.064	21.4	20.2	65.1

Note. The DZ site was regarded as a control site due to its relative distance from any industrial pollution sources (~25 km). The JLG site was about 70 m to an abandoned Pb smelter, and the YG site was about 500 m to a large operating Pb smelter. Values inside parentheses represent 1 SD of the mean. Different letters within the same column indicate significant differences at $p < .05$ as determined by the Tukey's honestly significant difference pairwise comparisons test.

TABLE 2

Pearson correlation coefficients of atmospheric element depositional concentrations at the YG, JLG, and DZ sites in Henan Province, China ($n = 45$)

Site	Element					
	Element	As	Cd	Cu	Pb	Zn
YG	As	1				
	Cd	0.397 *	1			
	Cu	0.564 **	0.660 **	1		
	Pb	0.481 **	0.698 **	0.912 **	1	
	Zn	0.128	0.764 **	0.584 **	0.644 **	1
JLG	As	1				
	Cd	0.375 *	1			
	Cu	0.644 **	0.501 **	1		
	Pb	0.154	0.513 **	0.613 *	1	
	Zn	0.481 **	0.492 **	0.579 **	0.290	1
DZ	As	1				
	Cd	0.491 **	1			
	Cu	0.411 **	0.237	1		
	Pb	-0.302 **	0.097	0.010	1	
	Zn	0.225	0.084	0.847 **	0.188	1

* Significant at the .05 probability level.

** Significant at the .01 probability level.

TABLE 3

Linear correlation between monthly deposition flux of As, Cd, Cu, Pb, and Zn and the monthly precipitation and mean wind speed at the YG, JLG, and DZ sites in Henan Province, China ($n = 15$)

		x		Monthly precipitation (mm)		Mean wind speed (m s ⁻¹)	
Y, deposition flux (kg (km ² 30 d ⁻¹))	As	DZ	$p > .1$			$p > .1$	
		JLG	$p > .1$			$p > .1$	
		YG	$p > .1$			$p > .1$	
Cd		DZ	$y = .01x + 0.090, p < .05$			$p > .1$	
		JLG	$p > 0.1$			$y = 0.271x - 0.199, p < .01$	
		YG	$p > .1$			$y = 0.964x - 0.572, p < .01$	
Cu		DZ	$p > .1$			$y = 0.289x - 0.068, p < .01$	
		JLG	$y = -0.009x + 1.50, p < .05$			$y = 0.706x - 0.261, p < .05$	
		YG	$p > .05$			$y = 2.362x - 0.906, p < .01$	
Pb		DZ	$y = 0.126x + 6.61, p < .05$			$p > .1$	
		JLG	$p > .05$			$p > .1$	
		YG	$p > .1$			$y = 22.98x - 4.90, p < .01$	
Zn		DZ	$p > .1$			$y = 1.22x - .51, p < .05$	
		JLG	$p > .1$			$y = 7.41x - 10.11, p < 0.01$	
		YG	$p > .1$			$y = 16.96x - 22.10, p < .01$	