EPA Public Access

Author manuscript

Environ Monit Assess. Author manuscript; available in PMC 2020 January 29.

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Published in final edited form as:

Environ Monit Assess. ; 191(2): 115. doi:10.1007/s10661-019-7254-1.

Spatial Distribution of Smelter Emission Heavy Metals on Farmland Soil

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Abstract

This work was conducted to explore heavy metal pollution in soils in an area near lead-smelters in Jiyuan City, which is one of the main lead production areas in China. Altogether, 88 topsoil samples (0–20 cm) were collected from farmlands near Yuguang lead-smelting facilities, the sampling sites were 1570 to 6388 m to the main stack of Yuguang. The samples were analyzed for total and diethylene triamine pentaacetic acid (DTPA)-extractable heavy metals. The results indicated that, i) Cd was the primary polluting heavy metal in the soil, the range of total Cd concentration was 1.95–5.70 mg kg⁻¹, with a mean pollution index (concentration in soil/background value, PI) of 51.4, the range of total Pb concentrations was 64.5–435 mg kg⁻¹, with a mean PI of 9.11, the concentrations of total Cu, Zn and Ni were slightly higher than the background values. Mean concentrations of DTPA-extractable Cd and Pb were 0.744 and 58.7 mg kg⁻¹, respectively. ii) The total concentrations of Cd, Pb and Pb/Cd ratios of samples decreased as the distance to the main stack of Yuguang increased. Abnormal variations of these trends suggested these parameters of certain samples were affected by pollution sources other than Yuguang. iii) Judged by the results of this work, the area of the heavy metal polluted land in Jiyuan was greater than 115 km², a value reported by an earlier investigation. The results of this work suggest that the soil in the study area was polluted by Cd and Pb emissions from more than one polluting source, the variation of Cd, Pb concentration and Pb/Cd ratios of samples to the distance of the pollution source can be potentially used for pollution source identification.

Keywords

lead smelting; soil; heavy metal; distance; Pb/Cd ratio; distribution; pollution source

1 Introduction

Heavy metal accumulation in soil has attracted increased attention recently from residents to regulators in China. According to the bulletin of Ministry of Environmental Protection and Ministry of Land Resources (2014), 16.1% of the land in China is polluted, with Cd, Hg, As, Cu and Pb ranked as priorities in the pollutant list. In China, heavy metal pollution in soil poses a more serious risk to the health of local inhabitants than in most other countries, due to the low farmland area per capita in the polluted areas and the short distance between smelters and resident communities, which is true for many smelters in China (Qiu et al, 2016; Ran et al, 2010; Cheng et al, 2014; Shao et al, 2016).

Among different pollution sources of heavy metal in soil, nonferrous metal (especially Pb and Zn) mining and smelting is the major source. Henan Province in northern China is the biggest lead production province in China at present, with lead output accounting for about one third of China's total (Xing et al. 2016). Main lead smelters in Henan Province lie in the three cities of Anyang, Jiyuan and Sanmenxia, resulting in elevated levels of Cd and Pb in soils and crop grains in the vicinity of these smelters (Zhang et al, 2012; Qiu et al, 2016; Xing et al, 2016; Zhao et al, 2017). High concentrations of Pb have also been found in hair and blood of people living near the smelters (Zhang et al, 2012; Zhou et al, 2013; Qiu et al, 2016). The lead smelting industry in Jiyuan City began in the 1950s. In 2016, Jiyuan produced 978,000 tonnes of Pb, which accounted for 21.0% of the total lead output of China that year (Jiyuan City Government, 2018), and the soils near the smelting plants have been inevitably polluted with Cd and Pb (Zhou et al, 2013; Ran et al, 2010; Cheng et al, 2014; Li et al, 2016; Qu et al, 2016; Zhao et al, 2017). There is no lead mining in Henan Province, thus the accumulation of heavy metals in soils near the lead smelters is predominantly from atmospheric deposition from the lead smelters. Compared with pollution from mining slags and waste water (Lü et al, 2018), atmospheric deposition from smelters affects a larger area, with relatively uniform heavy metals distribution in soils. Besides lead smelting, Jiyuan City also has heavy industries such as iron smelting, production of construction materials, chemical products and coal. These plants all contribute to the accumulation of heavy metals in soil. However, the contribution of heavy metal accumulation in soils in Jiyuan from different polluting sources has not been investigated yet. Published studies about heavy metal accumulation in soils in Jiyuan often assume the lead smelting plants are the unique source of heavy metal release to the environment, based on sampling sites around the lead smelters, typically less than 3000 m from the stacks (Zhou et al, 2013; Ran et al, 2010; Cheng et al, 2014; Li et al, 2016; Qu et al, 2016; Zhao et al, 2017). Investigation of farmland soils near a lead smelter which began production during the 1990s in Anyang City, Henan Province observed sampling sites which were more than 2.5 km to the stack and found total concentration of Cd in 0–20 cm depth to be about 2.50 mg kg^{-1} (Cheng et al, 2014). The farmland soil quality standard of China requires the total Cd concentration $<0.6 \text{ mg kg}^{-1}$. Thus, pollution of heavy metals in soils near the lead smelters in Jiyuan which began production from 1950s may cover a much wider area. In order to fully estimate the extent of the contaminated soil impacted by lead smelters, research studies must expand the area of sampling to assess the reach of deposition.

For source identification of heavy metals in soil, Pb isotopic analysis has been successfully utilized (Bi et al, 2009). Recently, Bi et al (2006) applied elemental correlation of the ratios between Cd and Pb in contaminated soils to discriminate the pollution from atmospheric deposition and that from solid waste of Zn smelting. They concluded that because of the lower boiling point of Cd than those of Pb and Zn, Cd will accumulate in particulate matters while Pb and Zn tend to accumulate in solid waste during the smelting process. Shen et al (2017) demonstrated that pollution of soil samples from different sampling sites with similar Cd/Pb ratios was distinguishable to identify the source. Non-linear correlation between Cd, Pb concentrations of soil samples to the distance of the smelters have been noticed in different works (Bi et al, 2006; Douay et al, 2008; Ran et al, 2010; Cheng et al, 2014; Ghayorane and Qishlaqi, 2017), due to the deposition characteristics of the particulate matters from the stack. Thus, if a soil is affected by pollution sources from more than one lead smelting stack, the correlation may very likely to change. As a result, it is possible to discriminate pollution sources of heavy metals in soils within an area predominantly affected by atmospheric deposition from a smelter.

The purpose of the work was to, i) investigate the distribution of heavy metals in soils in the vicinity of lead smelters by sampling a larger area than the previously reported studies in Jiyuan, and ii) use the distribution of heavy metals in soils to estimate the contribution of different sources on the accumulation of heavy metals in soils near a lead smelter.

2 Materials and methods

2.1 The study area

The samples in this work were collected from the northwest rural part of Jiyuan City (Fig. 1). Jiyuan City lies to the south of the Taihang Mountain. The annual mean temperature and precipitation of this area are 14.4 °C and 860 mm, respectively. There are three lead smelting plants in Jiyuan at present, and are identified as Yuguang, Jinli and Wanyang. Yuguang was founded in 1957, its present annual lead (Pb) and zinc (Zn) production capacities are 400,000 and 300,000 tonnes, respectively. Wanyang and Jinli were both founded in 1995, Wanyang produces 200,000 tonnes of Pb and 200,000 tonnes of sulfuric acid annually, while Jinli produces 300,000 tonnes of Pb and 250,000 tonnes of sulfuric acid annually. Atmospheric emissions from these facilities deposit heavy metals on local farmland soils as particulate matter; no pollution of solid waste or wastewater was found. Wanyang lies to the east side of hills, while Jinli and Yuguang both lie on plain areas (Fig. 1). Aside from residential areas, roads and factories, the predominant land use in the sampling area is agronomic production (~70–80% of land area) with residential vegetable gardens. Summer corn (*Zea mays* L.) and winter wheat (*Triticum aestivum* L.) rotation is widely practiced in this area.

2.2 Collection and processing of the soil samples

Samples were collected in October 2014. The sampling area lies to the northwest of Yuguang (Fig. 1). The samples were all collected from wheat fields at the depth of 0–20 cm. The sampling sites which were closest to the Jinli, Wanyang and Yuguang were 8.1, 3.2 and

1.57 km to the main stacks of these smelting facilities, respectively. In total, 88 soil samples were collected.

The distribution of the sampling sites is indicated in Fig. 1. The altitude, longitude and latitude values of the sampling sites were measured with a handheld GPS unit. The sampling began from the northern most sample in Fig. 1 (c), then went south to the area just north of Kejing. Sampling continued from the northwest of Fig. 1, west of Kejing, then to the area near Daguofu and Xinzhuang (Fig. 1). The first sample was labeled T1 and sequentially numbered to T88. Samples T1 to T19 lie on the slope of the Taihang Mountain, the altitude of these sampling site deceases from 353 m to about 210 m above sea level from north to south. At the location of sample T19, the altitude of the farmland is roughly similar with the rest sites (T20-T88). There were some small enterprises near the sampling sites of T1-T10, these operations process lead, coal or produces bricks. The small lead-processing enterprise near site T1 ceased its operation in about 2010.

For each composite sample, three soil sub-samples were collected in an area of about 10 m to 10 m at the depth of 0–20 cm with a shovel, then the three subsamples were combined and mixed to make one composite sample. For each subsample, a 20-cm deep pit was dug on the ground with the shovel, the wall of the pit was made vertical and smooth, and then a 5-cm thick cuboid of soil was carefully collected by cutting the soil on the wall to 20 cm with a knife. Subsamples for each composite sample were of similar weight.

The samples were taken to laboratory, air-dried, and ground gently to pass a 2-mm sieve, mixed thoroughly to homogenize. Then about 20 g of soil from each sample was ground with an agate mortar to pass a 0.149-mm sieve and mixed thoroughly.

2.3 Sample analysis

The 0.149 mm samples were digested on a hot plate with hydrogen peroxide, hydrofluoric acid, perchloric acid and nitric acid for analysis of the total concentration, the 2 mm soil samples were extracted with DTPA (0.005 mol L^{-1} diethylene triamine pentaacetic acid + 0.1 mol L^{-1} triethanolamine + $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$). The concentrations of cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) in the solution were determined with atomic absorption spectrometry (PGeneral-TAS 990, Beijing). The digestion or extraction of each sample was conducted in triplicate. A reference soil sample (GBW07427, Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences) was included in each batch of digestion for quality control. The analysis was conducted according to Lu (2000).

2.4 Data processing

The triplicate values of each sample were used to calculate the mean value of each sample. The data was processed with Microsoft Excel and SPSS (Statistical Product and Service Solutions) 19.0. The equation with the biggest F value in curve estimation was chosen. The longitude and latitude values of the sampling sites and the main stack of the smelting plants were used to calculate the distances between the sampling sites and the stack according to Wei (2008). The availability index (AI) was calculated as the percentages of the DTPA-extractable concentration of one metal to the total concentration of the metal in the same

sample. Pb/Cd ratio is the ratio of the total concentrations of Pb and Cd of the same sample. The pollution index (PI) was the ratio between the concentrations of a metal in the sample to the background concentration of this element in this area.

Normally in smelter impacted soils, the Pb concentration is much higher than Cd. Past studies (Bi et al, 2006) have utilized Cd/Pb ratios, which typically results in fractional values less than one. Here we utilized Pb/Cd ratios to emphasis the magnitude of the values to more clearly show the observational trends.

3 Results and Discussion

3.1 Total concentrations of heavy metals

The results of the total concentrations of the heavy metals in the soil samples are indicated in Table 1. The distances between all the sampling sites to the main stack of Yuguang varies between 1570 and 6388 m. With the exception of some Cu concentrations that were lower than the background value, concentrations of other heavy metals in individual samples were all higher than the background values.

The PIs of different metals ranked $Cd > Pb > Ni > Cu \approx Zn$. Generally, a $PI > 3$ is considered the threshold of pollution, which in this case, only the values of Cd (51.4) and Pb (9.11) exceeded this level. PI values of Cu, Ni and Zn were all less than 1.8. It appears there is serious Cd pollution and less serious pollution of Pb in the study area. Xing et al (2016) investigated the accumulation of Cd, Pb and As in wheat grains harvested in an area about 3.5 km to the west of the present sampling area, and found that compared with the national food quality standard of China, the concentrations of Cd in all the samples and of Pb in some of the samples were higher than the maximum permissible concentrations. The results of the soil concentrations of Cd and Pb in this study are in agreement with those identified in Xing et al (2016).

Previous research which studied the accumulation of heavy metals in soils near the lead smelters in Henan Province also found Cd and Pb as the primary polluting elements (Ran et al, 2010; Cheng et al, 2014; Li et al, 2016; Liang et al, 2016; Zhao et al, 2017). Concentrations of Cd and Pb in soils ranged 2.75–11.5 and 42.9–396 $mg\ kg^{-1}$, respectively, with medians of 5.0 and 96.9 $mg\ kg^{-1}$ in soils near a lead smelter in northern Henan Province (Cheng et al, 2014). The lead smelter examined in Cheng et al (2014) began its operation in 1993, while Yuguang began its operation in 1950s, but the median concentrations of Cd and Pb in Cheng et al (2014) were much higher than those in this work. Conversely, the median and maximum concentrations of Cd and Pb in the present work are higher than other works investigating heavy metals in soils near lead smelters in Jiyuan (Yao et al, 2015; Li et al, 2016; Qu, 2016; Zhao et al, 2017). These variations are partly due to the difference between the distributions of the sampling sites in previous works. For example, soil very close to the smelter was not sampled in this work, which often observes very high concentrations near the stack and directly attributed to the to the stack emissions. Hence, the concentrations of Cd and Pb starting in the zone of deposition near the smelters decreases as distance from the stack increases (Cheng et al, 2014; Douay et al, 2008). Further, we limited our sampling to cultivated wheat fields. Meadows were not sampled in this work since

smelting waste disposal may happen on meadows and our emphasis was on emission deposition.

3.2 Concentrations of DTPA-extractable heavy metals

Table 2 indicates the statistical results of DTPA-extractable heavy metal concentrations in the samples. Cd and Pb had higher availability than other metals, the mean concentrations of DTPA-extractable Cd (0.744 mg kg^{-1}) and Pb (58.7 mg kg^{-1}) were both higher than the background values of these two metals in Table 1.

Ran et al (2010) investigated the concentrations of DTPA-extractable heavy metals in soils near a lead smelter in northern Henan Province and found that the range of DTPA-extractable Cd and Pb concentrations were $0.25\text{--}2.35$ and $7.18\text{--}133 \text{ mg kg}^{-1}$, respectively, while the medians were 0.903 and 46.3 mg kg^{-1} , respectively, the medians were close to those in the present work (Table 2). Yao et al (2015) and Zhao et al (2017) found the maximum concentrations of DTPA-extractable Cd and Pb were about 14 and 738 mg kg^{-1} , with an average of 1 and $>60 \text{ mg kg}^{-1}$ of about 200 soil samples near the lead smelters collected in Jiyuan City. Their sampling areas partly covered the study area in this work, and the maximum concentrations of these two elements were much higher, while the mean concentrations were a little higher than those in this work.

Lead had the highest availability index (AI) (31.9%), followed by Cd (22.6%). Among the three metals with lower PI values, Cu had the highest AI, followed by Zn and Ni (Table 2). The results indicated that the AI are in agreement with the PI as in shown in Table 1.

3.3 Correlation between heavy metal in soil and the distance to the stack of the smelting plant

The values of the total and DTPA-extractable concentrations of these five metals all decrease as the distance between the sampling sites and the main stack of Yuguang increases. Significant correlations were found between total or DTPA-extractable concentrations of all five metals and the distance ($p < 0.01$), and the correlations were non-linear, except for total Ni (Table 3). The correlation between the heavy metal concentration and the distance to the pollution source is in good agreement with those of Bi et al (2006), Douay et al (2008), Rang et al (2010), Li et al (2012) and Cheng et al (2014). The equations of total Pb and total Cd had the highest r^2 values among all the correlations. The non-linear correlation between the heavy metal concentrations of soil samples to the distance to the smelter can be regarded as a characteristic of the spatial distribution of heavy metals predominantly from atmospheric deposition from a point source. It is predicted that this correlation would not be as strong when considering soils affected by ore mining and processing, as contamination would be more localized and linear (Lü et al, 2018).

The variation of the concentration of total Cd and Pb as a function of distance from Yuguang stack is shown in Figs. 2 and 3. These figures indicate that the concentrations of Cd and Pb decline with increasing distance from the stack; however, at a distance of about 6300 m, the concentrations of both Cd and Pb in some samples increases as the distance increases. This elevated concentration near 6300 m implies that the Cd and Pb concentrations of these samples were positively affected by another source other than Yuguang. Investigation of the

area near those sampling sites, we suspect the concentrations are affected by the small enterprises near sampling site T1. The most distant sampling site to is 6388 m to the main stack of Yuguang. Analysis of the curves in Figs. 2 and 3 suggests that even if there were no effect from the small enterprises near sampling site T1, the concentrations of Cd and Pb in the samples at 6300 m are still much higher than the background values. If we assume the polluted area resulting from Yuguang smelting facilities is a perfectly round circle with a radius of 6388 m, it would cover an area of 128 km². The present productivity of lead from Yuguang, Jinli and Wanyang facilities are all greater than 100,000 tonnes (Xing et al, 2016). Based on the distribution of heavy metals in soil near each smelting plant in this work and the lead outputs of these plants, the anticipated contamination area (where total Cd>0.6 mg kg⁻¹, the threshold concentration of farmland soil in China) near the smelters would be much greater (approximately 384 km²) than the previously reported area of 115 km² (Liang et al, 2016). More investigation is needed to identify if this area of contamination is even greater.

The variation of the availability index (AI) of Cd and Pb to the distance between the sampling sites and the main stack of Yuguang was indicated in Fig. 4. The AI values decline as the distance increases for both Cd and Pb, however, the values of Pb decline slower than those of Cd. At a distance about 4000 m, the AI values of some samples are less than 5%. At 6300 m, the AI values of Pb in some samples decrease sharply as the distance increases, while those of Cd increases sharply. The abnormal variation of the AI values to the distance suggests that the emission characteristics of the source that results in these variation is different from that of Yuguang. Pb from this other potential source has lower availability, while Cd has higher availability than the input from Yuguang. The variation at about 6300 m is probably due to the emission from the small enterprises near these sampling sites, this is in agreement with the variation of the total concentrations of Cd and Pb in Figs 2 and 3. Isotopic analysis would help to differentiate the sources.

Significant negative linear correlation was found between the Pb/Cd ratio to the distance between the sampling sites and the main stack of Yuguang (Fig. 5) ($p<0.01$). This implies that the Pb from the emission of the stack tends to deposit near the stack, while the Cd transfers a longer distance. The distance which a particle can transport in the atmosphere is affected by its mass, where lighter particles can travel longer distance than heavier ones (Ettler et al, 2016). Shen et al (1991) investigated the composition of particles from a Zn smelter, and found that smaller particles contained both Cd and Pb, while only Pb was found in larger particles. These results may explain the reason why Pb/Cd ratios of the soils decreases with increasing distance to the stack in this work.

In Fig. 5, the Pb/Cd ratio values of 19 samples at 2245–3260 m were much higher than the fitted linear regression. The mean value and the standard deviation of the Pb/Cd ratios of these 19 samples are 69.3 and 12.9. The values of these 19 samples with larger Pb/Cd ratios are T53-T71 as indicated in Fig. 1. These samples have the closest distance of all the samples in this work to the main stack of Wanyang (see Fig. 1(b) for the location of the Wanyang smelting facilities). Because shorter distance results in higher Pb/Cd ratios as discussed above, the particles from Wanyang are likely influencing higher Pb/Cd ratios of these 19 samples. The distance of the sampling sites of these 19 samples to the main stack of

Yuguang ranged 2245–3260 (mean 2759) m, while the distance to the main stack of Wanyang ranged 2709–4231 (mean 3959) m. Because the Pb/Cd ratios of these 19 samples were greater than most of the other samples in this work, this may imply that particles from Wanyang having higher Pb/Cd ratios than those from Yuguang.

The ratios of different elements in soil near smelters or the variation of the ratio in different particles has rarely been used for the correlation calculation to the distance to the pollution source. Bi et al (2006) proposed that because of the lower boiling point of Cd to those of Pb and Zn, Cd, and to some extent Pb, tends to partition onto lighter, carbon-based particulate matter while Pb and Zn will be left in the solid waste during Zn smelting process, thus a higher Cd/Pb ratio in contaminated soils implies that the heavy metal pollution is mainly from atmospheric deposition of smelting.

Li et al (2014) investigated the concentrations of heavy metals in soil fractions with different particle size near gold mines in Beijing with elevated concentrations of Pb and Cd. Calculated with their data, the Pb/Cd ratios in the fractions of 0–2, 2–5, 5–10 and 10–50 μm particles had very narrow variation (150–151), while the Pb/Cd ratios of 50–74, 74–165 and 165–300 μm particles were 185, 115 and 123. These results demonstrate that the Pb/Cd ratios of the different particle sizes vary greatly from the soil samples in this work. Shen et al (2017) investigated the heavy metal accumulation in soils near a zinc smelter in Shaanxi Province, and found that the Pb/Cd ratios in soil samples near the smelter ranged 0.8–5.3, and samples collected far away from the smelter had bigger Pb/Cd values (35.1–127). Eckel et al (2002) investigated the Sb/Pb, As/Pb, Cd/Pb ratios of soil samples collected from different areas, the Pb/Cd ratios calculated from their data ranged between 38.46–1428; these Pb/Cd values are much greater than the results of the present work. The background values of Pb and Cd of local soils in this work are 20.2 and 0.064 mg kg^{-1} , respectively (Wei, 2004), with a resulting Pb/Cd ratio of 315.6. Thus, the lead smelting activities increase the Pb/Cd ratios of soil. Still, the estimation of the effect of different pollution sources on the variation of Pb/Cd ratios to the distance is based on the hypothesis that the Pb/Cd ratios at different distances to the pollution source are different. This concept is similar to conclusions of Bi et al (2006), which stated that soils having similar Pb/Cd ratios had similar pollution sources.

The results of this work indicate that the variation of the concentrations of Cd, Pb and the Pb/Cd ratios of samples to the distance to the pollution source can be potentially used to discriminate the atmospheric deposition from different sources.

3.4 Correlation between concentrations of heavy metals

The Pearson correlation results of heavy metal concentrations were outlined in Table 4. Most of the correlations are statistically significant ($p < 0.05$), with the correlation between DTPA-Cd and DTPA-Pb, total Cd and total Pb having the biggest correlation coefficients. Correlation with total Ni have relatively poor significance. These results are in good agreement with similar studies (Ran et al, 2010; Cheng et al, 2014; Ghayorane and Qishlaqi, 2017). The poor correlation between total Ni concentrations with other elements implies that the total Ni concentration was not affected by the smelting.

3.5 Component analysis results

The variation of the total concentrations of Cd, Pb, Cu, Zn, and those of the DTPA-extractable-Cd, Pb, Cu, Zn and Ni in the soil were mainly affected by Component 1, which had positive effect on the concentrations of these elements (Table. 5). Accumulation of Cd and Pb in the samples was from the atmospheric deposition from the emission of Yuguang. Thus, Component 1 is the effect from Yuguang. Component 1 had negative effect on the concentration of total Ni in the samples. Component 2 had negative effect on the concentrations of total Cd, Pb, and concentrations of DTPA-extractable forms of all five metals; however, it had biggest positive effect on the concentration of total Ni. Because the concentration of total Ni was less affected by the lead smelting (Table 1, 2 and 3), Component 2 is the geological contribution in the soils. Component 3 had positive contribution to the concentrations of the total concentrations of all the five metals. In Figs. 2 and 3, the samples at about 6300 m had elevated concentrations of Cd and Pb than the trend, Component 3 is the contribution from the enterprises near sampling sites at 6300 m (sampling sites near sample T1) (Fig. 1).

Jiyuan City is important for Zn, Pb and coal production in China. Before the high blood lead levels in Jiyuan were reported by the media in 2009, there are about 200 lead smelting works in Jiyuan, most of them were small, with poor infrastructure facilities and high pollution by atmospheric deposition and solid waste from smelting. Some of these smelting facilities were located in remote areas, such as that was reported by Cheng et al (2017). After 2009, the government closed most of the smelting facilities (Qiu et al, 2016). Currently, only Yuguang, Jinli and Wanyang lead smelting plants are still in operation. Scientists and authorities have been actively investigating the accumulation of heavy metal pollution from the lead smelting plants in Jiyuan, but all the published investigations were conducted in the vicinities of the existing three lead smelting plants (Yao et al, 2015; Li et al, 2016; Qu et al, 2016; Zhao et al, 2017), while the contribution from the closed smelting plants was ignored. Compared with the pollution from the three existing lead smelting plants, the pollution from the closed smelting facilities had much lower output, thus assumed they affected much smaller areas. The variation of Cd, Pb and Pb/Cd of soils to the distance of one pollution source used in this work may be helpful to identify the contribution of different pollution sources, including those once-active sources.

4 Conclusions

Analysis of 88 topsoil (0–20 cm) samples collected near the lead smelters in Jiyuan indicated that, i) Cd is the most accumulated heavy metal in soil; the concentrations of Cd ranged 1.95–5.70 mg kg⁻¹, with an average pollution index (mean concentration/background value) of 51.4; the concentration of Pb ranged 64.5–435 mg kg⁻¹, with an average pollution index of 9.11. Average pollution indices of Cu, Ni and Zn are all less than 3. The mean DTPA-extractable concentrations of Cd and Pb are 0.744 and 58.7 mg kg⁻¹. ii) Significant correlation between the concentrations of total Cd, total Pb, and Pb/Cd ratios to the distance between the sampling sites and the main stack of the closest lead smelting plant (Yuguang) were found. The results indicate the accumulation of heavy metals were affected by Yuguang, Wanyang and other small emission sources near the sampling sites. iii) The

estimated area of heavy metal pollution, where Cd or Pb concentrations were above farmland soil quality standards for China, was 384 km², which is significantly larger the previously reported 115 km².

Acknowledgements

This work was sponsored by The National Key Research and Development Program of China (2016YFE0106400) and National Natural Science Foundation of China (41471253). The authors also want to thank Mr. Wuzheng Zhai, Ming Cai, Xiaojian Hu and Juntao Liu for their help in sample collection and processing. Although EPA contributed to this article, the research presented was not performed by or funded by EPA and was not subject to EPA's quality system requirements. Consequently, the views, interpretations, and conclusions expressed in this article are solely those of the authors and do not necessarily reflect or represent EPA's views or policies.

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Fig. 1.

Map of the study area. (a) Location of Jiyuan City in northern China. (b) The sampled area is situated to the northwest of urban Jiyuan and the locations of the three smelters in Jiyuan (Yuguang, Jinli and Wanyang). (c) The locations of the sampling sites are located to the west and northwest of the Yuguang.

Fig. 2. Variation of total Cd concentrations in farmland soils to the distance between sampling sites and the main stack of Yuguang smelting plant in Jiyuan, China ($n=88$)

Fig. 3. Variation of total Pb concentrations in farmland soils to the distance between sampling sites and the main stack of Yuguang smelting plant in Jiyuan, China ($n=88$)

Fig. 4. Variation of the availability indices of Cd and Pb in farmland soils to the distance between sampling sites and the main stack of Yuguang smelting plant in Jiyuan, China ($n=88$)

Fig. 5. Variation of Pb/Cd ratios of farmland soils to the distance between the sampling sites and the main stack of Yuguang smelting plant in Jiyuan, China ($n=88$)

Table 1

Statistical results of total concentration of heavy metals in farmland soils of near Yuguang smelting plant in Jiyyuan, China ($n=88$)

Element	Range(mg kg ⁻¹)	Mean(mg kg ⁻¹)	Median(mg kg ⁻¹)	SD	CV(%)	Background value(mg kg ⁻¹)	Mean pollution index
Cd	1.95~5.70	3.29	2.92	1.00	30.0	0.0640	51.4
Cu	16.2~52.7	31.8	31.5	6.58	20.7	21.4	1.49
Ni	35.9~54.5	45.6	45.6	3.68	8.07	25.3	1.80
Pb	64.5~435	184	143	99.9	54.2	20.2	9.11
Zn	68.2~158	99.2	93.9	19.9	20.1	65.1	1.52

Note: The background values of Cd, Ni and Pb are from Wei (2004), the background values of Cu and Zn are from Li et al (1991).

Table 2

Statistical results of concentration of DTPA-extractable heavy metals in farmland soils near Yuguang smelting plant in Jiyan, China ($n=88$)

Metal	Range (mg kg ⁻¹)	Mean (mg kg ⁻¹)	Median (mg kg ⁻¹)	SD	CV (%)	Mean availability index (%)
Cd	0.0513–2.16	0.744	0.635	0.525	70.6	22.6
Cu	1.29–8.11	3.03	2.70	1.34	44.3	9.53
Ni	0.187–0.769	0.387	0.377	0.104	26.9	0.860
Pb	15.0–151	58.7	40.8	39.1	66.6	31.9
Zn	0.963–9.18	3.91	3.19	2.01	51.3	3.94

Table 3

Regression between concentrations (y) of soil heavy metals and the distances (x) between the sampling sites and the main stack of Yuguang smelting plant in Jiyuan, China ($n=88$)

Forms of metal	Model	Equation	r^2	Significance
Total Cd	Quadratic	$y=3\times 10^{-7}x^2-0.0026x+8.86$	0.8001	$p<0.01$
Total Cu	Quadratic	$y=1\times 10^{-6}x^2-0.0127x+56.66$	0.3299	$p<0.01$
Total Ni	Linear	$y=0.0014x+40.11$	0.3231	$p<0.01$
Total Pb	Power	$y=3\times 10^6x^{-1.212}$	0.8093	$p<0.01$
Total Zn	Logistic	$y=-33.18\ln(x)+368.95$	0.4575	$p<0.01$
DTPA-Cd	Logistic	$y=-1.109\ln(x)+9.76$	0.7653	$p<0.01$
DTPA-Cu	Power	$y=2896x^{-0.856}$	0.6829	$p<0.01$
DTPA-Ni	Quadratic	$y=3\times 10^{-8}x^2-0.0003x+0.86$	0.4097	$p<0.01$
DTPA-Pb	Power	$y=1\times 10^7x^{-1.539}$	0.8421	$p<0.01$
DTPA-Zn	Logistic	$y=-3.57\ln(x)+32.90$	0.5541	$p<0.01$

Table 4

Correlation (Pearson) coefficient matrix between the concentrations of total and DTPA-extractable metals in farmland soil samples collected near Yuguang smelting plant in Jiyuan, China ($n=88$)

	Total Cd	Total Cu	Total Ni	Total Pb	Total Zn	DTPA-Cd	DTPA-Cu	DTPA-Ni	DTPA-Pb	DTPA-Zn
Total Cd	1									
Total Cu	0.462**	1								
Total Ni	-0.316**	0.227	1							
Total Pb	0.913**	0.428**	-0.431**	1						
Total Zn	0.816**	0.528**	-0.133	0.826**	1					
DTPA-Cd	0.839**	0.320**	-0.517**	0.924**	0.739**	1				
DTPA-Cu	0.657**	0.573**	-0.352**	0.724**	0.690**	0.745**	1			
DTPA-Ni	0.550**	0.345**	-0.078	0.495**	0.567**	0.576**	0.463**	1		
DTPA-Pb	0.884**	0.436**	-0.425**	0.940**	0.773**	0.959**	0.758**	0.526**	1	
DTPA-Zn	0.745**	0.563**	-0.271*	0.766**	0.738**	0.771**	0.874**	0.556**	0.803**	1

*and **for significant at 0.05 and 0.01 levels, respectively.

Table 5Results of principal component analysis of heavy metal in soils near Yuguang smelting plant in Jiyuan, China ($n=88$)

Variables	Components		
	1	2	3
Total Pb	0.948	-0.143	0.047
Total Cd	0.917	-0.045	0.142
Total Zn	0.869	0.182	0.124
Total Cu	0.547	0.682	0.088
Total Ni	-0.385	0.771	0.385
DTPA-Pb	0.954	-0.136	0.020
DTPA-Cd	0.936	-0.240	-0.038
DTPA-Zn	0.884	0.184	-0.233
DTPA-Cu	0.847	0.129	-0.269
DTPA-Ni	0.635	0.228	-0.018
Total variance (%)	61.313	12.902	9.046
Cumulative variance (%)	61.313	74.215	83.261