

Research Article

Distribution Characteristics of Heavy Metals and Pb Isotope in Profile Soils from a Mining and Smelting Area in Northwestern China

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The distribution characteristics of typical heavy metals (HMs) and Pb isotopic compositions in profile soils from different areas were investigated in Baiyin district, northwest China. The soil samples from the ore district and the sewage irrigation area showed an obvious enrichment of HMs in different depths, and the difference in the longitudinal migration depth of Pb, Cu, Zn, and Cd was insignificant, which might be due to the migration behavior of HMs mainly controlled by carbonate in alkaline soil. With the sewage irrigation activities, the content of soil organic matter was no longer the main controlling factor for the migration behavior of HMs. In ore district and sewage irrigation area, the HMs contents of nonresidual fractions in topsoil were much higher than that in the corresponding deep soil, which indicated that HMs activities in topsoil were significantly high. The Pb isotopic compositions of profile soils indicated that the long-term mining and smelting activities remained the main source of vertical enrichment of HMs in Baiyin district. Moreover, the Pb isotope ratios $^{206}\text{Pb}/^{207}\text{Pb}$ of nonresidual fractions (1.1359-1.1916) were all lower than that in the corresponding residual fractions (1.1641-1.2010), showing the characteristics that HMs input from anthropogenic source were in different degrees. The Pb isotopic compositions of residual fractions in the topsoil of ore district and sewage irrigation area (1.1641 and 1.1703) were between the two end-members composed of background soil and local mineral samples, which suggested that some anthropogenic HMs might enter into the residual components in the soil that was greatly affected by the input of HMs.

1. Introduction

The health and sustainable development of soil ecosystem are closely related to human well-being. In 2015, 13 of the 17 global sustainable development goals mentioned in “Transforming Our world: The 2030 Agenda for Sustainable Development” [1] released by the United Nations were directly or indirectly related to soil. However, with the rapid development of industrial society, the increasingly serious problem of soil pollution have become one of the main threats to food safety and human health, which have aroused widespread public concern [2, 3]. According to the *National Soil Pollution Survey Bulletin* announced by China’s Minis-

try of Environmental Protection and Ministry of Land and Resources in 2014 [4], from the perspective of pollution distribution, soil pollution in southern China had been more serious than that in northern China, especially in some regions such as the Yangtze River Delta and Pearl River Delta. Soil heavy metals (HMs) in southwest and central south China had exceed the relevant standard in a large range, and the proportion of heavy pollution points in the middle reaches of the Yangtze River and the region between the Yangtze River and the Huai River was the highest, reaching 7.1%. In addition, the soil HMs pollution in the main grain-producing areas in the South China was also more serious than that in the north China. At present, the research

on the sources, distribution, occurrence speciation, migration, and transformation of soil HMs in China mainly focused on the southern regions with rich mineral resources and high degree of soil HMs pollution. These previous research results have made important contributions to the evaluation of environmental risk, remediation, and treatment of soil contaminated with HM in the South China.

As is well known, the mineral resources, especially non-ferrous metal deposits, are very abundant in northern China and are the important economic mainstay. However, there is a consensus that the HMs pollution in soil is quite severe and should be paid more attentions, such as Fengxian ([5]; Fang et al., [6]), Jinchang [7, 8], Baiyin [9–12], and Inner Mongolia [13, 14]. Tian et al. [5] reported that the average contents of Pb in farmland, woodland, and grassland soil around the lead-zinc smelter in Fengxian County of Shaanxi Province were 410.1 mg/kg, 315.9 mg/kg, and 313.6 mg/kg, respectively, which were much higher than the background value of Pb in local soil (21.2 mg/kg). Zhang et al. [8] studied the characteristics of heavy metal pollution in urban soil based on different land-use types in the mining city—Jinchang in the western area of China. According to the Chinese standards of grading of the soil heavy metal pollution and the biotoxicity index of heavy metal, the ranking quality for soils from the dwellings was the level of III; the public infrastructure land was the level of IV; the industry land, the roads and paved areas, the agricultural land, and the city greenbelt were the level of V, where Ni and Cu were the worst offenders [8]. In fact, the synergistic effect of sand and dust storm, soil and water loss, and acid rain aggravated the pollution, and the serious pollution had been a “bottle-neck” problem in the sustainable ecological development, especially for the northwest China.

In China, the soil pH value is in the range of 4.5–8.5, where the soil pH is increasing from the south to north part. The soil pH is one of the key factors to control the environmental behavior of HMs. In general, most of the HMs in alkaline soil exist in the insoluble formation, such as hydroxide, phosphate, and carbonate, whilst the soluble fraction of HMs in acidic soil is high. Moreover, the mineral composition of soils between the South and the North China also shows significant differences [15–18]. In the South China, the mineral composition of soil is mainly composed of iron and manganese oxides, whereas clay minerals in the North China. The differences of soil pH and mineral composition between the north and south part would directly affect the occurrence and migration behavior of HMs. Therefore, it was unscientific to apply the remediation and control methods of HMs in southern soil directly to solve those problems in northern areas. It is necessary to carry out systematic and in-depth research on the source, spatial distribution, occurrence, migration, and enrichment behavior of soil heavy metal pollutants in northern China, which was of great significance to explore the migration and transformation behavior of HMs in alkaline soil and then provided scientific and effective schemes to prevention, remediation, and governance of soil heavy metal pollutants in northern China.

2. Materials and Methods

2.1. Study Area. Soil samples were collected from Baiyin city, which was once one of the important nonferrous metal mining and smelting bases and now a typical resource exhausted city in China. Baiyin is located in the middle of Gansu Province and the upper reaches of the Yellow River, in the transition zone between the Loess Plateau and the Tengger Desert. It has a typical arid and semiarid climate [19]. The annual average temperature is 6–9°C, the annual rainfall is 180–450 mm, the annual evaporation is the 1500–1600 mm which is 4.5 times of the average precipitation of Baiyin city [20], and the soil in Baiyin area is a calcareous soil [11]. The ore district was mainly engaged in mining and metal smelting activities over about half a century which have seriously impact on the local ecological environment [10, 21, 22]. Due to the lack of water resources, the irrigation activities with sewage that from the upstream had been applied in Baiyin for more than 40 years, and the two sewage irrigation areas had been formed in the east (Dongdagou) and west valleys (Xidagou) of Baiyin City, which not only polluted the surrounding soil but also caused potential harm to food safety and human health [10, 20, 23–28]. However, in both Silong and Shuichuan towns, the crops are mainly irrigated by the Yellow River. Previous studies have shown that the main HM pollutants in the featured soil were Pb, Cu, Zn, and Cd [12]; therefore, in this study, we mainly focused on the migration and enrichment behavior of these four HMs in the profile soils from grass land.

2.2. Sampling and Sample Preparation. In this study, six profile soils (approximately 0–52 cm in depth) were collected in April 2019, in which C1 ($n = 27$) was from the ore district (OD), C2 ($n = 27$) and C3 ($n = 13$) were from Dongdagou sewage irrigation area (DSIA), C4 ($n = 13$) was from Xidagou sewage irrigation area (XSIA), and C5 ($n = 27$) and C6 ($n = 13$) were from the Yellow River irrigation area (YRIA) (Silong town and Shuichuan town). The profile soil samples were all collected from the grassland without obvious human disturbance, and the detailed sampling sites were shown in Figure 1. In laboratory, each soil sample was removed from stones, plant roots, and other debris and then cryodesiccated, ground, and sieved through a 200-mesh nylon sieve for further analysis.

2.3. Elemental and Pb Isotope Analyses

2.3.1. Elemental Analysis. Soil samples (approximately 0.1 g) were completely digested by the mixture solution of HNO₃–HCl–HF–H₂O₂ in perfluoroalkoxy (PFA) vessels and then evaporated near drying. Finally, the digested samples were made 10 mL with 2.0% HNO₃ solution and then stored in a refrigerator at 4°C for further analysis. The procedure was clearly described in our previous work [21]. All reagents used in the above process were of high-purity grade. The concentrations of Pb, Cu, Zn, and Cd were determined using the voltammetry polarograph (Metrohm Switzerland, 848 VA), which has high analysis precision and wide analysis range, satisfying the analysis of HM concentrations in most natural samples. The precision and accuracy of the

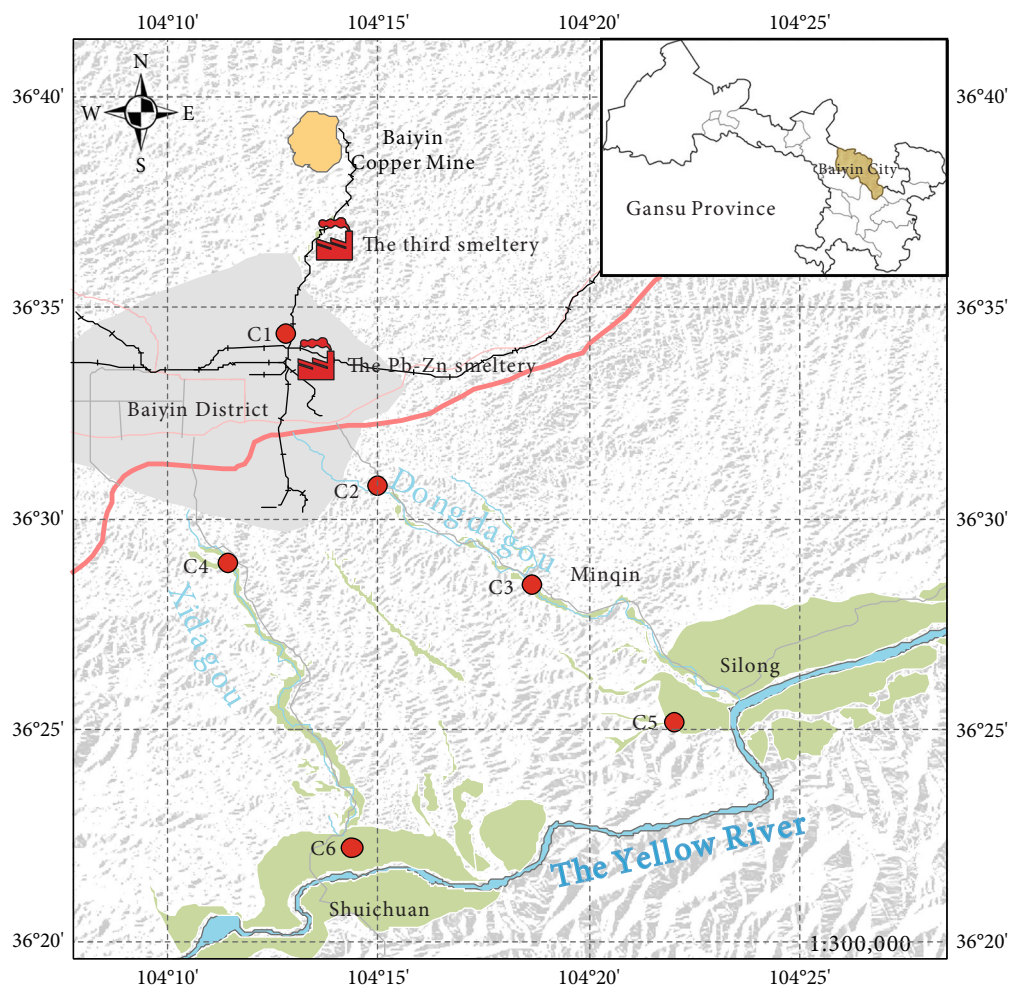


FIGURE 1: Sampling location in the study area (modified from [10, 21]).

measurements were verified using standard reference materials (GBW07407), and the relative standard deviations were typically lower than 5.0%. The HM concentrations of the soil shown in this study were all based on dry weight.

2.3.2. Pb Isotopic Analysis. The separation of Pb, instrumental analysis, and correction of lead isotope mass fractionation of the instrument had been described in detail in our previous work by He et al. [21]. All procedures for Pb isotopic analysis were performed in a high-efficiency air-filtered superclean laboratory (Class 100), and all acids used in the digestion were purified using subboiling distillation with high-purity reagents. The isotope ratios of Pb were measured using an ICP-MS (Nu Instrument, Nu Attom) at the Northwest Institute of Eco-Environment and Resources. In this work, the long-term precision of reference material NIST SRM 981 was 0.18% and 0.28% for the $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios, respectively.

2.4. Sequential Extraction Procedure. Chemical sequential extraction method is one of the most common and effective methods to study the occurrence species of HMs in soil and sediments. According to the order of interaction between

HMs and minerals from weak to strong, chemical extractants with different extraction capabilities are selected to continuously separate HMs with different binding species in soil.

The sequential extraction experiments were carried out on the surface soil samples (C1-1, C2-1, C3-1, C4-3, C5-1, and C6-1, approximately 0–12 cm in depth) and deep soil samples (C1-23, C2-16, C3-12, C4-12, C5-21, and C6-13, approximately 32–52 cm in depth) of each profile soil by the improved chemical sequential extraction method referenced from Pueyo et al. [29], and the detailed steps were shown in the Supplementary Material. The complicated formations of HMs in soil could be divided into four species: exchangeable fraction, reducible fraction, oxidizable fraction, and residual fraction.

2.5. Soil Organic Matter. Soil organic matter (SOM) content was analyzed in accordance with GB 9834-88 of the National Standards of China.

2.6. The Relative Contributions of Anthropogenic Activities. Our previous work showed that the Pb isotopic compositions of topsoil in the Baiyin area conformed to the binary

mixing model of mineral samples and background soils [21]. In this study, Equations (1) and (2) were used to calculate the relative contributions of HMs from the geogenic and anthropogenic sources, respectively. The two end-member values of $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{geo}}$ and $(^{206}\text{Pb}/^{207}\text{Pb})_{\text{anth}}$ were 1.1992 and 1.1494, respectively [21]. The contributions of geogenic and anthropogenic sources could be expressed by f_{geo} and f_{anth} , respectively, as follows:

$$\left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{sample}} = f_{\text{geo}} \times \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{geo}} + f_{\text{anth}} \times \left(\frac{^{206}\text{Pb}}{^{207}\text{Pb}}\right)_{\text{anth}}, \quad (1)$$

$$f_{\text{geo}} + f_{\text{anth}} = 1.0. \quad (2)$$

In Equations (1) and (2), the subscripts “geo” and “anth” referred to geologic and anthropogenic sources, respectively.

3. Results and Discussion

3.1. Longitudinal Distribution of HMs. The vertical distribution characterizations of HMs in soils collected from different regions of Baiyin were shown in Figure 2 and Table S1. From the regional point of view, there was no obviously vertical enrichment of HMs in the two soil profiles located in the YRIA, while the profile soils in the OD and sewage irrigation area clearly showed the enrichments of HMs in different depths and degrees. In OD, the contents of HMs (C1) were the highest in the profile soil from depth of 0-2 cm, in which the highest concentrations of Cu, Pb, Zn, and Cd were 86.30 mg/kg, 162.67 mg/kg, 528.94 mg/kg, and 14.45 mg/kg, respectively. The four typical HMs showed enrichment in depth of 0-32 cm, and the average concentrations of Cu, Pb, Zn, and Cd were 2.28, 5.08, 3.08, and 35.38 times higher than those of the soil background value (SBV) of Gansu Province (24.1 mg/kg for Cu, 18.8 mg/kg for Pb, 68.5 mg/kg for Zn, and 0.116 mg/kg for Cd), indicating that these four elements in soil have the same ability of vertical migration in OD although the enrichment degree of them was different, among which Cd was the highest. Given the fact that OD was close to the Baiyin Copper Mine (BCM) and smelters, and there was no history of sewage irrigation in that area, the enrichment of HMs in soil could be attributed to the atmospheric deposition.

In DSIA, the contents of HMs in the depth of 0-2 cm in soil profile C2 were the highest, in which the highest concentrations of Cu, Pb, Zn, and Cd were 140.42 mg/kg, 333.00 mg/kg, 510.53 mg/kg, and 12.20 mg/kg, respectively, and then quickly declined with the increase of the soil depth. The enrichment depths were 0-12 cm for Cu, 0-22 cm for Pb, 0-8 cm for Zn, and 0-22 cm for Cd, respectively. The average contents of Cu, Pb, Zn, and Cd in enrichment areas were 3.92, 6.10, 5.43, and 29.81 times higher than the SBV of Gansu Province. In the soil profile C3, the contents of HMs in the depth of 0-4 cm were the highest, in which the highest concentrations of Cu, Pb, Zn, and Cd were 357.85 mg/kg, 439.36 mg/kg, 1639.17 mg/kg, and 31.81 mg/kg,

respectively. Column samples showed significant enrichment characteristics of HMs, except for the low contents of HMs in the depth of 44-48 cm, and the concentrations of Cu, Pb, Zn, and Cd are 8.50, 12.88, 11.47, and 125.91 times higher than the SBV in Gansu Province on average. The soil profile C3 was collected at the middle section of Dongdagou area which is also the core area of sewage irrigation. The enrichment depth and degree of HMs were much deeper and higher than that of the soil profile C2, indicating that this area suffered heavier sewage irrigation and more HMs pollution. Meanwhile, the HM enrichment degree of soil profile C3 was also much higher than soil profile C1 in OD, suggesting that sewage irrigation leaves more influence on HM pollution depth and degree to soil compared with other input pathways of HMs, such as atmospheric deposition. In XSIA, the vertical distribution characteristics of HMs suggested that there were sewage irrigation activities in different periods in this area, which has not received due attentions before. The highest contents of HMs occurred in the depth of 8-12 cm, and the average concentrations of Cu, Pb, Zn, and Cd were the 230.53 mg/kg, 149.59 mg/kg, 364.75 mg/kg, and 5.89 mg/kg, respectively, which are 3.91, 4.34, 2.21, and 18.79 times higher than SBV of Gansu Province. The results suggested that the HMs pollution in XSIA soil should be paid more attentions, because XSIA is the main agricultural production for Baiyin.

Kong et al. [30] analyzed the vertical distribution characteristics of HMs in the karst area of Guilin, Guangxi Zhuang Autonomous Region, southern China. The results showed that there were significant differences in the enrichment depth of Cu, Pb, Zn, Cd, and Mn, among which the migration and enrichment depth of Pb and Cu were the shallowest (about 18-30 cm), and the Zn, Cd, and Mn were deeper (about 18-90 cm). However, in the typical arid and semiarid alkaline soil studied in this work, the differences in vertical migration depth of different HMs were insignificant. It might be related to the significant differences in physical and chemical properties (such as pH value) and mineral composition in soil between the south and the north area of China. For the acid soil mainly composed of the iron and manganese oxide minerals in south China, the interaction between metal elements (such as Pb and Cu) and soil components was more intense resulting in weaker migration and enrichment. However, Zn and Cd, the interaction with soil components was relatively weaker; thus, the migration and enrichment depth were stronger and deeper than that of Pb and Cu [9, 31]. The migration and enrichment behaviors of HMs were mainly controlled by carbonate and clay mineral for the northern alkaline soil in China. The interaction between the four typical HMs and carbonate or clay mineral was similar in strength, so the differences in vertical migration and enrichment depth of different HMs were insignificant. These results further suggested that there are some differences in the migration and enrichment behavior of metal elements in the soils from different areas; therefore, the corresponding remediation methods could be suitable for the local conditions.

The content of SOM in south China is generally high, which can significantly affect the migration behavior of metal ions in environmental media. In order to explore the

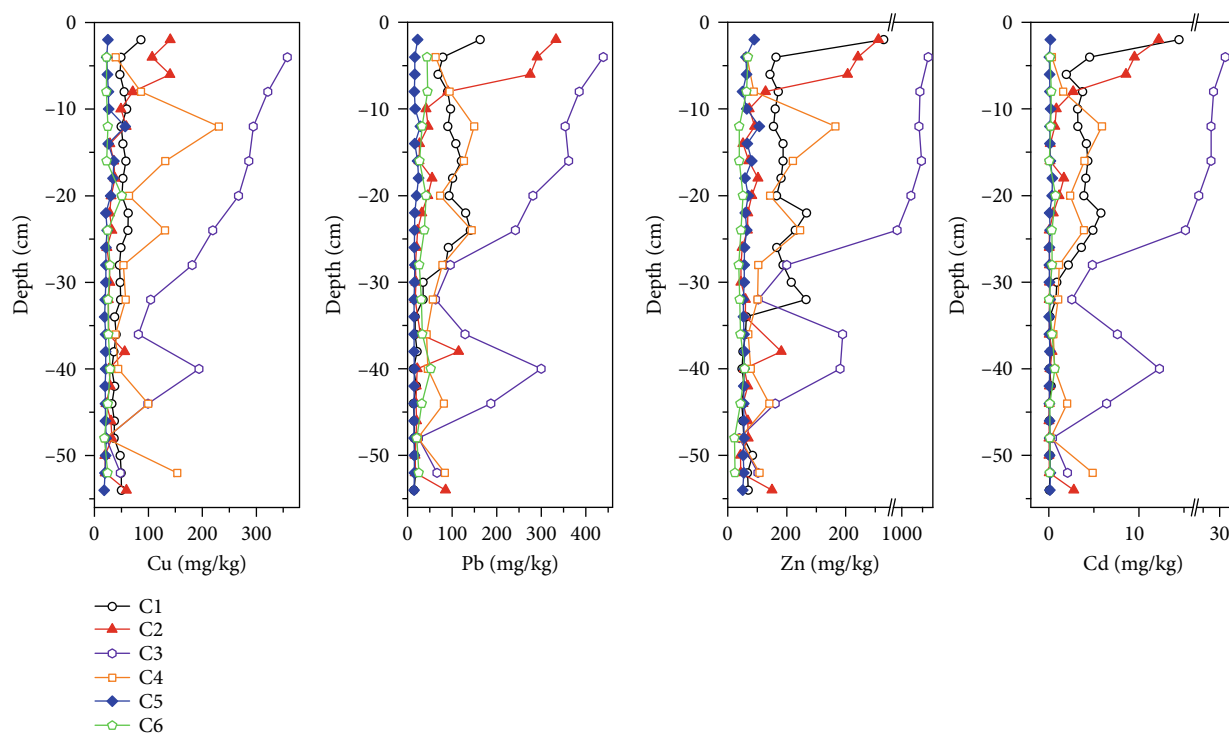


FIGURE 2: The distribution of HM concentrations for the different soil profiles.

effect of SOM on the vertical migration and enrichment of HMs in alkaline soils in arid and semiarid areas, the correlation between HM contents and SOM contents in different soil profiles was analyzed (as shown in Figure 3 and Table S1). The vertical distribution of HM contents and SOM showed a high positive correlation in the area without sewage irrigation history (C1) and less sewage irrigation activities (C2) in OD. The linear regression correlation coefficient R^2 between the contents of Cu, Pb, Zn, Cd, and SOM in C1 and C2 were 0.70, 0.60, 0.66, and 0.88 and 0.55, 0.58, 0.60, and 0.50, respectively (Figures 3(a) and 3(b)), which indicated that the vertical distribution of SOM would affect the vertical migration and enrichment behavior of HMs in alkaline calcareous soil in arid and semiarid areas. However, in the sewage irrigation area (C3 and C4), the correlation between HM contents and SOM was much lower. The correlation (R^2) between Cu, Pb, Zn, and Cd contents and SOM were 0.18, 0.49, 0.20, and 0.28 and 0.04, 0.29, 0.23, and 0.01, respectively (Figures 3(c) and 3(d)), which suggested that SOM was no longer the important factor controlling the vertical migration and distribution of HMs under the influence of sewage irrigation. In the soil samples (C5 and C6) irrigated by the Yellow River, the correlation between the contents of some HMs and SOM was also weaker. The correlations (R^2) between the contents of Cu, Pb, Zn, Cd, and SOM were 0.41, 0.60, 0.33, and 0.47 and 0.01, 0.45, 0.51, and 0.01, respectively (Figures 3(c) and 3(d)), which might be related to the less input of HMs in the soil. In general, the correlation between HMs from geogenic source and SOM was weaker. In addition, the vertical

distribution of S contents in the soil showed that the concentrations of S in the depth of 34-54 cm were extremely high (Figure 2), which suggested that the soil in the depth near the BCM might have been doped with sulfide minerals. The S contents of profile soil C3 collected from DSIA were generally high (Figure 2), which showed that the area suffered serious acid wastewater irrigation.

3.2. Vertical Distribution of Pb Isotopic Composition. A representative profile soil samples were selected from OD (C1), sewage irrigation area (C2), and YRIA (C5). As shown in Figure 4 and Table S2, at the depth of 0-28 cm, the $^{206}\text{Pb}/^{207}\text{Pb}$ values of C1 were at the low level (1.1443-1.1541), which were close to that of the local ore samples (1.1438-1.1520). At the depth of 28-32 cm, the $^{206}\text{Pb}/^{207}\text{Pb}$ values of C1 were in the range of 1.1663-1.1679. When the depth exceeded 32 cm, the $^{206}\text{Pb}/^{207}\text{Pb}$ values of C1 (1.1894-1.2062) were similar to that of the local background soil (1.1957-1.2022), which indicated that the enrichment depth of anthropogenic HMs in the soil of OD (C1) was mainly at 0-32 cm, and when the depth exceeded 32 cm, HMs in soil mainly came from geogenic source. For C2 samples collected from the sewage irrigation, the $^{206}\text{Pb}/^{207}\text{Pb}$ values showed a low level at 0-8 cm (1.1454-1.1520), which was closed to that of local ore samples (1.1438-1.1520). At the depth of 8-22 cm, the $^{206}\text{Pb}/^{207}\text{Pb}$ values of C2 samples were in the range of 1.1582-1.1809. In addition to the lower $^{206}\text{Pb}/^{207}\text{Pb}$ values, which were 1.1479 at depth of 36-38 cm and 1.1528 at depth of 52-54 cm, the Pb isotopic ratios $^{206}\text{Pb}/^{207}\text{Pb}$ were at the higher levels (1.1830-1.1986) that close to the background values

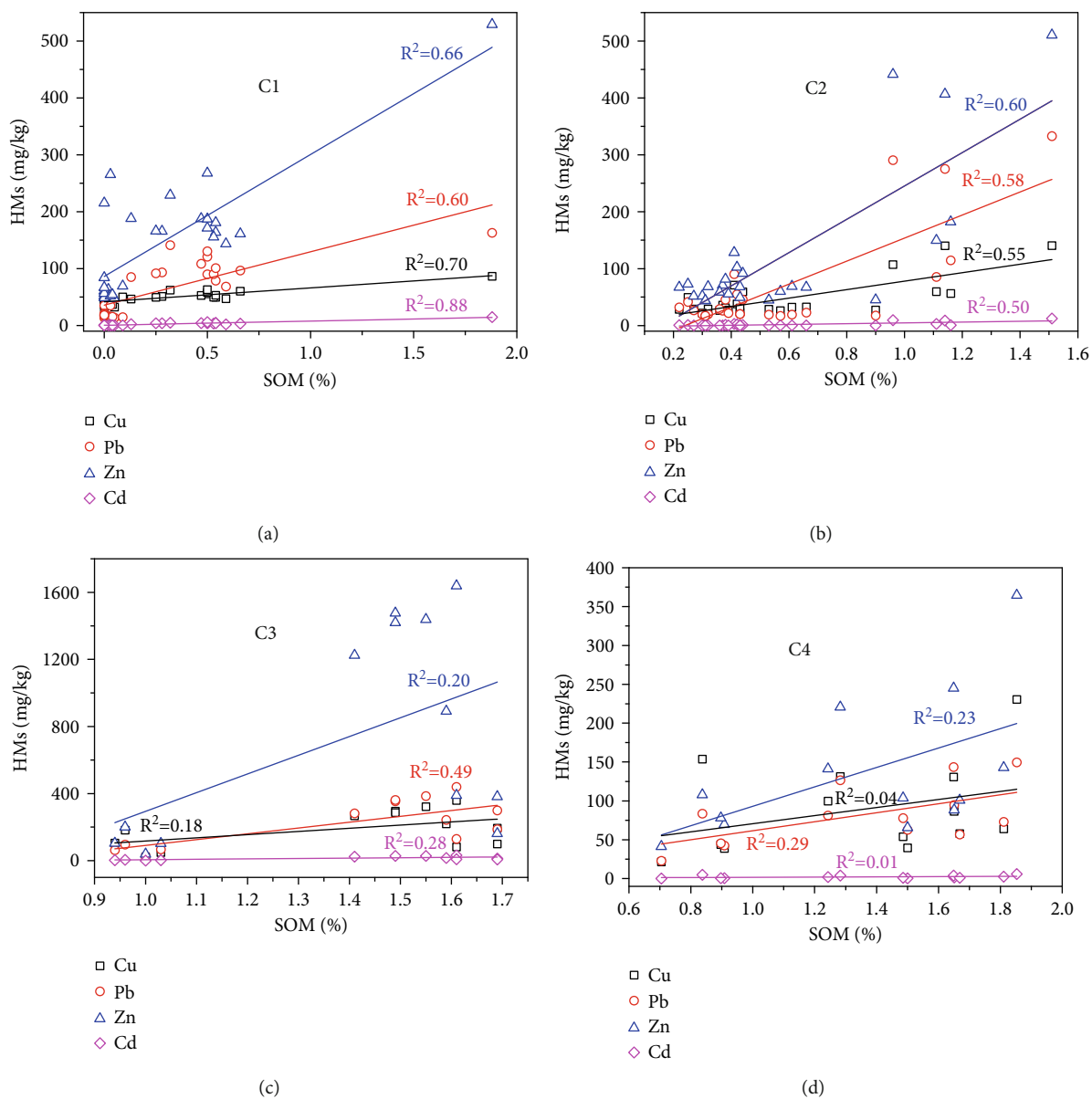


FIGURE 3: Continued.

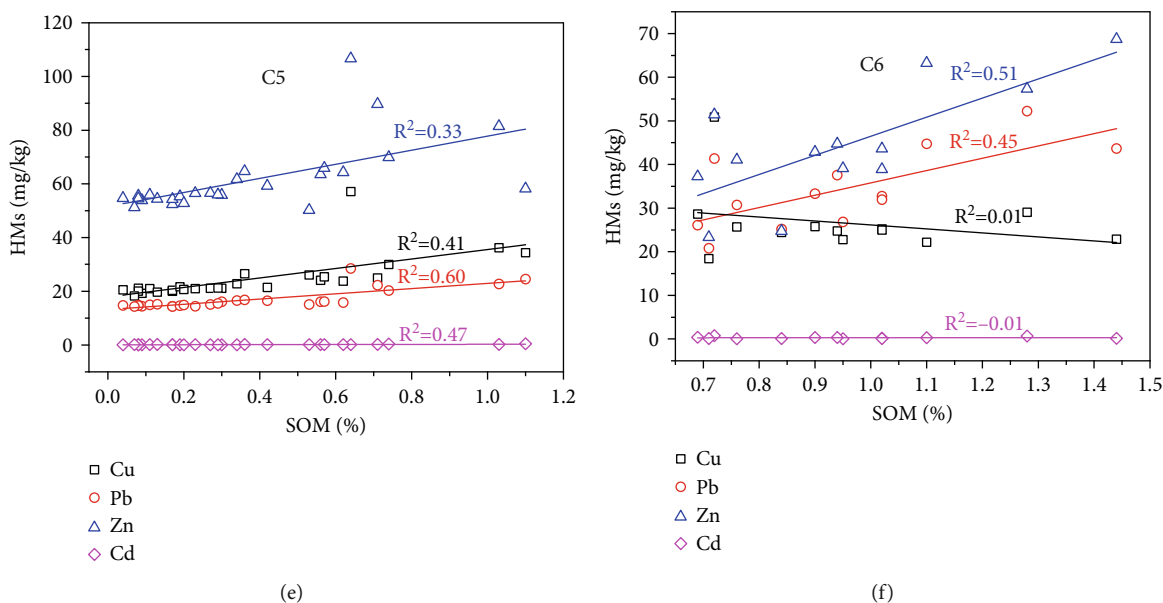


FIGURE 3: Correlation between HM contents and organic matter contents in different soil profiles.

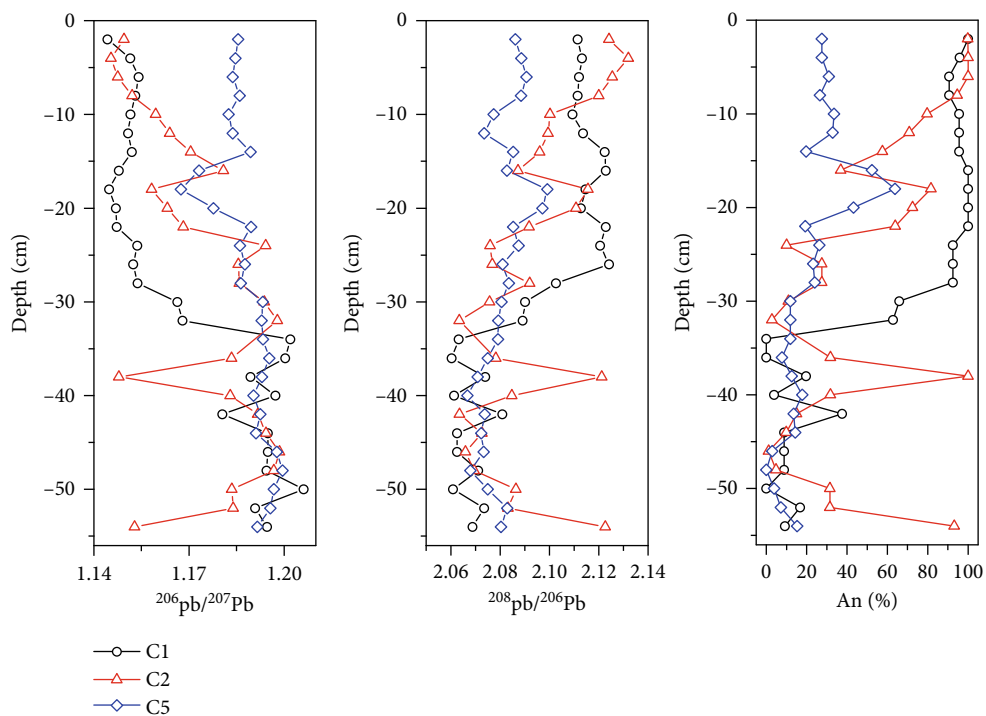


FIGURE 4: The Pb isotopic compositions and the relative contributions of heavy metal from anthropogenic source (An%) in different soil profiles.

(1.1957-1.2022) at the depth that over 22 cm, indicating that the enrichment depth of anthropogenic HMs in soil of sewage irrigation area (C2) was about 22 cm. For profile soil C5 collected from the YRIA, besides the depth of 14-20 cm where the $^{206}\text{Pb}/^{207}\text{Pb}$ showed relatively lower values (1.1674-1.1777), other samples showed higher level (1.1825-1.1995), indicating that there were no significant HMs input from anthropogenic sources except for the

depth of 14-20 cm. The Pb isotope ratios of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ were in good correspondence, which indicated that the isotopic data obtained had high reliability.

The HM contents, Pb isotopic composition, and the relative contribution of HM inputs from anthropogenic sources in the three profile soils were highly correlated. It showed that the higher HM contents, the lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, and the greater relative contribution of HM inputs

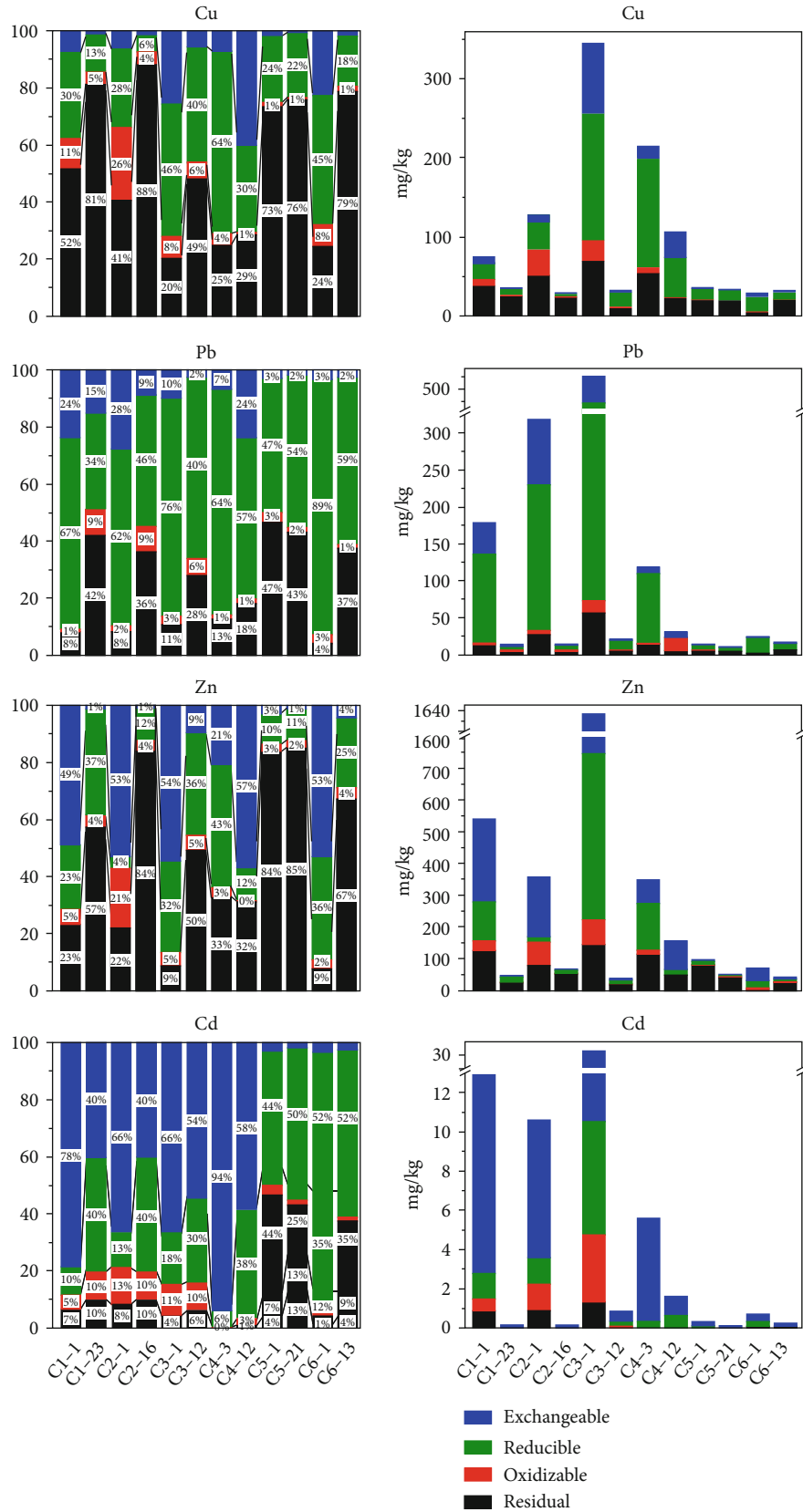


FIGURE 5: The concentrations and percentage of exchangeable, reducible, oxidizable, and residual Cu, Pb, Zn, and Cd in topsoil and deep soil from different areas.

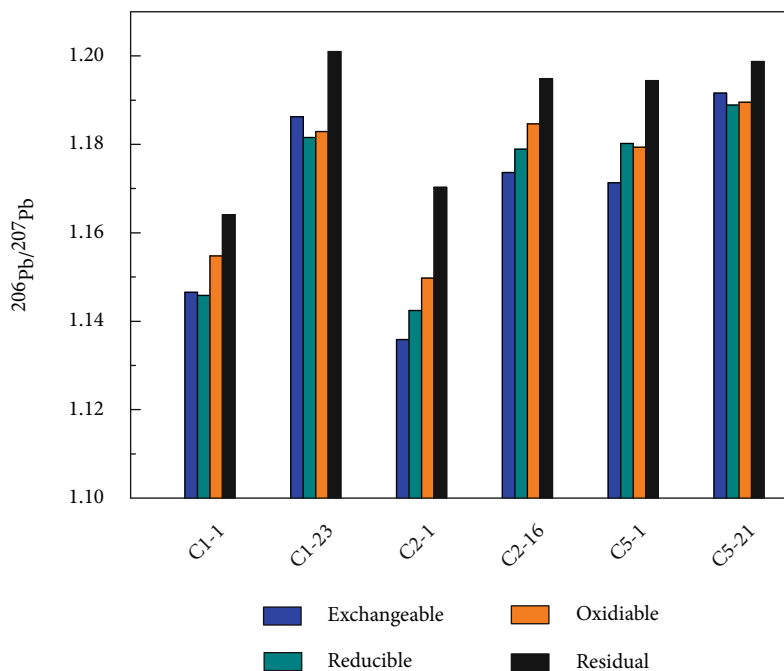


FIGURE 6: The Pb isotope ratios $^{206}\text{Pb}/^{207}\text{Pb}$ of topsoil and deep soil in different areas.

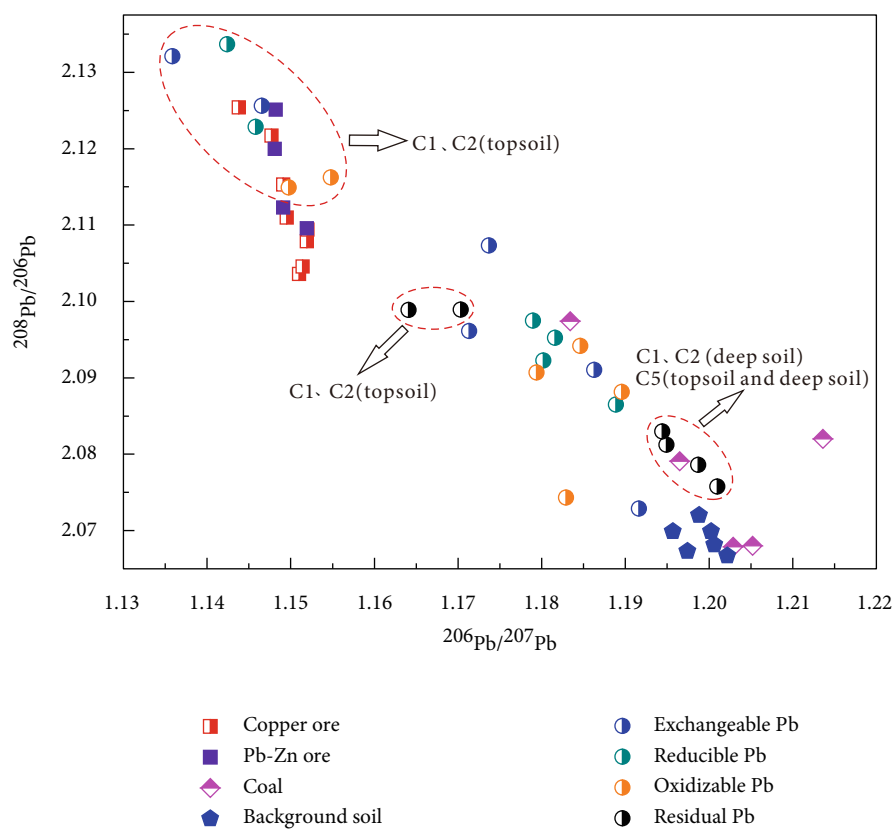


FIGURE 7: The Pb isotopic compositions ($^{208}\text{Pb}/^{206}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$) of topsoil and deep soil.

from anthropogenic sources (Figure 4, Table S2). For Baiyin area, the input of HMs in the soil around the mining area was mainly controlled by atmospheric transport and

deposition, while the sewage irrigation area was under the cooperative control of atmospheric deposition and water transport and was also significantly affected by the

degree of sewage irrigation. Therefore, the vertical distribution characteristics and enrichment depth of HMs in different regions of Baiyin area were not strictly consistent. This study can provide scientific guidance for the prevention and treatment of soil HM pollutants in Baiyin area.

3.3. Occurrence Species of HMs in Profile Soils. In soil and sediment, exchangeable HMs are the most unstable and easily absorbed and utilized by plants, followed by reducible specie, while the activity of oxidizable HMs is relatively poor, and the residual specie is generally considered to be the most stable. As shown in Figure 5 and Table S3, except for the two profile soils (C5 and C6) collected from the YRIA, the proportions of nonresidual HMs in the surface soil of the other four profile soils were much higher than that in the corresponding deep soil, indicating that there was a high activity and a risk of ecological environment on HMs in the surface soils from the mining and sewage irrigation area. In the surface soil of OD (C1), DSIA (C2, C3), and Shuichuan town (YRIA) (C6), the proportions of Cu, Pb, and Zn in the nonresidue fraction were much higher than that in the corresponding deep soil, indicating that the activities of Cu, Pb, and Zn in the surface soil were extraordinarily high. It should be noted that the proportions of Cu, Pb, and Zn in surface soil and deep soil of profile soil C3 were significantly higher than those of C1 and C2. Moreover, there were no significant differences in the proportions of Cu, Pb, and Zn in the surface soil and corresponding deep soil of XSIA (C4) and Silong town (YRIA) (C5), and the proportions of Cu, Pb, and Zn in C4 were higher than that in C5.

The residual fractions of Cd in all profile soils were small (0-10%), while the exchangeable fractions were dominant (40-94%). Except for the two profile soils (C5 and C6) in YRIA, the exchangeable Cd in the surface soil were higher than that in the corresponding deep soil, indicating that the activity of Cd in the soil was very high, especially in the surface soil. Besides, the occurrence species of Pb was also special. Compared with Cu, Zn, and Cd, the proportion of reducible fraction in Pb was the highest (34%-89%), showing the reducible > exchangeable > oxidizable. The contents of nonresidual Zn, with the maximum reaching 1487 mg/kg (C3 in DSIA), in the surface soil of mining area and sewage irrigation area were particularly high. The result indicated that the active Zn had a high content in surface soil of sewage irrigation, which also aggravated the risk of corresponding ecological environment.

3.4. Characteristics of Pb Isotopic Composition of Soils at Different Depths. Topsoil and deep soil of three profile soils (i.e., C1 in OD, C2 in DSIA, and C5 in YRIA) were chosen for the sequential chemical extraction experiment; meanwhile, the Pb isotopic composition of each fraction was analyzed. As shown in Figure 6, the Pb isotope ratios $^{206}\text{Pb}/^{207}\text{Pb}$ for the residual fractions were approximately 1.2010 and 1.1949 for the deep soil of OD and DSIA and 1.1944 and 1.1987 for the topsoil and deep soil in YRIA, respectively, which were all closed to the local soil back-

ground value (1.1992) [21]. The results clearly showed the obvious input characteristics of geogenic source. Moreover, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of all the nonresidue fractions were lower than those of the corresponding residual fractions, suggesting the different characteristics of HMs input from anthropogenic sources. In addition, the ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ in topsoil from OD and DSIA (C1 and C2) were significantly lower than those of corresponding deep soil, which indicated that the input of anthropogenic HMs in topsoil was higher compared with the C3 (in YRIA) which had little difference in the ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ between the topsoil and the deep soil, suggesting the limited impact of HM input from anthropogenic sources on soil in YRIA.

As shown in Figure 7, Pb isotopic compositions of the residual fractions in deep soil of the profile soils in OD and DSIA (C1 and C2) and the residual fraction in surface and deep soil in YRIA (C5) were all close to the values of local soil background end-member, and the relative contributions of anthropogenic HMs input were 0.0%, 8.7%, 9.6%, and 1.0% for deep soils in C1 and C2 and surface and deep soil in C5, respectively (Table S2), which indicated that there was no obvious input of HMs from anthropogenic sources. HMs mainly came from the geogenic source, causing a low environmental risk in these soils. The Pb isotopic compositions of the nonresidue fractions in the topsoil from the OD and DSIA (C1 and C2) were close to the end-members of local ore samples. The relative contributions of anthropogenic HM input in these soils were 89.2% and 100%, respectively (Table S2), indicating that the soils in OD and DSIA were greatly affected by mining, smelting, and other industrial activities. Besides, Pb isotopic compositions of other fractions were between the local ore samples and the soil background.

It was worth noting that Pb isotopic composition of the surface soil residual fractions in OD and DSIA (C1 and C2) were between the two HM end-members (anthropogenic and geogenic end-members), and the relative contributions of anthropogenic HMs in these soils were 70.5% and 58.0% (Table S2), respectively, which indicated that HMs from the anthropogenic sources might enter the residual fraction under certain conditions. This result was consistent with the residual HM contents measured by chemical sequential extraction experiment (Figure 5). In general, HMs in residual fractions mainly occurred in the lattice of silicate, primary, and secondary minerals. Therefore, in the case of no significant difference in soil mineral composition, the contents of residual HMs in surface and deep soil of the same profile soil sample should be similar. However, in OD and DSIA, the contents of residual HMs in surface soil was higher than that of in their corresponding deep soil (Figure 5). The above results confirmed that in the surface soils which were greatly affected by HM pollution, most of the anthropogenic HMs existed in the nonresidual components, and some might also exist in the residual components, which would reduce the overall activity of anthropogenic heavy metals to a degree. The specific mechanism needed advanced study.

4. Conclusion

In this work, we studied the distribution characteristics of typical HMs and Pb isotopic compositions in profile soils from different areas in Baiyin district, northwestern China. The results showed that, compared with the areas mainly suffered from the atmospheric deposition, sewage irrigation area was not only controlled by the coordinated control of atmospheric transport and water transport, but also greatly affected by the history of sewage irrigation, resulting in significant differences in the enrichment depth and the pollution degree of HMs in different regions. The vertical distribution characteristics of HMs and Pb isotopic composition in soil samples had a high correlation, indicating that the vertical enrichment of HMs in soil in Baiyin area was mainly caused by the industrial activities in OD. As the main components of soil, the contents of organic matter, iron and manganese oxides, might also affect the migration and enrichment of HMs in soil. The activity of HMs in surface soil of mining area and sewage irrigation area was higher, whereas that in surface and deep soil of YRIA were lower. The ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ of nonresidue fractions in all samples were lower than those in residual fractions, showing the different characteristics of HM input from anthropogenic sources. The ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ in topsoil from the OD and DSIA (C1 and C2) were significantly lower than those of corresponding deep soil, indicating that the input of anthropogenic HMs in topsoil was high. However, there was less difference of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of various speciation components in surface soil and deep soil among the samples (C3) irrigated by the Yellow River, which indicated that this area was less affected by the input of HMs from anthropogenic sources. HMs in soil nonresidue fractions mainly came from mining and smelting activities in OD. However, in the surface soil which was greatly affected by HMs pollution, some HMs from anthropogenic sources might also exist in residual components under certain conditions.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

There are no conflicts to declare.

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Supplementary Materials

Table S1: the vertical distribution of heavy metal concentrations, sulfur contents, soil organic matter contents, and Pb isotopic compositions in soil profiles. Table S2: the relative contributions of heavy metals from anthropogenic and geogenic sources of soil profiles in different sampling areas. Table S3: percentage contents and concentrations of heavy metals extracted from surface and deep soil samples in different soil profiles. (*Supplementary Materials*)

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