

Effects of heavy metal pollution on farmland soils and crops: A case study of the Xiaoqinling Gold Belt, China

Rui-ping Liu, You-ning Xu, Jiang-hua Zhang, Wen-ke Wang, Rafaey M Elwardany

Citation: Rui-ping Liu, You-ning Xu, Jiang-hua Zhang, Wen-ke Wang, Rafaey M Elwardany, 2020. Effects of heavy metal pollution on farmland soils and crops: A case study of the Xiaoqinling Gold Belt, China, China Geology, 3, 402-410. doi: 10.31035/cg2020024.

View online: https://doi.org/10.31035/cg2020024

Related articles that may interest you

Investigation of soil and groundwater environment in urban area during post-industrial era: A case study of brownfield in Zhenjiang, Jiangsu Province, China

China Geology. 2019, 2(4), 501 https://doi.org/10.31035/cg2018128

Deep gold mineralization features of Jiaojia metallogenic belt, Jiaodong gold Province: Based on the breakthrough of 3000 m exploration drilling

China Geology. 2020, 3(3), 385 https://doi.org/10.31035/cg2020048

LA-ICP-MS *in situ* analyses of the pyrites in Dongyang gold deposit, Southeast China: Implications to the gold mineralization China Geology. 2020, 3(2), 230 https://doi.org/10.31035/cg2018123

A new type U–Th–REE–Nb mineralization related to albitite: A case study from the Chachaxiangka deposit in the northeastern Qaidam Basin of China

China Geology. 2019, 2(4), 422 https://doi.org/10.31035/cg2018133

An integrated ore prospecting model for the Nyasirori gold deposit in Tanzania China Geology. 2019, 2(4), 407 https://doi.org/10.31035/cg2018127

Progress in the investigation of potash resources in western China China Geology. 2018, 1(3), 392 https://doi.org/10.31035/cg2018046







Journal homepage: http://chinageology.cgs.cn https://www.sciencedirect.com/journal/china-geology

Effects of heavy metal pollution on farmland soils and crops: A case study of the Xiaoqinling Gold Belt, China

Rui-ping Liu^{a, b, c, d,*}, You-ning Xu^{a, c, d}, Jiang-hua Zhang^{a, c, d}, Wen-ke Wang^e, Rafaey M Elwardany^{f, g}

^a Xi'an center, China Geological Survey, Ministry of Natural Resources, Xi'an 710054, China

^b Key Laboratory of Subsurface Hydrology and Ecological Effect in Arid Region of Ministry of Education, Xi'an 710054, China

° Key Laboratory for Geo-azards in Loess Area, Ministry of Natural Resources, Xi'an 710054, China

^d Field base of scientific observation of Shannxi Tongguan, Ministry of Natural Resources, Xi'an 710054, China

^e School of Environmental Science & Engineering of Chang'an University, Xi'an 710054, China

f School of Earth Science and Land Resources of Chang'an University, Xi'an 710054, China

^g Faculty of Science, Al-Azhar University, Assiut 71524, Egypt

A R T I C L E I N F O

Article history: Received 30 December 2019 Received in revised form 11 March 2020 Accepted 21 March 2020 Available online 7 August 2020

Keywords: Heavy metal pollution Crops Farmland Environmental investigation engineering of soil Xiaoqinling Gold Belt China

ABSTRACT

This paper focuses on the heavy metal enrichment and heavy metal pollution degree associated with mining activities in some crops and the soils of different parent materials in the Xiaoqinling Gold Belt. According to the geochemical analysis results of the soils observed in the gold belt, the soils are most highly enriched in Pb, followed by Cr, Cu, and Zn. Furthermore, they are relatively poor in Hg, Cd, and As. It is also shown that the heavy metals in all kinds of soils have the same geochemical characteristics in the gold belt. As for the crops (such as corn and wheat) in the gold belt, Zn and Cu are the most abundant elements, followed by Pb and Cr. Meanwhile, Hg, Cd, and As were found to have relatively low concentrations in the crops. The heavy metals in wheat and corn have the same geochemical characteristics in the gold belt in general. Compared to the aeolian loess soils and the crops therein, heavy metals are more enriched in diluvial and alluvial soils and the crops therein. As shown by relevant studies, the Hg, Pb, Cd, Cu, and Zn pollution are mainly caused by mining activities. Corn and wheat in the gold belt have a high tendency of risk exposure to heavy metal pollution since they are mostly affected by mining activities and feature high background values of heavy metal concentrations. Furthermore, wheat is more liable to be enriched in heavy metals than corn is grown in all types of soils. The Hg pollution in soils leads to Hg accumulation, increasing the risk of Hg uptake in crops, and further affecting human health. This study will provide a scientific basis for the control and management of heavy metals in farmland soils of mining areas.

©2020 China Geology Editorial Office.

1. Introduction

Once soils are contaminated by heavy metals, the heavy metals in the soils cannot be decomposed by physical or biological processes and may be accumulated by biota (He Y, 2008). Heavy metals not only affect the physicochemical properties of the soils but may also affect the ecosystem and human health (Xu YN et al., 2007). The development of metal resources, especially heavy metals, in farmland soils is one of the most important studies presently (Dai JR et al., 2018; Yan

HZ et al., 2018; Ding HJ et al., 2019; Alexander KA and Akoto R, 2018; Cai K et al., 2016). It also presents a big challenge to China where agriculture serves as the main industry while land resources are short and even other countries and regions in the whole world (Chu BB, 2009; Yong SO et al. 2011; Chen JD et al. 2012; Sun XP, 2013). Previous studies have shown that the increase in heavy metal content in wheat and corn plants near the mines that are under exploitation or abandoned is higher than in uncontaminated areas (Zeid AA et al. 2012; Sun QB et al. 2013). High-dose daily ingestion of heavy metals from crops may be the main cause of dropsy, skin ailments, cancers, and hepatopathy in mining areas (Singh N et al., 2008; Alothman ZA et al., 2012). Carcinogenic and non-carcinogenic health risk assessment of heavy metals exposure in gold mines has been

^{*} Corresponding author: E-mail address: lrp1331@163.com (Rui-ping Liu).

conducted (Belloa S et al., 2019). Scientists are increasingly aware of the concentrations, occurrence, bioavailability, and soil-to-crop transfer of heavy metals in farmland soils (Rai PK et al., 2019; Zhang JR et al., 2018; Doabi SA et al., 2018). Furthermore, according to relevant investigations, untreated industrial sewage and domestic wastewater irrigation have led to heavy metal contamination of agricultural soil-crop system (Li YP et al., 2019; Chaoua S et al., 2019). However, the concentrations of heavy metals in crops and soils consisting of different parent materials and the heavy metal pollution degree associated with mining activities are vet to be studied in mining areas. In this study, the heavy metal pollution of soils and farm crops in the Xiaoqinling Gold Belt was analyzed. This will provide a scientific basis for the environmental management of farmland (including farmland soil remediation) and the analysis of the effects of heavy metals in mining areas, aiming to ensure the safety of agricultural products.

The Xiaoqinling Gold Belt is the second largest gold mining area in China. It is located in the central part of China, adjacent to the Shaanxi-Henan boundary and along the west slope of the Xiaoqinling Mountains. The area is characterized by gold deposits of quartz vein type. According to large-scale mining of the gold deposits starting in the early 1970s, there are more than 1200 gold-bearing quartz veins, with an estimated Au reserve of 800 t and a proven Au reserve of 390 t (Yan HZ et al., 2018). Smelting activities are mainly conducted in the loess gully plateau, a region composed of fluvial terraces and alluvial fans (Fig. 1). The Xiaoqinling Gold Belt covers an area of about 1170 km², where wheat, corn, and other crops are grown. Gold mining and gold amalgamation may lead to heavy metal pollution of the soil environment as the soils are contaminated through wastewater irrigation, atmospheric dust deposition, and the leaching and runoff of tailings and slag. As suggested by previous research, heavy metal pollution of soils in mining areas has become one of the main environmental problems associated with mining activities (Fig. 2).

2. Research Methods

2.1. Sampling and analytical procedures

The Xiaoqinling Gold Belt is characterized by spatially varying soil environment and grows many important crops, which may lead to different geochemical processing degrees of minerals. Therefore, this paper mainly focuses on the accumulation of heavy metals in farm crops grown in different types of soils in the Xiaoqinling Gold Belt. The crops and the corresponding soils at a depth of 0–20 cm were collected following the investigation requirements of mining geo-environment, with sampling frequency set to 1 sample/1 km. Crops and soils were sampled on a one-on-one basis, and 84 sets of crop/soil samples were collected. The crops included wheat and corn, which are the primary crops grown in the area. The quincunx sampling method including soil sample collection, preparation, and storage (DB21T 1289–

2004) was adopted. According to this method, 2-3 sets of corn/soil samples were collected in every area with a length of 50 m, and then they were combined into one compound sample. After that, a quartering method was used to retain the weight of a sample to 1 kg. Soil samples were collected after scraping off the regolith on the surface and removing weeds, grass, roots, gravel, fertilizer, and other debris using bamboo as a sample shovel. Dry soil samples were successively sieved using a 60-mesh (250 µm) screen, placed into a plastic film bag, and sent to the lab for analysis. In the laboratory, the sieved samples were shattered and blended evenly using a high aluminum (Al) pot to reduce particle size (diameter) of the samples to 0.149 mm. Then the soils were analyzed to determine the concentrations of arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), mercury (Hg), lead (Pb), and zinc (Zn). The wheat and corn samples collected were processed indoors to obtain the "full" grains, which were then sent to the lab. As and Hg analyses of the soil and crop samples were conducted using AFS-230E dual-channel atomic fluorescence photometer in Beijing Kechuang Haiguang Instrument Co., Ltd. The Cd, Cr, Cu, Pb, and Zn analyses of soil samples were conducted using an Xseries2 inductively coupled plasma mass spectrometer (ICP-MS) produced by Thermo Fisher Scientific. The detection limits for As, Cd, Cr, Cu, Hg, Pb, and Zn in the soils are 2 µg/kg, 0.1 µg/kg, 0.05 µg/kg, 0.04 µg/kg, 2 µg/kg, 0.06 µg/kg, and 0.05 µg/kg, respectively. In contrast, the Cd, Cr, Cu, Pb, and Zn analysis of crop samples were conducted using the flame and graphite furnace atomic absorption spectrometer (F-AAS and GFAAS) manufactured by Analytik Jena AG from Germany. The detection limits for As, Cd, Cr, Cu, Hg, Pb, and Zn in the crops are 2 μ g/kg, 0.1 μ g/kg, 0.05 μ g/kg, 0.04 μ g/kg, 2 µg/kg, 0.06 µg/kg, and 0.05 µg/kg, respectively. Pulp was made from the crop samples of about 0.5-1 g and then was digested by nitric acid and hydrogen peroxide. The detailed steps are as follows: Place 0.5-1 g of dry crop samples into a polytetrafluoroethylene sample cup after being accurately weighed, then add 5 ml of HNO₃; soak the crops overnight (optional), and finally, add 1 ml of H2O2; after being immersed for 10 mins, the samples were loaded into digestion tanks, which were then placed in self-control closed microwave digestion unit; upon digestion, the aliquot was transferred to 25 ml colorimetric tubes and shaken; the As, Cd, Cu, Cr, Pb, and Zn analysis was conducted. Several national standard materials (GSB-2 or GSB-3) were also analyzed to assess analytical accuracy. Meanwhile, the results of multiple parallel sample tests were compared to determine the analytical precision. As a result, the precision was generally less than 5%.

2.2. Calculation of translocation factor

The translocation capability of heavy metals from the soil to the edible part of crops can be described using a transfer factor (TF). The soil-to-crop transfer factor (TF) was defined as follows:

$$TF = \frac{concentrat ion of heavy matals in crop(mg/kg)}{concentrat ion of heavy matals in soil(mg/kg)}$$
(1)

Agrochemical analysis of soils was carried out by standard techniques (Arinushkina EV, 1970).

3. Results

3.1. The heavy metal pollution of the different types of soils

Soil samples were collected from three kinds of soils, namely diluvial soils, alluvial soils, and eolian loess soils. As



Fig. 1. Distribution of crop and soil sampling locations in the Xiaoqinling Gold Belt, China.



Fig. 2. Remote sensing interpretation map of mining pollution sources in the study area.

used herein, the diluvial soils refer to the soils developed in sediments deposited by a river during flooding, and they are characterized by a mixture of sand, gravel, and loess; the alluvial soils are those developed in other types of sediments deposited by a river. The term eolian loess was defined by Richthofen FV in 1877 (Sun J, 2005). It refers to windblown particles with nearly uniform sizes, which may be transported and deposited outside of their original region (such as a desert). Loess is typically characterized by uniform particle sizes, large pores, and a loose structure. The eolian loess soils in the Xiaoqinling Gold Belt are mainly the Late Pleistocene Malan Loess, which consists of fine sandy powder after long-term cultivation, maturation, and fertilization.

According to the geochemical characteristics of the soils given in Table 1, Pb features the highest average metal content in the three kinds of soils, followed by Cr, Cu, and Zn, and the soils are relatively poor in Hg, Cd, and As. That is, the heavy metals in all types of soils have the same geochemical characteristics in the study area. The heavy metal concentrations in the diluvial and alluvial soils are higher than those in the eolian loess soils. Spatially, Pb, Zn, and Cu vary greatly compared to the other five elements in the soils. As compared with the second-level standard of soil environmental quality, the soils in the Xiaoqinling Gold Belt are mainly polluted by Hg, Pb, Cd, and Cu (the soils of second-level standard refer to those mainly suitable to use as general farmland for vegetables, tea, and orchards, with the soil quality not causing damage to plants or the environment).

The content of heavy metals in food grains grown on different soil parent materials is shown in Tables 2, 3. Zn and Cu are the most abundant heavy metal elements in the food grains, followed by Pb and Cr. Besides, Hg, Cd, and As were found to have relatively low concentrations in crops. In general, the heavy metals in wheat and corn in the study area have the same geochemical characteristics. The diluvial and alluvial soils are more liable to be enriched in heavy metals than the eolian loess soils. According to spatial statistics, Zn, Cu, and Pb elements in crops also vary spatially. Compared to food/crop standards (GB 2762-2005; GB13106-91) in terms of Pb concentrations, the grains may pose a risk to human health. Meanwhile, the maximum content and average content of heavy metals in wheat are far higher than those in corn (except for Pb).

3.2. Heavy metal content in unpolluted and polluted soils

To clearly show the statistical difference in the heavy metal content measured in wheat and corn grown on the

| Soil parent material | Statistical characteristic | Hg | Pb | Cd | Cr | As | Cu | Zn |
|---|----------------------------|-------|--------|-------|-------|-------|--------|--------|
| | | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg |
| Alluvial soil | Average | 1.96 | 408.23 | 1.26 | 53.18 | 8.93 | 116.64 | 89.64 |
| | Maximum | 17.43 | 4244 | 8.11 | 66.73 | 12 | 1278.0 | 265.41 |
| | Minimum | 0.09 | 28.66 | 0.19 | 40.24 | 6.9 | 17.49 | 57.24 |
| | Standard deviation | 3.7 | 845.9 | 1.8 | 4.8 | 1.1 | 248.7 | 49.6 |
| Eolian loess soil | Average | 1.244 | 126.16 | 0.56 | 55.42 | 9.24 | 10.97 | 32.74 |
| | Maximum | 7.374 | 560.6 | 1.222 | 61.36 | 11.79 | 16.58 | 50.30 |
| | Minimum | 0.066 | 25.95 | 0.191 | 51.15 | 7.77 | 4.84 | 19.40 |
| | Standard deviation | 1.8 | 114.3 | 0.3 | 2.3 | 0.9 | 24.6 | 26.6 |
| Diluvial soil | Average | 2.83 | 368.21 | 1.93 | 54.07 | 9.27 | 90.97 | 93.31 |
| | Maximum | 29.57 | 2940 | 11.31 | 60.86 | 12.4 | 594.90 | 206.01 |
| | Minimum | 0.12 | 21.1 | 0.15 | 46 | 7.53 | 15.39 | 53.18 |
| | Standard deviation | 5.9 | 613.6 | 2.7 | 3.7 | 1.2 | 125.6 | 41.2 |
| The second-level standard of soil environmental quality | | ≤1.0 | ≤350 | ≼0.6 | ≤250 | ≤25 | ≤100 | ≤300 |

Table 1. Content of heavy metals in the different types of soils.

| Table 2. | Content of heavy | metals in wheat o | n the different types | of soils. |
|----------|-------------------------|-------------------|-----------------------|-----------|
| | | | | |

| Soil parent material | Statistical characteristic | Hg | Pb | Cd | Cr | As | Cu | Zn |
|--|----------------------------|-------|-------|-------|-------|-------|-------|-------|
| | | mg/kg |
| Alluvial soil | Average | 0.01 | 0.66 | 0.08 | 0.37 | 0.05 | 4.21 | 23.11 |
| | Maximum | 0.08 | 1.69 | 0.33 | 1.06 | 0.15 | 5.50 | 29.00 |
| | Minimum | 0 | 0.06 | 0.01 | 0.13 | 0.02 | 3.19 | 15.00 |
| | Standard deviation | 0.0 | 0.4 | 0.1 | 0.2 | 0.0 | 0.6 | 3.6 |
| Eolian loess soil | Average | 0.01 | 0.56 | 0.05 | 0.47 | 0.05 | 4.08 | 20.61 |
| | Maximum | 0.05 | 1.56 | 0.14 | 0.88 | 0.14 | 7.88 | 30 |
| | Minimum | 0 | 0.06 | 0.02 | 0.19 | 0.025 | 2.94 | 13.00 |
| | Standard deviation | 0.0 | 0.4 | 0.0 | 0.2 | 0.0 | 0.8 | 4.2 |
| Diluvial soil | Average | 0.01 | 0.68 | 0.08 | 0.46 | 0.06 | 4.27 | 23.32 |
| | Maximum | 0.12 | 1.44 | 0.15 | 1 | 0.16 | 5.81 | 29.0 |
| | Minimum | 0 | 0.22 | 0.02 | 0.13 | 0.03 | 3.06 | 16.0 |
| | Standard deviation | 0.0 | 0.3 | 0.0 | 0.3 | 0.0 | 0.6 | 3.5 |
| Standards of contaminants in foods (GB 2762-2005; GB 13106-91) | | 0.02 | 0.2 | 0.1 | 1 | 0.5 | 10 | 50 |

| Soil parent material | Statistical characteristic | Hg | Pb | Cd | Cr | As | Cu | Zn |
|---|----------------------------|-------|-------|-------|-------|-------|-------|-------|
| | | mg/kg |
| Alluvial soil | Average | 0.002 | 0.87 | 0.07 | 0.15 | 0.02 | 1.38 | 10.97 |
| | Maximum | 0.006 | 1.95 | 0.21 | 0.31 | 0.05 | 2.18 | 16.58 |
| | Minimum | 0.00 | 0.18 | 0.01 | 0.08 | 0.01 | 0.81 | 4.84 |
| | Standard deviation | 0.0 | 0.5 | 0.1 | 0.1 | 0.0 | 0.3 | 2.7 |
| Eolian loess soil | Average | 0.002 | 0.47 | 0.05 | 0.14 | 0.02 | 1.25 | 10.81 |
| | Maximum | 0.005 | 1.51 | 0.16 | 0.26 | 0.08 | 2.08 | 15.61 |
| | Minimum | 0.00 | 0.08 | 0.00 | 0.05 | 0.00 | 0.84 | 6.95 |
| | Standard deviation | 0.0 | 0.4 | 0.1 | 0.1 | 0.0 | 0.3 | 2.4 |
| Diluvial soil | Average | 0.002 | 1.16 | 0.09 | 0.17 | 0.02 | 1.41 | 12.15 |
| | Maximum | 0.006 | 2.01 | 0.23 | 0.47 | 0.10 | 2.40 | 21.69 |
| | Minimum | 0.000 | 0.23 | 0.02 | 0.08 | 0.01 | 0.85 | 7.92 |
| | Standard deviation | 0.0 | 0.5 | 0.1 | 0.1 | 0.0 | 0.4 | 3.4 |
| Standards of contaminants in foods (GB 2762-2005; GB13106-91) | | 0.02 | 0.2 | 0.1 | 1.0 | 0.5 | 10 | 50 |

Table 3. Content of heavy metals in corn on the different types of soils.

different types of soils, the concentrations were converted into log values and plotted as box and whisker diagrams, as shown in Fig. 3. In this paper, the boxplots were prepared using the software ORIGIN7.5. T-test and f-test were carried out in the statistical process.

As shown content of heavy metal in soils, wheat, and corn in unpolluted and polluted soils consisting of different parent materials in Fig. 3, compared to unpolluted alluvial soils, the alluvial soils in the mining areas have much higher median and maximum concentrations of Hg, Pb, Cd, and Cu, a slightly higher concentration of Zn, and non-obviously different As and Cr content. Compared to the wheat grown in unpolluted alluvial soils, the wheat grown in the alluvial soils in the study area has far higher median concentrations of Cd, Hg, and Pb and similar concentrations of As, Cu, Cr, and Zn. As for the corn planted on alluvial soils, the content of the heavy metals in the study area is non-obviously different from that in polluted areas.

As shown in Fig. 3, compared to unpolluted eolian loess soils, the eolian loess soils in mining areas have much higher median and maximum content of Hg and Pb, slightly higher Cu and Zn content, and non-obviously different content of Cd, Cr, and As. Compared to the crops planted in unpolluted eolian loess soils, the crops planted in eolian loess soils in mining areas have lower average Pb content, and nonobviously different content of As, Cd, Cu, Cr, and Zn. Furthermore, the wheat grown on the eolian soils in the mining areas has a higher maximum and median concentrations of Hg than those grown in unpolluted eolian soils, while there is no significant difference in the Hg concentration in corn.

As also shown in Fig. 3, compared to unpolluted diluvial soils, the diluvial soils in the mining areas have a much higher median and maximum content of Cu, Cd, Hg, and Pb, slightly higher Zn content, and non-obviously different As and Cr content. Compared to the wheat grown in unpolluted diluvial soils, the wheat grown in the diluvial soils in mining areas has far higher median and maximum content of Hg, Pb, and Cd, and non-obviously different average concentrations of As, Cu,

Cr, and Zn. Meanwhile, compared to the corn grown in unpolluted diluvial soils, the corn grown in the diluvial soils in mining areas has non-obviously different concentrations of heavy metals.

3.3. Migration of heavy metals from soils to crops

The ability of heavy metal to move from soils to edible parts of crops can be described using the transfer factor (TF). The TFs of heavy metals from the alluvial soils to wheat are as follows. It can be seen from Fig. 4 [Transfer factors (TFs) of heavy metals calculated for the soils consisting of different parent materials] that the average TFs of Cu, Cd, and Zn in mining areas are lower than those in unpolluted areas, while average TFs of other heavy metal elements are non-obviously different in the two kinds of areas. However, the maximum TFs of Hg in mining areas are far higher than those in unpolluted areas, suggesting that mining activities promote the migration of Hg. As for the TFs of heavy metals from the alluvial soils to corn, the average TFs of Cu, Cd, and Zn in mining areas are lower than those in unpolluted areas, while the average TFs of other elements shows a non-obvious difference.

The TFs of heavy metals from eolian loess soils to wheat are as follows. It can be seen from Fig. 4 that the average TFs of Cd, Cu, Pb, and Zn calculated in mining areas are lower than those in unpolluted areas, while the average TFs of other heavy metal elements exhibit a non-obvious difference in the two kinds of areas. However, the maximum Hg TFs in mining areas are far higher than those in the non-polluted areas, implying that mining activities promote the migration of Hg from eolian loess to wheat grains. As for the TFs of heavy metals from eolian loess soils to corn, the average TFs of Cd in mining areas are lower than those in the unpolluted areas, while the TFs of other heavy metal elements exhibit a nonobvious difference in the two kinds of areas.

As for the TFs of heavy metals from diluvial soils to crops, the average and maximum TF values of Cu, Cd, and Zn in mining areas are lower than those in unpolluted areas (Fig. 4),

while the TFs of other heavy metal elements exhibit a nonobvious difference in the two kinds of areas.

4. Discussion

Tables 1-3 illustrate the difference in heavy metal concentrations in different kinds of soil parent materials in the study area. It can be seen that the diluvial and alluvial soils

are more liable to be enriched in heavy metals than the eolian loess soils. According to the comparison of the average content of heavy metals in wheat and corn, the content of the heavy metals in the crops grown in the three kinds of soils shows a similar rule, i.e., the crops in diluvial and alluvial soils are more liable to be enriched in heavy metals than the eolian loess soils. The difference may be mainly due to the different gradations of soil particles (Fig. 5). The increase in



Fig. 3. Content of heavy metal in soils (top row), wheat (middle row), and corn (bottom row) in unpolluted (left column) and polluted soils (right column) consisting of different parent materials. a–concentrations of heavy metals in unpolluted soils (log values); b–concentrations of heavy metals in polluted soils (log values); c–concentrations of heavy metals in unpolluted wheat (log values); d–concentrations of heavy metals in unpolluted wheat (log values); e–concentrations of heavy metals in unpolluted corn (log values); f–concentrations of heavy metals in polluted corn (log values).

clay content in soils may slightly increase the total content of heavy metals in the soils through the ionic exchange. Other factors affecting bioavailability include soil organic matter, pH, and Eh (Zhang JH et al., 2014).

Based on the above results presented in Fig. 5, it can be concluded that the pollution of Hg, Pb, Cd, Cu, and Zn is mainly caused by mining activities. Different types of soils have some different pollution performance. For example, the Cd content in eolian loess soils is different from that in the soils consisting of other two kinds of parent materials (i.e., diluvial soils and alluvial soils). However, elements with higher risks associated with mining activities are limited to Hg, Pb, and Cd in general, which are much more extensive than other heavy metal elements in soil pollution.

Mining activities appear to affect the heavy metal content in popular crops grown in the three kinds of soil parent materials. For example, mining activities affected the concentrations of Hg, Pb, Cd in wheat and corn grown in alluvial soils, eolian loess, and diluvial soils (Tables 1, 2).

As shown in Fig. 4, soil substrate with high-concentration heavy metals could inhibit some heavy metals (e.g., Cd, Cu, and Zn) from migrating into crops while promoting the



Fig. 4. Transfer factors (TFs) of heavy metals calculated for the soils consisting of different parent materials. a–TFs of heavy metals in unpolluted wheat; b–TFs of heavy metals in polluted wheat; c–TFs of heavy metals in unpolluted corn; d–TFs of heavy metals in polluted corn.



Fig. 5. Separator-size distribution of the soils consisting of different parent materials.

migration of other elements such as Hg. However, Cr and As content are basically not affected by mining activities. Then a concern is raised according to the data, i.e., why is Hg liable to migrate? Hg in soils is accumulated in roots through suction and moisture migration. In addition, Hg in the water containing organic and inorganic substances tends to have a certain affinity for a variety of chelating ligands. There exist two chemical forms of Hg in the soils with normal Eh and pH values, namely organic and inorganic forms. Inorganic mercury compounds include HgS, HgO, HgCO₃, HgHPO₄, HgSO₄, HgCl₂, and Hg(NO₃)₂, while organic mercury compounds include alkyl mercury, complex mercury, and organic mercury, and pesticides (Chen HM, 1996) such as $HgCl_2$, $Hg(NO_3)_2$, and methyl mercury. The latter is soluble, although more than 95% of the mercury is fixed quickly in sorption processes that take place through a series of transformation (Zhu X et al., 1996). Studies revealed that mercury transformation is closely related to soil quality and soil environment (Li LJ, 2015; Liu JH et al., 2001). In the case of irrigation-induced reduction, at least part of mercury in various substrates can be converted into soluble methyl mercury or methyl mercury complexes; both of them can increase the biological migration of mercury from soils into the plants, thus producing negative effects on plant growth (Wang YW and Wei FS, 1995).

The primary forms of inorganic mercury in the soils include $HgSO_4$, Hg (OH)₂, $HgCl_2$, and HgO, with relatively low concentrations, and the ability of Hg itself to migrate in soils is very weak. However, Hg^{2+} can be methylated as follows subject to the action of soil microorganisms:

$$Hg^{2+} \xrightarrow{Enzyme \text{ or anaerobe}} (CH_3)_2 Hg \leftrightarrow CH_3 Hg^+$$
(2)

In the case of sufficient oxygen, HgS can become soluble $HgSO_4$ —a chemical substance that can be formed by biological methylation process:

$$HgS + 2O_2 \rightarrow HgSO_4 \rightarrow CH_3Hg^+$$
(3)

Biologically, methyl mercury is a thousand times more toxic than Hg^0 because methyl mercury is strongly fat-soluble and thus is easy to cross the cell membrane and penetrate cells. As a result, it accumulates in organisms in a thousand times higher content than others in the accumulation sequence (from lowest to highest uptake): Hg^{2+} , CH_3Hg^+ , and CH_3HgCH_3 .

5. Conclusions

(i) Heavy metals are more liable to be enriched in the diluvial and alluvial soils than in eolian loess soils. This finding provides insights into polluted soil restoration and the reclamation of tailings and slag in the study area. It may be more favorable to choose uncontaminated eolian loess soils than diluvial soil and alluvial soils.

(ii) The Cu, Cd, Hg, Pb, and Zn elements mainly originate from mining activities. Different types of soils have different pollution performance. Mining activities combined with high background values of heavy metal concentrations will make the area unsuitable to grow mass crops of wheat and corn.

(iii) Polluted fine-grained substrates can inhibit some heavy metals (Pb, Cd, Cu, and Zn) from migrating from soils to crops but may promote the migration of Hg. This will increase the risks posed by Hg to crops and human health.

CRediT authorship contribution statement

Rui-ping Liu and You-ning Xu conceived of the presented idea. Rui-ping Liu developed the theory, performed the computations and verified the analytical methods. Rui-ping Liu and El-Wardany RM supervised the findings of this work. All authors discussed the results and contributed to the final manuscript.

Declaration of competing interest

The authors declare no conflict of interest.

Acknowledgment

This study was funded by the survey projects initiated by the Ministry of Natural and Resources of the People's Republic of China (DD20189220, 1212010741003, 1212011220224, and 121201011000150022), the Public Welfare Scientific Research Project launched by the Ministry of Natural and Resources of the People's Republic of China (201111020), the project of 2015 Natural Science Basic Research Program of Shaanxi (2015JM4129), and the project of 2016 Fundamental Research Funds for the Central Universities (open fund) (310829161128). The authors ' thanks also go to the experiment and testing lab of Xi 'an Center, China Geological Survey for the statistical analysis of the data conducted.

References

- Alexander KA, Akoto R. 2018. Assisted phytoremediation of heavy metal contaminated soil from a mined site with Typha latifolia and Chrysopogon zizanioides. Ecotoxicology and Environmental Safety, 148, 97–104. doi: 10.1016/j.ecoenv.2017.10.014.
- Alothman ZA, Naushad M, Khan MR, Wabaidur SM. 2012. A comparative study on characterization of aluminum tungstate and surfactant-based aluminum tungstate cation exchangers: Analytical applications for the separation of toxic metal ions. Journal of Inorganic and Organometallic Polymers, 22, 352–359. doi: 10.1007/ s10904-011-9594-3.
- Arinushkina EV. 1970. Manual for soil chemistry analysis. Moscow, Moscow University Publishing House.
- Belloa S, Nasirub R, Garbab NN, Adeyemo DJ. 2019. Carcinogenic and non-carcinogenic health risk assessment of heavy metals exposure from Shanon and Bagwai artisanal gold mines, Kano state, Nigeria. Scientific African, 6, 00197–00203. doi: 10.1016/j.scitotenv.2019. 06.414.
- Cai K, Du YM, Luan WL, Li Q, Ma YC. 2016. Geochemical behavior of heavy metals Pb and Hg in the farmland soil of Hebei plain. Geology in China, 43(4), 1420–1428 (in Chinese with English abstract). doi: 10.12029/gc20160425.

Chaoua S, Boussaa S, Gharmali AE, Boumezzough A. 2019. Impact of

irrigation with wastewater on an accumulation of heavy metals in soil and crops in the region of Marrakech in Morocco. Journal of the Saudi Society of Agricultural Sciences, 18, 429–436. doi: 10.1016/j.jssas.2018.02.003.

- Chen HM. 1996. The Soil Heavy Metal Pollution in a Plant System. Beijing, Science Press, 1–9 (in Chinese).
- Chen JD, Dai QG, Xu XH, Zhong XC, Guo BW, Zheng C, Zhang HC, Xu K, Huo ZY, Wei HY. 2012. Heavy metal contents and evaluation of farmland soil and wheat in a typical area of Jiangsu Province. Acta Ecologica Sinica, 32(11), 3487–3496 (in Chinese with English abstract). doi: 10.5846/stxb201105080598.
- Chu BB. 2009. The Pollution Research on Heavy Metals in Farmland Soil around Lead-Zinc District, Nanjing Qixiashan. Wuhan, China University of Geosciences, Master dissertation (in Chinese with English abstract).
- Dai JR, Pang XG, Song JH, Dong J, Hu XP, Li XP. 2018. A study of geochemical characteristics and ecological risk of elements in soil of urban and suburban areas of Zibo City, Shandong Province. Geology in China, 45(3), 617–627 (in Chinese with English abstract). doi: 10.12029/gc20180314.
- Ding HJ, Lei TG, Nie YN, Ji HB. 2019. Characteristics and Interactions of heavy metals with humic acid in gold mining area soil at an upstream of a metropolitan drinking water source. Journal of Geochemical Exploration, 200, 266–275. doi: 10.1016/j.gexplo. 2018.09.003.
- Doabi SA, Karami M, Afyuni M, Yeganeh M. 2018. Pollution and health risk assessment of heavy metals in agricultural soil, atmospheric dust and major food crops in Kermanshah province, Iran. Ecotoxicology and Environmental Safety, 163, 153–164. doi: 10.1016/j.ecoenv. 2018.07.057.
- He Y. 2008. The Research on Heavy Metals Pollution of Soil and Cropper in Typical Area of Plain in the North of Zhejiang Province. Xi'an, Chang'an University, Master dissertation, 15 (in Chinese with English abstract).
- Li LJ. 2015. Delayed Geochenmical Hazard and Soil Environmental Quality Assessment of Hg in the Soil of Qiu Village. Chengdu, Chengdu University of Technology, Ph.D. dissertation, 1 (in Chinese with English abstract).
- Li YP, Wang SL, Nan ZR, Zang F, Sun HL, Zhang Q, Huang W, Bao LL. 2019. Accumulation, fractionation and health risk assessment of fluoride and heavy metals in soil-crop systems in northwest China. Science of the Total Environment, 663, 307–314. doi: 10.1016/j/ sitotenv.2019.01.257.
- Liu JH, Chen LT, Wang WH, Shen ZM, Peng A. 2001. The estimation of mercury deposition in Beijing. Journal of environmental science, 21(5), 643–645 (in Chinese with English abstract). doi: 10.13671/ j.hjkxxb.2001.05.030.
- Rai PK, Lee SS, Zhang M, Tsang YF, Kim KH. 2019. Heavy metals in

food crops: Health risks, fate, mechanisms, and management. Environment International, 125, 365–385. doi: 10.1016/j.envint.2019. 01.067.

- Singh N, Kumar D, Raisuddin S, Sahu AP. 2008. Genotoxic effects of arsenic prevention by functional food –jaggery. Cancer Letters, 268(2), 325–330. doi: 10.1016j.envint.2019.01.067.
- Sun J. 2005. Richthofen and his theory of the eolian origin of loess. Quaternary Sciences, 25(4), 438–433 (in Chinese with English abstract).
- Sun QB, Yin CQ, Deng GF, Zhang L. 2013. Investigation on heavy metal contamination of farmland Soil and wheat (Triticum Aestivum) mearby mining Areas. Journal of Henan Agricultural Sciences, 42(4), 80–84 (in Chinese with English abstract).
- Sun XP. 2013. Study of the different concentrations of lead, zinc to ecotoxic effects of maize growth. Territory & Natural Resources Study, 1, 57–60 (in Chinese with English abstract).
- Wang YW, Wei FS. 1995. Soil environmental element chemistry. Beijing, China Environmental Science Press, 133–134 (in Chinese).
- Xu YN, Ke HL, Zhao AN, Liu RP, Zhang JH. 2007. Assessment of heavy metals contamination of farmland soils in some gold mining area of Xiao Qinling. Journal of Soil Science, 38(4), 732–737 (in Chinese with English abstract).
- Yan HZ, Zhou GH, Sun BB, He L, Liu YF, Hou SJ. 2018. Geochemical characteristics of the bayberry producing area in Longhai, Fujian. Geology in China, 45(6), 1155–1166 (in Chinese with English abstract). doi: 10.12029/gc20180606.
- Yong SO, Adel RA Usman, Sang SL, Samy AM A El-A, Bonysu C, Yohay H, Jae EY. 2011. Effects of rapeseed residue on lead and cadmium availability and uptake by rice plants in heavy metal contaminated paddy soil. Chemosphere, 85, 677–682. doi: 10.1016/j.chemosphere.2011.06.073.
- Zeid AA, Rahmat A, Abdulaziz MA, Jawad A, Mohamed AH. 2012. Assessment of toxic metals in wheat crops grown on selected soils of Khyber Pukhtoon Khaw, Pakistan, irrigated by different water sources. Arabian Journal of Chemistry, 4, 1878–5352. doi: 10/1016/j.arabjc.2012.04.006.
- Zhang JH, Wang KY, Li H, Chen HQ, Ke HL, Liu RP, Zhao AN. 2014. Factors affecting bioavailability of heavy metal elements Pb and Cd in the soil of the Tongguan gold ore district and their significance. Geological Bulletin of China, 33(8), 1188–1195 (in Chinese with English abstract).
- Zhang JR, Li HZ, Zhou YZ, Lei D. 2018. Bioavailability and soil-to-crop transfer of heavy metals in farmland soils: A case study in the Pearl River Delta, South China. Environmental Pollution, 235, 710–719. doi: 10.1016/j.envpol.2017.12.106.
- Zhu XC, Qing CG, Pi GJ. 1996. The study of soil mercury forms and their influencing factors. Journal of Soil, 33, 194–100 (in Chinese with English abstract).