Factors Affecting the Levels of Pb and Cd Heavy Metals in Contaminated Farmland Soils

Jianghua ZHANG
Northwestern Polytechnical University
Shaaxi, 710072, PR China
e-mail: 53235266r@qq.com

Yaoguo WU
Northwestern Polytechnical University
Shaaxi, 710072, PR China
e-mail: wuygal@nwpu.edu.cn

Youning XU
Xi'an Center of Geological Survey, CGS
Shaanxi, 710054, China
e-mail: ksdzhj@sohu.com

Abstract—**The toxicity and bioavailability of heavy metals depends upon characteristics of the surrounding soil matrix. To assess the risk of heavy metals in soil, it is necessary to understand the relationships between the heavy metals and other soil chemicals. Lead (Pb) and cadmium (Cd) in soils affected by gold mining in China were studied. The influences of organic matter, cosmids and pH on the bioavailability of Pb and Cd were determined. Soil organic matter and pH were the main factors influencing bioavailability of Pb and Cd. The total amount of Pb or Cd was positively associated with soil organic matter content but the levels of water-soluble and ion-exchangeable Pb and Cd decreased when organic matter increased. Soil cosmids did not significantly affect the bioavailability of Pb and Cd. Activity and bioavailability of heavy metals increased with low soil pH, while the content of Cd in the carbonated and ferric-manganese oxidation states increased. For farmland soil contaminated by Pb and Cd, the use of organic fertilizers and soil maintenance at neutral to alkaline pH can help reduce heavy metal risks in agricultural products.**

Keywords-bioavailability; soil; lead; cadmium; gold mine

I. INTRODUCTION

Gold mining soil is often polluted with heavy metals that result from mining activities. Methods for remediation of heavy metal contaminated soils have been intensively studied. The persistence and toxicity of heavy metals pose a threat to the health of humans and other species through direct contact and passage into the food chain. The reduction or elimination of heavy metal soil contaminants is urgently needed for protection of the environment and human health. See [1-3].

Heavy metal toxicity is influenced by both concentration and by distribution. The availability of a heavy metal in soil refers to the amount that can be absorbed by plants or other organisms. The accumulation, migration and transformation of a heavy metal in soil are affected by several factors and a variety of physical and chemical effects. These include biological processes in the soil system as well as the soil organic and inorganic component capabilities for absorbing the heavy metal ions in the solid phase. Plant capability for adsorption and enrichment of heavy metal ions is related to the amount and bioavailability of the element in the soil and also affected by plant species, soil properties, light intensity, and temperature. See [4]. Therefore, it is important to study transformation forms of heavy metals in soil. This provides a better understanding of the environmental effects on restoration of the heavy metal contaminated soil through these transformations.

The Xiaoqinling goldfield has frequently been used to study heavy metal pollution and prevention. After many years of mining, the heavy metals, which are one of the "three wastes" in the mining industry, have polluted the soils of the gold mining district through dust fallout, use of mining waste water for crop irrigation, and tailing waste leaching. The main soil contaminant is a complex mixture of Hg-Pb-Cd. This finding is based on an examination of the accumulation of heavy metal elements and damages within the Xiaoqinling goldmine district in surface water, groundwater, soils, crops, and human hair. See [5-9]. The migration and transformation characteristics of Hg in this goldfield have been studied. See [10]. The relationship between amounts of heavy metals in the soil and different forms and bio-availabilities as well as contents within organisms has also been examined. See [11]. However, factors affecting and controlling the chemical changes of heavy metals in the Xiaoqinling goldfield remain undefined. We chose two typical pollutants of gold mining, Pb and Cd, for analysis of the main factors influencing the chemical forms of heavy metals and bioavailabilities related to different geochemical landscape types. We also determined the migration and accumulation of Pb and Cd, and provide data useful for the restoration of Pb and Cd polluted soil and reduction of Pb and Cd in agricultural products.

II. SITE DESCRIPTION

The Xiaoqinling gold mining region is the second largest gold producing area in China. It is located in the eastern Shaanxi and western Henan provinces (N 34°29'–34°35' and E 110°11'–110°34') (Figure 1). The

average, annual rainfall is 587.4 mm and the average annual evaporation is 1193.6 mm. This area has a warm temperate continental semi-arid climate. The main soil types in the research area are sand clay, loam, loess and river silt soil. Soil moisture content ranges from 15–20%.

Figure 1.   Location of the study region.

III.   MATERIALS AND METHODS

A total of 79 soil samples were collected from the plowed soil surface layer (0–20 cm), at the rate of one sample per 2 km², within 4 geochemical landscapes. These were alluvial slope tableland, gully region of the loess plateau, Yellow River alluvial plain, and Shuangqiao river terrace (Figure 2). Soil was air dried, sifted by 20-mesh, and 1 kg samples were packed into plastic bags. These samples were sent to the Hefei Mineral Resources Supervision and Inspection Center, Hefei Anhui province, China. (The lab is authorized by China Metrology Accreditation, is located in Hefei Anhui province. China). Samples were processed by grinding in aluminum bowls to achieve a particle size diameter of <0.097 mm (<200 mesh). Pb and Cd content was studied using inductively coupled plasma mass spectroscopy (Nexion 350x. PE). The Cd and Pb detection limits were 30 ng/g, and 2 μg/g, respectively. The pH value was studied using a Phs-3C acidometer. The organic matter in soil was studied by High-TOCn. The 7 forms of each heavy metal, including the water-soluble state, ion-exchangeable state, carbonate state, humic acid state, ferric-manganese oxidation state, strong organic state and residual state, were analyzed using a Forstner continuous extraction approach (extractants were H_2O, $MgCl_2$, CH_3COONa, $Na_4P_2O_7$, $NH_2OH \cdot HCl$ and HNO_3).

The morphological analysis procedure was as follows: (1) Water soluble state: weigh 2.50 g of 100 mesh sample, transfer to a 250 mL polyethylene beaker, add 25 mL distilled water, ultrasonically extract for 30 min, centrifuge to separate, filter the supernatant using a 0.45 μm membrane, use the AFS method to determine heavy metals, wash precipitate with fresh water, discard the aqueous phase, and retain the precipitate. (2) Ion exchange state: add 25 mL $MgCl_2$ solution to the precipitate, shake to mix, ultrasonically extract for 30 min, centrifuge to separate, keep the supernatant for further tests, wash the precipitate using water, discard the aqueous phase, and retain the precipitate. Take 10 mL supernatant, add 5 mL HCl, increase the volume to 25 mL, shake well, and adopt AFS method to determine heavy metals. (3) Carbonate-bound state: add 25 mL sodium acetate solution to the precipitate, shake well, ultrasonically extract for 60 min, centrifuge to separate and retain the supernatant for further test, wash the precipitate using water, discard the aqueous phase, and retain the precipitate. Take 10 mL supernatant, add 5 mL HCl solution, increase the volume to 25 mL, shake well, and use the AFS method to determine heavy metals. (4) Humic acid-bound state: add 50 mL sodium pyrophosphate solution to the precipitate, shake well, ultrasonically extract for 40 min, let stand for 2 h, then centrifuge to separate, retain the supernatant for further tests, wash the precipitate using water, discard the aqueous phase, and retain the precipitate. Put 25 mL supernatant into a 50 mL beaker, add 15 mL nitric acid solution and 3 mL perchloric acid solution, heat until the white smoke of perchloric acid is completely evaporated, add 5 mL (1+1) HCl to dissolve the salts, increase the volume to 25 mL, shake well, and use the AFS method to determine heavy metals. (5) Iron and manganese oxide-bound state: add 50 mL hydroxylamine hydrochloride-hydrochloric acid solution to the precipitate, shake evenly, ultrasonically extract for 60 min, centrifuge to separate, retain the supernatant for additional tests, wash the precipitate using water, discard the aqueous phase, and retain the precipitate. Take 20 mL supernatant, add 5 mL HCl solution, increase the volume to 25 mL, shake well, and use the AFS method to determine heavy metals. (6) Organic-bound state: add 3 mL HNO_3 solution and 5 mL H_2O_2 to the precipitate, shake well, keep in a water bath at 83 ℃ for 1.5 h, add 2.5 mL ammonium acetate-nitrate mixture, increase the volume to 25 mL, stand for 10 h and then centrifuge to separate, dilute the supernatant to 50 mL and retain for further test, wash the precipitate using water, discard the aqueous phase, and retain the precipitate. Put 25 mL supernatant into a 50 mL beaker, add 10 mL nitric acid solution and 1 mL perchloric acid solution, heat till the white smoke of perchloric acid is all evaporated, 5 mL (1+1) HCl to dissolve the salts, increase the volume to 25 mL, shake well, and use the AFS method to determine heavy metals. (7) Residual state: dry, ground and weigh the residue, and calculate the residual correction coefficient d. Then weigh 0.20 g residue, add 15 mL HNO_3 and 3 mL $HClO_4$, heat until the white smoke of $HClO_4$ evaporates for 2 min, extract using hydrochloric acid, increase the volume to 25 mL, and use the AFS method to determine heavy metals.
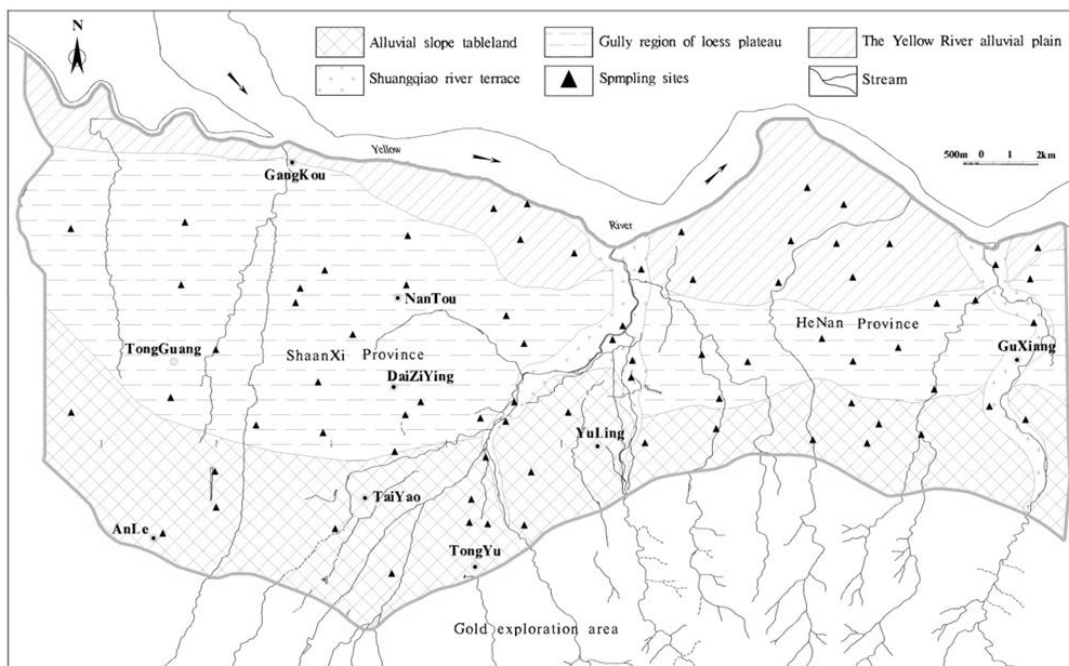
Figure 2.   Sample locations and landscape distribution.

Soil size samples were collected from unscreened unprocessed field soil and dispersed. Samples and dispersants were introduced into a laser grain instrument (measuring range from 0.02 mm to 2000 mm), and soil particle diameters were recorded by computer. The particle diameters were the diameters of equivalent particles based on the actual particles. Irregular particles were transferred to the diameter of equivalent particles using equivolumetric principles.

The test results were simulated by data dynamic equations of Origin 8.0 (Origin lab Corporation, USA, 2008), and monadic regression analysis. Significance tests as well as the correlation analysis were conducted using DPS2005 (data processing system developed by Zhejing University, 2005).

IV.   RESULTS AND DISCUSSION

A. *Effects of Gold Mining on Pb and Cd Bioavailability*

Compared with the heavy metal content in soil from the western development zone, Pb and Cd values in the gold mining area were higher by 6.5 and 2.8 times respectively. Compared with the average heavy metal content in Guanzhong China, Pb and Cd values in the gold mining area were higher by 10.5 and 10.8 times respectively. Compared with the values of China's Land Quality Standards (GB15618-1995), Pb and Cd values in the gold mining area exceeded the standards by 1.2 and 2.6 times respectively. The high concentration region of heavy metals includes patches along the Shuangqiao River where mining activity is concentrated. Pb residues are typically associated with Au and Cd is associated with Zn. In the processes of gold mining a portion of the heavy metals is released as dust, which is spread by wind and is eventually deposited on regional soils.

B. *Effects of Organic Matter on Pb and Cd Bioavailability*

Animal, plant and microorganism residues decompose and become soil organic matter including humus and bimolecular. Bimolecular mainly comes from dead cells, faeces, and some biomolecules by the leaching effects of rain. Soil humus includes mostly stable materials, and some partially decomposed organic matter undergoing biological and physico-chemical processing. Soil organic matter also includes secretions of animals and microbes. These secretions can be decomposed in soil and absorbed by organic and inorganic matter to form compounds involved with soil acidification and weathering. Organic matter content is an important index of soil fertility. The content varies considerably in different soils but it is usually below 5% in the surface layer of agricultural soil. See [12].

Table I shows the organic content of soils by region. The percentages of organic matter in agricultural soils were all below 2%. The maximum organic matter percentage was found in the Piedmont pluvial oblique tableland soil and the minimum organic matter percentage was in the Yellow River alluvial plain. However, the differences of organic matter among the soil parent materials were minor, ranging from 0.77% to 1.05% and averaging 0.92%.

TABLE I.   MASS FRACTION OF ORGANIC MATTER IN THE SOILS OF DIFFERENT GEOCHEMICAL LANDSCAPES

Geochemical landscape types	Organic matter/%			Number of Samples
	Min.	Max.	Avg.	
alluvial slope tableland	0.47	1.86	1.05	22
gully region of loess plateau	0.28	1.50	0.86	32
Yellow River alluvial plain	0.40	1.31	0.77	14
Shuangqiao river terrace	0.37	1.50	0.99	11

The percentage of organic matter in soil controls the geochemical activities of heavy metals, affecting soil productivity and ecological processes. See [13]. Organic matter influences mobility and bioavailability of heavy metals by electrostatic adsorption and by coordination and chelation. The mobility of heavy metals is limited by attachment to solid organic matter, but dissolved organic matter, which contains active radicals such as N and O, probably also combines with heavy metals, increasing their mobility. See [14]. In theory, organic matter in soil has two influences on the fate of heavy metals. Each influence is based on specific environment conditions. Figure 3 and Figure 4 show the relationship between soil organic matter in gold mining areas and the total amount of Pb and Cd. Soil organic matter is positively correlated to the amount of Pb and Cd, indicating that the soil organic matter can directly influence the amount of Pb and Cd in the soil (Figure 3).
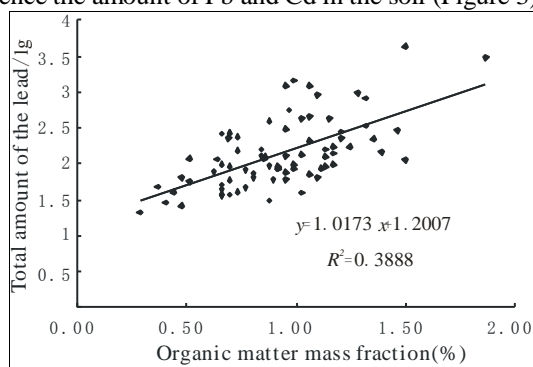
The main effects are ion exchange, complexation, and adsorption. Under certain pH values, the maximum adsorption of Cd is significantly correlated to levels of organic matter and iron-aluminum oxides ($R^2 = 0.804$, confidence coefficient $P < 0.05$) See [15]. Heavy metal behavior is influenced by interactions with organic matter. Humus contains a large number of functional groups, which play key roles in forming chelates. The heavy metal ions chelated by humus can be immobilized in the soil, significantly reducing risks to ecological systems. See [16].

$y=-0.0002x+0.0031$

$R^2=0.0016$

Figure 5.   Correlation between soil organic matter mass fraction fraction and Pb bioavailability

$y=1.0173x+1.2007$

$R^2=0.3888$

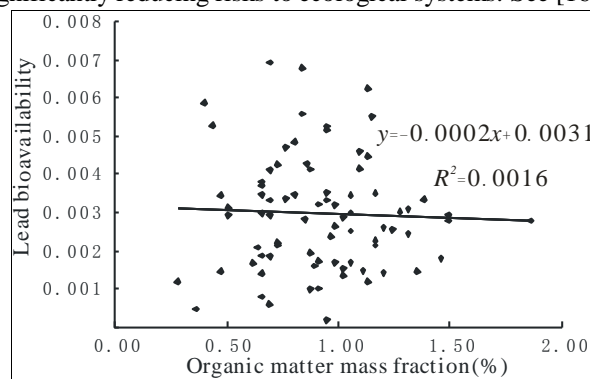Figure 3.   Correlation between soil organic matter mass fraction and the total amount of Pb

$y=0.7731x-0.8729$

$R^2=0.3187$
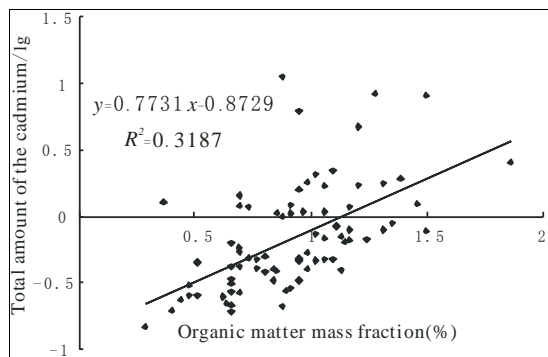
Figure 4.   Correlation between soil organic matter mass fractionand the total amount of Cd.
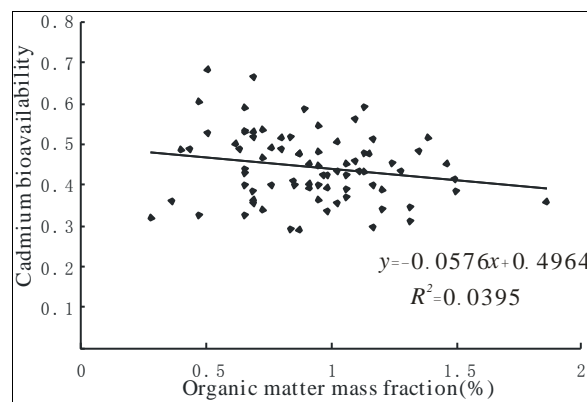

$y=-0.0576x+0.4964$

$R^2=0.0395$

Figure 6.   Correlation between soil organic matter mass and Cd bioavailability.

Figures 5 and 6 show low correlation between the mass fraction of organic matter and available forms of Pb and Cd. Increased organic matter in soil reduces the ion state and exchangeable states of Cd. Cd in these states moves into crop plants more readily. Application of organic fertilizer

may improve the safety of agricultural products produced in farmland contaminated by Pb and Cd. See [17]. This may occur because organic fertilizer and humus have a strong affinity for adsorbing heavy metals and reducing free metal ions in soil solutions.

C. Effects of Cosmid Contents in the Soil on the Bioavailability of Pb and Cd

Clay minerals, with diameters < 2 μm, adsorb Pb and Cd ions and reduce their activity. Colloidal clay minerals carry a large number of negative charges on their surface and the number of the exchangeable cations exceeds that of anions. See [18]. Soil capacity for absorbing and exchanging ions is a fundamental factor of its capacity for reducing heavy metal pollution. Various components of soil have different adsorption ability for heavy metals. The adsorption function of clay minerals such as aluminosilicate and oxides plays an important role in attenuating the toxicity of heavy metal elements by bonding and rendering them temporarily inactive. The total amount of absorbed heavy metal depends upon the amount of exchanged soil cations, which is affected by clay mineral types, surface areas, adsorption sites, and ionic strength. See [10]. It is therefore reasonable to conclude that the development stages of the cosmid in the soil have an influence on the chemical interactions of heavy metals.

TABLE II. COSMID CONTENT IN SOILS FROM DIFFERENT GEOCHEMICAL LANDSCAPES

Geochemical landscape type	Cosmid/%			Number of Samples
	Min.	Max	Avg.	
alluvial slope tableland	11.74	18.99	16.73	22
gully region of loess plateau	9.99	23.95	16.66	32
Yellow River alluvial plain	8.58	14.22	11.19	14
Shuangqiao river terrace	7.79	17.04	14.22	11

Table II shows cosmid levels of different geochemical landscapes in the study area. The amount of cosmid is between 7–17% in the surface area of cultivated soil. In spite of the different terrain partition, there is no significant difference in the amounts of cosmids in the soil, which ranges from 11.19 to 17.73. Geology theory suggests that in the parent materials comprising the sediments in the piedmont alluvial areas, the particles should be coarse and rough. However, the percentage of the cosmid located at the piedmont pluvial fan in Qiaoqinling area is slightly higher than the other three landscape types. In the Yellow River alluvial plain, in contrast, loess composed of sediments from the fluvial facies had the least amount of cosmid. This

phenomenon may have resulted from the following. In the Yellow River alluvial plain, the topsoil sand bed vanished due to prolonged cultivation, or the continuous downward leaching of the cosmid that makes the clay particles in the plow pan. In the alluvial slope tableland, it is affected by both the loess and the proluvial, which creates an even distribution of the sands and results in a relatively high cosmid content in the surface soil. Ordered, highest to lowest, by average percentage amount of cosmid, the alluvial slope tableland is greatest followed by the gully region of loess plateau, Shuangqiao river terrace, and the Yellow River alluvial plain.
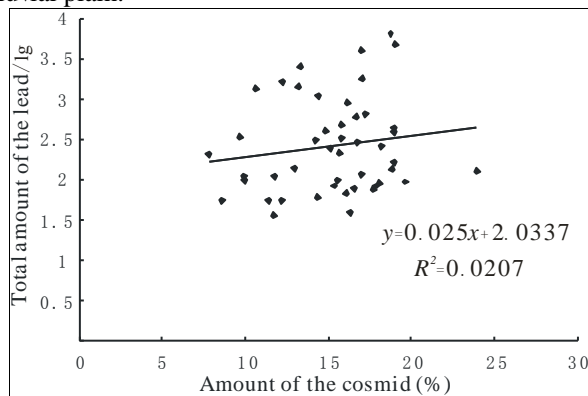

$y = 0.025x + 2.0337$

$R^2 = 0.0207$

Figure 7. Correlation between the cosmid content and total amount of lead in the soil.
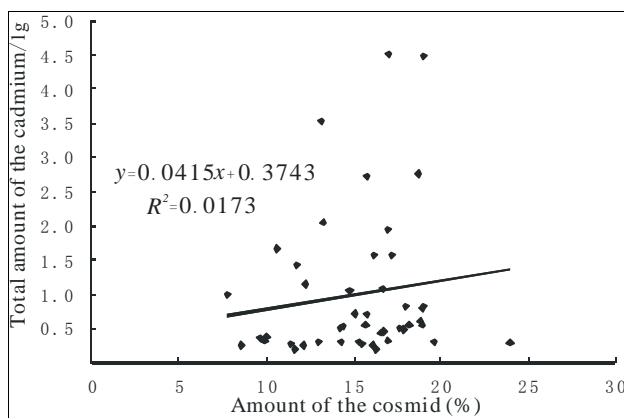

$y = 0.0415x + 0.3743$

$R^2 = 0.0173$

Figure 8. Correlation between the cosmid content and total amount of cadmium in the soil.

Figures 7 and 8 indicate that there is no significant relationship between the total amount of Pb and Cd and content of the cosmid in the soil, which suggests that the amount of the cosmid may not play an effective role in the accumulation of Pb and Cd in the soil.
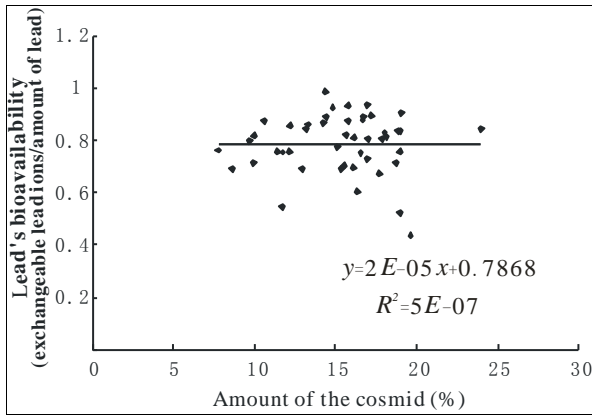
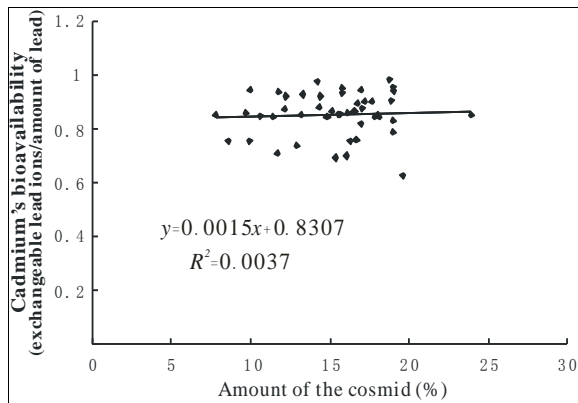Figure 9. Correlation between amount of the cosmid and Pb bioavailability.

Figure 10. Correlation between amount of the cosmid andCd bioavailability

Figures 9 and 10 show the relationship between the contents of the cosmid and bioavailability of Pb and Cd, measured by the ratio of exchangeable ions in the total. There is no evidence that soil clay influences the ionic state of the two metals. The amount of the cosmid in farmlands of the gold mining district appears to have no significant effect on the heavy metal bioavailability.

D. Effects of Soil pH to the Bioavailability of Pb, Cd

Soil pH alters the effectiveness of heavy metals by influencing the composition and charge characteristics of the soil heavy metals-precipitation/dissolution, adsorption/desorption and ligand/dissociation equilibrium. The microbial activity can also indirectly affect the metal validity. See [14,18-20].

TABLE III. SOIL PH FROM DIFFERENT GEOCHEMICAL LANDSCAPES

Geochemical landscapes types	pH			Number of Samples
	Min.	Max.	Avg.	
Alluvial slope Tableland	8.04	8.42	8.24	22
Gully region of loess plateau	8.07	8.66	8.34	32
Yellow River alluvial plain	8.01	8.59	8.37	14
Shuangqiao river terrace	7.91	8.48	8.22	11

Table III shows that among the different geomorphological units, the Yellow River alluvial plain soil had the highest pH value, and the soil of river terraces had the lowest pH value. The soil pH of the different geomorphic units showed only minor differences, ranging from 8.22 to 8.37, with a mean value of 8.29. The soils in the study area are alkaline. Under alkaline conditions, the majority of heavy metals in the soil occur as hydroxides, which are not easily absorbed by plants and are less subject to migration. See [21].
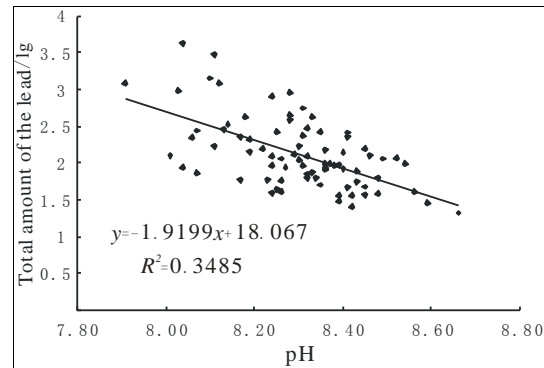

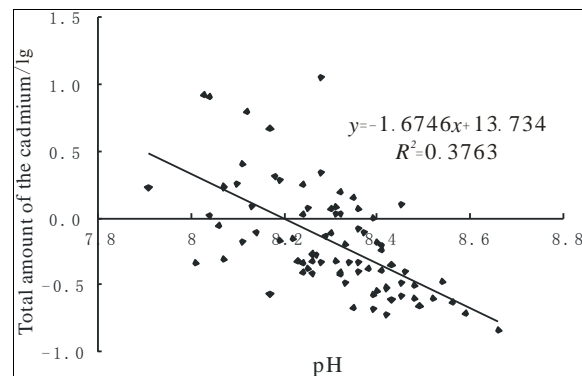Figure 11. Correlation between soil pH and total amount of Pb.

Figure 12. Correlation between soil pH and total amount of Cd.

Figures 11 and 12 show significant negative correlations between soil pH and the content of Pb and Cd. Soil acidification increases the accumulation of Pb and Cd in soil.
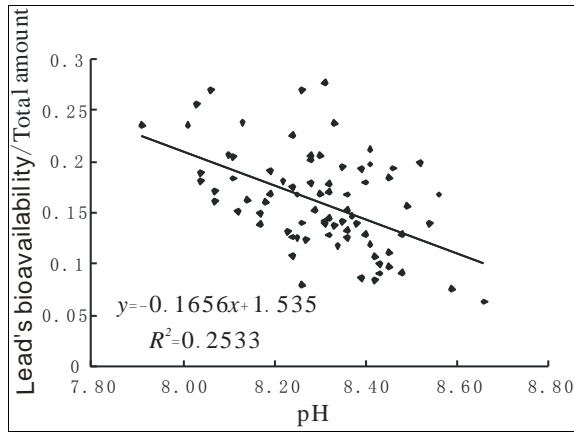

Figure 13. Correlation between soil pH and lead bioavailability.
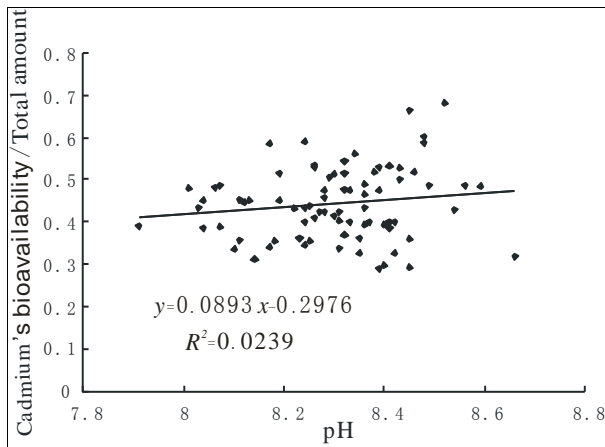

Figure 14. Correlation between soil pH and Cd bioavailability.

There is no correlation between the proportions of the effective states and soil pH. Thus, we determined the tendency analysis of the proportions and soil pH. The proportions include the water soluble state, ion-exchangeable state, humic acid state, and the strong organic state which accounted for the total soil carbonate state accounts for total soil; ferric-manganese oxidation state accounts for total soil respectively. Figure 13 shows the negative correlation between the effective state of Pb and the soil pH. It indicates the effect of pH on the activity of Pb ions, which is reflected by the negative correlation between Pb (water soluble state + ion-exchangeable state + humic acid state+ strong organic state) and the soil pH. Figure 14 shows that in a slightly alkaline soil, Cd content (water soluble state + ion-exchangeable state + humic acid state+ strong organic state) may increase slightly as the soil pH increases.
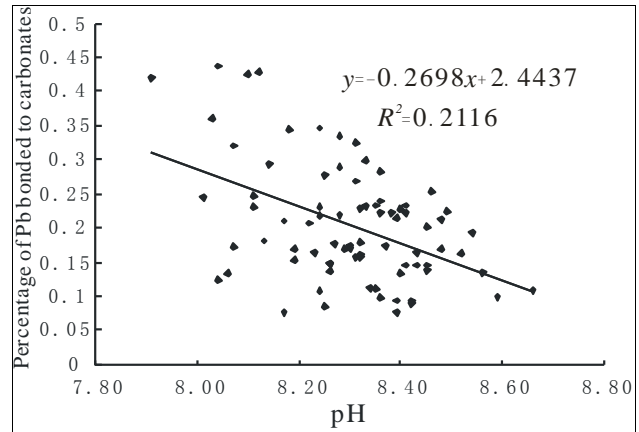

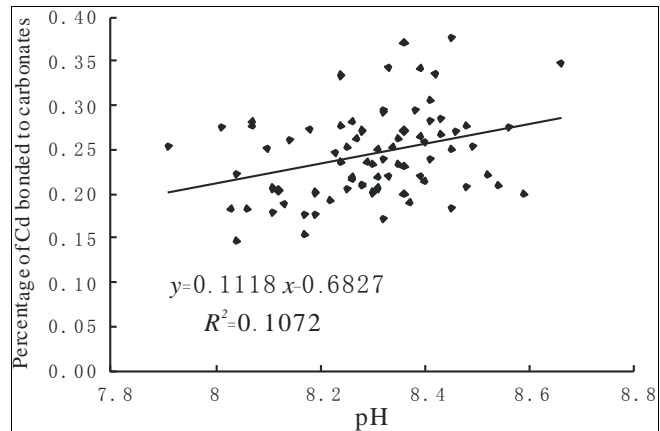Figure 15. Correlation between soil pH and the percentage of Pb bonded to carbonates.

Figure 16. Correlation between soil pH and the percentage of Cd bonded to carbonates.

Figure 15 shows a negative correlation between the percentage of Pb bonded to carbonates and soil pH. The content of Pb bonded to carbonates shows a trend consistent with Pb (water soluble state + ion-exchangeable state + humic acid state+ strong organic state).The percentage of Cd bonded to carbonates is positively correlated with the soil pH (Figure 16). This indicates that, under alkaline conditions, the increased content of Cd in carbonate form will enhance the Cd bioavailability.
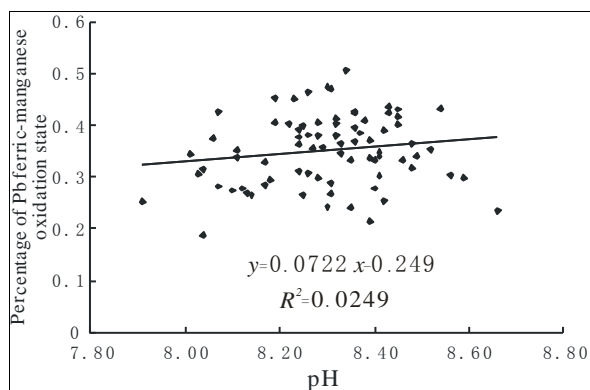
Figure 17. Correlation between soil pH and the percentage of Pb ferric-manganese oxidation state.
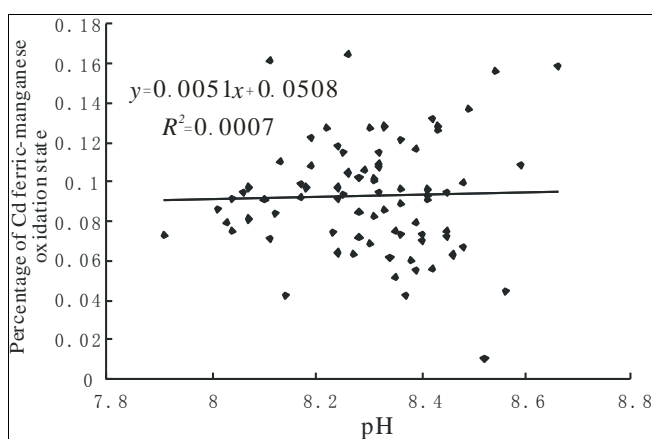

Figure 18. Correlation between soil pH and the percentage of Cd ferric-manganese oxidation state.

Figures 17 and 18 illustrate the relationship between the levels of of Pb and Cd ferric-manganese oxidation state and soil pH changing. The correlation between these variables is not significant. There is a slight tendency for the content of Pb and Cd ferric-manganese oxidation state to increase with soil pH. This may be caused by the desorption of specific adsorption of Pb and Cd.

The bioavailability of Pb and Cd have different responses to soil pH. For Pb, a lower pH improves the distribution of Pb in the soil, and promotes transformation from the carbonate-bound state to the ion-exchangeable state. Since the ion-exchangeable state is more active than the carbonate-bound state, bioavailability is enhanced. For Cd, a higher soil pH will increase the content of the carbonate-bound state and ferric-manganese oxidation state. If the pH of heavy metal contaminated soil can be modified, it should be maintained in a narrow range between weak acid and mildly alkaline.

V. CONCLUSIONS

Correlations between organic matter, clay particles, pH and Pb and Cd content show that soil organic matter and pH are main factors influencing the biological effectiveness of Pb and Cd in the soil.

Organic matter in soil is positively correlated with the total content of Pb and Cd. When organic matter content increased, the water soluble and ion exchange states of Pb and Cd decreased. Increasing levels of organic fertilizer may reduce the migration of Pb and Cd and improve the safety of agricultural produce.

The study region is arid to semi-arid. Heavy metal ions adsorbed by soil is the main method of transfer from an unsaturated solution to the solid phase. However, the percentage of clay matter in this area lies within a small range (7–17%) so this probably has a minor impact on the bioavailability of Pb and Cd.

Although lower soil pH will increase the activity of heavy metal ions, and enhance bioavailability, excessive pH may increase the carbonate state and ferric-manganese oxidation state of Cd. Therefore, considering the entire Pb and Cd soil contamination area, soil acidification should be avoided and soil should be maintained within a pH 7 ± 1 range. Also soil salinization should be controlled.

REFERENCES

[1] Luo Y.M., *Contaminated Site Remediation in China: Progresses, Problems and Prospects*. The Administration and Technique of Environmental Monitoring. 23 (2011), pp. 1–6.

[2] Han C.M., Wang L.S., and Gong Z.Q., *Chemical forms of soil heavy metals and their environmental significance*. Chinese Journal of Ecology. 24 (2005), pp. 1499–1502.

[3] Wang H.B., Shu W.S., and Lan C.Y., 2005. *Ecology for heavy metal pollution: recent advances and future prospects*. Acta Ecologica Sinica. 25 (2005), pp. 597–605.

[4] Zhou Q.X., and Huang G.H., *Environmental biogeochemistry and global environmental change*, Science Press, Beijing, 2001.

[5] Xu Y.N., Ke H.L., and Zhao A.N., *Assessment of Heavy Metals Contamination of Farmland Soils in Some Gold Mining Area of XiaoQinling*. Chinese Journal of Soil Science. 38 (2007), pp. 732–736.

[6] Xu Y.N., Zhang J.H., and Chen S.B., *Distribution of Contents of Heavy Metals in Soil Profile Contaminated in Different Ways in Xiaoqinling Gold Mining Area*. Journal of Agro-Environment Science. 27(2008), pp. 200–206.

[7] Xu Y.N., Zhang J.H., and Zhao A.N., *Evaluation of the potential ecological risk of heavy metals in farmland soils in a certain gold mining area, Xiaoqinling*, Geological Bulletin of China. 27(2008), pp. 1272–1278.

[8] Xu Y.N., Zhang J.H., and Xie.J., *Contrast analysis on heavy metals contents in villagers' hair in contaminated areas of the Xiaoqinling gold belt*. Geological Bulletin of China. 27(2008), pp. 1279–1285.

[9] Xu Y.N., Zhang J.H., and Zhao A.N., *Water and soil contamination and environmental effect in a certain gold area in Xiaoqinling*. Hydrogeology and Engineering Geology. 36 (2009), pp. 131–134.

[10] Dai Q.J., Feng X.B., and Qiu G.L., *Preliminary study on mercury contamination in gold mining in gold mining in Tongguan County of Shaanxi Province*, Environmental Chemistry. 23 (2004), pp. 460–464.

[11] Wang X.W. *The Research about the Relationship between Heavy Metals Contamination and Crops on Farmland Soil in the Goldfield*, Ph.D. diss., Chang'an University, 2010.

[12] Mou S.S., and Qing C.L., *Environmental Edaphology*, China Agriculture Press, Beijing, 1999.

[13] Pyatt F B,Pyatt A J, and walker C., *The heavy metal content of skeletons from an ancient metalliferous polluted area in southern Jordan with particular reference to bioaccumulation and human health*, Ecotoxicol Environ Saf. 60(2005), pp. 295–300.

[14] Luo Y.M., 2009. *Soil environment and ecological safety*, Science press, Beijing, 2009.

[15] Bolton A., *Cadmium adsorption capacity of selected on triosoils*. Canadian Journal of Soil Science. 2(1996), pp. 183–187.

[16] Buffle J., *Complexation reactions in aquatic systems*, Ellis Horwood, Chichester, 1988.

[17] Huang C.Y., *Edaphology*, China Agriculture Press, Beijing, 2000.

[18] Yang Z.F., Chen Y.L., and Qian X., *A study of the effect of soil pH on chemical species of cadmium by simulated experiments*, Earth Science Frontiers. 12(2005), pp. 252-260.

[19] Yu T., Yang Z.F., and Zhong J., *Factors affecting the geochemical behavior of heavy metal elements Pb and Cd in soil*, Earth Science Frontiers. 15(2008), pp. 67-73.

[20] Mo Z., Wang C.X., and Chen Q., *Form Distribution and Transformation of Heavy Metals of Cu, Pb, Zn, Cr and Cd in Soils*, Journal of Agro-Environment Science. 21 (2002), pp. 9–12.

[21] Hu N.J., Luo Y.M., and Huang P., *X-Ray Adsorption Spectroscopic Evidence for the Formation of Pb(II)Inner-Sphere Adsorption Complexes and Precipitates at the Alkaline Soil-Water Interface*, Spectroscopy and Spectral Analysis. 31 (2011), pp. 560–564