Cd pollution and ecological risk assessment for mining activity zone in Karst Area

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Abstract. The monitored soil samples were collected from farmland in the area with mining activity in Karst area in Liupanshui. In this article, moss bag technology and TSP were used simultaneously for Cd transportation and deposition in the study area. Geostatistics and GIS were then used for the spatial distribution of Cd in the soil. Afterwards, Cd pollution to the soil environment and human health was studied by using the geo-accumulation index and potential ecological risk index methods. The results indicated that atmospheric deposition is the major route of Cd pollution. A moderate to strong pollution of Cd in the area and the degree of potential ecological risk was in a high level in the study area. Furthermore, Cd pollution in Liupanshui may originate from mining activity and atmospheric deposition.

1. Introduction
Cadmium (Cd) is one of air pollutant which is harmful to human beings [1], and it plays a key role in the agricultural soil quality which has been a hot topic in the field of environmental research in recent years [2].

One of the important environment issues today is the pollution due to atmospheric deposition. Atmosphere works as a part of environment and has a significant effect on the ecosystem. Atmospheric deposition is a kind of circulation from earth to atmosphere through the earth’s surface. Atmospheric deposition helps the transportation of trace metal in environment, while it’s the main external origin of bio-available heavy metal in the environment [3]. There are reports on atmospheric deposition which is the main route for exchange of substances between the land surface and atmosphere and the atmospheric Cd content in urban area and rural areas and industrial district. Nriagu [4] reported atmospheric deposition made crucial contribution to Cd content in soil as external source. Atmospheric deposition has been one of global environmental problems and has led to the effect of agricultural soil interface with potential ecological risk.

A series of ecological environmental problems (e.g. water and soil loss) in Guizhou Province due to Karst environment is fragile and vulnerable [5]. Mining activities in Karst area as rich mineral resource regions cause heavy metal emission from atmosphere to the soil [6].

Guizhou Province has abundant lead and zinc resources. During the process of zinc or lead smelting, Cd is obtained as a by-product and can be emitted into atmosphere [7, 8]. The variation of metallic element ratio and equilibrium concentration in soil pose is a potential ecological risk to the local field. The study is focused on determining the atmospheric deposition of Cd and concentration level of agricultural soil. The potential ecological risk of surrounding agricultural soil is assessed as well.
2. Material and methods

2.1. Sampling collection

2.1.1. Study site. In the study, the effect of gradient atmospheric sediment of Cd to soil was evaluated in the primitive zinc production area.

300 samples were collected within an area of 50 km² in Laoingshan town (N 26°30’, E 105°03’), which is located in Shuicheng (a town in Liupanshui area), Guizhou Province (the sampling points showed in figure 1). The samples were collected at a depth of 20 cm at different distances.

![Figure 1. Location of the soil samples.](image1)

2.1.2. Sampling and analytical methods. Moss-bag techniques were used for domestic investigation of deposition of mercury in mercury and zinc production area [9, 10].

![Figure 2. The geometry dimension of moss bag.](image2)
Fabrication Method of Moss Bag *Hypnum plumaeforme* Wils (with > 6 cm height) from Fanjing Mountain with good environment conditions was collected for packing moss bag. The chosen *H. plumaeforme* was cleaned with distilled water and immersed in 0.5 mol/L HCl for 24 hours and rinsed thoroughly with distilled water before drying. Dry moss (~3.2 g) was packed in a small nylon net with a mesh of 1.5 × 2.0 mm [11]. The installed bag with 100 cm² surface area is shown in figure 2. In addition, the concentration of Cd in moss was measured for eight times, and the average blank value of Cd was 0.077 mg kg⁻¹.

2.1.3. Monitoring of Moss Bag. The bags were exposed to the air by hanging 3-3.5 m off the ground and were away from the main road at least 100 m. Samples were collected from downwind direction. Each sample was collected with covered and uncovered moss bag, while total deposition of Cd was collected for 30 days under normal climate in 2005. All sites were dried at 60±2°C and weighed with loss <5%.

2.2. Geo-accumulation index

The geo-accumulation index (Igeo) for Cd concentrations was calculated by using the following formula [12, 13].

\[ I_{\text{geo}} = \log_2 \left( \frac{C_n}{k\cdot B_i} \right) \]

where, \( C_n \) = measured concentration of Cd (mg/kg) in soil; \( B_i \) = geochemical background value (mg/kg) of the element in the background sample; \( k \) = factor introduced to minimize the effects of possible due to lithogenic effect [14, 15]. The Cd background value in the primitive zinc production area was chosen as \( B_i \). The classification of pollution degree is shown in table 1. In the study, \( B_i \) is 0.31 mg·kg⁻¹ [16].

| Igeo value | Igeo Class | Pollution level |
|------------|------------|----------------|
| ≤0         | 0          | Unpolluted     |
| 0-1        | 1          | Unpolluted to moderately polluted |
| 1-2        | 2          | Moderately polluted |
| 2-3        | 3          | Moderately to strongly polluted |
| 3-4        | 4          | Strongly polluted |
| 4-5        | 5          | Strongly to very strongly polluted |
| >5         | 6          | Very strongly polluted |

2.3. Potential ecological risk assessment

The methods for heavy metal potential ecological risk assessment including Geo-accumulation Index (GI), Sediment Enrichment Factor Method (SEF), Toxicity Characteristic Leaching Procedure (TCLP), Potential Ecological Risk Index (PERI) etc. were used [17-22]. In the study, PERI method was to evaluate heavy metal contamination from the perspective of sedimentology. PERI was calculated by using the following formula:

\[ RI = \sum E_i = \sum \left[ T_i \left( C_i^t / C_i^r \right) \right] \]

where \( E_i \) = potential ecological risk index of single element; \( T_i \) = toxic-response factor for the given element (i.e. Cd=30); \( C_i^t \) = concentration of given element in the soil; \( C_i^r \) = reference value of given element.
Table 2. Classification of PERI parameters.

| E<sub>i</sub> | RI   | Potential ecological risk grade |
|-------------|------|--------------------------------|
| <40         | <150 | Low                            |
| 40-80       | 150-300 | Moderate                      |
| 80-160      | 300-600 | Considerable                  |
| 160-320     |       | High                           |
| >320        | >600 | Very high                      |

2.4. Geostatistical analysis

Semi-variogram was used for analyzing the spatial variability in a region. The formula is:

\[
\gamma(h) = \frac{1}{2} \text{Var}[Z(x + h) - Z(x)]
\]

Where \(\gamma(h)\) measures the mean variability between two points \(x\) and \(x+h\), as a function of their distance \(h\) [23]. The geostatistical analysis was carried out using GIS 9.3. Based on the fitted semi-variogram models, the ordinary Kriging provided by the software Arc/GIS 9.3 was used to map the distribution of heavy metals.

3. Results and discussion

3.1. Cd concentration in soil

In order to study the extent of metal contamination in this area, investigation of Cd concentration in soil at various distance to the zinc working industries are recorded. Table 3 shows the distribution of Cd from selected sites of the zinc production area. Exponential curve of the trend of Cd pollution in soil of zinc-smelting area is shown in figure 3. The average concentration decreased along the distance to the zinc working industries.

Table 3. Concentration of Cd in different distance of soil samples in farmland.

| Distance (km) | Average (mg kg<sup>-1</sup>) | Max (mg kg<sup>-1</sup>) | Min (mg kg<sup>-1</sup>) | SD | CV (%) |
|---------------|-------------------------------|---------------------------|--------------------------|----|--------|
| 5             | 3.68                          | 3.92                      | 3.37                     | 0.16 | 4.3%   |
| 10            | 2.75                          | 3.06                      | 2.44                     | 0.17 | 6.2%   |
| 15            | 2.32                          | 2.76                      | 1.89                     | 0.25 | 10.8%  |
| 20            | 2.01                          | 2.44                      | 1.63                     | 0.22 | 10.9%  |
| 25            | 2.53                          | 2.89                      | 2.02                     | 0.21 | 8.1%   |
| 30            | 1.54                          | 1.82                      | 1.25                     | 0.17 | 11.3%  |
| 35            | 1.34                          | 1.66                      | 0.98                     | 0.22 | 16.4%  |
| 40            | 0.91                          | 1.14                      | 0.76                     | 0.11 | 12.0%  |
| 45            | 0.68                          | 1.04                      | 0.33                     | 0.22 | 31.8%  |
| 50            | 0.52                          | 0.84                      | 0.22                     | 0.21 | 40.4%  |
3.2. Cd deposition rate by Moss-bag techniques
The Cd content in 3.2 g moss indicates the Cd deposition rate during 30 days in the investigated area. The ratio of dry deposition rate ranged from 58% to 96%, with an average of 79%. It showed that dry deposition accounts a large proportion of total deposition rate. Therefore, the process of Cd to the mark from the atmosphere is a gravitation-induced mechanism which corresponds to the report.

Table 4. Deposition rate of Cd by monitoring of moss bag.

| Distance/ (km) | Total Deposition Rate/(mg·m²·mon⁻¹) | Dry Deposition Rate/(mg·m²·mon⁻¹) | Dry/Total (%) |
|---------------|-------------------------------------|-----------------------------------|--------------|
| 5             | 8.14                                | 4.72                              | 58%          |
| 10            | 5.18                                | 3.62                              | 70%          |
| 15            | 3.59                                | 2.12                              | 59%          |
| 20            | 1.43                                | 1.35                              | 94%          |
| 25            | 0.91                                | 0.86                              | 95%          |
| 30            | 0.43                                | 0.31                              | 72%          |
| 35            | 0.24                                | 0.23                              | 96%          |
| 40            | 0.16                                | 0.12                              | 75%          |
| 45            | 0.09                                | 0.08                              | 89%          |
| 50            | 0.05                                | 0.04                              | 80%          |

3.3. Estimation of pollutant indicators
The Geo-accumulation index value of Cd from 2.25 to 3.66 indicates a range of Geo-accumulation index class from 3 to 4. It showed all the sediments in these stations were moderately contaminated to be strongly polluted by Cd.

3.4. Potential ecological risk assessment
Potential ecological risk indexes for Cd in the topsoil were computed, and the value ranged between 143 and 380. Mean value of Cd was 241 and represents high level of potential ecological risk. The graph showed the ecological risk assessment of the study area. The primitive zone area along the wind direction indicated a very high level of potential ecological risk as shown in figure 4.

Figure 3. The trend of Cd pollution in soil along the wind direction in the area.
3.5. Geostatistical analysis

The results of the best-fit spatial model and model parameters are shown in Table 5. In Table 5, $C_0$ is nugget, $C_1$ is sill, and $A$ is range. The nugget/sill ratios were <25%, suggesting that the variable had strong spatial dependence. The ratios were between 25% and 75%, suggesting that the variable had moderate spatial dependence. The ratios were >75%, suggesting the variable had weak spatial dependence [24]. The ratio of Cd was 44.6%, showing that the factors had moderate spatial dependence.

**Table 5.** Semivariance function model and parameters of Cd content.

| Sample Size | Model   | Nugget | Sill   | Range  | Nugget/sill |
|-------------|---------|--------|--------|--------|-------------|
| 300         | Gaussian| 0.0906 | 0.2031 | 0.0291 | 0.446       |

**Figure 4.** Spatial distribution of potential ecological risk index of Cd.

**Figure 5.** Spatial distribution of Cd content in topsoil.
Karst Area in Guizhou showed a high Cd background level due to mining activity. The characterization (rich in calcium and magnesium, alkaline) of Karst ecosystem indicated soil heterogeneity. Because the karst environment is sensitive and fragile, it is impossible to be restored once destroyed. The present repair mechanism of heavy metal pollution in other area is not applicable for Karst environment. Therefore, a series of researches about heavy metal pollution in karst area can provide a different theoretical system for Cd pollution. The topsoil in the study site has a high-level risk of Cd pollution which caused by mining activity as showed in the result of PERI and pollutant indicators as shown in figure 5.

4. Conclusion
Cd content in TSP, soil and the deposition rate of Cd decreased with the distance away from the pollutant source. Eighty percent dry deposition is the dominated process of Cd to the mark from the atmosphere. It suggested that dry deposition determination is better due to the loss of moss bag derived from the effect of precipitation to the total deposition rate. Furthermore, heavy metal potential ecological risk assessment was done based on Geo-accumulation Index (GI) and potential ecological risk index (PERI) method. The calculation indicates all the sediments in these stations were from moderately to strongly pollute by Cd and a high level of potential ecological risk to the study area by Cd. Nugget/sill ratio implied that Cd pollution in Liupanshui may have originated from mining activity and atmospheric deposition.

In the polluted central zone, the usage of soil is classified based on legislation “Soil Pollution Control Plan” for release the impact on Cd pollution [25]. In order to protect this area, more risk assessment and agricultural quality investigation should be done in this area and we need an integrated control system for water-soil-agricultural products. On the other hand, several measures helped decrease the impact on Cd pollution, including culturing microbial communities, spraying organic fertilizer, increasing the pH value of soil and planting less solanaceae.

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References
[1] He Z L, Zhou Q X and Xie Z M 1998 Balance of Soil Beneficial and Harmful Elements (Beijing: China Environmental Science Press)
[2] Egwurugwu J N, Ufearo C S, Abanobi O C, et al 2007 Effects of ginger (Zingiber officinale) on Cd toxicity Afr. J. Biotechnol. 6(18) 2078-82
[3] Quan Q, Ying C, Qingwei M A, Wang F, Xi M and Bo W 2016 The impact of atmospheric deposition of cadmium on dominant algal species in the east china sea J. Ocean Univ. Chin. 15(2) 271-82
[4] Nriagu J O 1984 Changing Metal Cycles and Human Health (Berlin: Springer)
[5] Xiao D, Zhang W, Xiong K, et al 2009 Study on Karst landscape spatial pattern based on remote sensing and GIS Proc. Spie 7498 74981D-7
[6] Lin W J, Xiao T F, Zhou W C, Ao Z Q and Zhang J F 2009 Environmental concerns on geochemical mobility of lead, zinc and cadmium from zinc smelting areas: Western Guizhou, China Environ. Sci. 30(7) 2065-70
[7] Zhou Q X 1994 Cd contaminated soil ecosystem and its theoretical model release mechanism Journal of Zhejiang University (Natural Science) 28 283-44
[8] Sun T H, Zhou Q X and Li P J 2001 Pollut. Ecol. (Beijing: Science Publisher)
[9] Tan H, He J L and He T T 1997 Study of Hg deposition near a Hg mine by moss bag adsorption Environ. Sci.18(6) 71-2
[10] Xie F, Tan H, Yang B, et al 2014 The study of atmospheric transport and deposition of Cd emitted from primitive Zinc production area Water Air Soil Pollut. 225(11) 1-7
[11] Temple P J 1981 Moss bag as monitors of atmospheric deposition J. Air Pollut. Control Assoc.
Wan J B, Wang J Y and Wu D 2008 Current assessment on heavy metal pollution in the sediment on Le’an River Environ. Sci. Technol. 31(11) 130-3
Hanif N, Ali S M, Cincinelli A, Ali N, Katsoyiannis I A and Tanveer Z I, et al 2016 Geo-accumulation and enrichment of trace metals in sediments and their associated risks in the chenab river, Pakistan J. Geochem. Explor. 165 62-70
Wang L, Yu R, Hu G and Tu X 2009 Speciation and assessment of heavy metals in surface sediments of Jinjiang River tidal reach, southeast of china Environ. Monit. Assess. 165(1-4) 491-9
He S I, Long C L, Liu Y Z, et al 2004 Geochemistry and environment of the Cd in the soil and sediments at the surface of Guizhou Province Guizhou Geol. 21(4) 245-50
Yi X, Gu X J, Hou Y Q, et al 2010 Assessment on soil heavy metals pollution by geoaccumulation index in Jinhuiqu irrigation district of Shanxi Province J. Earth Sci. Environ. 32(3) 288-91
Müller G 1979 Schwermetalle in den sedimenten des Rheins-Vera E’nderungenseit 1971’ Umschau 79 778-83
Nobi E P, Dilipan E, Thangaradjou T, et al 2010 Geochemical and geo-statistical assessment of heavy metal concentration in the sediments of different coastal ecosystems of Andaman Islands, India Estuar. Coast. Shelf S. 87(2) 253-64
Gopinath A, Nair S M, Kumar N C, et al 2010 A baseline study of trace metals in a coral reef sedimentary environment, Lakshadweep Archipelago Earth Sci. Environ. 59(6) 1245-66
Guo W, Liu X, Liu Z, et al 2010 Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin Procedia Environ. Sci. 2(1) 729-36
Gargouri D, Azri C, Serbaji M M, et al 2011 Heavy metal concentrations in the surface marine sediments of Sfax Coast, Tunisia Environ. Monit. Assess. 175(1-4) 519-30
Nemr A E, EI-Said G F, Khaled A, et al 2016 Distribution and ecological risk assessment of some heavy metals in coastal surface sediments along the Red Sea, Egypt Int. J. Sediment Res. 31(2) 164-72
Wang Z Q 1999 Geo-statistics and Its Application in Ecology (In Chinese) (Beijing: Science Press) pp 25-31
Journel A G 1993 Quantitative Geology and Geostatistics//Quantitative geology and geostatistics (U.S.A.: D. Reidel Pub. Co.; Canada: Kluwer Academic Publishers; Kluwer Academic Publishers Group) pp 213-24
Shen G Y 2016 The State Council issues soil pollution control action plan Fine and Specialised Chemicals 6 12