

Simulation of Heavy Metals Migration in Soil of Rare Earth Mining Area

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ABSTRACT. The study of heavy metal interactions with soils under specific climatic circumstances might lead to a better understanding of heavy metal migration and provide further information for local pollution control. In this work, we collected soil samples from the world's largest light rare earth mining district, Bayan Obo mine district, and assessed the heavy metal content in the soil at various depths. The extraction effectiveness of Diethylenetriaminepentaacetic acid (DTPA) and Toxicity Characteristic Leaching Procedure (TCLP) for heavy metals in surface soil were compared. Furthermore, we studied the longitudinal transport of heavy metals under precipitation conditions using simulated experiments and kinetic fitting. We discovered that pH has a significant impact on heavy metal release. Precipitation easily transports Zn, Pb, and Cr to deeper layers of the soil. The modified Elvoich equation could better describe heavy metal release patterns.

Keywords: mine soil, heavy metals, leaching, migrate, curve fitting

1. Introduction

Soil is one of the most important sinks for many pollutants, such as organic pollutants (Alharbi et al., 2018), heavy metals (Su, 2014), and emerging pollutants (Dimpe and Nomngongo, 2016). Contaminated soil could directly affect the local population's health through the food chain (Csavina et al., 2014). In some areas that can generate large amounts of contaminants such as chemical plants, mines, and oil fields, local climate change may change the migration pathways of these contaminants, which poses a significant to the health of the local population (Ettler, 2016; Seo and Hong, 2020). Therefore, paying attention to the levels and transport patterns of pollutants in the soils of these areas can help reduce the risks posed by pollutants to the surrounding areas.

Soils in semi-arid climates are often wind-classified and deposited, resulting in the formation of loose soil structures that are not conducive to contaminant control. Semi-arid soils have higher exchange capacity (CEC) and higher pH than tropical soils, therefore heavy metals are more likely to be adsorbed on soil particles for movement (Moghal et al., 2016). In addition, under the influence of prevailing winds, soil particles will migrate rapidly from the source of pollution to other areas, elongating the contaminated area and causing extensive pollution, this feature is more obvious in mining areas (Křibek et al.,

2014; Mihaljevič et al., 2015; Křibek et al., 2016). Precipitation is also regarded as a major factor influencing the migration of heavy metals (Sharma et al., 2008). Different precipitation conditions can impact heavy metals migration behavior. Atmospheric particulate matter can carry heavy metals to soil and surface water under precipitation (Sternbeck et al., 2002). Also, heavy metals can be moved from the surface to the lower layers due to infiltration of rainwater, and enriched in the lower soil layers, increasing the risk of groundwater pollution.

Changes in soil properties also have an impact on the transport of heavy metals (Lalah et al., 2009). Generally speaking, soils with a high proportion of sand particles have a low water content and a small soil surface area per unit volume, which reduces the adsorption capacity of the soil for heavy metals and increases the chances of heavy metal migration (Zhang et al., 2005; Frimpong and Koranteng, 2019). The higher the soil organic matter (SOM) content, the stronger the sorption properties of the soil, thus reducing the leaching capacity of heavy metals (Fan et al., 2016). The lower the pH, the less the ability of the soil to retain heavy metals (Chen et al., 2007).

Therefore, as an extension of the previous study (Wang et al., 2021), this study aims to simulate the heavy metal migration in soils of rare earth mining areas under semi-arid climatic conditions. In detail, leaching experiments of heavy metals were conducted on soils in the Bayan Obo mining area, the largest light rare earth mining area in China, to investigate: (1) levels of heavy metals in soils at different depths in the Bayan Obo mining area, (2) the release capacity of local soils for heavy metals, and (3) the longitudinal migration pattern and release mechanism of heavy metals under rainfall.

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2. Materials and Methods

2.1. Study Area

Bayan Obo mining area ($109^{\circ}47' \sim 110^{\circ}04' \text{ E}$, $41^{\circ}39' \sim 41^{\circ}53' \text{ N}$) is located in Baotou City, Inner Mongolia Autonomous Region, with a population of about 27,600 inhabitants by the end of 2019. The average elevation is 1,605 m, the total annual average temperature is 2.5°C , the annual precipitation is 248.5 mm, and the local soil type is mainly chestnut calcium soil, with a small amount of meadow soil and saline soil. The local climate is inland arid and windy (Li et al., 2015). Location map is shown in Figure 1.

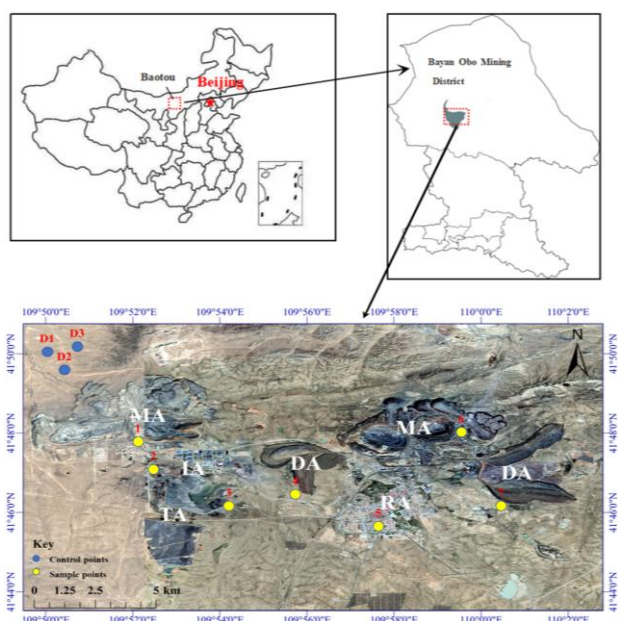


Figure 1. Location of the study area.

2.2. Sampling and Analysis

2.2.1. Field Sampling

The sampling design was based on the distribution of mining areas, different functional areas, and wind directions. The control site was set up in the northwest direction of the study area away from the influence of all suspected pollution sources. Based on the previous research (Wang et al., 2021), we selected seven representative points to represent different functional areas and named Points 1 ~ 7 in order. (Points 1 and 6 represent the mining area (MA), Point 2 represents the industrial area (IA), Point 3 represents the tailing area (TA), Points 4 and 7 represent the dumping area (DA), and Point 5 represents the residential area (RA). We also collected soil samples at different depths (0 ~ 20, 20 ~ 40, and 40 ~ 60 cm) at these points to determine the longitudinal content of heavy metals in the soil. All samples were collected in August 2019, 3 ~ 5 subsamples from each sampling site were mixed, and the soil was collected with the stainless-steel shovel, preserved in plastic self-sealing bags after collection, transported back to the laboratory, and the latitude and longitude coordinates of the sampling sites were recorded with GPS.

2.2.2. Measurements

The soils were dried at room temperature, and the $\text{HCl-HNO}_3\text{-HF-H}_2\text{O}_2$ (1:4:1:1) digestion method was used to digest. The concentrations of heavy metals were determined by a flame-atomic absorption spectrophotometer (FAAS, PerkinElmer AA800, USA). The recoveries of standard addition were also carried out and the recovery of each heavy metal ranged from 93.2 to 101.4%.

2.2.3. Extraction Experiments

Diethylenetriaminepentaacetic acid (DTPA) and Toxicity Characteristic Leaching Procedure (TCLP) extraction procedures were used to compare the metals extraction concentrations in the soil samples.

(1) DTPA

Extraction solution preparation: 0.005 mol/L DTPA, 0.01 mol/L CaCl_2 , 0.1 mol/L Triethylamine (TEA). 1.967 g of DTPA and 14.92 g of TEA were dissolved in deionized water as solution A. Another 1.47 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in deionized water as solution B. The two solutions were mixed and transferred to a 1000 ml volumetric bottles, adjust pH to 7.30 with HCl, and finally fix volume was with deionized water.

Extraction experimental: 25.00 g of air-dried 20 mesh sieved soil sample was weighed into a 150 mL triangular flask, 50.0 mL of DTPA extraction solution was added, shaken for 2 hrs at 25°C , filtered, pretreated, and used for analysis.

(2) TCLP

Extraction solution preparation: Add 5.7 mL of acetic acid to 500 mL of deionized water, then add 64.3 mL of 1 mol/L NaOH and fix the volume to 1000 mL. Make sure that the pH was between 4.88 and 4.98.

Extraction experiment: Put 100 g of soil into a 2 L wide mouth flask and pour the extraction solution into the wide mouth flask according to the ratio of 20:1. The wide mouth flask was stoppered tightly and shaken horizontally at 25°C for 18 ± 2 hrs. After that, the mixture was removed, centrifuged and filtered. Collect the filtrate for heavy metal testing.

2.2.4. Simulation Experiments on the Migration of Heavy Metals

Longitudinal transport patterns of soil heavy metals under different rainfall conditions were simulated in the room. Leaching solutions of different pH (4.48, 6.80, and 7.30) were prepared to simulate rainfall. The simulation experiment is divided into two parts. The device (a) adds only surface soil samples (Point 6) to research the release of heavy metals under simulated rainfall. In device (b), unpolluted soil (control sites) and surface soil samples (Point 6) are added to the device separately to study the migration of heavy metals from the surface soil to the lower soil during the simulated rainfall. Leaching samples were obtained at 75, 150, 225, 300, 600, and 900 mL. After pretreatment, heavy metals content was determined.

The determination of pH and electrical conductivity (EC)

of soil columns under simulated rainfall was also carried out at the same time as the determination of heavy metals, and all mentions of experimental devices and simulated rainwater configurations can be found as follow:

Leaching devices (Figure 2): The main body is a PVC cylindrical pipe with an inner diameter of 4 cm and a height of 25 cm. A 100-mesh nylon net was laid at the bottom of the tube, and about 50 g of quartz sand and glass beads washed with deionized water were weighed and laid at the bottom of the cylindrical tube (about 2 cm), and the bottom of the soil column was sealed. Weigh 100 mesh sieved air-dried soil (or clean soil) and fill the cylindrical tube with soil at a field capacity of 1.16 g/cm to form a mock soil column about 15 cm high. The top of the column is covered with quartz sand, glass beads, and nylon mesh to ensure that the soil surface structure is not damaged during leaching. The soil column was placed on the fixture and 100 ml PVC bottles were used to collect the leaching solution, with three replicates per group. To prevent the edge effect of the soil column, the soil at the edge of the column was compacted as much as possible to reduce the occurrence of the phenomenon of excessive water flow.

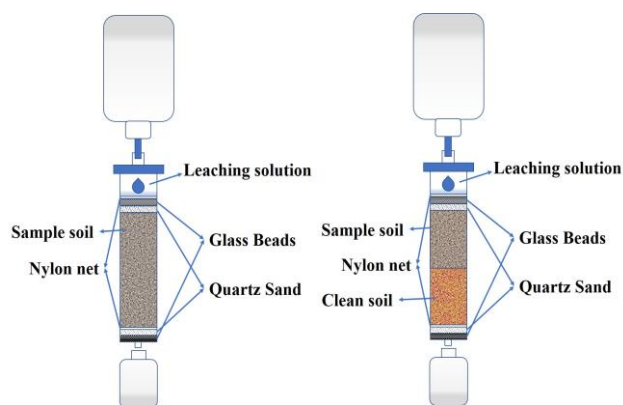


Figure 2. Leaching experimental devices (device (a) was used in the experiments to study the release pattern of heavy metals; device (b) was used in the experiments to study the migration of heavy metals in the longitudinal direction).

Configuration of simulated rainwater: The local annual average precipitation from 2012 to 2018 was between 208.2 and 422.8 mm, with an average value of 301.7 mm. 300 mm was taken as the annual average precipitation. The minimum value of rainwater pH was 4.46, the mean value was 6.80, and the maximum value was 7.30. The chemical composition of simulated rainwater was Ca^{2+} 1.564 mg/L, K^{+} 0.04 mg/L, Na^{+} 0.023 mg/L, Mg^{2+} 0.047 mg/L, Cl^{-} 0.11 mg/L, CO_3^{2-} 0 mg/L, HCO_3^{-} 0.47 mg/L, SO_4^{2-} 0.078 mg/L.

2.2.5. Adsorption Kinetics

Soil is an open system, and all chemical reactions occurring in this system are in dynamic change (Li et al., 2019). The cumulative release of heavy metals from soils under leaching can be further examined by chemical kinetic methods. The commonly used dynamic models include first-order kinetic equation,

double-constant rate equation, parabolic diffusion equation, modified Elovich equation, and so on. The fitted equations used in this paper are as follows:

First-order kinetic equation:

$$\ln y = a + bx \quad (1)$$

Double-constant rate equation:

$$\ln y = a + b \ln x \quad (2)$$

Parabolic diffusion equation:

$$y = a + bx^{0.5} \quad (3)$$

Modified Elovich equation:

$$y = a + b \ln x \quad (4)$$

3. Results and Discussion

3.1. Levels of Heavy Metals in Soil

Table 1 shows the concentration of heavy metals in the soil at different depths. It can be observed that the concentration of heavy metals in the soil at all layers exceeds the control point, indicating that human actions have interfered with the dispersion of heavy metals at these places (Liang et al., 2023). In the mining area, the heavy metal content at Point 6 is much higher than that at Point 1, which may be related to mining activities (such as blasting and mineral transportation). Mining areas' unique geological formations may also be one of the reasons for the abnormal heavy metal content in this area (Zhu et al., 2016). The concentration of heavy metals at Point 4 was much higher than that at Point 7 for the dump area, which may be related to local transportation activities. The dump area at Point 7 has reached its maximum capacity, and no transport activity has occurred nearby, thus no additional pollutants have been brought into the region. Furthermore, the region is densely vegetated, which helps to stabilize and minimize heavy metal concentrations in the soil (Zhang et al., 2020). However, the dump area around Point 4 is still in use, and the excess soil and ore obtained after ore mining will be continuously poured into the area, which leads to the entry of a large number of heavy metals, resulting in the increase of heavy metal concentration in the soil.

The concentration of heavy metals in the topsoil is substantially higher in the tail mining area than in the deep soil, which may be due to the action of wind (Li et al., 2018). The northwest wind dominates in this location, which allows tail sand from the tailings pond in the northwest to readily infiltrate the surface soil and pollute it. The concentration of heavy metals in the residential area's surface soil is low, yet it is more than the control point. On the one hand, this might be attributable to domestic rubbish dumping and traffic exhaust emissions (Affum et al., 2007; Long et al., 2009). Dust from mining blasting, on the other hand, may be transported to the topsoil of

Table 1. Concentrations of Heavy Metals in Soils at Different Depths

| 0 ~ 20 cm | Mn (mg/kg) | Cu (mg/kg) | Zn (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Cr (mg/kg) |
|--------------|------------|------------|------------|------------|------------|------------|
| MA(1) | 1176.36 | 24.61 | 131.52 | 41.14 | 0.24 | 83.76 |
| MA(6) | 9789.38 | 29.81 | 697.04 | 343.22 | 2.23 | 102.64 |
| DA(7) | 632.73 | 19.18 | 91.23 | 23.41 | 0.16 | 60.76 |
| DA(4) | 4365.83 | 22.34 | 284.36 | 126.62 | 0.77 | 60.77 |
| TA(3) | 14283.48 | 22.58 | 671.96 | 502.35 | 2.53 | 37.36 |
| RA(5) | 584.29 | 20.20 | 107.20 | 27.33 | 0.23 | 49.47 |
| IA(2) | 4021.80 | 37.84 | 339.12 | 191.01 | 0.89 | 71.45 |
| Control site | 524.12 | 20.63 | 93.26 | 15.94 | 0.08 | 58.50 |
| 20 ~ 40 cm | Mn (mg/kg) | Cu (mg/kg) | Zn (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Cr (mg/kg) |
| MA(1) | 864.00 | 24.72 | 196.78 | 36.28 | 0.11 | 80.01 |
| MA(6) | 9655.97 | 24.86 | 629.80 | 307.96 | 1.87 | 81.30 |
| DA(7) | 1350.87 | 18.42 | 135.69 | 42.40 | 0.12 | 65.40 |
| DA(4) | 521.30 | 15.36 | 89.93 | 19.50 | 0.07 | 42.60 |
| TA(3) | 1338.14 | 12.53 | 142.85 | 29.88 | 0.19 | 29.30 |
| RA(5) | 579.84 | 20.46 | 120.29 | 25.44 | 0.14 | 50.30 |
| IA(2) | 429.02 | 27.34 | 494.54 | 21.30 | 0.11 | 68.40 |
| Control site | 406.67 | 19.47 | 73.56 | 12.45 | 0.05 | 43.50 |
| 40 ~ 60 cm | Mn (mg/kg) | Cu (mg/kg) | Zn (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Cr (mg/kg) |
| MA(1) | 1270.90 | 24.09 | 138.88 | 40.76 | 0.19 | 80.02 |
| MA(6) | 7075.77 | 22.67 | 439.49 | 211.40 | 1.34 | 70.68 |
| DA(7) | 1875.06 | 25.32 | 118.70 | 63.13 | 0.19 | 69.75 |
| DA(4) | 246.35 | 13.13 | 53.14 | 16.91 | 0.09 | 34.88 |
| TA(3) | 3439.43 | 10.76 | 190.42 | 111.48 | 0.44 | 27.18 |
| RA(5) | 661.28 | 22.17 | 76.12 | 29.72 | 0.20 | 52.42 |
| IA(2) | 585.82 | 31.66 | 321.20 | 28.25 | 0.23 | 66.16 |
| Control site | 356.90 | 16.94 | 51.34 | 12.66 | 0.10 | 42.29 |

residential areas by prevailing winds. The copper concentration in industrial locations is higher than in other places, which may be attributed to local copper smelting plants. The smoke of copper and its compounds enters the soil with the flue gas during the smelting process (Rastmanesh et al., 2010).

3.2. Extraction Experiments

The results of the extraction experiments are shown in Figure 3. In general, the concentration of heavy metals extracted by the DTPA method is slightly higher than that of the TCLP method, which may be due to the DTPA method's higher elution ability in soils containing Ca^{2+} (The local soil is dominated by chestnut calcium soil). TCLP, on the other hand, is an acidic leaching solution, and the high concentration of H^+ in the leaching solution allows active metal ions to enter the leaching solution more easily, increasing the concentration of heavy metal ions in the leaching solution. The concentrations of heavy metals in the two extraction solutions were Mn, Zn, Pb, Cr, Cu, and Cd in order, which was consistent with the performance of total heavy metals in local soils. The concentrations of each heavy metal in the extraction solution (except for Cu in the DTPA method) exceeded the background values of Inner Mongolian soils, which may be related to local industrial activities and special geological formations (Wang et al., 2021). However, such high levels of releasable heavy metals may have some potential impact on the local environment and the safety of the inhabitants.

In addition, we found that both methods were not effective in terms of their ability to extract lead (12.2 and 16.3%, respectively, while the extraction rates of the other heavy metals are above 20%), which was similar to the results from other mines (Liu et al., 2018). In mines or smelters, lead minerals may be encapsulated in other stable soil lattices (e.g., quartz), which reduces the bioavailability of lead (Mbengue et al., 2015). Among the two extraction methods, the highest extraction rate is Cd (66.28 and 82.56%, respectively). On the one hand, this may be due to the decreased Cd concentration of the soil. On the other hand, this shows that Cd is more active in local soils. After inhaling or ingesting contaminated soil, active Cd (e.g., in water-soluble, ion-exchange, and carbon-binding states) may be absorbed into the intestines, stomach, and lungs residents, posing a risk of carcinogenic effects when accumulated over time (Orell et al., 2013).

3.3. Simulation Experiments

3.3.1. pH

Soil has a strong buffering capacity due to its complex composition (Li et al., 2019). The pH of the leachate can reflect the buffering capacity of the soil against changes in acidity and alkalinity (Burns et al., 2006). The changes in pH of the experimental leaching solutions are shown in Figure 4. The pH of all three leaching solutions increased rapidly with the increase of volume at the beginning, reaching about 7.5 at 225 ~ 300 mL. The pH of the leaching solution gradually decreased with the

leaching process at 300 ~ 900 mL. This trend is probably due to the neutralization reaction between the soil exchangeable salt-based ions and the exogenous H^+ , which leads to a sharp increase in pH at the pre-leaching stage due to the consumption of H^+ . At the same time, the leaching solution also contains anions such as SO_4^{2-} , which are ligands exchanged with the hydroxyl groups of the soil oxides after adsorption. It leads to an increase in hydroxyl groups in the leaching solution. However, the pH of the leaching solution no longer increases when the exchangeable salt-based ions and hydroxyl groups of the soil are fully reacted.

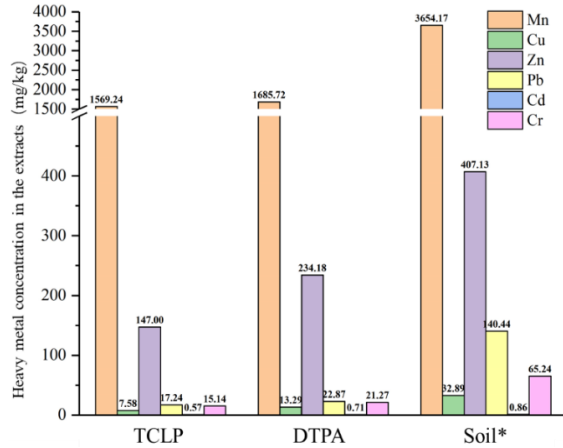


Figure 3. Concentration of heavy metals in extracts and soil (heavy metals concentrations in soils can be found in Wang et al. (2021)).

3.3.2. EC

The magnitude of EC reflects the content of electrolytes in the soil leaching solution. As the leaching process continued, the trend of EC of the leaching solution was shown in Figure 5. The EC decreased sharply from 938.78 to 479.08 $\mu\text{S}/\text{ms}$ for pH = 4.48 during the 0 ~ 300 mL process, and slowly decreased during the 300 ~ 900 mL process, with the conductivity of all three leaching solutions stabilized at about 350 $\mu\text{S}/\text{ms}$. The explanation for this tendency may be related to the quick transfer of salt-based ions and adsorbed oxides from the soil surface to the aqueous solution and their rapid leaching out with the leaching solution in the early stage of leaching. The number of exchangeable ions in the soil decreased as the leaching progressed, resulting in a drop in exchange capacity. It indicates that after acidic precipitation, heavy metals in the surface soil will be swiftly dissolved into rainfall and infiltrate into the deep soil, potentially polluting the nearby groundwater.

3.3.3. Heavy Metal Concentration in the Leaching Solution

The heavy metal content in the leaching solution increased sharply at the initial stage of leaching, and slowly decreased to a stable level after the end of leaching (Figure 6). At the beginning of leaching, the content of heavy metals in the leaching solution increased rapidly, and then the trend of increase gradually slowed down when the leaching reached about 225 ~ 300

mL. The more active heavy metal ions on the soil surface may have been desorbed from the particles and released into the leaching solution, resulting in a rapid increase in heavy metal content. The heavy metal content on the particle surface gradually decreases and changes to slow internal soil diffusion, resulting in a slower rate as the leaching progresses.

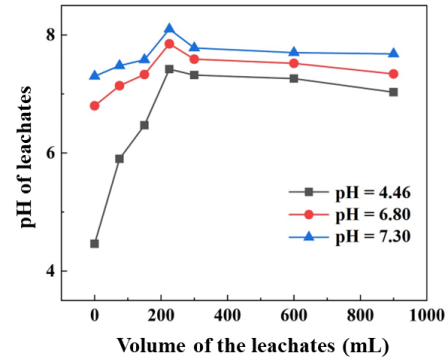


Figure 4. Change of pH under the leaching conditions.

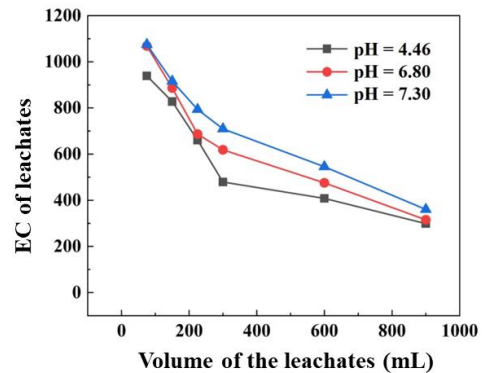


Figure 5. Change of EC under the leaching conditions.

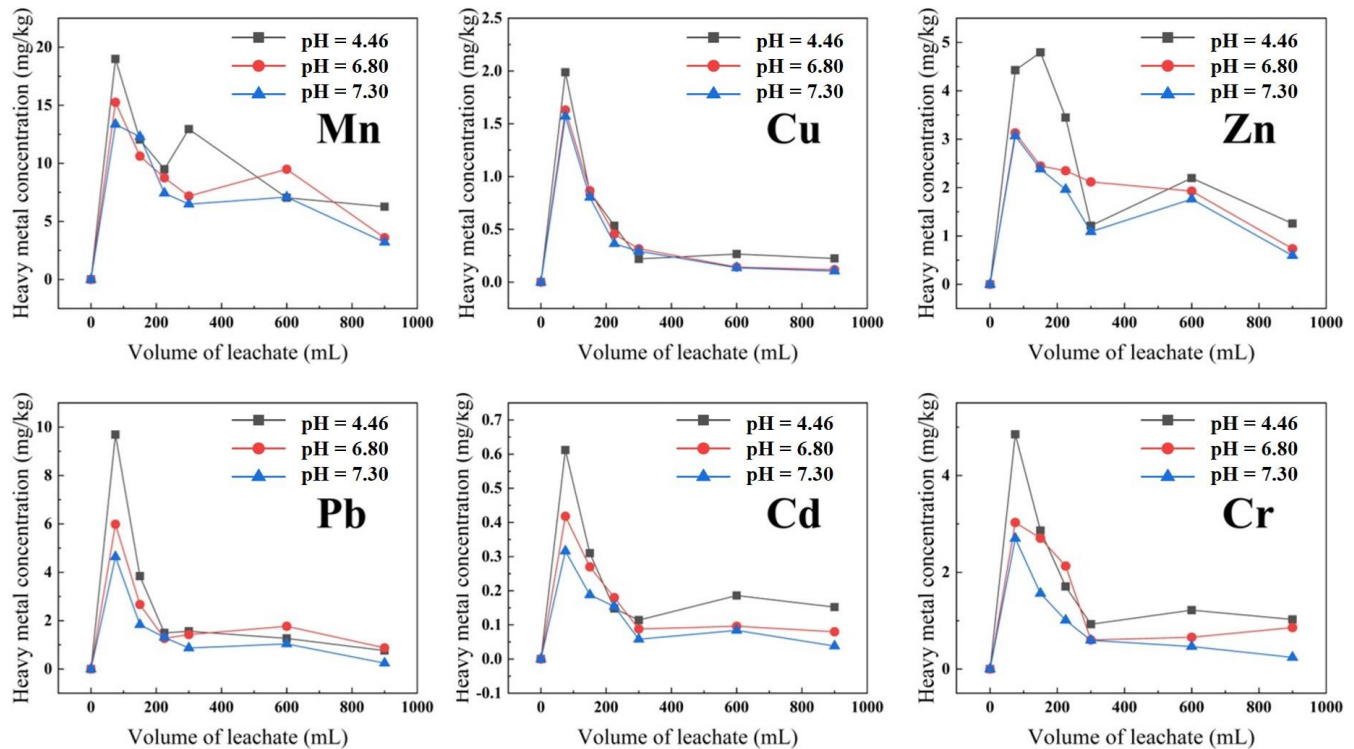
The pH = 4.48 leaching solution contained more heavy metals than the other two at the start of leaching under the three pH conditions. The possible reason for this is the high content of H^+ , which reacts with exchangeable salt ions in large quantities at the beginning of the leaching (Wang et al., 2020). Cu, Pb, and Cd all exhibited similar behavior. Mn declined slowly in the late stage of leaching, possibly due to the high total amount of Mn in local soil and more exchangeable ions, resulting in partial ions that were still not completely desorbed in the late stage of leaching. Zn has a slower peak value than other heavy metals and thus enters the solution concentration at a later stage.

3.3.4. Longitudinal Migration Characteristics of Heavy Metals

The clean soil columns in the device were divided into four equal parts after three different rainfall simulation leaching experiments, and each column's concentration results are shown in Table 2. Longitudinally, heavy metal concentration was higher near contaminated soil and lower away from contaminated soil, indicating that some of the heavy metal ions entering the

Table 2. The Concentration of Heavy Metals in Each Soil Column

| Soil Columns Parts | pH = 4.46 Mn | pH = 6.80 | pH = 7.30 | pH = 4.46 Cu | pH = 6.80 | pH = 7.30 |
|--------------------|-----------------|-----------|-----------|-----------------|-----------|-----------|
| 1 | 8.01% | 6.89% | 6.16% | 7.90% | 7.05% | 6.31% |
| 2 | 7.32% | 6.11% | 4.79% | 6.88% | 5.65% | 6.50% |
| 3 | 6.16% | 4.20% | 4.05% | 5.47% | 4.54% | 3.10% |
| 4 | 5.56% | 3.71% | 3.05% | 4.11% | 3.54% | 1.69% |
| | Zn | | | Pb | | |
| 1 | 11.46% | 7.75% | 6.01% | 13.18% | 10.01% | 7.82% |
| 2 | 7.44% | 5.81% | 5.13% | 9.31% | 7.20% | 5.78% |
| 3 | 3.84% | 3.01% | 2.67% | 5.82% | 4.54% | 2.87% |
| 4 | 2.38% | 2.16% | 1.20% | 3.30% | 2.19% | 1.57% |
| | Cd | | | Cr | | |
| 1 | 8.16% | 6.80% | 6.22% | 9.99% | 7.38% | 5.81% |
| 2 | 6.88% | 4.86% | 4.52% | 6.31% | 4.92% | 4.47% |
| 3 | 4.27% | 3.52% | 3.23% | 4.08% | 2.81% | 2.90% |
| 4 | 3.43% | 2.92% | 2.63% | 2.36% | 1.66% | 1.37% |

**Figure 6.** Concentration of heavy metals released from the soil column.

leach solution were adsorbed and retained by soil particles. Besides, heavy metal content decreased with the increase of the pH value of rainfall simulation leaching solution. It suggests that a larger concentration of H^+ in the leaching solution promotes heavy metal longitudinal movement. This could be because a low pH environment promotes stronger heavy metal adsorption-desorption in the soil, allowing for faster replacement or desorption of ions adsorbed in the soil into solution, resulting in rapid accumulation of heavy metals in the soil's vertical direction.

3.3.5. Adsorption Kinetics of Heavy Metal Release

The first-order kinetic equation was used to fit the kinetic processes of soil heavy metals released from three different pH leaching solutions. The first-order kinetic equation fits the release curves of the three pH leaching solutions relatively poorly, as shown in Figure 7, with R^2 ranging from 0.45 to 0.70 for all of them. Mn provided the best overall fit to the first-order kinetic equation, with R^2 values ranging from 0.62 to 0.68 for the three pH leaching solutions. Cu had the worst fit, with R^2 ranging from 0.45 to 0.55. These findings suggest that the first-order

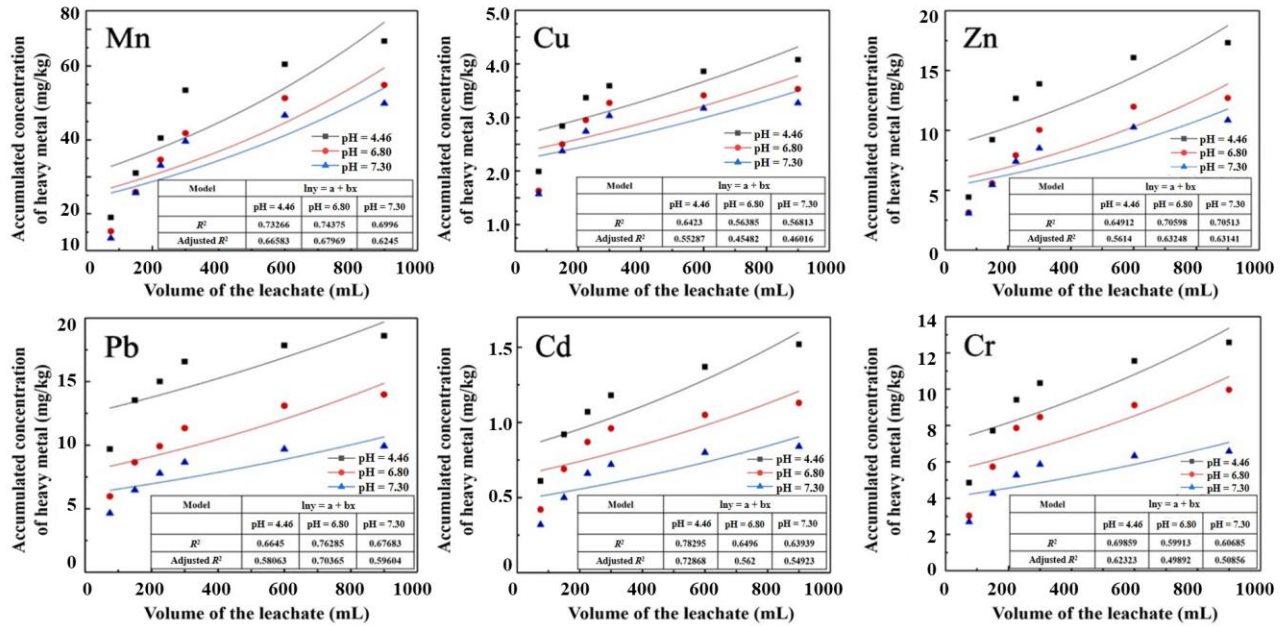


Figure 7. Results of fitting the first-order kinetic equation.

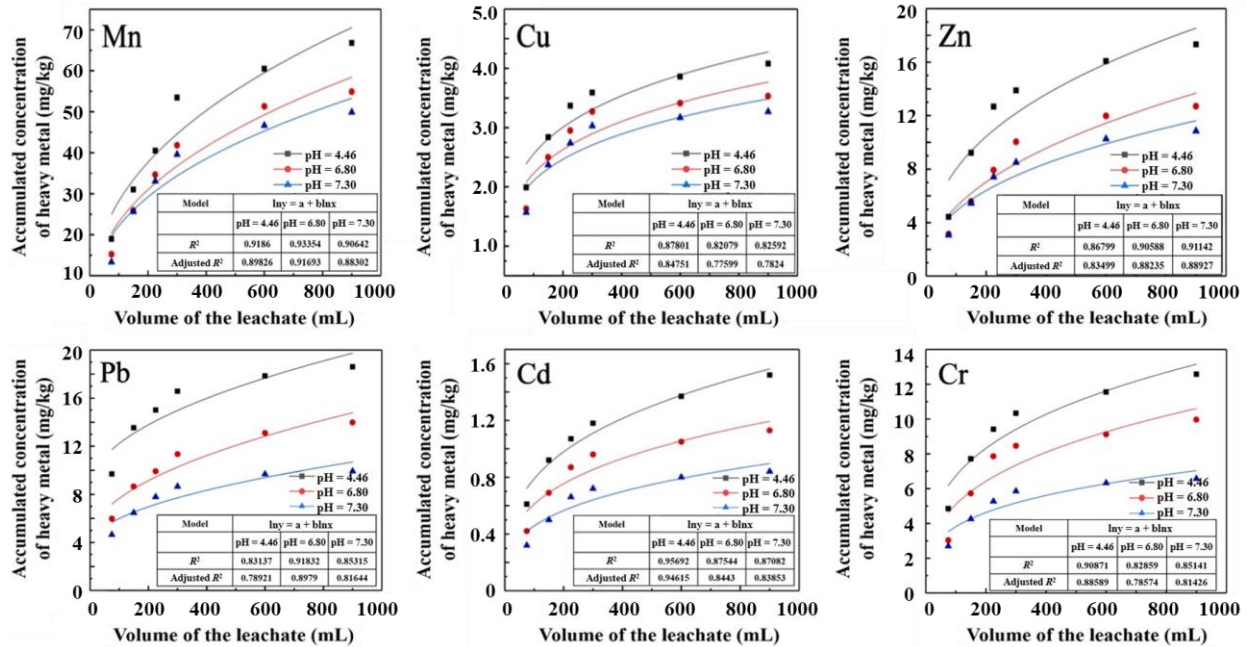


Figure 8. Results of fitting the double-constant rate equation.

kinetic equation does not adequately explain heavy metals' local longitudinal migration pattern.

The double-constant rate equation fit results are shown in Figure 8, and they are overall better than the first-level kinetic equation. The adjusted R^2 for all heavy metals ranged from 0.78 to 0.94, with Pb at pH = 6.80 of the leaching solution fitting best and Cu at pH = 6.80 fitting worst. The relatively well-fitted elements were Mn and Pb (adjusted R^2 were greater than 0.87),

and the badly-fitted elements were Cu (adjusted R^2 are less than 0.85).

The results of the parabolic equation fit are shown in Figure 9. The result of this equation is like the double constant rate equation and better than the first-order kinetic equation. The best fit for Mn ($R^2 > 0.85$ in all three cases) and the worst fit for Cu ($R^2 < 0.77$ in all three cases). The other three fitted equations also exhibit this feature.

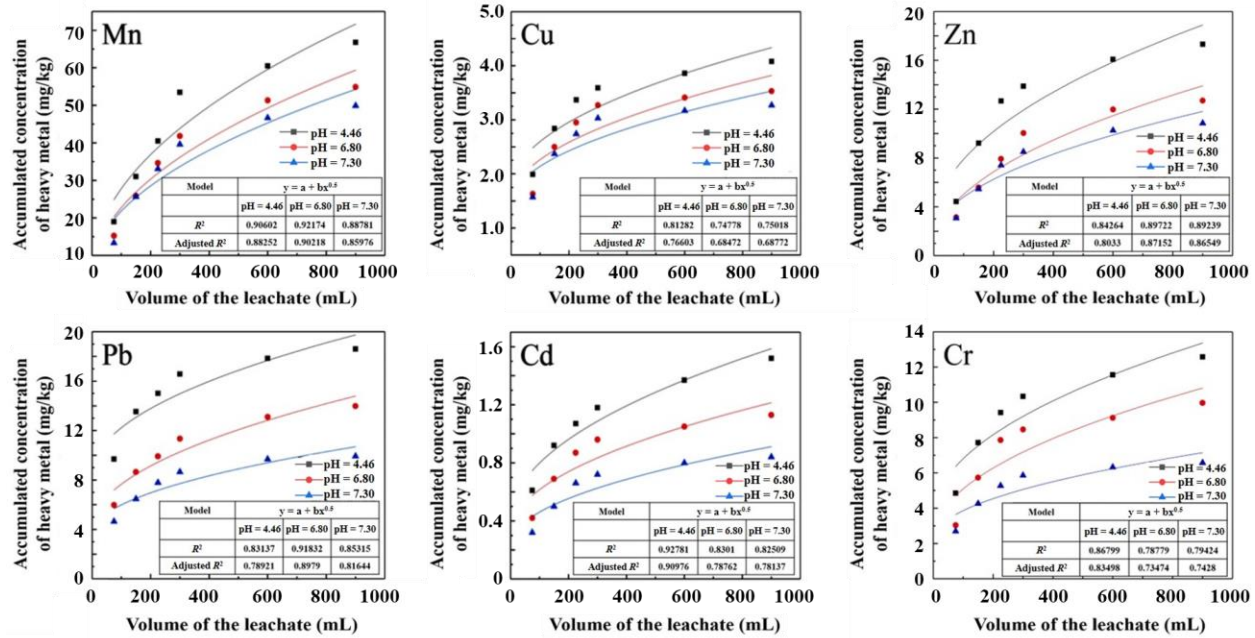


Figure 9. Results of fitting the parabolic equation.

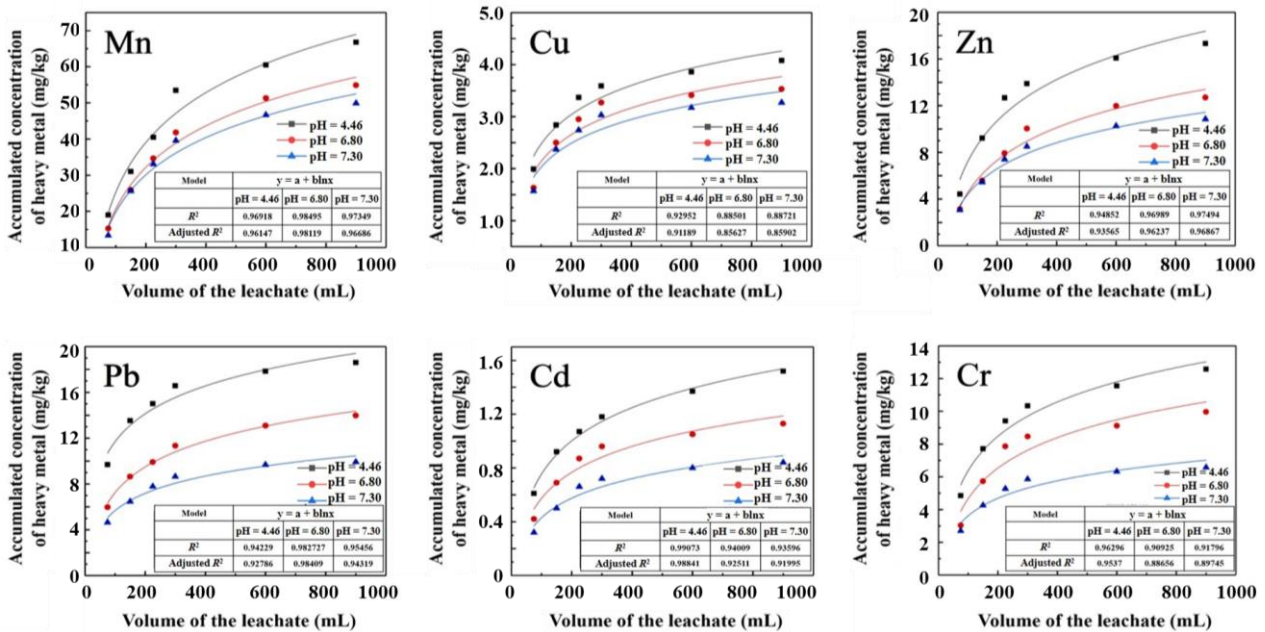


Figure 10. Results of fitting the modified Elovich equation.

The kinetic process of soil heavy metal release was fitted using the modified Elovich equation, and the results are shown in Figure 10. From the fitting data using the modified Elovich equation, R^2 (0.86 ~ 0.99) is higher than all the other three obtained. The best fits were obtained for Mn (adjusted R^2 0.96 ~ 0.98), Zn (adjusted R^2 0.94 ~ 0.97), Pb (adjusted R^2 0.93 ~ 0.98), and Cd (adjusted R^2 0.92 ~ 0.99), all of which had adjusted R^2 greater than 0.90. The fits for Cu, Cd, and Cr were better than those for the other two leaching solutions at pH = 4.46. Mn and

Pb were better fitted at pH = 6.80 than the other two leaching solutions, which may be related to the pH of the leaching solution and local soil properties.

Overall, on the one hand, the results of the four kinds of fitted equations are in order of the modified Elovich equation, the double constant rate equation, the parabolic diffusion equation, and the first-order kinetic equation. It indicates that the modified Elovich equation can better explain the effect of rainfall leaching on local heavy metal pollution. On the other hand,

in terms of pH, the four fitted equations were better fitted for Mn and Pb at pH = 6.80 and Cu, Cd, and Cr at pH = 4.46. Zn was similarly fitted at pH = 6.80 and pH = 7.30, both of which were better fitted than the pH = 4.46 leaching solution.

4. Conclusions

Heavy metal concentrations in soil at various depths are high, which is caused by both human activity and geological factors. Mining and related industrial activities are the most significant polluters in the entire study area. Reduced human activity and plant growth can help to reduce heavy metal deposits in the soil.

The extraction experiments revealed that the concentration of heavy metals in the extraction solution was proportional to the total amount present in the soil. The results of the two extraction methods were essentially consistent, but the DTPA method had a slightly higher extraction rate than the TCLP method. Both methods were less effective in extracting Pb, which may be due to the more stable Pb in the soil. Cd was extracted at the highest leaching rate in the extraction solution, potentially putting the local population's health at risk.

The simulation experiments revealed that pH had a significant effect on heavy metal precipitation in the soil, and the heavy metal release pattern was initially rapid and then gradually leveled off. It means that if the rain is acidic, heavy metals in the topsoil will be released quickly when the rain starts. The migration results revealed that Zn, Pb, and Cr migrated easily to the lower layers of the soil, whereas Cu and Cd did not. The kinetic fitting results revealed that the modified Elovich equation could best explain the release of heavy metals under leaching.

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