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REVIEWED BY Xiaokai Zhang, Jiangnan University, China Liang Pei, Chinese Academy of Sciences (CAS), China

*CORRESPONDENCE Hepeng Li, 157880063@gg.com

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Effects of landscape restoration on migration of lead and cadmium at an abandoned mine site

Feiying Zhang and Hepeng Li*

Zhejiang Academy of Forestry, Hangzhou, China

Abandoned lead and zinc (Pb/Zn) mining wastes represent a serious environmental hazard because heavy metals (e.g., Pb and Cd) are continuously released into the environment, threatening ecological and human health. This study was devoted to investigate the stability of Pb and Cd in the soil at an abandoned Pb/Zn mine site after landscape restoration by five-year monitoring. Chemical extraction was applied to measure the distribution of metals. The results showed that the bioavailability of Pb and Cd in soil increased, during the accumulation of soil organic matter of about seven g/kg, and that the soil pH value decreased from 4.82 to 4.44. Soil organic matter and soil pH significantly affected the distribution of metals. Long-term afforestation can lead to continuous soil acidification. There was a significant negative correlation between the carbonate-bound state distribution and soil pH. With the decrease in pH, the decomposition of carbonates was promoted, and relative abundances of Pb and Cd in the distribution associated with the fulvic and humic complex of organic matter increased by 0.54% and 3.17%, respectively. Pb and Cd showed different migration behavior in pine. Compared with Cd, Pb was more concentrated in roots. These results have important implications for the long-term sustainable management of forests formed by the phytostabilization of contaminated soil.

KEYWORDS

abandoned mines, phytostabilization, remediation, lead, cadmium, redistribution

Introduction

Lead/zinc ores are highly dispersed throughout the earth and could be found in most countries. According to statistics, 29 provinces, autonomous regions, and cities have found and explored Pb/Zn deposits, and China's Pb/Zn reserves rank the second in the world (Zhao et al., 2015; Luo and Teng, 2018). According to the communique of China's National Investigation of Soil Contamination (2014), 13.3% of all the soil samples and 33.4% of the soils collected from mining areas exceeded the upper limit concentrations of the China Soil Environmental Quality Standards for heavy metals (GB15168-1995). The long-term mining, smelting, and tailings accumulation of Pb/Zn mines lead to a high content of metal elements Pb and Zn in soil, and Cd is a hazardous metal element and

synergic with Zn, resulting in serious soil compound pollution. Erosion of particulate-bound Pb (Pb-P) and particulate-bound Cd (Cd-P) is the main cause of metal pollution in the soil around the mining area (Gutiérrez et al., 2016). The original forest landscape is seriously damaged, and there are also geological hazards such as collapse, landslides, and debris flows, as well as water and soil environmental pollution. Therefore, mining activities are considered to be the main driving force associated with soil degradation (Xu et al., 2021). Soil metal pollution has the characteristics of concealment, long-term, and irreversibility, and is highly toxic. Naturally, soils have Pb levels of 2 ~ 200 mg/kg, while Cd makes 0.01 ~ 0.7 mg/kg (Mahdi et al., 2019). High Cd/Pb concentration in soils threatens environmental safety and food security. The wastes at the abandoned Pb/Zn mine are considered one of the most serious environmental problems and pose serious hazards to ecosystems and human health.

For abandoned Pb/Zn mines, in situ fixation is a better approach than ex situ removal because these in situ fixation methods are usually more cost-effective and environmentally friendly, considering that many abandoned mining areas are located in remote mountains (Puga et al., 2015). The goal of ecological restoration is to keep the metals in place, restore the landscape, and reduce the pollution to the surrounding land and downstream water bodies (Lebrun et al., 2018). Phytostabilization helped by adding organic matter-based soil amendments, and is a cost-effective and environmentally friendly remediation that can be implemented on mining slopes and waste slag heap slopes to reduce the erosion of heavy metals (Lee et al., 2014). Plants can stabilize the soil and minimize the wind's ability to transport metal-rich dust (Galende et al., 2014). Phytostabilization, as a natural and solar-driven in situ strategy, has great potential in dealing with large areas of moderately polluted soil and sites (Gutiérrez et al., 2016). The premise is that plants are carefully selected and appropriate agronomic methods are adopted to properly manage them. Organic matter-based soil amendments like manure, which can improve the rhizosphere nutrition conditions and the growth of vegetation and their roots help stabilize soil, have been used in several abandoned mining areas to reduce metal migration in runoff (Arco-Lazaro et al., 2017). The mechanism of the influence of organic matter, especially the dissolved organic matter in soil, on the bioavailability of metals may be that the active functional groups (such as R-OH, -COOH, Ar-OH, -COR, and -CHO) combines with metal ions through adsorption, reduction, complexation, and chelation, which lead to the different distribution of metals in soil matrix and soil solution, resulting in the change of bioavailability (Angst et al., 2021). However, the effects of landscape restoration on metal migration in abandoned mine sites have not been widely described, and critical knowledge gaps remain regarding the potential for physical and chemical properties of the soil changes to increase metal mobility.

The total amount of metals in soil determines the amount of various chemical fractions of metals in soil to a certain extent, especially the content of bioavailable metal (Vareda et al., 2019). Therefore, the total amount of metals in soil has been widely used in risk assessment of soil metal pollution and soil environmental quality assessment for a long time (Sun et al., 2018). However, further studies have shown that the chemical distribution, or fractionation, of metals could reveal more important details about their mobility, release potential, and potential ecotoxicity. The bioavailable concentration of metals is increasingly used as an indicator of risk. Many different methods have been and are being developed to utilize bioavailability in environmental risk assessment (Zhang et al., 2017). The mobile distribution of metals refers to the metals retained in the unstable fraction of the soil, which is the form of the amount and toxicity of metals available to the organism. Sequential extraction methods were originally developed to study the geochemical equilibrium distribution of metals in soils and to predict their biological effectiveness on plants (Tessier et al., 1979; Gismera et al., 2004; Alvarez et al., 2006; Sebei et al., 2020). It is a useful tool for studying the source, destination, biological and physicochemical effectiveness of particulate elements, and the migration of adsorbed elements. According to the target and the physical characteristics of the target sample, appropriate reagents are used in each stage.

Our research focuses on the mobility of metals in the soil of landscape restoration mining areas, which is based on the actual environment rather than laboratory simulation. Five-year monitoring was conducted to 1) investigate the changes in the distribution of Pb and Cd at an abandoned mine site after five years of landscape restoration, and 2) assess the management and implications for long-term sustainability after phytostabilization in abandoned mining areas. The results of our study would provide a better perspective for the long-term sustainable management of the restored landscape around the tailings ponds.

Materials and methods

Study area

The abandoned mine is located in the hills and mountain area, about 500 m above sea level, 2.5 km to the northwest of Qingyuan County, Zhejiang Province. Its central geographical location is E $119^{\circ}02'18''$, N $27^{\circ}37'59''$. It belongs to the subtropical humid monsoon climate, with an average annual temperature of $16-19^{\circ}$ C and an average annual precipitation 1,600-1,800 mm. The study area is mountainous red loam, with 20%-30% gravel content, angular, generally 3-5 cm in size, 10-20 cm in size, covered by the Quaternary residual slope deposit (Q4^{e1-d1}). The hydrology of the abandoned mining area is relatively simple; it is mainly composed of atmospheric



FIGURE 1

Abandoned Pb/Zn mining area and sampling site in Qingyuan County (the satellite imagery was obtained from the Bigemap version 29.6.3.0 software and can be downloaded for free from https://map.tianditu.gov.cn).

precipitation and the natural flow of the gully along the slope to the downstream Songyuan Stream. The rainfall in the area is mainly concentrated in the plum season from April to June and the flood season from July to October. The non-flood season is from November to next March, with less rainfall. In 1985, the seventh Geological Brigade of Zhejiang Province, after three years of exploration, proved the lead resource reserves of 14.5×10^6 kg in 1988, with a mining area of 1 km². It was officially put into production in June 1992, with a daily production capacity of 1.10×10^3 kg. The mine is mainly open-pit mining, supplemented by underground mining, forming more than 20,000 m² of open-mining slope, 16,000 m² of tailing pond, and about 30,000 m² of waste slag heap slope. In April 2003, due to the depletion of resources and the protection of the ecological environment, the mine was abandoned. The concentration of Pb and Cd in the abandoned mining area is several orders of magnitude higher than the background content (Pb is about 7 times the tertiary limit value of the soil background value in Zhejiang Province, and Cd is about 40 times).

Landscape restoration

Pinus massoniana as a native plant has no strict requirements for soil, and can grow on gravel soil, sandy soil, clay, thin ground scoured by ridges and sunny slopes, and in steep rock crevices. In 2015, ecological restoration was carried out in the abandoned mining area, and *P. massoniana* were planted on the open mining slope and waste slag heap slope. Before planting *P. massoniana*, commercial manure (organic matter content: 20.5 g/kg, pH: 7.25, Pb and Cd were not detected) was applied to improve the agronomic potential of the soil in order to establish vegetation and reduce soil erosion. The amount of commercial manure was 10×10^3 kg/km², and the soil was reclaimed after application so that the organic fertilizer could be evenly mixed into the slope soil.

Soil and plant tissue analyses

Soil samples were collected in the first ten days of April every year (2016–2020). On each slope, multi-point sampling was applied and displayed, as in Figure 1. A total of 500 g of samples were collected from a depth of 0–20 cm using the quarter method (Campos-M and Campos-C, 2017) from multi-point sampling sites.

Plant tissues (roots, branches, and pine needles) of *P. massoniana* planted for landscape restoration were collected to determine the Pb and Cd contents inside. In the first 10 days of April 2020, the pine plants were collected based on the multi-point collection method of soil. The roots, branches, and pine needles were then collected. Plant tissues were digested with high-purity HNO₃ using a microwave digester (CEM, Mars, United States).

The plant of *P. massoniana* was collected in April 2015 in Qingyuan, Zhejiang Province, China. The material was identified by Dr. Hong Zhu (Nanjing Forestry University, Nanjing, China). The voucher specimen (No. P150409) was deposited at the Zhejiang Academy of Forestry, Hangzhou, China.

Soil pH was determined using a pH electrode in CO₂-free deionized water, with a soil–liquid ratio of 1:2.5 (w/v). Organic matter (OM) in soil is estimated to be 1.724 times that of organic

Step	Fractions	Distribution	Reagent	Shaking time and temperature
1	Exchangeable (f ₁)	Exch	10 ml of m mg(NO ₃) ₂ (pH 7)	4 h at 25°C
2	Bound to carbonates (f ₂)	Adsorbed	25 ml of m CH ₃ COONa (pH 5)	6 h at 25°C
3	Metal–organic complex bound ^a (f ₃)	Fulvic humic	30 ml of 0.1 m $Na_4P_2O_7$ (pH 10)	20 h at 25°C
4	Easily reducible metal oxide bound (f_4)	Reducible	20 ml of 0.1 m $\rm NH_2OH \cdot HCl$ in 0.01 m $\rm HNO_3$	30 min at 25°C
5	Organic bound (f ₅)	Organic	5 ml of 30% $\rm H_2O_2$ (pH 2), 3 ml of 0.02 m $\rm HNO_3$	2 h at 85°C
			3 ml of 30% $\rm H_2O_2$ (pH 2), 1 ml of 0.02 m HNO_3 cool, add 10 ml of 2 m $\rm NH_4NO_3$ in 20% HNo_3	2 h at 85°C
				30 min at 25°C
6	Bound to Al–Si minerals (f_6)	Residual	Digestion with hf -HClO ₄	

 a 30 ml of 0.1 M Na₄P₂O₇ extract was brought to pH 1.0 with the addition of 6 M HCl, and the suspension was left overnight for the coagulation of humic acid. The suspension was centrifuged at 12,000 rmp for 10 min. The acid-soluble metals, designated as fulvic complex-bound, were determined in the supernatant. The residue was solubilized with 0.1 M Na₄P₂O₇, and the metals, designated as humic complex-bound, were determined in the solution.

carbon (OC). Soil organic carbon (SOC) was measured by the solid direct injection method using a total organic carbon analyzer (Multi N/C 3100, Analytikjena, Germany).

The distribution of Pb and Cd in the soil was analyzed according to the sequential extraction method of Krishnamurti and Naidu (2002). In the first step of extraction, Mg(NO₃)₂ was used to replace NH₄NO₃ used in the original scheme because the strong acid and weak base salt of ammonium nitrate would reduce the pH value of the soil and promote soil hydrolysis, which might lead to excessive release of metals (Filgueiras et al., 2002). Table 1 shows the details of the method. During the extraction process, 1.0 g of each soil sample was weighed, and three parallel samples were made at the same time. After each extraction, the supernatant was centrifuged with a high-speed centrifuge at 12,000 rpm for 10 min, and then the residual sample was cleaned with 5 ml of deionized ultrapure water twice, mixing all supernatants, fixing the volume, and then carrying out the next extraction. The supernatants were filtered (0.45 µm) for analysis using inductively coupled plasma mass spectrometry (NexION 300X, Perkin Elmer, United States). The final residual fraction was dissolved for complete determination using the digestion procedure of HF-HClO₄.

Certified reference materials (GSW07445 for soil and GBW10019 for *Pinus massoniana*) were used in the digestion and analyzed as part of the QA/QC protocol. Repeated analyses of the certificated reference materials yielded a recovery rate of 92%–114% (n = 6) for Pb and 92%–105% (n = 6) for Cd.

Statistical analysis

Statistical analysis was carried out using the SPSS version 22.0 software. Pearson correlation coefficients were determined

between the SOM, soil pH, and the distributions of Pb and Cd in soil. Figures were developed using the Origin 85 program. The satellite imagery in Figure 1 was obtained from the Bigemap version 29.6.3.0 software.

Results

Soil organic matter and soil acidity

After ecological restoration, the SOM of the slopes reached about 30 g/kg (Table 2), and the soil pH value decreased by 0.38 units (Figure 2). The fertility of the slope prior to remediation was very low, and the organic matter content of the slope was only 1.3 g/kg in 2015. The native plant *Pinus massoniana* could grow in barren soil. Therefore, we did not choose commercial organic fertilizer with a high organic matter content to improve soil fertility. De Valle et al. (2020) have found that excessive soil organic carbon content cuts off the connection between plants and microorganisms.

Distribution of metals lead and cadmium

Soil properties after afforestation are listed in Table 2. Relative abundances of Pb and Cd in the exchangeable (F₁), adsorbed (F₂), fulvic and humic complex (F₃), reducible (F₄), organic (F₅), and residual (F₆) fractions following the sequential extraction procedure of soils are graphically illustrated in Figure 3. Observing the fractions in Figures 3, 4, whether it is Pb or Cd, the relative abundance of the residual and the amount of F₆ fraction were falling, which illustrated an assignment from a stable F₆ distribution to F₁₋₅ distribution. After ecological

Time (year)	Soil organic matter (g/kg)	рН	Pb-P (mg/kg)	Cd-P (mg/kg)
2016	23.01 ± 0.23	4.82 ± 0.04	3,568.32 ± 4.26	46.42 ± 2.01
2017	24.13 ± 0.26	4.79 ± 0.03	3,523.26 ± 3.68	46.05 ± 1.68
2018	26.59 ± 0.35	4.71 ± 0.02	3,546.12 ± 3.13	44.58 ± 1.74
2019	28.06 ± 0.46	4.63 ± 0.02	3,509.68 ± 3.30	42.36 ± 1.85
2020	29.98 ± 0.42	4.44 ± 0.02	3,496.21 ± 3.21	38.69 ± 1.56

TABLE 2 Descriptive statistics of soil properties after afforestation (mean \pm standard deviation, n = 7).



restoration, the fractions' content was redistributed. The bioavailability of Pb/Cd was increasing.

The metals Pb and Cd in the slope soil of an abandoned mining area showed different distribution patterns. The exchangeable (F1) fraction, that is, metals adsorbed on clay, humus, and other constituents, was ranked in the following order of relative abundance: Cd > Pb. The F_1 fraction in soil is the main fraction of metal release into the soil solution and is readily ion exchanged (Lyu et al., 2021). Exchangeable fraction is sensitive to environmental changes, easy to migrate and transform, and can be absorbed by plants, and relative abundance of the adsorbed (F_2) fraction is Cd > Pb. It is related to the co-precipitation-bound state of metals in soil formed on carbonate minerals. The F2 fraction is also most sensitive to soil environmental conditions, especially the soil pH value. When the pH value decreases, it is easy to release again and enter the environment. In the fulvic and humic complex (F₃) fraction, relative abundances are in the following order: Cd > Pb.



Relative abundances of Pb and Cd in the exchangeable (F_1), adsorbed (F_2), fulvic and humic complex (F_3), reducible (F_4), organic (F_5), and residual (F_6) fractions following the sequential extraction procedure of the soils.



The F₃ fraction is related to components of dissolved organic matter (DOC) such as humic and fulvic acids. Low molecular weight substances, like amino acids, carbohydrates, and organic acids, and high molecular weight substances, like humic substances (i.e., fulvic, humic acids, and humin), are referred to as well-known DOC matrices. Although the process and function of DOC have been extensively studied, there are still some ambiguities about the source of DOC (Lehmann and Kleber, 2015; Ramesh et al., 2019). Relative abundance of the reducible (F_4) fraction is Pb > Cd. The F_4 fraction is generally formed by the external capsule and fine powder particles of minerals, the active iron manganese oxide with a large specific surface area, adsorption, or co-precipitation of anion. Many previously published studies have reported that the reducible fraction (usually associated with Fe and Mn oxyhydroxides) dominates in sequestering large amounts of Pb (Li et al., 2015; Meng et al., 2018; Sebei et al., 2020; Haris et al., 2022). In the organic (F₅) fraction, which is metal associated with organics other than humic and fulvic acids, relative abundances are in the following order: Cd > Pb.

Discussion

Variability in organic matter and soil acidity

Commercial manure was applied to improve the agronomic potential of soils so that vegetation could be established and erosion reduced. Atmospheric nitrogen deposition, water content, temperature, and litter entering into the soil all affect the accumulation of SOM. According to the mining area environment, we choose the native plants which are resistant to barrenness, developed root system, easy to survive, and have certain tolerance to heavy metals. Planting *P. massoniana* can improve the landscape of the mining area and the surrounding area with low cost. Plants can stabilize the soil and minimize the wind's ability to transport metal-rich dust. The damaged soil fertility had been repaired to a certain extent.

The 5-year monitoring results showed that the soil pH value decreased. Soil acidification was related to the decomposition of accumulated organic matter to produce organic acid, the secretion of acid by Pinus massoniana, and acid deposition. Conifer litter contains tannin, resin, and lignin, which are difficult to be decomposed. After decomposition, acid substances are produced, which inhibit soil microbial activities and make the soil become acid. A study shows that conifer litter is difficult to be biodegraded, and conifer evergreen characteristics strengthen the fixation of acid pollutants. As pointed out by Binkley, Valentine, and Jönsson (Binkley and Valentine, 1991; Jönsson et al., 2002), Norway spruce can acidify the soil because plants absorb only soluble forms of Cd/Pb and release protons back to the soil solution. While anions do not exist in the same content absorbed by plants, metal ions are unbalanced, and proton leaching on plant outer membranes controlled by proton pumps may acidify soil. Arshad et al. (2016) have reported that Pelargonium hortorum has this exact acidification effect on soil. On the other hand, in recent decades, with the development of China's industry, a large number of acid gas emissions, and the increasing impact of acid sediment on the environment, the frequency and intensity of acid deposition in southern China have increased. Acid deposition may be the main cause of forest soil acidification.

Distribution	$Pb(F_1)$	Pb (F ₂)	Pb (F ₃)	Pb(F ₄)	$Pb(F_5)$	Pb(F ₆)
pН	-0.989**	-0.990**	-0.936*	-0.953*	0.658	0.966**
Soil organic matter	0.980**	0.956*	0.987**	0.848	-0.722	-0.988**
** <i>p</i> < 0.01.						

TABLE 3 Pearson's correlation among soil pH, soil organic matter, and distribution (F1~F6) of Pb.

p < 0.05.

TABLE 4 Pearson's correlation among soil pH, soil organic matter, and distribution (F1~F6) of Cd.

Distribution	Cd(F ₁)	Cd(F ₂)	Cd(F ₃)	Cd(F ₄)	$Cd(F_5)$	Cd(F ₆)
pH	0.314	-0.992**	-0.977**	0.974**	0.986**	0.987**
Soil organic matter	-0.058	0.924*	0.985**	-0.898*	-0.952*	-0.971**

**p < 0.01.

*p < 0.05.

Relationships among soil pH, soil organic matter, and distribution of lead and cadmium

The Pearson's correlation among soil pH, SOM, and the distribution $(F_1 \sim F_6)$ of Pb and Cd is shown in Table 3 and Table 4. There was a significant positive correlation between the F₆ distribution and soil pH. The amount of the F₆ distribution decreased with the decrease in soil pH. The plants decrease soil pH by root exudation (e.g., amino acids, organic acids, phenols, terpenoids, carbon dioxide, and water) and plant litter, and these, in turn, increase the bioavailability of Pb and Cd for plant uptake (Gul et al., 2021). In contrast, there was a significant negative correlation between the F2 distribution and soil pH. Carbonatebound metals are co-precipitated bound states of metals on carbonate minerals formed in the soil, which are sensitive to soil acidity. With the decrease in the pH, the decomposition of carbonates such as CdCO₃ was promoted. The F₃ distribution is positively correlated with the SOM. The F₃ distribution represents the metals associated with metal-organic complexes. With the ecological restoration of slope soil, plant litter, root exudation, and soil humus, microorganisms affect the accumulation of the SOM. Humus is the main form of SOM, accounting for 85%–90% of the total SOM, so most of SOM refers to soil humus. Humic acid and fulvic acid are the main components of dissolved organic matter with better solubility (Eckley et al., 2021). Functional groups in dissolved organic matter have high activity or functionality in soil and aquatic environments. For example, humic acids interact with metals, which affect the soil pH and metal migration. With the accumulation of organic matter, the relative abundances of Pb and Cd in the distribution F3 increased by 0.54% and 3.17%, respectively. The decrease in the soil pH and the increase in soil SOM after landscape restoration resulted in the increase in

exchangeable forms of Cd and Pb, which implied that the bioavailability of Pb and Cd has improved.

The fractions of Cd are more sensitive to soil acidity than those of Pb. Except the distribution F_1 , there was a significant correlation between the remaining distributions and soil pH. Soil pH significantly affects the mobility and phytoavailability of Cd, and has a crucial role in retaining Cd in soil. Increasing soil pH by liming is effective in reducing plant Cd accumulation (Wang et al., 2020).

Spatial distribution of lead and cadmium within the P. massoniana, and implications for phytostabilization

After landscape restoration, lead and cadmium in the soil migrated to P. massoniana. Spatial distributions of Pb and Cd within P. massoniana are illustrated in Figure 5. Compared with cadmium, lead was more concentrated in roots. The concentration of cadmium in pine needles, branches, and roots was relatively uniform. Lead and cadmium showed different migration behavior. Cd is more mobile than Pb, and it is synergic with Zn. Some studies have confirmed that cadmium in plants is more likely to be present in the form of Cd-thiol-rich proteins, Cd-carboxylic acid compounds, and Cdhistidine bound (Gu et al., 2020).

Our data corroborated that the mobility of lead and cadmium was increased at the abandoned mining area after landscape restoration. Different from farmland, woodland has no habit of applying lime, so long-term afforestation can lead to continuous soil acidification. Soil acidification may increase the solubility and mobility of metals in soil (Gao et al., 2019). Alkaline amendments (e.g., lime application) should be appropriately used for long-term sustainable management after



phytostabilization in abandoned Pb/Zn mining areas. Some studies have shown that lime can increase soil respiration by increasing the concentration of organic carbon in soil solution (Li et al., 2020). CaCO3 amendment has been shown to be effective in reducing Cd accumulation in rice grains (Yan et al., 2021). Biochar remediation might be a scheme that can be tried. Biochar prepared by anaerobic pyrolysis is generally alkaline. The inorganic carbonate crystal in biochar is consistent with the traditional lime in composition (Meng et al., 2022). Therefore, adding it to the soil can significantly improve the soil pH (Tang et al., 2022). Biochar has the characteristics of porosity and a large specific surface area, which directly affects its adsorption and fixation of metals (Xu et al., 2016; Moradi et al., 2019; Yu et al., 2019; Yuan et al., 2019; Xiang et al., 2021). The soil in abandoned mining areas needs continuous tracking and monitoring after ecological restoration, and corresponding remedial measures shall be implemented.

Conclusion

After landscape restoration, SOM accumulated and the soil acidified with time affected the redistribution of metal fractions and certainly promoted the remobilization of metals. One of the most obvious changes was that it promoted the activation of carbonate-bound distribution metals sensitive to soil acidity. The second is to promote the activation of metals associated with the fulvic and humic complex, which are the main components of dissolved organic matter. The introduction of unstable carbon sources may stimulate metal migration. The study of pollutants' occurrence and sources, the pollution effect on forests, and changes in pollutant processes after land use modification would contribute to providing tools for their sustainable management. Implications from this study indicate that alkaline amendments should be appropriately used for long-term sustainable management after phytostabilization in abandoned Pb/Zn mining areas.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

Author contributions

FZ: methodology, investigation, experimental and lab work, and writing—original draft; HL: review and editing, and overall supervision.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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