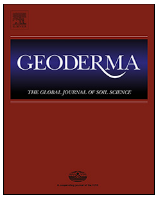
Geoderma 326 (2018) 123–132

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma



# Dominant factor affecting Pb speciation and the leaching risk among land-use types around Pb-Zn mine

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ARTICLE INFO

Handling Editor: Junhong Bai

*Keywords:*
Land-use
Pb
Speciation
Leaching risk
Mine

ABSTRACT

Soil lead (Pb) pollution around the mining area has severely threaten human health. However, Pb leaching risk in soils with different land uses and which is the proper land use are still unknown. In this work, Pb speciation characteristics and the dominant soil factors affecting Pb speciation in three land uses (farmland, woodland, and grassland) surrounding the Pb-Zn mine in Feng Country, Shaanxi province were investigated. Moreover, the Pb leaching risk and associated determining factors were evaluated by the combination of leached Pb concentration and structural equation model (SEM). The results showed that farmland presented the highest total Pb content (410.1 mg kg$^{-1}$) among three land use types. The reducible fraction of Pb (Fe-Mn oxides bound) was the major speciation (> 50%) in all tested soils of three land-use types. Soil total phosphorus (TP), water content (WC), and pH play major role in regulating Pb speciation. Though soil biological properties, like microbial communities, catalase, and microbial biomass nitrogen (MBN) exhibited distinct responses to three different land uses, they showed minor influence on Pb speciation. More interestingly, SEM analysis indicated that Pb leaching risk was directly linked with bacteria abundance, total Pb content, clay content, and C/N. Grassland presented the higher predicted Pb leaching concentration (85.03 mg kg$^{-1}$), compared with that in woodland, suggesting that grassland was the worst land-use type to buffer the Pb toxicity. Woodland could be recommended as the proper native land use to alleviate environmental risk. Overall, our results demonstrated the dominant factor to regulate Pb speciation and pointed out the proper land-use in relieving Pb leaching risk around Pb-Zn mine. These finding provides the new strategies to the remediation and management of metal-contaminated soil.

## 1. Introduction

Soil pollution by lead (Pb) in the mine tailings and surrounding area has been the focus due to the high health risk (Li et al., 2014). Pb, which is emitted from smelters in flue gases or incorporated into solid wastes, would reach the soil and result in significant contamination at local-to-regional scale. However, these large area of polluted soil was still utilized in various land-use types, such as woodland, farmland, grassland, etc. (Wei and Yang, 2010). Land-use types can affect soil quality to regulate Pb bioavailable and biotoxicity (Marzaioli et al., 2010). Thus, it is necessary to investigate Pb mobilization in soil with different land uses and find out the key factors that determine Pb biotoxicity. Furthermore, the evaluation of environmental risks under different land use patterns and the seeking of safe land use type are of great significance to human health.

As it is known, the toxicity and mobility of Pb in soil were not only affected by the total concentration, but also by its geochemical speciation i.e. exchangeable, iron-manganese oxide-associated, organic-associated and residual forms. Exchangeable fractions are considered to be bioavailable; oxide- and organic matter-bound fractions may be potentially bioavailable; while the residual fraction is mostly not available to either plants or microorganisms (Rodriguez et al., 2009). These fraction distributions are affected by complex environmental factors, like soil properties, plant species, and microbiological processes, which were mainly determined by land use types (Li et al., 2009). Wang et al. (2008) have concluded that soil particle-size distribution was significant different under 5 land-use types (woodland, shrub land, grassland, terrace, and abandoned slope farmland). Subsequently, Marzaioli et al. (2010) proved that several physical, chemical and biological parameters in soils were affected by different land use

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https://doi.org/10.1016/j.geoderma.2018.04.016
Received 15 December 2017; Received in revised form 26 March 2018; Accepted 17 April 2018

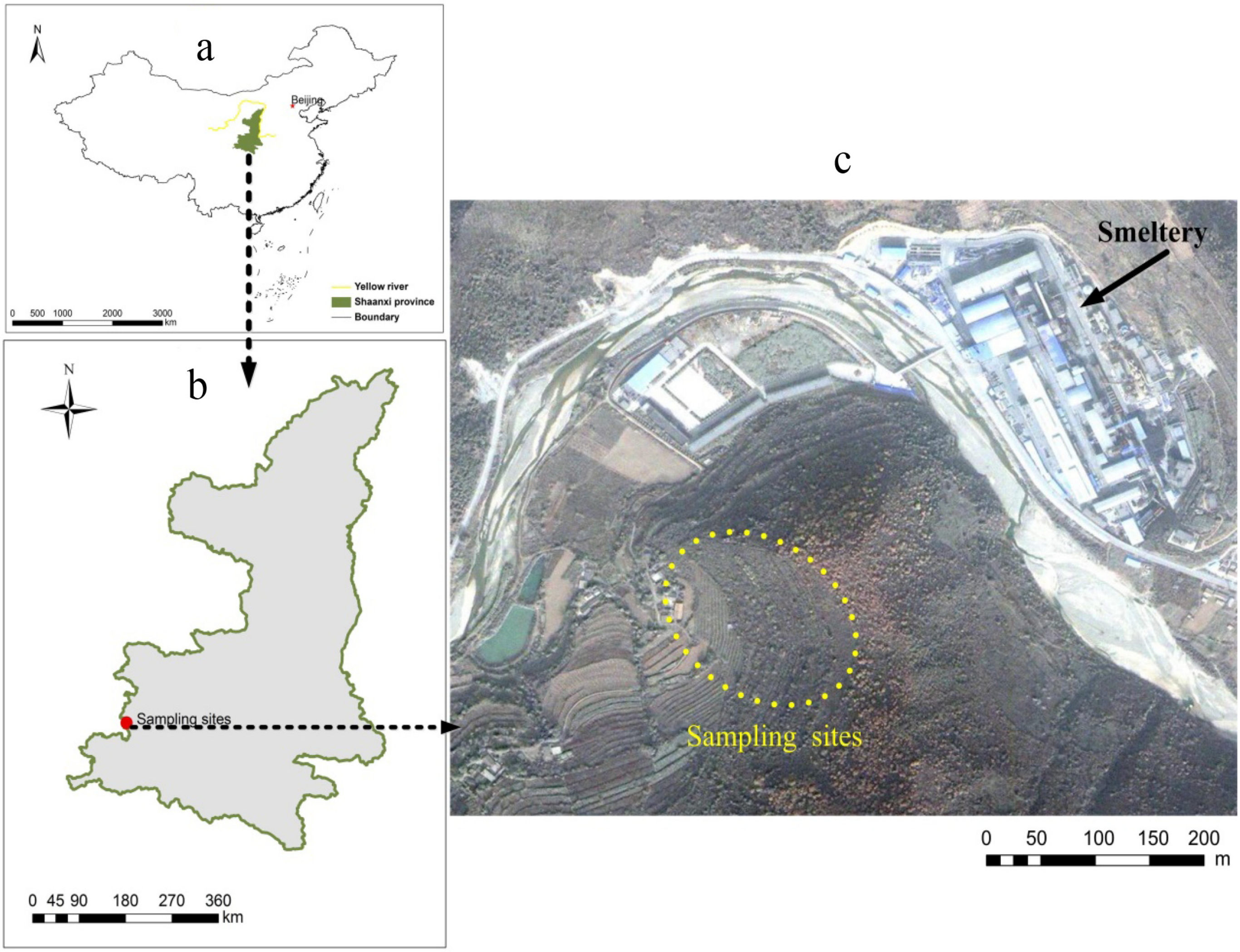

**Fig. 1.** Map of sampling area. a and b show the map of China and Shaanxi province, respectively. c shows the specific sampling area which is marked with the yellow dots. The smeltery was marked by black arrow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

types (i.e. permanent crops, grazing lands, shrublands, coniferous and mixed forests). They also concluded that different land uses led to distinct heavy metal contents (chromium, copper, and zinc) in soils. Total Pb content in classical garden was reported to be almost twice than in other land use types (business area, public green space, residential area, and roadside area) (Xia et al., 2011). Zheng et al. (2005) also stated that Pb in greenbelt and orchard were significantly higher than those in other land use types (paddy field, vegetable field, and wheat field). Moreover, land use type could change the distribution of diethylene triamine pentacetate acid (DTPA) exactable form of heavy metals in the soils through affecting soil organic matter (Mahmoudabadi et al., 2015). Metals (except Ni) mobility decreased in the following order: wetland > dryland ≥ paddy field > forest land (Zheng et al., 2016).

Thus, it is believed that land-use type influence on Pb speciation should be considered in the Pb contamination evaluation systems. Limited relevant studies have been carried out and proved that heavy metals i.e. Cd, Cu, Pb and Zn had distinct concentration among several land uses (Wei and Yang, 2010; Xia et al., 2011; Zheng et al., 2005). However, these primary studies focused only on total Pb contamination with neglecting of Pb speciation distribution. Therefore, the dominant soil properties under different land uses regulating Pb speciation and toxicity are still unknown, which hinders the effective strategies to the remediation and management of Pb-contaminated soil around Pb-Zn mine. Moreover, in most previous studies of evaluating Pb biotoxicity, stimulated Pb polluted soils by artificial addition were employed. For example, the effects of plant species coexistence on soil biotoxicity under Pb pollution were studied by adding 200 and 500 mg Pb [applied as $Pb(NO_3)_2$] into 1 kg dry weight soil (Gao et al., 2010). Another study of Pb effects on soil biotoxicity was undertaken with brown soil in a greenhouse by adding different $Pb(NO_3)_2$ contents for a period of 10 weeks. (Pan and Yu, 2011). Zheng et al. (2017) also carried out the study of Pb influence on soil enzymes by supplementing $Pb(Ac)_2$ as the simulated Pb pollution in a plastic vessel for 15 days. These short-term and simulated Pb pollution results may obtain some unrealistic conclusions due to the different Pb pollution sources, which underestimate or overestimate the Pb exposure risk. Besides, in studies referring to the actual Pb pollution, the biotoxicity evaluation mainly depended on plant accumulation and limited microorganisms. For example, a study was designed to investigate the potential human health risks associated with the consumption of okra vegetable crop contaminated with toxic heavy metals. The crop was grown on a soil irrigated with treated wastewater. It was concluded that the okra tested was not safe for human use, especially for direct consumption by human beings. (Balkhair and Ashraf, 2016). Some native wild plant species were used to assess the Pb toxicity. The examination of Pb content in them showed that *Inula viscosa* L. and *Allium ampeloprasum* L have the potential to be used for the phytostabilization of Pb (Christou et al., 2017). As to microorganism, *Escherichia coli* DH5α as a reporter microorganism was used to disclose toxicity ranking of various ashes of municipal solid waste incinerator. The results showed that low solubility of metallic ions (e.g., Pb(II) and Cu(II)) in ashes likely resulted in low mobility in the environment and low risk to humans (Lin and Chen, 2006). Bacteria strains from *Pseudomonas* were employed to assess their resistance to Pb under the effects of humic substances (HS). This study demonstrated that Pb toxicity to bacteria could be reduced through complexation with HS and their fractions (Perelomov et al., 2018). All these conclusions were generally disparate due to the confine of plant species and unicity of microbe variety. These limitation and gaps motivate our study of Pb actual contamination evaluation under various land uses using more reliable indexes.

Here, Pb speciation distribution, soil physical (texture, water content), chemical (pH, organic carbon, total nitrogen, total phosphorus), and biological (microbial biomass, community, soil enzyme) characteristics were investigated under three land uses (farmland, grassland, and woodland). The aims of this study were to: 1) explore the Pb speciation characteristics among different land uses and find out the dominant soil factors affecting Pb speciation; 2) seek for the proper land-use type in relieving environmental risks.

## 2. Materials and methods

### 2.1. Experimental site and soil sampling

Soil samples were collected in the surroundings of the Pb-Zn mine located in Feng County, Shaanxi province, China (106°33′E, 33°48′N). The mine was the fourth largest zinc producer and the smelter near the mine has been in operation for over 50 years. The smelter has an annual output of 150, 000 tons of zinc ingots and one million tons of coke. The prevailing wind direction in Feng County during the sampling period was east and the wind speed varied from 3.4 to 7.6 $m\,s^{-1}$. The long-term smelter dust emission was the main source of Pb pollution in the sampling area (Shen et al., 2017).

Farmland, woodland, and grassland were selected as three different land uses. The sampling lands around the smelter have similar gradients and altitudes. The location of the sampling is shown in Fig. 1. A total of 47 samples were collected from farmland (30 samples), woodland (9 samples), and grassland (8 samples) surrounding the mining areas. Soil samples from 0 to 20 cm depth were taken using shovel at each point. The samples were placed in labelled Ziploc plastic bags for transport to the laboratory. All samples were sieved to an adequate size for further analysis (< 2 mm). Half of each sample was stored at 4 °C for the determination of soil bio-properties and the rest was air-dried for the subsequent physicochemical analyses.

### 2.2. Soil physical-chemical properties analysis

Soil pH was determined at a soil to water ratio of 1:2.5 using a pH meter (Startorius PB10). The soil texture was determined using a Malvern Mastersizer 2000 particle size analyzer with alcohol as a dispersant. Soil organic carbon (SOC) was determined by $K_2Cr_2O_7$-$H_2SO_4$ oxidation method. Total nitrogen (TN) was measured after $H_2SO_4$-$H_2O_2$ digestion via Kjeldahl distillation (KETUO KDY-9820, China) and total phosphorus (TP) was determined after digestion by Mo-Sb colorimetric method with a UV–vis spectrophotometer (Shimadzu UVmini-1240, Japan). Water content (WC) was measured by the gravimetric method. Total Pb content in soil samples were measured by digestion with three acid ($HNO_3$, HCl, and $HClO_4$) and analyzed using a flame atomic absorption spectrometer (VARIAN-GTA120AA240FS). Certified standard reference materials NIST 2709 San Joaquin soil (National Institute of Standards and Technology, USA) was used in the analysis as part of the Quality Control and Quality Assurance (QC/QA) protocol.

### 2.3. Mineralogy and chemical composition in clay fraction of soil

The mineralogy characteristics of phyllosilicate composition of clay fractions in soil were analyzed by X-ray diffraction (XRD). Prior to the XRD analysis, free Al and Fe phases were removed by the dithionite-citrate-bicarbonate (DCB) extraction method (McKeague et al., 1971). All X-ray diffractograms were recorded by a Bruker D8 X-ray diffractometer equipped with CuKα radiation, under a voltage of 40 kV and an intensity of 40 mA. The XRD patterns were recorded from 3 to 30° (2θ) at a scanning speed of 10° (2θ) $min^{-1}$.

Identification of the clay minerals was mainly based on the comparison of the XRD patterns obtained under the seven different measurement conditions: Mg-glycerol, K-25 °C, K-110 °C, K-250 °C, K-350 °C, K-450 °C, and K-550 °C. Montmorillonite was identified by the presence of the 1.8 nm peak in the Mg-glycerol sample and the absence of this peak in all K samples. Vermiculite was identified when the 1.4 nm peak in the K-25 °C sample was absent compared to that in the Mg-glycerol sample. Illite was recognized by its 1.0 nm peak in all treatments. Kaolinite was identified by the presence of a peak at 0.71 nm in the Mg-glycerol, K-25 °C and K-300 °C sample and the absence of this peak in the K-550 °C sample.

Semi-quantitative estimates of the proportions of the clay minerals in the samples were derived from the integrated peak areas of the characteristic peaks. The relative percentages of montmorillonite, illite, vermiculite, and kaolinite were determined using empirically estimated weighting factors (Biscaye, 1964).

The chemical compositions of clay samples were determined with wavelength dispersive X-ray fluorescence spectrometry (WD-XRF, a PW4400). Briefly, 0.6 g clay sample was mixed with 6 g dry lithium tetraborate ($Li_2B_4O_7$) and fused into a 32 mm diameter glass bead. Calibrations were carried out with 28 nationally certified reference materials of soil (GBW07401-GBW07416 and GBW07301-GBW07312). The analytical uncertainty, as checked by parallel analysis of two national standards (GSS-8 and GSD-12), was 1–2%.

### 2.4. Determination of chemical forms of Pb in soils

The BCR sequential extraction procedure (proposed by the European Community Bureau of References) (Rauret et al., 1999) was modified and then applied to fractionate the chemical forms of Pb in soil samples. Briefly, it consists of four extraction steps, namely: Step 1 (acid extractable/exchangeable fraction, F1), extraction with 0.11 M acetic acid; Step 2 (iron- manganese oxide-associated fraction, F2), extraction with 0.5 M hydroxylamine hydrochloride at pH 1.5; Step 3 (organic-associated fraction, F3), reaction with 8.8 M $H_2O_2$ followed by extraction with 1.0 M ammonium acetate at pH 2, and Step 4 (residual fraction, F4), is calculated by subtracting the non-residual fraction from the total metal concentrations. Pb concentration in each extracts was analyzed using a flame atomic absorption spectrometer (VARIAN-GTA120AA240FS).

### 2.5. Soil bio-properties analysis

Microbial biomass carbon (MBC) and nitrogen (MBN) were determined by the chloroform fumigation-extraction method previously described by Vance et al. (1987). A $k_{EC}$ factor 0.45 was used to convert microbial C flush into MBC, while a $k_{EN}$ of 0.54 was used for MBN (Maharjan et al., 2017). Microbial quotient ($q_{mic}$ as MBC/SOC) was calculated for the present study (Anderson and Domsch, 1989). Microbial community consisted of bacteria, fungi, actinomycetes was determined by plate count method (Takahashi et al., 2017).

Soil enzyme activity was determined by the method described by Guan (1987). Briefly, urease activity was measured by the sodium phenolate-sodium hypochlorite colorimetry method and was expressed as micrograms of $NH_3$-N per g soil per hour (μg $NH_3$-N·$g^{-1}$·$h^{-1}$). Alkaline phosphatase activity (ALP) was determined using the orthophosphoric monoester phosphohydrolase method with alkaline optimum and was expressed as milligrams of phenol per g soil per h (mg phenol·$g^{-1}$·$h^{-1}$). Catalase activity was defined as milliliters of 0.02 mol·$L^{-1}$ $KMnO_4$ per g soil per h (mL 0.02 mol·$L^{-1}$ $KMnO_4$·$g^{-1}$·$h^{-1}$) and was measured by the potassium permanganate titration method.

### 2.6. Assessment of Pb pollution and potential leaching risk

Contamination factor (CF) reflects the anthropogenic input in elemental pollution and was calculated by dividing the concentration of element in the soil by the background concentration ($CF = C_i/B_i$) (Pandey et al., 2016). Here, $C_i$ is the Pb concentration, and $B_i$ is the geochemical background value of Pb (21.2 mg $kg^{-1}$) in Shaanxi province (Chen et al., 2015b). The contamination grades in an increasing order of contamination are rated from 1 to 6 (0 = none, 1 = none to medium, 2 = moderate, 3 = moderate to strong, 4 = strongly polluted, 5 = strong to very strong, 6 = very strong).

The geoaccumulation index ($I_{geo}$) is a geochemical criterion to evaluate pollution level in soils or sediments and calculated using $I_{geo} = \log_2 (C_n/1.5B_n)$ (Chen et al., 2015b). In this work, $C_n$ is the measured concentration of Pb, $B_n$ is the geochemical background value of Pb in Shaanxi province. Factor 1.5 is the background matrix correction factor due to lithospheric effects. The Pb pollution level was classified based on $I_{geo}$ value as follows: unpolluted ($I_{geo} \le 0$), unpolluted to moderately polluted ($0 < I_{geo} \le 1$), moderately polluted ($1 < I_{geo} \le 2$), moderately to heavily polluted ($2 < I_{geo} \le 3$), heavily polluted ($3 < I_{geo} \le 4$), heavily to extremely polluted ($4 < I_{geo} \le 5$), or extremely polluted ($I_{geo} > 5$).

The potential Pb leaching risk was estimated by the concentration of leached Pb, which was calculated from the concentration and leached portion of four fractions using $Conc_{pb} = Conc_1 \times \eta_1 + Conc_2 \times \eta_2 + Conc_3 \times \eta_3 + Conc_4 \times \eta_4$. $Conc_i$ and $\eta_i$ are the concentrations and leached portions of four different Pb speciation. In this work, 1, 0.176, 0.008 and 0 were employed for $\eta_1$, $\eta_2$, $\eta_3$, and $\eta_4$ values, respectively (Bao et al., 2016).

### 2.7. Statistical analysis

One-way analysis of variance (ANOVA) and Duncan's multiple range tests were used to assess the statistical significance of three different land uses based on soil properties and Pb content using SPSS 20.0 ($P < 0.05$). The correlation matrix between Pb speciation concentration and soil properties was based on the Pearson's correlation coefficients and was described by heatmap using R software 3.3.1. Canoco 4.5 program was selected to conduct redundancy analysis (RDA). The structural equation modeling (SEM) framework was applied to investigate direct and indirect effects of soil properties on Pb leaching risk (PLR). The $\chi^2$ values and P-values were adopted to evaluate the overall goodness of structural equation model fit. Finally, we calculated the standardized total effects of pH, clay, C/N, Pb, and bacteria on PLR. The SEM was carried out by using the Amos 21.0 software package (Smallwaters Corporation, Chicago, IL, USA).

## 3. Results

### 3.1. Soil physico-chemical and mineralogy properties

Three land uses with different vegetation types and ages were employed in this study (Table S1 in the Supplemental file). Means and standard error for the general soil characteristics are presented in Table 1. In general, 47 soil samples with three land uses featured different soil properties. The pH of studied soils among three land use were similar with the mean value about 7.9. Though soils from grassland has significantly distinct particle size distribution compared to that from other two land uses, all tested soils had silt loam texture (USDA classification) with silt mean contents ranging from 57.6 to 65.4%. The SOC and TN contents showed no significant differences among three land uses. Soils from farmland had the significantly highest TP content due to the possible fertilization. Three land uses could result in the extremely various WC with the highest mean value of 27.2% for grassland.

The X-ray diffraction shows the bulk mineralogy of the compounds that may be present in clay fraction of soil. The diffractogram (Fig. S1) and semi quantitative analysis (Table 2) showed that vermiculite ranged from 31 to 36%, montmorillonite 24–29%, illite 25–32%, and kaolinite 10–13% in all tested soils. Based on the clay fraction contents in three land uses (Table 1), it could be concluded that compared to farmland and woodland, grassland has significantly lower mineral contents. Pb compounds were not observed in all tested soils, probably due to the low total Pb level on phyllosilicate composition that would render its crystalline compounds non-detectable by XRD (Dermatas et al., 2006). The major elements results indicated that silicon (47.7–48.5%), aluminum (18.2–19.4%), and iron (8.3–8.6%) were the dominant oxides in all tested soils (Table 2). Also, it was shown that grassland had the lowest dominant oxides contents among three land uses.

### 3.2. Pb speciation distribution in soils

For the total Pb content, it was shown that farmland had the extremely polluted value of 410.1 mg $kg^{-1}$, significantly higher than that in woodland (315.9 mg $kg^{-1}$) and grassland (313.6 mg $kg^{-1}$) (Fig. 2). As Shen et al. (2017) reported, the studied sites were polluted by atmospheric deposition of Pb dusts from point of emissions. Thus, the different total concentrations of Pb in three land use might be led by the distinct cover types intercepting different Pb contents going into the soil (Pouyat et al., 2007). All soils from three land uses were strongly polluted assessed by the CF > 6 and $I_{geo} > 5$ (Table 3). For all three land uses, Fe-Mn oxides bound Pb (F2) was the dominant speciation accounting for 60% of the total Pb amount. The second Pb speciation was the residual fraction (F4) with about 20% and followed by acid exchangeable Pb (< 19%) and organic matter/sulfides-bound fraction (< 5%). Comparing Pb speciation among three land uses, it was shown that for F1 (acid exchangeable Pb), grassland had a greater portion than the other two land uses (Fig. 3). For F2, in contrast, grassland showed a lower portion. However, for F3 (organic matter and sulphides bound Pb) in the farmland, it was significantly higher than that in other two land uses. For F4 (residual Pb), there were no significant differences among three land uses. When employing the leached portion ($\eta$) to assess the potential Pb leaching risk, it was found that the Pb leaching concentration was 60.62 mg $kg^{-1}$ in woodland. This value was comparable with farmland (74.65 mg $kg^{-1}$), however, lower than grassland (85.03 mg $kg^{-1}$) ($P < 0.05$) (Table 3).

### 3.3. Soil microbial performance

The microbial community results (Fig. 4) showed that in all collected soil samples, bacteria was dominant with the amount of $10^6$ cfu $g^{-1}$, followed by actinomycetes (about $10^5$ cfu $g^{-1}$) and fungi ($10^3$ cfu $g^{-1}$). Among three land uses, woodland had the largest microbe amount including bacteria, actinomycetes, and fungi. However, three land uses had no significant differences for fungi. For three soil enzymes related to C, N, and P nutrient cycling, they displayed various changes among three land uses. For example, urease exhibited the maximum value in woodland, followed by farmland and grassland. Grassland showed the minimum value of ALP activity, and there were no significant differences between farmland and woodland. For catalase, the maximum and minimum values were observed in woodland and farmland, respectively. For MBC and MBN, they both showed the maximum values in woodland, followed by farmland and grassland. Also, the microbial quotient ($q_{mic}$) value followed the same order as

**Table 1**
Physicochemical properties of soils with three land uses.

| Parameters[a] | Farmland | | Woodland | | Grassland | |
|---|---|---|---|---|---|---|
| | AV. ± SD.[b] | C.V.[c] (%) | AV. ± SD. | C.V. (%) | AV. ± SD. | C.V. (%) |
| pH | 8.0 ± 0.1 a | 1.3 | 7.9 ± 0.05 a | 0.7 | 7.9 ± 0.03 a | 0.4 |
| Clay (%) | 24. ± 1.4 a | 5.5 | 23.5 ± 3.5 a | 14.9 | 14.1 ± 6.1 b | 42.6 |
| Silt (%) | 65.4 ± 1.1 a | 1.6 | 64.6 ± 1.7 a | 2.7 | 57.6 ± 10.1 b | 17.6 |
| Sand (%) | 10.0 ± 1.8 b | 18.2 | 11.9 ± 4.8 b | 40.7 | 28.2 ± 15.0 a | 53.3 |
| SOC ($g\,kg^{-1}$) | 11.2 ± 1.5 a | 13.5 | 11.8 ± 1.9 a | 16.8 | 10.8 ± 2.6 a | 24.5 |
| TN ($g\,kg^{-1}$) | 1.2 ± 0.1 a | 10.5 | 1.2 ± 0.1 a | 15.2 | 1.1 ± 0.4 a | 38.4 |
| TP ($g\,kg^{-1}$) | 7.6 ± 0.7 a | 10.1 | 6.0 ± 1.2 b | 21.0 | 6.1 ± 1.0 b | 16.5 |
| C/N | 9.3 ± 0.9 b | 10.6 | 16.1 ± 2.4 a | 14.9 | 10.4 ± 1.5 b | 15.0 |
| WC (%) | 16.6 ± 2.0 c | 12.2 | 19.5 ± 2.9 b | 15.1 | 27.2 ± 7.0 a | 25.9 |

[a] SOC: soil organic matter. TN: total nitrogen. TP: total phosphate. C/N: the ratio of SOC to TN. WC: water content.

[b] AV. means the average value. SD. means standard deviation. Same letter denotes no significant difference between values in each land use.

[c] C.V. means coefficient variation.

**Table 2**
Mineralogy and major elements as weight percent (%) in the clay fraction (< 2 μm) in soils.

| Land uses | Clay mineral composition | | | | Major elements | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Montmorillonite | Illite | Kaolinite | Vermiculite | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $TiO_2$ |
| Farmland | 27 | 25 | 12 | 36 | 48.5 | 18.2 | 8.4 | 2.7 | 2.1 | 0.4 | 3.4 | 0.3 | 0.7 |
| Woodland | 29 | 27 | 10 | 34 | 48.3 | 19.4 | 8.6 | 2.8 | 2.3 | 0.4 | 3.2 | 0.2 | 0.8 |
| Grassland | 24 | 32 | 13 | 31 | 47.7 | 19.1 | 8.3 | 2.7 | 2.1 | 0.4 | 3.3 | 0.2 | 0.7 |

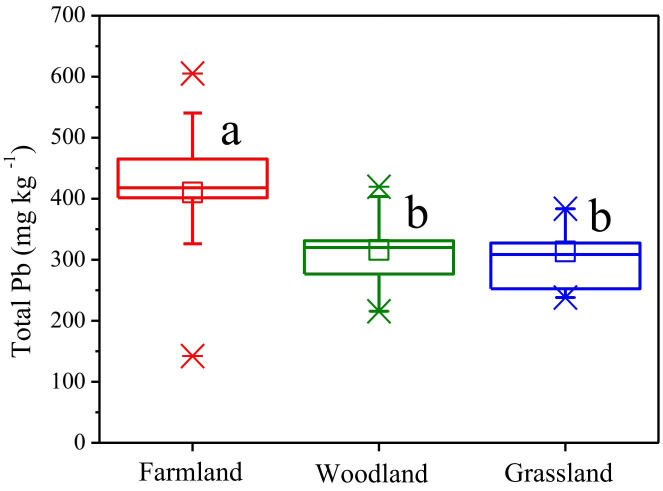

**Fig. 2.** Boxplots of total Pb concentration in soils of three land uses ($n = 30$ for farmland, $n = 9$ for woodland, $n = 8$ for grassland). Same letter denotes no significant difference between values in each land use.

MBC and MBN in three land uses. In all, woodland led to the highest microbial activity, in contrast to grassland. Combined with the results of Pb leaching risk, it was found that high microbial activity might result in the inevitably high Pb leaching risk in three land uses. Then, the question we concern is that which factor in soil bio-chemical properties regulate the Pb speciation distribution and then lead to the high Pb leaching risk.

### 3.4. The relationship between soil properties and Pb speciation

The correlation between Pb speciation and soil properties was shown as the heatmap (Fig. 5). The red and blue colors represented the positive and negative relations, respectively. Except F4 (the residual fraction), other Pb speciation showed significant relations with at least two parameters of soil properties. For example, F1 was positively significantly related with sand, however, negatively significantly affected by six soil properties, including clay, silt, bacteria, actinomycetes, urease, and MBN. Both clay and TP had positively significant influence on F2. However, sand, WC, fungi, and catalase had the contrary effect on F2. Moreover, it was found that the same soil properties showed various performances towards different Pb speciation. pH exhibited its stably positive effect on Pb speciation. However, for clay and silt, they showed negative influence on F1, while positive effect on F2 and total Pb, which is contrast to WC. Thus, it is difficult to intuitively identify the main regulator for each Pb speciation from the complex relationships.

The redundancy analysis (RDA) was employed to identify the dominant factor regulating the Pb speciation distribution. Canonical correlations for the soil properties for each axis indicated that both Axis 1 and Axis 2 were primarily TP, pH, and WC gradients (Table S2). The plot can be interpreted qualitatively by the length of the arrow to indicate how much variance being associated with that factor. Arrows for pH, TP, and WC were about twice as long as those for TN, MBN, MBC, urease, and SOC, indicating that these three factors accounted for a much greater proportion of variance in the Pb speciation than other soil properties (Fig. 6). For soil biological properties, like soil enzymes, microbial mass, and structure, they might regulate Pb speciation distribution and leaching risk. However, the RDA analysis proved that these biological properties could not dominantly regulate these processes. Furthermore, for each Pb speciation, according to the angle between Pb speciation and three soil properties, F1 was positively related with WC and pH, and negatively correlated to TP. For F2, F3, and total Pb, there were positive relations with TP and pH, while, negative relation with WC. F4 was positively related with pH and TP, but negatively related to WC. Thus, higher pH and TP would present a positive effect in relieving Pb leaching risk, and higher WC could increase leaching risk. Moreover, the structural equation model (SEM) was used to assess the direct and indirect effects of explanatory variables on PLR. The fitted models explained 81% of the variance in PLR (Fig. 7a). Bacteria abundance, total Pb content, clay content, and C/N exerted direct effect on PLR. pH played an indirect but important role in affecting on PLR. From one respect, pH mainly indirectly impacted PLR by regulating Pb content. Furthermore, bacteria could be also the link of relationships between pH and PLR. Standardized total effects derived from the SEM indicated that PLR was mainly driven by bacteria,

**Table 3**
Pb speciation distribution and the assessment of Pb pollution.

| Speciation | Items[a] | Farmland[b] | Woodland | Grassland |
|---|---|---|---|---|
| Acid exchangeable (F1) | P. (%) | 5.9 ± 4.5 | 7.2 ± 2.7 | 17.4 ± 5.2 |
| | C.V. (%) | 87.6 | 48.5 | 23.4 |
| Fe-Mn oxides (F2) | P. (%) | 69.7 ± 12.3 | 67.8 ± 13.5 | 57.2 ± 10.0 |
| | C.V. (%) | 26.6 | 28.5 | 30.8 |
| Organic matter and sulphides (F3) | P. (%) | 4.5 ± 2.2 | 3.2 ± 2.2 | 3.9 ± 3.1 |
| | C.V. (%) | 47.7 | 59.5 | 67.6 |
| Residual (F4) | P. (%) | 19.8 ± 12.2 | 21.9 ± 12.9 | 21.5 ± 9.8 |
| | C.V. (%) | 73.7 | 65.6 | 43.8 |
| Total | Conc. (mg kg$^{-1}$) | 410.1 ± 104.7a | 315.9 ± 65.8b | 313.6 ± 52.3b |
| | C.V. (%) | 25.5 | 20.8 | 16.7 |
| Contamination factor | CF | 19.4 ± 4.9a | 14.9 ± 3.1 b | 14.8 ± 2.5b |
| | $I_{geo}$ | 12.4 ± 0.5a | 12.1 ± 0.3 b | 12.1 ± 0.3b |
| Potential leaching risk | Conc. (mg kg$^{-1}$) | 74.7 ± 26.9ab | 60.6 ± 15.2b | 85.0 ± 13.5a |

[a] P. represents the percentage of every Pb speciation in total. C.V. is the abbreviation of coefficient variation. Conc. is the abbreviation of concentration.
[b] Same letter denotes no significant difference between values in each land use.

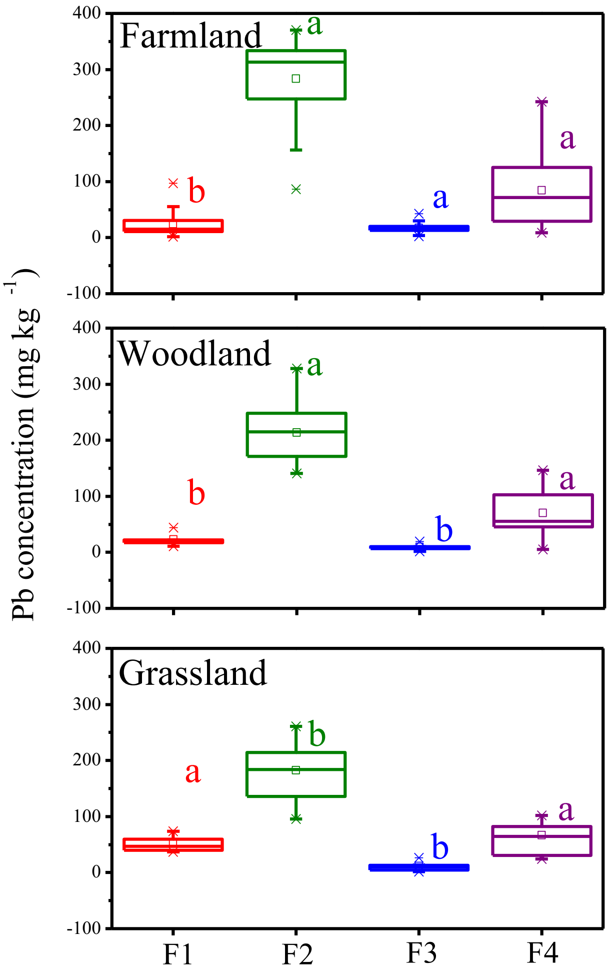

**Fig. 3.** Fractionation of Pb in soil of three land uses. F1, F2, F3, and F4 represent acid exchangeable, Fe-Mn oxides, organic matter and sulphides, and residual fractionation of Pb, respectively. The same letter within the same color denotes no significant difference between values in each land use.

followed by Pb content, pH, clay content, and C/N (Fig. 7b).

## 4. Discussion

### 4.1. Dominant factors regulating Pb chemical form in soils with three land uses

Over decades, Pb gangue and flyash from the industrial and mining production in Feng Country, Shaanxi province have no doubt seriously damaged the surrounding soil function. Soil land uses should be considered when evaluating Pb pollution due to their distinct responses. Chen et al. (2015a) suggested that heavy metals such as arsenic, cadmium, and Pb concentrations were significantly higher in soil samples from abandoned industrial land than from farmland and forested land. Land uses could affect Pb mobility by changing soil physical, chemical, and biological parameters (Marzaioli et al., 2010). Soils from permanent crops generally showed lower values of microbial parameters, nutrient and organic C content and the higher values of heavy metal content, compared to the other soils, while mixed forest soils showed opposed characteristics. Moreover, instead of total Pb concentration determination in soil, Pb associated with the different soil compartments help ascertain for the mobility and bioavailability of Pb in the ecosystem (Kelebemang et al., 2017).

Here, we quantified the Pb partition in four soil fractions. Generally, the sum of F1, F2, and F3 are typically considered the mobile and potentially bioavailable ones for living organisms. These three fractions include metal from anthropogenic sources. The metals present in F4 are not available and can be regarded as a measure of the contribution by natural sources (Ghayoraneh and Qishlaqi, 2017). It was found that the Pb distribution among four speciation exhibited the same trend in three land-uses and was shown in the order of F2 (Fe-Mn oxides bound) > F4 (residual) > F1 (acid exchangeable) > F3 (organic/sulphides bound). In other Pb polluted soils, F2 was also the most relevant abundances (Ghayoraneh and Qishlaqi, 2017; Rodriguez et al., 2009). All these studies underlined the strong affinity of Pb for both Fe and Mn compounds, and was in line with early findings which showed that Fe and Mn hydrous oxides are vital scavengers of Pb in soils. These compounds were supposed to sorb Pb via formation of steadily inner sphere sorption complexes, and play an important role in controlling its mobility in the environment (Ghayoraneh and Qishlaqi, 2017). F3 was the fraction with the lowest Pb content in all tested soils. Similar percentages of Pb in F3 were found in mine surrounding areas reported by previous studies (Li and Thornton, 2001; Rodriguez et al., 2009). This low portion of Pb in F3 might be led by the low organic matter (about 1%) in the studied soils.

Although the Pb dominant speciation in four fraction was not affected by land uses, there were still significant differences for each

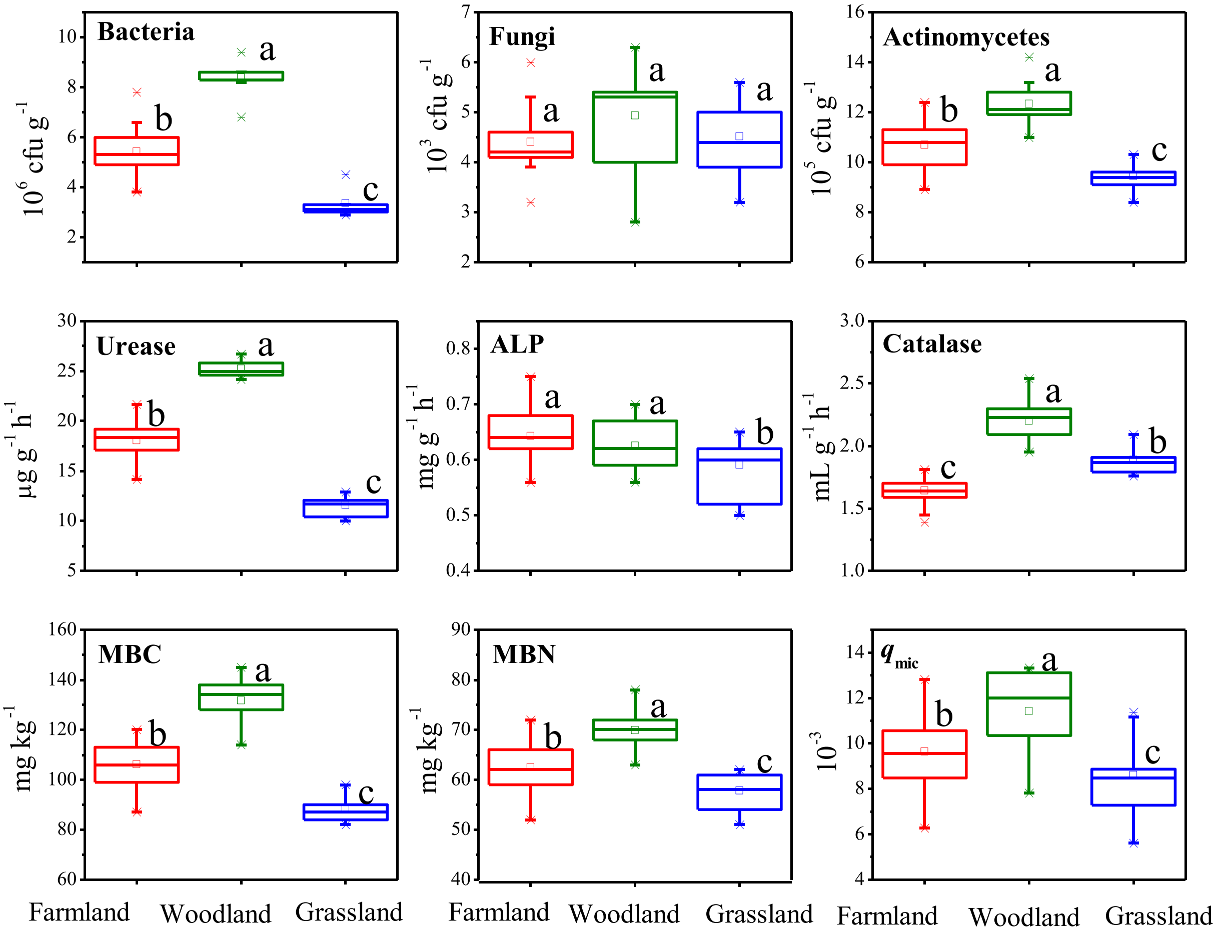

**Fig. 4.** Microbial responses including microbe community, soil enzyme activities, and microbial biomass to Pb pollution under three land uses. ALP: alkaline phosphatase; MBC: microbial biomass carbon; MBN: microbial biomass nitrogen. $q_{mic}$ is the ratio of MBC to SOC. Same letter denotes no significant difference between values in each land use.

fraction among three land uses (Fig. 3). As it is known, the partitioning of Pb in the different soil fractions is largely dependent on the soil properties such as the soil pH, organic matter, CEC, microbe population, enzymes activities, and microbial mass (Gao et al., 2010; Kelebemang et al., 2017). Among these soil properties, soil pH was found to play the most important role in determining metal speciation, solubility from mineral surfaces, movement, and eventual bioavailability of metals, due to its strong effects on solubility and speciation of metals both in the soil as a whole and particularly in the soil solution. Heavy metal mobility decreases with increasing soil pH due to the precipitation of hydroxides, carbonates or the formation of insoluble organic complexes (Balkhair and Ashraf, 2016). Apart from soil pH, organic matter content in soil is also one of most important soil properties affecting heavy metal mobility. It was reported that heavy metal adsorption onto soil constituents declined with decreased organic matter content in soils (Antoniadis et al., 2008). The combination of soil pH and organic matter content would produce the more precise regression models for estimation of EDTA-Cu, Pb and Zn contents in soils, demonstrating the distinct effect of the two factors on the availability of these heavy metals in soils (Zeng et al., 2011). Gao et al. (2010) concluded that bacteria and actinomycetes were sensitive to heavy metals, while fungi seemed not be sensitive, which is consistent with our results (Fig. 4). Soil enzyme activities and microbial mass are also severed as sensors towards any natural and anthropogenic disturbance (Khan et al., 2010; Duan et al., 2018). However, among so many soil properties, which factor mainly govern the Pb speciation distribution is still unknown. Based on our RDA analysis results, TP, pH, and WC were identified as three main factors to regulate the Pb speciation partition in soils. In a similar study of Pb speciation in water system, it was found that TN and pH were the controlling factors (He et al., 2017). It could be concluded that pH always play a dominant role in Pb speciation distribution regardless of water or soil samples. TP could be served as another important regulator, which was due to that Pb exists as lead phosphate ($Pb_3(PO_4)_2$) and lead chloride phosphate ($Pb_5(PO_4)_3Cl$) in residual fractions (the secondary partition of Pb speciation). These compounds make Pb unreachable and therefore less potential risk to the biota (Kelebemang et al., 2017). Also, because of the significant differences of WC among three land uses (Table 1), it was considerable that WC was regarded as the nonnegligible factor affecting Pb speciation. Moreover, it was evidenced that lower water contents would favor lower rates of Pb weathering and subsequent release (Dermatas et al., 2006). Thus, our study not only demonstrated the leading role of pH but also proposed other two key factors (TP and WC) involved in regulating Pb speciation under three land uses.

Interestingly, we found that TP and WC were not important contributors to the SEM model, despite the strong relationship between these metrics and Pb speciation. Perhaps it is because that TP and WC were severed as intrinsic factor of total Pb content due to their significant relationships (Fig. 5). Previously, SEM is always used for disentangling complex sets of direct and indirect interactions, but remains relatively underutilized in soil pollution evaluation (Collins et al., 2016). For example, Hill et al. (2017) studied the direct impact of cover crops on nutrient cycling and yield in many different systems by SEM models. They demonstrated that C/N ratio and shorter time were two vital indirect factors affecting yield. Another study was to test for the direct and indirect effects of climate, spatial factors, soil fertility, soil

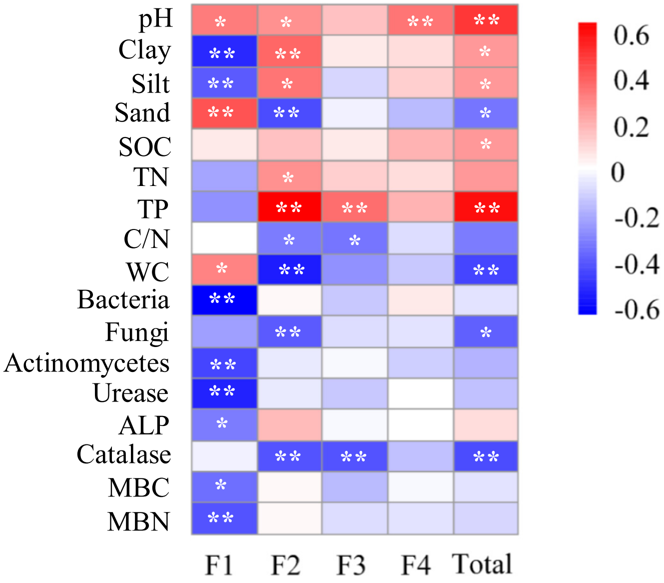

**Fig. 5.** The heatmap of correlation coefficients between Pb speciation and soil properties. "*" and "**" mean that the regression is significantly related between soil properties and Pb speciation at P < 0.05 and P < 0.01 level. SOC: soil organic matter. TN: total nitrogen. TP: total phosphate. C/N: the ratio of SOC to TN. WC: water content. ALP: alkaline phosphatase. MBC: microbial biomass carbon. MBN: microbial biomass nitrogen. F1: acid exchangeable Pb. F2: Fe-Mn oxides bound Pb. F3: organic matter and sulphides bound Pb. F4: the residual Pb.

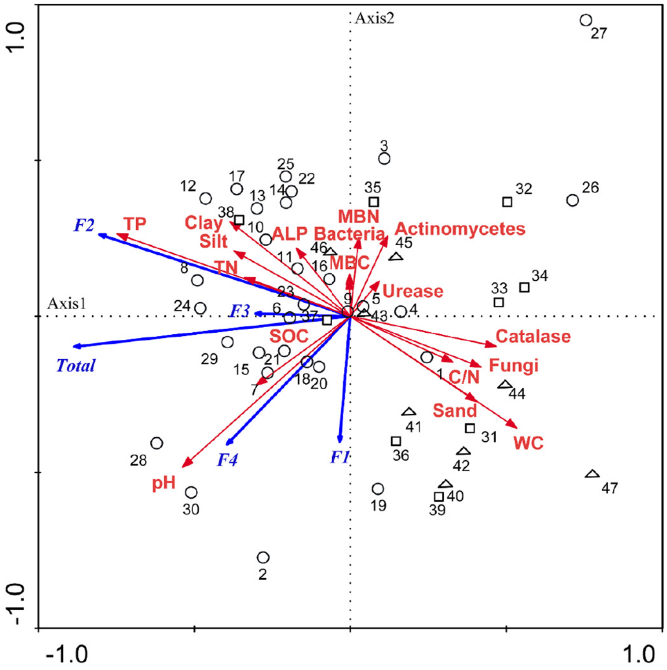

**Fig. 6.** Redundancy analysis (RDA) triplot to investigate the relationship between Pb speciation and soil properties. F1, F2, F3, F4, and total represent five Pb speciation marked with blue arrow. All soil properties are marked with red arrow. The circle, square, and triangle represent samples came from farmland, woodland, and grassland, respectively. SOC: soil organic matter. TN: total nitrogen. TP: total phosphate. C/N: the ratio of SOC to TN. WC: water content. ALP: alkaline phosphatase. MBC: microbial biomass carbon. MBN: microbial biomass nitrogen. F1: acid exchangeable Pb. F2: Fe-Mn oxides bound Pb. F3: organic matter and sulphides bound Pb. F4: the residual Pb. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

texture and plant diversity on the fungal richness (Chen et al., 2017) The SEM results showed that plant species richness played significant role in determining soil fungal richness. Herein, using this model, we have uncovered interesting connections between soil properties, Pb content, and PLR for the first time. As expected, pH plays a key role in regulating Pb leaching risk. In a study of the interacting roles of soils on microbial communities, soil pH was also identified as a master and indirect variable due to its impact in biogeochemical processes (such as organic matter hydrolysis and acid-base reactions in soil pore waters) (Waldrop et al., 2017). Clay and C/N ratio both could directly or indirectly affect PLR through bacteria. Under different land-use management, bacterial 16S rRNA gene abundance was previously proved to have the highest correlation with clay content, followed by total-P, CEC, pH, and silt (Lynn et al., 2017). Besides, SEM can provide a way to interpret a causal theory such as the three-step bioavailability concept. In SEM, the causal relationships between the three steps of bioavailability can be modeled and analyzed based on the structure of the covariance between the variables. Beaumelle et al. (2016) demonstrated that SEM highlights that the metals present in the soil solution and easily extractable are not the main source of available metals for earthworms. This study further highlights SEM as a powerful tool that can handle natural ecosystem complexity, thus participating to the paradigm change in ecotoxicology from a bottom-up to a top-down approach. We believe that coupling heavy metal speciation with soil biotic and abiotic measurements in a SEM framework would offer exciting opportunities for disentangling the complex network of heavy metal-soil interactions.

### *4.2. The proper land use based on Pb leaching risk evaluation*

Currently, numerical methods to estimate the potential risk from heavy metals in soils have been reported, such as the Enrichment Factor, the Index of Geo-accumulation, risk index (RI) (He et al., 2017). However, these risk assessment methods have been based only on the total heavy metal content. Considering the available content of heavy metals into ecological risk assessments is necessary. The risk assessment code (RAC) was determined based on the percentage of the total metal content that was found in the first sediment fraction in BCR method (% F1). When this percentage mobility is < 1%, the sediment has no risk to the environment. Percentages of 1–10% reflect low risk, 11–30% medium risk, and 31–50% high risk (Nemati et al., 2011). According to the RAC, in this work, it was found that the percentages of F1 in farmland (5.9%) and woodland (7.2%) were both in the range reflecting low risk. While, in grassland, the F1 percentage (17.4%) was in the range of 11–30% reflecting medium risk. However, except the residual solid, which hold elements with the crystal structure and showed a neglectable change under the conditions normally encountered in nature, F2 and F3 both have the potential Pb release risk to the environment. Thus, according to the toxicity characteristic leaching procedure (TCLP), Bao et al. (2016) proposed leached portion ($\eta$) for different species of heavy metals to comprehensively evaluate the leaching risk. In this study, when Bao's method was employed, the predicted Pb leaching concentration was calculated (Table 3).

Recently, land use patterns have been frequently proved having strong influence on the mobility of heavy metals, as well as the transfer in soil-plant system (Fang et al., 2017). Thus, in the remediation of heavy metal pollution, land use types should be seriously considered. In this work, the proper land use type for relieving Pb pollution was therefore sought based on the Pb leaching risk. The results showed that grassland has the significantly higher Pb leaching risk due to the highest WC (27%) compared with the other two land uses. On the other hand, grassland had the lowest clay mineral contents, especially for montmorillonite, which was reported to have significant potential to bind Pb through sorption and cation exchange (Dermatas et al., 2006). As previously illustrated by major element analysis, silicon, aluminum, and certainly iron oxides in the clay fraction may also comprise

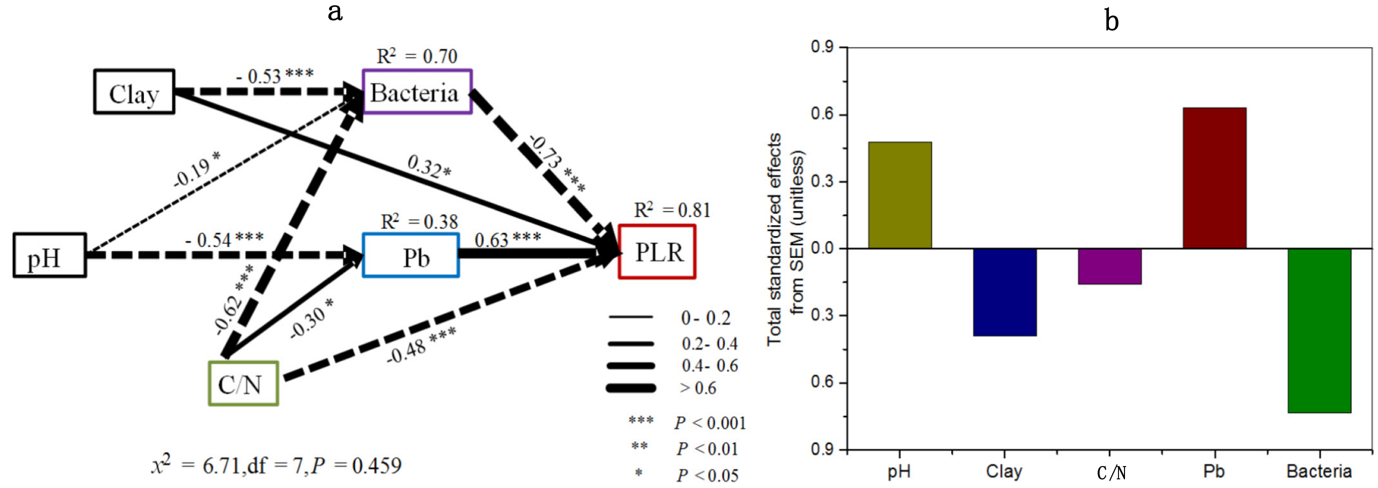

**Fig. 7.** The structural equation model (SEM) examining the multivariate effects on potential leaching risk (PLR) (a) and total standardized effects from SEM (b). The width of the arrows indicates the strength of the standardized path coefficient. The solid lines indicate positive path coefficients and dashed lines indicate negative path coefficients. $R^2$ values represent the proportion of the variance explained for each endogenous variable. C/N is the ratio of soil organic matter to total nitrogen.

available surfaces for Pb sorption in the soil. These dominant oxides were also the least abundant in grassland. Furthermore, in the similar slope, grassland was reported to have generally higher water content than forest and farmland (Fu et al., 2000). Therefore, grassland should be the last choice to minimize the Pb leaching concentration. Compared to grassland, woodland has larger and deeper root systems than herbaceous plants, which lead to high clay, SOC, TP, and TN contents in the soils (Li et al., 2016; Wang et al., 2015). This land-use type would effectively improve soil properties and decrease Pb mobility. Moreover, shrubs and trees could provide an extensive canopy and establish a deep root network to remediate metal-polluted soil and meanwhile prevent soil erosion (Padmavathiamma et al., 2014). Many native woody plants (*Pinus sylvestris*, *Betula pubescens*, *Empetrum nigrum*, and *Arctostaphylos uva-ursi*) have been proved to be suitable for revegetating heavy metal-polluted sites (Helmisaari et al., 2007). In copper polluted soils, forestland was also suggested as the optimum land use type due to the lower metal concentration (Ettler et al., 2014). The spatial distribution of concentration with different land uses indicated that mangrove forests play an important role in preventing the spread of heavy metals to other land uses (clam and shrimp farms) (Van et al., 2016). As to farmland, it has the highest total Pb content and lower Pb leaching concentration. However, the value is still beyond the background ($> 35\ \mathrm{mg\ kg^{-1}}$). Furthermore, even if permanent crop in farmland soils have actually a good productivity, this could suffer a reduction for the next several years because of the deterioration of soil chemical and biological properties (Marzaioli et al., 2010). It was found that the conversion of farmland from wetland resulted in an increase in the concentration of Pb and Cr in the soil. Soil erosion was identified as the major factor that enhances heavy metal losses in the cultivated lands (Wang et al., 2015). The sustainable agricultural activities may induce the more even distribution of heavy metals throughout the soil profiles of dryland and paddy field in the study area (Zheng et al., 2016). Thus, woodland would be suggested as the proper one reducing the Pb leaching and health risk among three land-use types.

## 5. Conclusions

In the present study, soil samples with three land uses surrounding of the Pb-Zn mine in Feng Country were strongly polluted assessed by the CF > 6 and $I_{geo}$ > 5. These soil samples had various soil properties. However, regardless of land use types, the chemical fraction of Pb in soils distributed in the same order F2 (Fe-Mn oxides bound) > F4 (residual) > F1 (acid exchangeable) > F3 (organic/sulphides bound). Soil physicochemical properties, such as TP, WC, and pH, severed as the dominant factor regulating Pb speciation partition. While, soil biological properties, like microbe communities, catalase, and MBN, were related with Pb speciation and regarded as minor factors affecting Pb speciation. SEM further demonstrated that bacteria abundance, total Pb content, clay content, and C/N exerted direct effect on Pb leaching risk, while pH plays an indirect but critical role. In terms of Pb leaching risk prediction, grassland had the highest potential risk compared to woodland and farmland. Woodland could be recommended as the proper native land use to alleviate heavy metal pollution. These results provide some innovative approaches to the phytomanagement and control of metal-contaminated soil around mine.

## 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.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (41571314, 41201226, 41425006), and CAS “Light of West China” Program (XAB2016A03).

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2018.04.016.

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