Migration and speciation of heavy metal in salinized mine tailings affected by iron mining

Xu Zhang, Huanhuan Yang and Zhaojie Cui

ABSTRACT

The negative effects of heavy metals have aroused much attention due to their high toxicity to human beings. Migration and transformation trend of heavy metals have a close relationship with soil safety. Researching on migration and transformation of heavy metals in tailings can provide a reliable basis for pollution management and ecosystem restoration. Heavy metal speciation plays an important role in risk assessment. We chose Anshan tailings for our study, including field investigations and laboratory research. Four typical heavy metal elements of mine tailings (Fe (373.89 g/kg), Mn (2,303.80 mg/kg), Pb (40.99 mg/kg) and Cr (199.92 mg/kg)) were studied via Tessier test in vertical and horizontal direction. The main speciation of heavy metals in Anshan tailings was the residual. However, heavy metals have a strong ability for migration and transformation in vertical and horizontal directions. Its tendency to change from stable to unstable speciation results in increasing bioavailability and potential bioavailability. Fe, Mn, Pb and Cr showed different ability in the migration and transformation process (Mn > Pb > Fe > Cr) depending on the characteristics of heavy metals and physicochemical properties of the environment.

Key words | heavy metal, migration, mine tailings, speciation

INTRODUCTION

Soil pollution caused by heavy metals has led to enormous concerns in recent years (Belviso et al. 2012). High levels of some heavy metals (e.g. Fe, Mn, Cr, Pb) in soils could induce phytotoxicity to plants, thus negatively affecting crop yield due to their high toxicity, bioaccumulation and biomagnification (Meers et al. 2006). Bioavailable types of heavy metals cause greater environmental risks, whereas heavy metal fraction tightly bound with soil organic matter and minerals has lower risks to be released to soil and water (Ashraf et al. 2012). Heavy metals directly released into the environment will not only affect physical and chemical properties of soil, but also deteriorate the quality of the water, ultimately threatening human health (Krishnani & Ayyappan 2006).

Anshan city located in northeast China was famous for mineral resources and mining (Li & Gan-Guo 2005). During mining processes, a large amount of heavy metals was present in mine tailings, waste water discharge, and dusts (Candeias et al. 2015). Inappropriate treatments of these wastes often result in extremely high concentrations of heavy metals in soils near mining sites (Mitchell et al. 2016). The change of the properties of soil, such as organic matter, Eh, and pH, could further affect the bioavailability of heavy metals (Zhang et al. 2016). Considering the complicated environmental factors, we must study on migration and transformation characteristics of heavy metals in the vertical and horizontal direction to assess the environmental risk (Li et al. 2015).

Total heavy metal concentrations are usually used to evaluate heavy metal pollution, but these poorly reflects the mobility and bioavailability of the heavy metals. Speciation of heavy metals can efficiently assess the reactivity and toxicity of heavy metals (Larios et al. 2012). Heavy metal speciation in soils plays an important role in environmental risk assessment of soil heavy metal pollution. Emission sources, soil pH, redox potential, organic matter and mineralogy can affect the speciation of soil heavy metals (Nwachukwu et al. 2010). The Tessier sequential extraction method which separates the heavy metals into five kinds has been widely used to investigate heavy metal speciation in various environmental media (Singh & Kalamdhad 2013). The objective of this research was to assess the heavy metal pollution and potential risk in Anshan tailings.
MATERIALS AND METHODS

Soil sampling

Anshan city located in northeast of China engaged in exploiting mineral resources, mining tailings and other wastes required a large area of the site, finally resulting in destruction of ecosystems in a stacked field. There was much heavy metal in tailings shown in Figure 1. Large amount of toxic heavy metals released and migrated through surface runoff and airborne particulates had serious impact on the surroundings. Concentrations of heavy metal in tailing and background value of China are shown in Table 1. Concentration of Fe, Mn, Pb and Cr in mine tailings was significantly higher than background value of China. Taking four typical heavy metal elements (Fe, Mn, Pb and Cr) as examples, we studied migration of heavy metals in the vertical direction, in order to know the effects of heavy metals on deep soil and groundwater. We dug a 1 m profile which was divided into five 20 cm depth intervals from the surface to different depths (P1, P2, P3, P4 and P5) (Rosling et al. 2005). According to the flow direction of tailings, we set up five sampling points located in upstream, center and downstream of the lake (Y1, Y2, Y3, Y4, and Y5) (Muntean & Rusu 2011).

Tessier test

‘Exchangeable’ (Step 1): 8 mL 1 mol/L MgCl2 solution, pH = 7.0, 25 °C continuous shock 1 h, centrifuged (3,000 r/min) 20 min, the supernatant was extract to be tested (Pérezcid et al. 1999). ‘Carbonate-bound’ (Step 2): residue of Step 1 added 8 mL 1 mol/L NaoAc solution, pH = 5.0, at (25 ± 1) °C continuous shock 8 h, centrifuged (5,000 r/min) 20 min, the supernatant was extract to be tested. ‘Oxide-bound’ (Step 3): residue of Step 2 added 8 mL 0.04 mol/25% HAc solution of NH2OH · HCl, (96 ± 3) °C, constant intermittent shock 4 h, centrifuged (3,000 r/min) 20 min, supernatant was extract to be tested. ‘Organic-bound’ (Step 4): residue of Step 3 added 3 mL 0.02 mol/L HNO3 and 5 mL 30% H2O2, NH4Ac and then adjusted to pH = 2, the mixture was heated in a water bath (85 ± 2) °C, in this process interrupted shock 2 h, then add 5 mL H2O2 adjusting the pH to 2, the mixture was placed at (85 ± 2) °C, heat 2 h, and intermittent shocks, cooled to (25 ± 1) °C, added 5 mL 3.2 mol/L NH4Ac of 20% HNO3 solution was diluted to 20 mL, continuous shake 30 min, centrifuged (5,000 r/min) 20 min. Supernatant was extract to be tested. Residual (Step 5): residue of Step 4 added 2 mL of concentrated HClO4 and 10 mL HF, dry out, 1 mL HClO4 and 10 mL HF, bake until nearly dry, add 1 mL HClO4, the residue was dissolved in 12 mol/L HCl, 70 °C, 1 h.

Concentration detection

After air drying, mixing, drying and sieving, soil samples were digested by microwave method with HNO3-HClO4-HF (3:1:1, v/v) (Madiseh et al. 2009). The concentration of heavy metals in the soil samples were measured by inductively coupled plasma-atomic emission spectrometry (Ramesh et al. 2001). Geochemical standard soil samples were provided by the National Research Center.

Self-organizing map

The data were analyzed by MATLAB 2009 (© 1984–2009 The MathWorks, Inc.). The self-organizing map (SOM) was subsequently used to classify migration characteristics and major influencing factors. The learning process of the

Table 1 | Concentration of heavy metal in tailing and background value of China

<table>
<thead>
<tr>
<th>Item</th>
<th>Concentration</th>
<th>Background value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu, mg/kg</td>
<td>10.0</td>
<td>22.6</td>
</tr>
<tr>
<td>Zn, mg/kg</td>
<td>49.0</td>
<td>74.2</td>
</tr>
<tr>
<td>Cd, mg/kg</td>
<td>0.066</td>
<td>0.097</td>
</tr>
<tr>
<td>Hg, mg/kg</td>
<td>0.003</td>
<td>0.065</td>
</tr>
<tr>
<td>Ni, mg/kg</td>
<td>11.0</td>
<td>26.9</td>
</tr>
<tr>
<td>Co, mg/kg</td>
<td>&lt;5.0</td>
<td>12.7</td>
</tr>
<tr>
<td>Mn, mg/kg</td>
<td>2,303.8</td>
<td>583.0</td>
</tr>
<tr>
<td>Fe, g/kg</td>
<td>375.89</td>
<td>29.43</td>
</tr>
<tr>
<td>Pb, mg/kg</td>
<td>40.99</td>
<td>26.00</td>
</tr>
<tr>
<td>Cr, mg/kg</td>
<td>199.92</td>
<td>61.00</td>
</tr>
</tbody>
</table>
SOM was conducted using the SOM Toolbox developed by the Laboratory of Information and Computer Science, Helsinki University of Technology in MATLAB environments. The SOM has been used effectively for extracting information from ecological data.

RESULTS AND DISCUSSION

Heavy metal speciation in the vertical direction

Speciation of Fe, Mn, Pb and Cr in the vertical direction is shown in Figure 2. The main speciation of Fe was residual form and organic-bound, accounting for 50.2% and 32%. Organic-bound of Fe was susceptible to release caused by oxidation (Dang et al. 2002). Carbonate-bound and oxide-bound proportion occupied a small share, but the content of carbonate-bound and oxide-bound were respectively 35.25 g/kg and 27.26 g/kg. With the increasing of depth, the exchangeable form gradually increased which caused direct impact on contaminated soil (Liu et al. 2010). Fe has a serious effect on soil and groundwater because of its great migration and transformation capacity in the vertical direction. The residual form of Mn accounted for 39.01% of the total in mine tailings, followed by organic-bound, carbonate-bound and oxide-bound, accounting for 25.77%, 19.22% and 15.92%, respectively. Potential bioavailability (organic bound, carbonate-bound and oxide-bound) (Ogunfowokan et al. 2009) amount up to 60.92%, which poses seriously potential threat to the ecosystem. Exchangeable form of Pb was not detected. Residual form accounted for 75.61% (30.99 mg/kg), followed by oxide-bound, carbonate-bound and organic-bound. Potential bioavailability amounts to 24.38%, which is easily released into the environment and damages the ecosystem. With the increasing of depth, the carbonate-bound significantly increased, finally increasing the potential hazard (Cai et al. 2007). The main speciation of Cr is residual form, up to 93.39–98.78%, followed by organic-bound, accounting for 0.74–4.38%. With the increase of soil depth, speciation of Cr has slightly changed. Chemical properties of the residual are stable which is not easily released into the environment (Yang et al. 2009). Therefore, Cr has little effect on surroundings, whether direct impact or potential impact.

Clustering of concentration in association with different heavy metals and depth is shown in Figure 3. The main speciation of heavy metals in mine tailings was the residual which indicated that the heavy metals have little direct toxic effect on the ecosystem because of the stable form. Fe and Mn showed similar rules in the vertical direction. The composition of the speciation in each layer had little changes. Exchangeable of Fe increased, carbonate-bound
of Mn and Pb increased and organic-bound of Cr increased, respectively, with the increasing depth. Potential bioavailability (organic-bound, carbonate-bound and oxide-bound) of Fe, Mn, Pb and Cr increased and enhanced potential risk on groundwater (Figure 2). With the increase of soil depth, organic-bound and residual decreased. Oxide-bound and carbonates bound of Fe, Mn, Pb and Cr obviously increased which resulted in potential threat to groundwater. If the soil conditions change, such as decreasing pH value and increasing oxidizing ability caused by acid rain, it will lead to the release of heavy metals into the environment (Hogstrand & Wood 2010). Fe, Mn, Pb and Cr have certain

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**Figure 3** | Clustering of concentration in association with different heavy metals and depth by the SOM. Five clusters classified by the SOM, cluster distances according to dendrogram by the Ward’s linkage method. HM means heavy metals; Lo means location; Sp means speciation; Co means concentrations; Ra means the proportion.
migration and transformation capacity in the vertical direction which exacerbates the potential threat of heavy metal pollution (Ma et al. 2015).

Considering the impact factors (chemicals and soil depth) and measurement (concentrations and proportions) as variables the response data were trained by SOM (Ren 2014). Types of heavy metal had good correlation with the speciation, showing that the distribution of speciation mainly depend on the characteristics of heavy metals. The proportion of speciation had close relationship with the sampling location. The composition of speciation was mainly decided by the soil depth and physicochemical properties of each layer. In short, Fe, Mn, Pb and Cr showed different characteristic and ability of migration and transformation (Mn > Pb > Fe > Cr). The speciation changes of heavy metals in the process of migration are affected by tailings soil physicochemical properties and heavy metal properties (Liao et al. 2016).

Heavy metal speciation in the horizontal direction

Speciation of Fe, Mn, Pb and Cr in the horizontal direction is shown in Figure 4. The main speciation of Fe was residual form and organic-bound in tailings center. Along direction of the flow, exchangeable form was gradually increased. The direct toxicity of Fe significantly increases because of the high concentration of Fe. Potential bioavailability (Organic bound, Carbonate-bound and Oxide-bound) obviously rose up to 52.8% which is easily affected by changes of soil properties, and finally released into the soil and water (Szymczychamadeja et al. 2013). The speciation of Mn significantly changed. Residual form and carbonate-bound obviously reduced, but oxide-bound and exchangeable form increased. Oxide-bound was unstable and easily released under reducing conditions. Considering the high content (292.78 mg/kg), the surrounding environment could be seriously damaged due to changing conditions. Organic-bound was susceptible to oxidation and released by the erosion of acid rain which is likely to migrate to the surroundings. Exchangeable form of Mn was 37.77 mg/kg which cause direct impact on the environment. Mn has great migration and transformation ability in the process of water erosion (Wang et al. 2001). In the center of mine tailings, the main form of Pb was the residual fraction, accounting for 71.9%, but significantly reduced along the flow direction. Carbonate-bound and oxide-bound obviously increased to 76.2%, because of the strong migration and transformation ability of Pb. Potentially bio-availability substantially increases and poses potential threat to the surrounding environment (Adamo et al. 2014). Speciation of Cr slightly changed along the river. Carbonate bound, oxide-bound and organic-bound slightly increased.

Figure 4 | Speciation of Fe, Mn, Pb, Cr in the horizontal direction. I – Exchangeable, II – Carbonate-bound, III – Oxide-bound, IV – Organic-bound, V – Residual.
However, the main speciation is still residual form, which accounted for more than 95.9%. Cr has little migration and transformation ability, which is stable and has less impact on the surrounding environment (Zou & Zhang 2015).

Clustering of concentration in association with different heavy metals and locations is shown in Figure 5. The speciation of heavy metals changes from stable to unstable along the flow direction. Residual decreased and exchangeable slightly increased. Organic-bound, carbonate-bound and oxide-bound significantly increased which could result in enhancing potential bioavailability. Fe and Cr showed similar regularity in the horizontal direction. The composition of heavy metal speciation slightly changed. Oxide-bound of Fe increased, carbonate-bound of Fe decreased and residual of

![Figure 5](https://iwaponline.com/wst/article-pdf/76/7/1867/449992/wst076071867.pdf)
Cr increased along the flow direction indicating the decreasing of bioavailability and toxicity. Residual of Pb and Mn obviously decreased but showed different rules. Oxide-bound and carbonate-bound of Pb increased. Oxide-bound and exchangeable of Mn increased. Direct bioavailability and potential bioavailability of Pb and Mn significantly increased and had great impact on the surrounding environment (Figure 4). Fe, Mn and Pb have certain migration and transformation ability in the horizontal direction which expands the scope and impact of the heavy metal pollution (Qian & Jiang 2020). Therefore, detection and remediation efforts must be made to control heavy metal pollution.

CONCLUSION

The main speciation of heavy metals in mine tailings was the residual form, followed by organic-bound. Fe and Mn should be classified as priority pollutants because of the high concentration. Fe, Mn, Pb and Cr showed different characteristics in migration and transformation process (Mn > Pb > Fe > Cr) depended on the properties of heavy metals and the environmental conditions (Liu et al. 2015). Heavy metals had strong migration and transformation ability in the vertical and the horizontal direction. Potential bioavailability (organic-bound, carbonate-bound and oxide-bound) significantly increased. Bioavailability (exchangeable form) slightly increased, which could cause bioaccumulation and magnification of heavy metals along the food chain (Li et al. 2010). The trend of speciation changes not only expand the range of heavy metal pollution, but also exacerbate the threat to deep soil and the surrounding environment. All in all, we should be real-time monitoring the heavy metals pollution of tailings and the surroundings. Bioremediation technology is also supposed to be applied for controlling the heavy metal pollution (Li et al. 2012).

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