Geochemical approach for toxic metal leaching and migration from defunct mining site

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Abstract

Toxic metal migration in the geo-environment spreads pollution and it is necessary to conduct reasonable and economical risk management. This work analyses the leaching of toxic metals from rock and soils around a hydrothermal alteration region, and estimates the effect of coexisting minerals and soluble elements on leaching and migration of toxic elements. The leaching of toxic metals is controlled by mainly Fe, Al and Ca concentrations in host rock, and high contents of them prevent leaching. Leaching and migration also strongly depend on colloidal materials, especially iron oxide and Al/Fe-humus complex. These materials prevent the leaching of toxic elements but toxic elements adsorb on them and are transported downstream. In particular, arsenic transport is clearly observed in the research area.

Key Words

Leaching, colloid, toxic metal, migration, chelate

Introduction

The concentration of contaminants in subsurface soils is estimated by public environmental measurements and assessment methods in each country. However, the migration of toxic metals in soil media is variously changed by coexisting ion species and colloids. Some parts of contaminants leached from subsurface soils migrate and accumulate as adsorbate on colloids, and this migration behaviour is affected by physicochemical parameters. In particular, crystalline – amorphous aluminosilicate, hydroxide, and humic matter adsorb and retain ion species in pore water, and are reported to control the soil physicochemical character by acting on water retention and aggregation of soil (Jonge et al. 2004).

This research aimed to clarify the speciation of mineral and colloids in soil media, and the effect of coexisting ion or colloids on toxic metal – pore water interaction. In addition, we explored which speciation has high potential to migrate the toxic metals in this research area.

Methods

Research area

This research field is Osaru River basin in northern part of Japan. In the watershed of this river, many mining sites used to work until scores of years ago and several hydrothermal alteration zones were distributed in each tributary around mining sites. Surface sediments in Osaru River basin are quaternary volcanic sediments and fluvial sediments. Only the downstream part is not covered by volcanic ash and exposes the fluvial or deltaic sediments. High-level Arsenic, Zinc, Copper, Mercury sites are detected in some alteration zones. Among them, 790mg/kg of arsenic was accumulated in the outcrop layer in a pyrophyllite-kaolinite alteration zone. The rock samples in alteration site were collected from each tributary as host materials, and alluvial soils were also collected from the main Osaru River. Figure 1 shows the distribution of alteration area and mining sites in the Osaru River basin. The soil sampling points of this study are also pointed out in Figure 1. The collected samples were sealed in plastic bags and kept in a refrigerator at 4°C.

Analytical methods

Soil and rock samples were air-dried at room temperature, crushed and sieved to <2 mm. In the case of soil samples, plant and coarse fragments were removed in this procedure and a part of the sieved samples was crushed to powder. On the other hand, the rock samples were homogeneously crushed to powder. The <2 mm sieved rock samples were also sieved to obtain 1–2 mm samples. The <2 mm soil samples and 1–2 mm rock samples were used for water leachate tests for metals. The leachates tests were conducted under the following conditions: 3 g of rock or soil sample was reacted with 30
ml of water and shaken at 200 rpm for 6 h in a 50 ml centrifuge tube. These procedures were carried out at room temperature and atmospheric pressure. After centrifugation at 3000 rpm for 20 min, the leachate was filtered through a 0.45 μm membrane. The heavy metal concentrations of the leachates were analysed using ICP-MS (ICPM-8500, Shimadzu, Co. Ltd.). In addition, pH was measured at a soil/water ratio of 1:2.5, and EC at a soil/water ratio of 1:5. Total organic carbon (TOC) was determined by ignition weight loss methods, and the phosphate absorption coefficient (PAC) was measured by the ammonium phosphate method using UV/VIS (PharmaSpec UV-1700, Shimadzu Co. Ltd.). The bulk chemical composition of powdered rock and soil samples was also measured by X-ray fluorescence analysis (EDX-720, Shimadzu Co. Ltd.). The CEC was measured by strontium chloride-ammonium acetate solution method (Kamewada and Shibata 1997). The colloid content in soils was estimated by using 3 type of chelating agent (dithionite-citrate, acidic oxalate and pyrophosphate). This method is mainly based on speciation and quantification of amorphous colloids by using the difference of leaching ability for each chelate (Parfitt and Childs 1988). Acidic oxalate selectively elutes amorphous ~ quasicrystalline aluminosilicate, amorphous iron minerals, alumina- or iron-humus complexes. Pyrophosphate elutes alumina and iron-humus complexes. Dithionite act as reducer and reduces free iron oxide, so that dithionite-citrate can elute free amorphous ~ crystalline iron oxide as citrate chelate. The concentration of Si, Al and Fe were measured by ICP-MS to calculate the colloid content of five fractions: goethite + hematite colloid, ferrihydrite colloid, allophane + imogolite colloid, alumina-humus complex, and iron-humus complex. Additionally, arsenic concentration in each leachate was also measured and estimates made of the arsenic rich colloidal fraction.

**Results**

**Soil chemical property**

Quartz and plagioclase were identified from every soil sample, and smectite (montmorillonite and nontronite) were also detected from the soils in mainstream ~ downstream regions. Some soils include chlorite, cristobalite, magnetite and dolomite under the influence of a hydrothermal alteration zone. Table 1 shows the chemical aspect of soil samples. Only upstream soil sample denotes slightly acidic condition (pH=5.3), high TOC (21%) and low CEC as compared with the other samples. The soils in mainstream to downstream have pH=6.07 ~ 6.68 and about 5% TOC. Average CEC is 15~20 [cmol(+)/kg] and major exchangeable cation is Ca. The leaching concentration of arsenic increases downstream. Figure 2 shows the relation between CEC and leaching concentration of heavy metals in water leachate test. Although the selectivity of heavy metal adsorption to smectite is changed by content of organic materials, reduced iron and carbonate, the adsorption selectivity among Cu, Pb and Zn are reported as Cu + Pb ≫ Zn under neutral pH and about 5% of TOC condition (Sipos et al. 2009). The leaching concentration of Cu is increased in proportion to CEC increase. Although Pb leaching represents a small concentration due to the originally lower content than Cu and Zn, Zn is also increased with CEC but decreases above 18 cmol(+)/kg of CEC. This phenomena indicates that Cu has higher adsorption selectivity and preferentially adsorbs on smectite.

![Figure 1](image1.png)  
**Figure 1.** The spatial distribution of mining site and alteration region in Osaru River basin, northern Japan. Circle points (○) are soil-sampling points. Rock samples were collected within alteration region.

![Figure 2](image2.png)  
**Figure 2.** The relationship between CEC and leaching concentration of heavy metals in the water leachate test.
Table 1. Soil chemical property and metal concentration of water leachate test.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>7.11</td>
<td>5.59</td>
<td>1.95</td>
<td>2.86</td>
<td>6.78</td>
<td>3.00</td>
<td>4.93</td>
<td>6.83</td>
</tr>
<tr>
<td>TOC [wt%]</td>
<td>21</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>PAC [%]</td>
<td>20.9</td>
<td>7.8</td>
<td>4.2</td>
<td>4.1</td>
<td>3.8</td>
<td>3.5</td>
<td>4.9</td>
<td>5.4</td>
</tr>
<tr>
<td>CEC [cmol(+)/kg]</td>
<td>5.73</td>
<td>15.63</td>
<td>18.80</td>
<td>14.07</td>
<td>19.60</td>
<td>23.99</td>
<td>13.75</td>
<td>15.81</td>
</tr>
<tr>
<td>Ca [cmol(+)/kg]</td>
<td>3.92</td>
<td>12.41</td>
<td>15.57</td>
<td>11.06</td>
<td>14.09</td>
<td>13.99</td>
<td>13.75</td>
<td>15.81</td>
</tr>
<tr>
<td>Mg [cmol(+)/kg]</td>
<td>0.85</td>
<td>1.67</td>
<td>2.19</td>
<td>2.19</td>
<td>2.33</td>
<td>2.33</td>
<td>2.28</td>
<td>3.37</td>
</tr>
<tr>
<td>K [cmol(+)/kg]</td>
<td>0.73</td>
<td>1.32</td>
<td>0.38</td>
<td>0.37</td>
<td>0.37</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
</tr>
<tr>
<td>Na [cmol(+)/kg]</td>
<td>0.23</td>
<td>0.23</td>
<td>0.66</td>
<td>0.45</td>
<td>0.26</td>
<td>0.46</td>
<td>0.42</td>
<td>0.37</td>
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<tr>
<td>Pb [ppb]</td>
<td>1.08</td>
<td>2.57</td>
<td>3.13</td>
<td>1.89</td>
<td>1.70</td>
<td>1.23</td>
<td>1.41</td>
<td>1.54</td>
</tr>
<tr>
<td>Zn [ppb]</td>
<td>4.56</td>
<td>11.55</td>
<td>16.56</td>
<td>8.08</td>
<td>8.24</td>
<td>5.75</td>
<td>10.94</td>
<td>12.18</td>
</tr>
<tr>
<td>As [ppb]</td>
<td>0.92</td>
<td>0.88</td>
<td>1.32</td>
<td>1.62</td>
<td>1.90</td>
<td>3.37</td>
<td>8.00</td>
<td>17.92</td>
</tr>
</tbody>
</table>

Leaching phenomena of toxic elements

Figure 3 shows the pH dependence of metal leaching. Elution ratio shows the ratio of leaching concentration to bulk contents for each element. Both of arsenic and lead show the amphoteric metal character in this leachate test. In the case of arsenic, high ferric contents (Fe > 10 wt%) prevent arsenic leaching, and especially low arsenic leaching samples are rich in goethite and metahalloysite. On the other hand, the low lead leaching sample is rich in sulphur. The kaolinite or goethite rich rock samples also prevent arsenic leaching under a slightly acidic condition, and Ca rich rocks poor leaching ratio with neutral to basic conditions.

Figure 3. The pH dependence of lead and arsenic leaching from soil and rock samples.

Amorphous ~ quasicrystalline colloid

The contents of amorphous ~ quasicrystalline colloid in each soils is summarised in Figure 4. The soil in upstream region includes 350 mg/kg of colloid, which is highest in this river basin. Ferrhydrite and alumina-humus complex are the main colloids. The content of alumina-humus complex decreases downstream, and 70 ~ 80 % of colloid become ferrhydrite. Ferrhydrite was observed in arsenic rich river sediments in the some tributaries near the mining site (Hara 2008). The leaching concentration of arsenic increases downstream in the Osaru River basin (Table 1), arsenic contents in the main 3 colloid fractions are summarized in Figure 5. Most arsenic exists with ferrhydrite colloid. Arsenic is assumed to adsorb on ferrhydrite and transport downstream with ferrhydrite colloid. Ferrhydrite is easy to form in ferric rich condition and easily fixes the arsenic (Klaus et al. 1998), but it exists as a metastable phase in natural environments. Therefore it transforms to goethite under neutral pH condition over several months to several years (Schwerthmann and Cornell 1991). Although phase transition is delayed by metal adsorption (Jambor and Dutrizac 1998), the goethite content in soil in river mouth is increasing (Figure 5). One of the reasons is that soil environment becomes reductives due to high groundwater level around river mouth. Arsenic adsorbs on ferrhydrite as As(V) under an oxidative condition, but if it alters to a reductive condition, arsenic is reduced to As(III) and As(III) continuously reduced to HAsO$_2$ (As(0)) under pH=3 ~ 6.5 based on a thermodynamic phase equilibrium calculation. So that the adsorption of arsenic on iron oxide is decreased. Goethite is widely distributed in this river basin, but arsenic adsorption is only observed on goethite in
downstream. Arsenic is assumed to desorb from ferrihydrite and adsorb again on goethite in the downstream part. Arsenic is fixed stably by the goethite colloid. On the other hand, the content of Al/Fe-humus colloid is low (Figure 4) but arsenic concentration in humus complex colloid is high downstream (Figure 5). The humus complex also assumed to have a high potential to accumulate arsenic and carry it through the river. Considering colloid speciation, arsenic mainly adsors on ferrihydrite and Al/Fe-humus complex. Arsenic is transferred as a colloid in subsurface oxidative and neutral pH conditions.

Figure 4. The colloid contents of soils in the Osaru River basin.

Figure 5. As concentration in the main colloids.

Conclusion
This work discusses toxic metal migration and leaching phenomena using field research data. The leaching of toxic metals is affected by co-existing mineral and major leaching elements, significantly Fe, Al and Ca. These elements prevent metal leaching, but some adsorbed metals also migrate as colloid. In this research area, the elements leached from hydrothermal alteration region adsorb on clay minerals or colloidal material. Especially arsenic adsorbs on ferrihydrite and Al/Fe-humus complex, and is transported downstream. It also accumulates in alluvial soil around the river mouth. In addition, accumulated arsenic exists under reductive condition at this river mouth, so that migration underground is assumed to be low.

References