The Content of Heavy Metals in Bottom Sediments of the Streams of the Sikhote-Alin Biosphere Reserve and the Streams Draining Mines of the Transit Zone of the Reserve

E.N. Chernova a,c,⁎, E.V. Potikha b, O.E. Nesterenko c

a Pacific Institute of Geography FEB RAS, Vladivostok, Russia
b Sikhote-Alin Nature Reserve, Ternei, Primorsky Krai, 692150 Russia
c Far Eastern Federal University, Vladivostok, Russia

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ABSTRACT

The concentrations of heavy metals in the bottom sediments (fraction <0.1 mm) of streams of the Sikhote-Alin Nature Reserve and streams draining the mines of the protective and transit zone of the reserve, as well as in the tailing material, was examined. The background ranges of the Fe, Cu, Ni, Zn, and Cd concentrations in bottom sediments of streams of the eastern and central Sikhote-Alin were defined. The concentrations of Zn are elevated, and the concentrations of Cd are comparable in the bottom sediments of the reserve compared to the approximate permissible concentration in the soil. Elevated concentrations of Zn, Cu, Cd, Mn, Pb, and Ni compared to the background were found in the bottom sediments of the streams draining the territory of the tin mines. The concentrations of Zn and Cd in these bottom sediments exceeded the approximate permissible concentration. Elevated concentrations of Cu were observed in the bottom sediments of the streams, even at a distance of 10 km from the mine. The content of metals in the bottom sediments in the stream draining the tin and silver mine did not exceed the approximate permissible concentration, whereas the concentrations of Cu, Mn and Pb were increased compared to the background. The surface layer of the sediments of the tin mines tailing ponds was enriched in Cu and Pb and starved of Cd, Ni, and Zn compared to the bottom sediments and the approximate permissible concentrations in the soil.

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Introduction

In the second half of the last century, there was intensive development of the taiga regions of Primorsky Krai. Mining operations were actively conducted in remote areas of the taiga, which were previously considered unreachable. Three mining fields were developed near the modern boundaries of the Sikhote-Alin State Nature Reserve. Development of the Lysogorskiy tin deposit located on the main watershed of Sikhote-Alin begun with excavations on the western slope. Only one tunnel was located on the eastern slope within the current territory of the reserve. At the present time, the territory of the mine is located within the protective zone of the reserve. Another tin deposit, Tayozhniy, was located near the northern boundaries of the reserve. It was named after the settlement next to which it was founded. These tin deposits, located on the western spurs of the Sikhote-Alin,
were in operation until the 1990s, with hundreds of millions of cubic metres of processed rock changing the look of vast territories and violating the hydrological regime of water bodies. However, the greatest anthropogenic stress was experienced by small streams that drained the territory of mining and processing, which were not protected from salted drainage water from the tunnels and tailings. The gold and silver mining complex Serebryanii, located at the eastern boundary of the reserve, was built in the late 1980s with all accessible contemporary technology that restricted the flow of mine drainage water into streams. Since 1995, the Serebryanii mining complex was operated occasionally and was finally sealed off at the end of 2012. Biological indices obtained by us for the watercourses draining the territory of these mines showed that over time certain changes occurred in the structure of zoobenthos (Potikha, 2012; Potikha & Zorina, October 23–27 2006) in relation to the watercourses of the Sikhote-Alin Nature Reserve (Potikha, 2011).

The goal of this work is to evaluate the metal pollution of watercourses of the Sikhote-Alin Nature Reserve and the streams in the protective and transit zones of the reserve that drain the territory of the sealed off and closed mines by analysing the content of metals in the bottom sediments.

Fig. 1. The map of the sampling locations of the bottom sediments in watercourses and tailing dumps in the study area
Materials and Methods

Bottom sediment samples from the watercourses and tailing ponds were collected during research expeditions by employees of the Sikhote-Alin Nature Reserve from August 2011 to October 2012. Sampling was performed on the perimeter of the Sikhote-Alin Reserve at the territories of the closed mining complexes Lysogorskiy (Pravaya Pritochnaya River, Kolumbe River basin) and Tayozhniy (Dalnaya River, Obilnaya River basin) and sealed off gold and silver mining complex Serebryaniy (Zolotoy Stream, Tayozhnaya River basin) (Fig. 1). To determine the background concentrations of heavy metals, samples of the bottom sediments were taken at the territory of the reserve (rivers Tayozhnaya, Zabolochenennai, Yasnaya, Serebryanka, Golubichnaya and Dzhigitovka).

Bottom sediment samples were collected from pools of watercourses, and soil samples were collected from the surface horizon at different areas of the tailing dump. All samples were placed in clean plastic bags, labelled, and dried to dry-air condition. In the lab, the bottom sediment and tailing samples were sieved, and the fraction less than 0.1 mm was separated. Weighed quantities of 0.2 g were taken at the territory of the reserve (rivers Tayozhnaya, Zabolochennaya, Yasnaya, Serebryanka, Golubichnaya and Dzhigitovka).

To determine the background concentrations of heavy metals, samples of the bottom sediments of the background area, the mean values, median, and double median absolute deviations (MAD) were calculated. The median value + 2MAD was used as the threshold value of the background concentrations of metals.

The degree of contamination of the sediments in the watercourses of mines was calculated using the total pollution index (Guidelines for assessing the danger of soil contamination with chemicals, 1987) by the formula:

\[ Z_c = \sum K_{ci} - (n - 1). \]  

Table 1

<table>
<thead>
<tr>
<th>Watercourse</th>
<th>Sampling area</th>
<th>Sampling point</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Cd</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. Dzhigitovka</td>
<td>Isakov Stream mouth</td>
<td>1</td>
<td>11.1</td>
<td>458.4</td>
<td>10.3</td>
<td>1.4</td>
<td>21.9</td>
<td>145.4</td>
</tr>
<tr>
<td>300 m down from</td>
<td>(Plastun-Terney road)</td>
<td>2</td>
<td>11.8</td>
<td>620.5</td>
<td>14.0</td>
<td>0.9</td>
<td>41.2</td>
<td>135.3</td>
</tr>
<tr>
<td>R. Dzhigitovka</td>
<td>Upstream, near cabin Kabaniy</td>
<td>3</td>
<td>562.2</td>
<td>997.4</td>
<td>23.8</td>
<td>2.1</td>
<td>81.8</td>
<td>445.2</td>
</tr>
<tr>
<td>R. Kuruma</td>
<td>Upstream, near cabin Kuruma</td>
<td>4</td>
<td>12.5</td>
<td>525.5</td>
<td>12.8</td>
<td>1.2</td>
<td>24.6</td>
<td>106.1</td>
</tr>
<tr>
<td>Str. Kabaniy</td>
<td>Mouth, near cabin Kabaniy</td>
<td>5</td>
<td>10.1</td>
<td>313.7</td>
<td>14.5</td>
<td>1.2</td>
<td>24.6</td>
<td>87.2</td>
</tr>
<tr>
<td>R. Kunaleika</td>
<td>Midstream, up from Khovar Stream mouth, up from</td>
<td>6</td>
<td>9.1</td>
<td>485.3</td>
<td>8.4</td>
<td>0.7</td>
<td>16.3</td>
<td>86.6</td>
</tr>
<tr>
<td></td>
<td>the bridge at cabin Kunaleika, boundary of the</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reserve</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R. Golubichnaya</td>
<td>Midstream, near Verhnyaya</td>
<td>7</td>
<td>11.9</td>
<td>875.3</td>
<td>6.4</td>
<td>1.2</td>
<td>14.3</td>
<td>93.1</td>
</tr>
<tr>
<td></td>
<td>Golubichnaya cabin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Str. Sukhoy</td>
<td>Downstream, near cabin Blagodatnoye</td>
<td>11</td>
<td>5.9</td>
<td>460.1</td>
<td>5.2</td>
<td>0.6</td>
<td>13.2</td>
<td>51.5</td>
</tr>
<tr>
<td>R. Zabolochenennai</td>
<td>Down from Yasnaya River mouth, near cabin</td>
<td>9</td>
<td>10.5</td>
<td>2140.3</td>
<td>7.4</td>
<td>2.9</td>
<td>30.3</td>
<td>267.0</td>
</tr>
<tr>
<td></td>
<td>Yasnaya</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R. Yasnaya</td>
<td>Mouth</td>
<td>10</td>
<td>10.0</td>
<td>628.6</td>
<td>9.0</td>
<td>2.9</td>
<td>26.1</td>
<td>209.8</td>
</tr>
<tr>
<td>Str. Krivoy</td>
<td>Mouth, near cabin Nechet</td>
<td>12</td>
<td>7.7</td>
<td>635.5</td>
<td>7.7</td>
<td>1.2</td>
<td>15.3</td>
<td>69.7</td>
</tr>
<tr>
<td>R. Tayozhnaya</td>
<td>Up from the mouth of Krivoy stream, near cabin</td>
<td>13</td>
<td>16.2</td>
<td>536.4</td>
<td>19.3</td>
<td>1.6</td>
<td>24.2</td>
<td>172.4</td>
</tr>
<tr>
<td></td>
<td>Nechet</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Min–max 5.9–5622 313–2140 6.4–23.8 0.6–2.9 13.2–81.8 51.5–445 442.2 804 11.3 1.6 27.4 161 10.9 620 9.0 1.2 24.2 135 1.9 321 5.1 0.9 12.4 98 12.9 941 14.0 2.1 36.3 233 37.2 1183 32.2 0.68 33.8 144.8 70.4 1150 61.3 1.1 55.3 240

Approximate permissible concentrations for soils

in numerator - arithmetical mean, in denominator - range.

\( ^a \) (Chudaeva & Chudaev, 2011).

\( ^b \) (Savenko, 2006).
where \( n \) — number of metals; \( K_d \) — concentration ratio:

\[
K_d = \frac{C}{C_b},
\]

where \( C \) — concentration of an element in the sample, \( \mu g/g \); \( C_b \) — background concentration, equal median + 2MAD of the background territory, \( \mu g/g \).

**Results and Discussion**

The content of metals in the bottom sediment samples of the background streams is presented in Table 1. The calculation of the background range and background threshold concentrations of metals proved that streams with elevated concentrations of heavy metals are located in and near the territory of the reserve. For example, elevated concentrations of metals are characteristic for the bottom sediments of the upper reaches of the Dzhigitovka River. The sediments of this river are also characterized by an increased amount of dissolved Zn (Shulkin et al., 2009) due to the presence of polymetallic ore occurrences in the catchment area. The bottom sediment samples taken in rivers Yasnaya and Zabolochennaya also contained elevated concentrations of Zn and Cd, in Tayozhnaya River, Cu and N are associated with polymetallic rocks found in the catchment area of the northeast Sikhote Alin (Radkevych et al., 1962).

Acid-soluble forms of metals in the bottom sediments were determined because they interact with the living matter in watercourses. Metals that are contained in crystal lattices of minerals and can pass into a solution only after treatment with explosive perchloric acid are available to the organisms only when the minerals are destroyed in the process of weathering. There are no threshold allowable concentrations for bottom sediments in Russian regulatory documents. According to the geochemical properties and mineral compositions of the components, soil is the closest to the bottom sediments (although there is less organic matter in the sediments). The approximate permissible concentrations are determined for acid-soluble forms of metals in soil (Hygienic Standards 2.1.7.020-94, 1994; Hygienic Standards 2.1.7.2511-09, 2009). Regulations apply to soil at settlements, agricultural areas, sanitary protection zones of water sources, and territories of resort areas.

Watercourses of the protected area were studied as the background, so it makes sense to compare the concentrations of metals in the bottom sediments of these streams to the approximate permissible concentrations in soils (close to neutral and neutral (loam and clay) \( pH_{KCl} > 5.5 \)). As shown in Table 1, the threshold background concentrations of Zn and Cd in the bottom sediments of the streams to the north-east of Sikhote-Alin are slightly higher than the approximate permissible concentrations for soils. In particular, the concentrations of Zn are increased in the bottom sediments of rivers Dzhigitovka and Zabolochennaya, and the concentrations of Cd are elevated in the bottom sediments of rivers Zabolochennaya and Yasnaya compared to the approximate permissible concentrations. Elevated concentrations of Zn in the bottom sediments of a number of streams in the reserve are confirmed by the results obtained during the analysis of the heavy metal content in water moss and periphyton (Chernova et al., 2013).

Four main watercourses with elevated concentrations of heavy metals in the sediments were discovered in the reserve: rivers Dzhigitovka, Yasnaya, Zabolochennaya and Tayozhnaya.

The natural characteristics of this anomaly due to polymetallic mineralization of rocks is confirmed by the following facts: this area has been a Nature Reserve since 1935; the population density in Ternei and Krasnoarmeiskiy regions and Dalnegorsk urban area (within which the nature reserve is located) is low; and water streams flow into the area from mineral mining sites.

Streams draining tin mines (Lysogorsky, Tayozhniy) and silver mines (Serebristy) contained increased concentrations of microelements in the ecosystem components, in particular, in mosses and water periphyton (Chernova et al., 2013) due to the mines and tailings present in the territory. It is expected that the concentrations of heavy metals in the sediments of the streams near the mines will also be increased.

Therefore the sediments of Pravaya Pritochnaya River located directly downstream of the tailings pond of Lysogorsky mine have concentrations of Cu, Cd, Zn, Pb, Mn and Ni that exceeded the background threshold by 23, 9, 10, 7 and 3 times, respectively. At a distance of 5–10 km from the tailing pond of the mine, the concentrations of metals in the bottom sediments of the stream decreased dramatically but still exceeded the background threshold (Cu — by 6 and 5 times, the other elements by 1–2 times, respectively — see Table 2).

**Table 2**

<table>
<thead>
<tr>
<th>Bottom sediments of watercourses located downstream from the tailings</th>
<th>Mine</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Cd</th>
<th>Pb</th>
<th>Zn</th>
<th>( Z_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. Pravaya Pritochnaya</td>
<td>Lysogorsky</td>
<td>23.0/2.2</td>
<td>6.9/−</td>
<td>3.1/0.5</td>
<td>8.8/9.2</td>
<td>3.9/1.1</td>
<td>9.9/10.5</td>
<td>44.8</td>
</tr>
<tr>
<td>5 km from the mine</td>
<td></td>
<td>5.9/0.6</td>
<td>1.3/−</td>
<td>1.0/0.2</td>
<td>1.2/1.3</td>
<td>1.5/0.4</td>
<td>1.8/1.9</td>
<td>12.7</td>
</tr>
<tr>
<td>10 km from the mine</td>
<td></td>
<td>5.0/1.1</td>
<td>2.4/−</td>
<td>1.6/0.3</td>
<td>1.2/2.5</td>
<td>1.5/0.5</td>
<td>1.5/3.9</td>
<td>13.2</td>
</tr>
<tr>
<td>R. Dalnaya</td>
<td>Tayozhniy</td>
<td>36.3/3.5</td>
<td>5.1/−</td>
<td>3.0/0.5</td>
<td>13.0/13.4</td>
<td>5.1/1.4</td>
<td>8.3/8.8</td>
<td>61.6</td>
</tr>
<tr>
<td>Str. Stradniy</td>
<td>Serebristy</td>
<td>4.2/0.4</td>
<td>6.7/−</td>
<td>1.0/0.2</td>
<td>0.5/0.5</td>
<td>5.1/1.4</td>
<td>0.7/0.7</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Anomaly coefficients \( K_A = C/C_{background} \). Danger coefficients \( K_D = C/C_{approximate permissible concentrations} \). \( Z_c = \sum K_A - (n - 1) \).
The bottom sediments of Dalnaya River near mine Tayozhniy are enriched in Cu, Cd, Zn, Mn, Pb and Ni by 36, 13, 8, 5 and 3 times, respectively, compared to the background values. In the bottom sediments of streams Zolotoy and Stradniy, which drain the territory of Serebristiy Mine, the concentration ratios \( K_a = \text{anomaly coefficient} \) are lower: for Cu, Mn, Pb they reached 4, 7 and 5, respectively. Thus, most anomalous sediments come from watercourses located near the tailings of tin mines (Tayozhniy Mine) or draining these tailings (Lysogorskiy Mine). Much less anomalous bottom sediments are found in the watercourse draining the gold and silver mine, which is related to the chemical composition of the tailings (Fig. 2). This is supported by the values of the total pollution index of the bottom sediments \( Z_c \), calculated according to the guidelines (Guidelines MU 2.1.7.730-99, nd) and comparing with the soils (Table 2).

Bottom sediments with concentrations of chemical elements exceeding the level of approximate permissible concentrations for soils are likely to be toxic to the inhabitants of the water bodies. Relying upon the excess of concentrations compared to the approximate permissible concentrations for soils (danger coefficient \( K_d \)), the most polluted sediments are in the waterways from the tin mines Lysogorskiy and Tayozhniy downstream from the tailings, and Zn and Cd \( (K_d = 9–13) \) should be considered the most dangerous metals. Cu and Pb, with high anomaly coefficients \( (K_a = 23–36 \) and \( 4–5 \), respectively), should be excluded from the pollutant group because they do not exceed the approximate permissible concentrations (Table 2).

For the tailings, the concentrations of Cu and Pb in the tailings materials at mines Lysogorskiy and Tayozhniy were relatively high compared to the sediments and the approximate permissible concentrations for soils (Fig. 2). The concentrations of Cd, Ni, and Zn in tin mine tailings are largely comparable with the approximate permissible concentrations and are significantly lower than the concentrations in the bottom sediments. The tailings of Serebristiy Mine contained heavy metals in lower concentrations than the approximate permissible concentrations in the bottom sediments of the waterways around the tailings. This confirms leaching of some chemical elements from the top layer of the tailings and creation of conditions for their natural overgrowth. High concentrations of metals in the bottom sediments indicate that the sediments are enriched in metals both through the rock at the catchment and through reprecipitation of tailings weathering products on the particles of suspended matter.

Thus, the bottom sediments of a number of background watercourses of central and eastern Sikhote-Alin contain increased concentrations of Zn and comparable concentrations of Cd compared to the approximate permissible concentrations for soils due to the presence of natural sources of metals in the catchment area.

The content of metals in the bottom sediments in the watercourses draining the mines is significantly above the background concentrations (Cu, Zn, Cd, Pb, Ni, and Mn) and exceeds the approximate permissible concentrations (Zn and Cd). Heavy metal compounds are carried by water for considerable distances from the sources of pollution, leading to cutback in the structure of the invertebrate community, indicating the creation of a negative habitat for most species (Potikha & Zorina, October 23–27 2006). Soils from the surface of tin tailings are characterized by high concentrations of copper and lead and lower concentrations of Zn, Cd, and Ni compared to the sediments due to leaching, dissolution and removal of metals from the tailing areas. The content of metals in material of silver and gold tailings is generally on par with the approximate permissible concentrations and significantly lower than the concentration of metals in the bottom sediments of the stream from underneath the tailings.

![Fig. 2. Concentrations of metals (µg/g dry mass) in mine tailings. APC – approximate permissible concentrations in soils](image-url)
References


