Risk Assessment on Human Health: the Case of Primorsky Krai Abandoned Sulfide-Rich Tailings Dump

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Abstract. To evaluate the human health risk, the Vetvisty creek (Vysokogorsk settlement, Primorsky krai) water quality monitoring was performed, and health risk associated with exposure to metals via oral ingestion was calculated. The results of inductively coupled plasma-mass spectrometry analyses for six samples collected in May, August, and November 2019 demonstrated a spatial variation of dissolved metals concentrations in the Vetvisty creek flow at stations before and after the tailings dam. The obtained characteristics of creek water samples allowed us to reveal, that the greatest contribution to carcinogenic risk is made is made by arsenic (up to 0.00160 mg/L and 2.99×10⁻⁵ of individual lifetime risk). The obtained cancer risk associated with exposure to metals via oral ingestion have the values of 3.17×10⁻⁵ and 2.28×10⁻⁵ before and after the Vysokogorsk tailings dam, respectively. All the risk levels are in carcinogenic risks range acceptable by United States Environmental Protection Agency and do not require any additional measures except of dissolved metals content control.

1. Introduction
The Vysokogorsk settlement is in Kavalerovsky District of Primorsky Krai, Russia. It is 30 kilometers northeast of the district's administrative center of Kavalerovo. Initially founded as a wealthy mine working village, nowadays it became uninhabited rural locality. From 1954 to 1976, 0.9 million tons of the sulfide-rich mining wastes were placed in the tailings dump on the settlement territory. After the enterprise bankruptcy in the beginning of 1990-s, mine and concentration mill were permanently closed, and then demolished by marauders.

Since the best settlement years, mining has had a negative impact on all the environmental components: atmosphere, soil, and hydrosphere. As the mine and mill were closed, no one is maintaining the tailings dump. Thus, the tailings dump became so called “object of accumulated environmental damage”. The same results are seen in many mine districts in Russia [1] and all around the world [2-6].

The increase in the surface contact of finely ground sulfides with weathering agents in layers of mines and tailings leads to the activation of supergene (hypergenic) processes, which then transitions to the technogenic stage [7]. Mine wastes oxidize and release acid, SO₄²⁻, and dissolved metals to all the natural waters [3, 4, 7]. The atmosphere pollution occurs when dry tailings are goes up and moves with the wind. The soil contaminating occurs with wind transport and deposition of tailings on the soil cover [3].
As the Vetvisty creek is runs along the ruined edge of the tailings dump, natural water is continuously contacting with tailings. Both slurry and drainage water are continuously discharged from the tailings dump into the creek (figures 1 and 2). Moreover, the Vetvisty creek flows into the Vysokogorskaya river – the settlement drinking water intake (figure 2).

The aim of this study was to evaluate the human health risk. To achieve this goal, we wanted to: (1) perform the Vetvisty creek water quality monitoring, (2) calculate the health risk associated with exposure to metals via oral ingestion with drinking water. Some work has been done in Kavalerovsky district on the surface water quality assessment [7–11], no work on human health risk has been considered until now.

![Figure 1. Vetvisty creek and the Vysokogorsk tailings dump ruined edge, 2018.](image)

2. Materials and methods

2.1. Sampling and analyses

Water samples were collected from Vetvisty creek upstream and downstream the tailings dump three times: in May, August, and November 2019. The sampling stations are given in figure 2.

![Figure 2. Map of the study area.](image)
Three replicates were collected on every sampling station, and then subsequently mixed and collected in HDPE containers. Sample analysis was performed by the Laboratory of Analytical Chemistry, Far East Geological Institute FEB RAS. The samples were filtered through pre-washed 0.45-μm Millipore filters. Concentrations of As, Cd, Cr, and Pb were determined in water using inductively coupled plasma-mass spectrometry (ICP-MS) on the Agilent 7700.

2.2. Risk assessment on human health
Three main pathways may occur when target analytes expose to human being: direct ingestion, inhalation through the mouth and nose, and dermal absorption [12, 13]. Nevertheless, the most harmful for water is ingestion pathway [14].

The lifetime average potential daily dose for individual substance was estimated using United States Environmental Protection Agency (US EPA) standard exposure assessment algorithm [15]:

\[
LADD_{pot} = \frac{(C_i CR ED F)}{(BW AT)},
\]

where \(LADD_{pot}\) is potential average daily dose, unit in mg/day, \(C_i\) is contaminant concentration (mg/L), \(CR\) is contact rate (L/day), \(ED\) is exposure duration (years), \(F\) is frequency of exposure events (days), \(BW\) is body weight (kg), and \(AT\) is averaging time (days).

The individual lifetime risk was estimated by multiplying the \(LADD_{pot}\) by the cancer potency slope factor as follows [15]:

\[
R_i = LADD_{pot} SF,
\]

where \(R_i\) is excess individual lifetime cancer risk level (unitless), \(LADD_{pot}\) is lifetime average potential daily dose (mg/day), \(SF\) is cancer potency slope factor (mg/kg/day)^{-1}.

And the cancer risk was calculated by summarizing the individual lifetime risks of all the substances under consideration:

\[
Cancer risk = \sum R_i.
\]

The obtained estimated value shows the incremental probability of an individual developing any type of cancer over a lifetime.

3. Results and discussions
The determined concentration ranges of individual contaminant metals at May, August, and November 2019, and their mean concentrations are shown in table 1.

| Contaminant     | Range (mg/L)             | Mean \(C_i\) (mg/L) |
|-----------------|--------------------------|---------------------|
| Arsenic (As)    | 0.00024–0.00160          | 0.00016–0.00059     |
|                 | Before tailings dam      | After tailings dam  |
|                 | 0.00073                  | 0.00036             |
| Cadmium (Cd)    | 0.00002–0.00008          | 0.00044–0.00087     |
|                 | Before tailings dam      | After tailings dam  |
|                 | 0.00004                  | 0.00067             |
| Chromium (Cr)   | 0.00008–0.00016          | 0.00005–0.00007     |
|                 | Before tailings dam      | After tailings dam  |
|                 | 0.00011                  | 0.00006             |
| Lead (Pb)       | 0.00003–0.00008          | 0.00007–0.00036     |
|                 | Before tailings dam      | After tailings dam  |
|                 | 0.00006                  | 0.00017             |

As it seen from table 1, the natural background concentrations of arsenic (May 2019, 0.00160 mg/L) and chromium (August 2019, 0.00016 mg/L) were high in the sampling station before the Vysokogorsk tailings dam. From the opposite site, cadmium and lead maximum concentrations (0.00087 mg/L in August, and 0.00036 mg/L in May, respectively) were observed after tailings dam. It
means, that as a result of interaction of Vetvisty creek water and abandoned tailings dam, the amounts of dissolved As and Cr are decreasing with the water flow, but Cd and Pb are increasing.

Next, lets calculate $LADD_{pot}$ lifetime average potential daily doses using the equation (1) and $C_i$ mean concentrations from table 1. The $CR$ contact rate of water is assumed as 2 L/day, $ED$ exposure duration is 70 years, $F$ frequency of exposure events – 365 days, $BW$ body weight – 70 kg, and $AT$ averaging time is 25550 days (365 days over 70 years). The results of $LADD_{pot}$ calculations are shown in the table 2.

**Table 2.** Lifetime average potential daily dose.

| Contaminant   | Before tailings dam | After tailings dam |
|---------------|---------------------|--------------------|
| Arsenic (As)  | 0.0000199           | 0.0000104          |
| Cadmium (Cd) | 0.0000011           | 0.0000191          |
| Chromium (Cr) | 0.0000031           | 0.0000018          |
| Lead (Pb)    | 0.0000017           | 0.0000047          |

The obtained $LADD_{pot}$ values (table 2) and the cancer potency slope factor $SF$ [16] (table 3) allowed us to calculate the individual lifetime risks $R_i$ (table 4).

**Table 3.** Cancer potency slope factor [16].

| Contaminant   | CAS Registry Number | Cancer potency slope factor $SF$ (mg/kg/day)$^{1}$ |
|---------------|---------------------|-----------------------------------------------|
| Arsenic (As)  | 7440-38-2           | 1.500                                         |
| Cadmium (Cd) | 7440-43-9           | 0.380                                         |
| Chromium (Cr) | 18540-29-9          | 0.420                                         |
| Lead (Pb)    | 7439-92-1           | 0.047                                         |

**Table 4.** Individual lifetime risks.

| Contaminant   | Individual lifetime risk $R_i$ | Contribution (%) |
|---------------|-------------------------------|------------------|
|               | Before tailings dam | After tailings dam | Before tailings dam | After tailings dam |
| Arsenic (As)  | $2.99 \times 10^{-5}$ | $1.49 \times 10^{-5}$ | 94.28 | 64.45 |
| Cadmium (Cd) | $4.33 \times 10^{-7}$ | $6.96 \times 10^{-6}$ | 1.37 | 30.51 |
| Chromium (Cr) | $1.30 \times 10^{-6}$ | $7.08 \times 10^{-7}$ | 4.10 | 3.10 |
| Lead (Pb)    | $1.00 \times 10^{-7}$ | $2.13 \times 10^{-7}$ | 0.25 | 0.93 |
| Cancer risk  | $3.17 \times 10^{-5}$ | $2.28 \times 10^{-5}$ | 100.00 | 100.00 |

As it seen in table 4, the greatest contribution to carcinogenic risk at sampling station after the Vysokogorsk tailings dam is made by arsenic and cadmium (65 and 30 %, respectively). Moreover, As exceeds the value $1 \times 10^{-5}$, but this level cannot be a reason for any major concern of residents.

Summarizing the individual lifetime risks $R_i$ (equation (3)) reveals, that the cancer risk associated with exposure to metals via oral ingestion have the values of $3.17 \times 10^{-5}$ and $2.28 \times 10^{-5}$ (before and after the Vysokogorsk tailings dam, respectively). It is obviously seen that the cancer risk is decreasing with the water flow because of interaction “creek water – tailings”.
All the obtained risk values are in US EPA acceptable carcinogenic risks range of $1 \times 10^{-6}$ to $1 \times 10^{-4}$ [17]. Following to [18], the unconditionally acceptable risk level is assumed below $1 \times 10^{-6}$, risks above $1 \times 10^{-4}$ are sufficiently large for some sort of remediation, and a risk of $1 \times 10^{-3}$ is mandatory requires protective measures. Thus, the observed risk levels do not require any additional measures except dissolved metals content control.

4. Conclusion
Concentrations of dissolved metals in the Vetvisty creek demonstrated a spatial variation. In the sampling station after the Vysokogorsk tailings dam the amounts of dissolved As and Cr are decreasing, but Cd and Pb are increasing because of interaction “creek water – tailings”.

The greatest contribution to carcinogenic risk is made by arsenic (up to 0.00160 mg/L in May 2019, and the highest individual lifetime risk is $2.99 \times 10^{-5}$), but it cannot be a reason for any major concern of residents. The obtained cancer risk associated with exposure to metals via oral ingestion have the values of $3.17 \times 10^{-5}$ and $2.28 \times 10^{-5}$ before and after the Vysokogorsk tailings dam, respectively. All the risk levels are in acceptable by US EPA carcinogenic risks range and do not require any additional measures except of dissolved metals content control.

5. References
[1] Blokov I P, Targulyan O Y, Moustache E I 2020 Accumulated environmental damage: destruction of health and budgets (Moscow: Greenpeace Council) p 61
[2] Salomons W 1995 J. Geochem. Explor. 52(1–2) 5–23
[3] Razo I, Carrizales L, Castro J, Diaz-Barriga F, Monroy M 2004 Water Air Soil Pollut. 152 (1–4) 129–152
[4] Moncur M, Ptacek C, Blowes D and Jambor J 2005 Appl. Geochem. 20 639–659
[5] Hudson-Edwards K A, Jamieson H E, Lottermoser B G 2011 Elements 7 (6) 375–380
[6] Kossoff D, Dubbin W E, Alfredsson M, Edwards S J, Macklin M G, Hudson-Edwards K A 2014 Appl. Geochemistry 51 229–245
[7] Zvereva V P, Lysenko A I, Frolov K R 2020 Minerals 10 (2) 91
[8] Frolov K R, Lysenko A I, Pyatakova A D 2019 IOP Conf. Ser.: Earth Environ. Sci. 272 022124
[9] Zvereva V P 2019 Rus. J. Gen. Chem. 89 2808–2817
[10] Elpatevsky P, Lutsenko T 2000 The mining complex as the factor of formation of the water chemical composition Materials: Scientific and practical aspects of extraction of non-ferrous and precious metals 2 407–415
[11] Frolov K R 2020 Assessment of the Rudnaya River Geochemical Barriers Water Composition Using Physico-Chemical Modeling Method (Dalnegorsk Ore District, Russia) Sustainable Development of Water and Environment ed H Y Jeon chapter 17 pp 177–189
[12] Kim E, Little J C, Chiu N 2004 Environ. Sci. Technol. 38 (6) 1799-1806
[13] Wu B, Zhao D Y, Jia H Y, Zhang Y, Zhang X X, Cheng S P 2009 Bull. Environ. Contam. Toxicol. 82 (4) 405–409
[14] IPCS 2004 IPCS Risk Assessment Terminology: Part 2: IPCS Glossary of Key Exposure Assessment Terminology (Geneva, Switzerland: World Health Organization)
[15] US EPA Environmental Protection Agency 1992 Guidelines for Exposure Assessment EPA/600/Z-92/001 (Washington DC: US Environmental Protection Agency)
[16] US EPA Risk Assessment Portal Integrated Risk Information System (IRIS) https://cfpub.epa.gov/ncea/risk/recorddisplay.cfm?deid=2776
[17] US EPA 1991 Role of the Baseline Risk Assessment in Superfund Remedy Selection Decisions (Memorandum from D. R. Clay, OSWER 9355.0–30, April 1991) (Washington DC: US Environmental Protection Agency)
[18] US EPA 2005 Guidelines for carcinogen risk assessment EPA/630/P-03/001F (Washington DC: US Environmental Protection Agency)