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Content Estimation of Heavy Metals and Arsenic in Waters and Soils of the Unal Tailings Pond

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Abstract: The purpose of this study is to estimate the migration of heavy metals (HMs) and As into the water of the Ardon river, and their content in the soils of the areas adjacent to the Unal Tailings Pond (UTP) caused due to the industrial waste of the Mizur Ore Mining and Processing Enterprise (OMPE) (North Ossetia). The main survey loops for experimental research and collection of biogeochemical materials are located in the Ardon river basin where the major abandoned polymetallic fields of the Republic are located. Soil samples were taken from 20 sites throughout the Ardon river and within the UTP. HMs and As levels in the water, alluvium, soils samples were determined using the atomic-absorption spectroscopy (AAS) in its flame version and/or electrothermal atomisation. We have determined that UTP wastewater discharge into the Ardon river along with Me introduction with waters of the Unaldon river, as well as the dust/pulp coming from UTP followed by the formation of bottom polymetallic anomalies provide a significant contribution to the Me pollution of the Ardon. High Me content in soil and slurry as a result of its deflation and in UTP effluents may lead to Me absorption by plants and other organisms. The data obtained reflect the processes of modern transformation of mountain taxa of the biosphere with a technogenic component and can be used for remediation of contaminated areas.

Key words: Arsenic, biogeochemical anomalies, North Ossetia, pulp deflation, river alluvium, soils, tailings pond.

Introduction

Biogeochemical provinces and anomalies are unique natural and anthropogenic survey loops for studying the formation of modern ecosystems, mass transfer, accumulation of chemical elements and the interaction of organisms with their natural habitat.

From the geomorphological and biogeochemical points of view, mountainous areas exhibit the most complicated taxa of the biosphere. The movement of chemical elements, and the matter in general, in the mountains is associated with both gravitational processes and atmospheric and water migration. While in the horizontal conditions the migration of chemical elements is relatively stable, within the mountainous areas it is complicated with altitudinal zoning (Chendev, 2020).

Among the anthropogenic factors existing in mountainous areas, the tailing dump waste of concentrating factories and/or rock waste dumps are of great danger. As a result of natural disasters or violation of the storage conditions for such materials, migration of toxic components is possible which results in the formation of geochemically extreme and ecologically hazardous landscapes (Hazrat et al., 2019; Rylnikova et al., 2020).

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In this respect, the Ardon river basin in North Ossetia with its developed mining industry is one of the potentially dangerous mountain subregions of the biosphere.

The authors of this report have been repeatedly carrying out biogeochemical studies in the Ardon subregion of the biosphere since 1994. Under the influence of natural and/or man-made factors, a local increase in Pb, Cd, Cu and/or Zn, both in soils and organisms, was found to occur in comparison with background areas, together with some distortion of biological diversity. The increased level of metals (Me) in the soils and the plants of the Ardon flood bed is accompanied by an increase in their concentrations in the blood and hair of animals and is considered as a risk factor regarding their adverse effect on physiological processes in the organisms of the examined animals (Efimov et al., 2020; Ermakov et al., 2016, 2017).

It was found that as a result of mudflows and floods, along with geomorphological and hydrochemical changes, a noticeable differentiation of living matter (namely, herbaceous plants and algae) occurs. The differentiation of the algal flora species depends on their habitat substrate, type of water and hydrological regime. Nevertheless, algae can be successfully used to monitor toxic metals at natural disasters in the cases when other indicator organisms are not available as a result of mudflows and water runoff, or death of the main group of plants and poikilothermic animals (Ermakov et al., 2018, 2020a, 2020b).

Today the evaluation of the ecological status of the chemical elements, in particular, Me and As, in the abiotic components of the biosphere and the biota is becoming one of the most important factors that either directly or indirectly impact the populations of living organisms, thus determining the quality of their habitat and ultimately giving rise to anthropogenic microevolution (Bolshakov and Moiseenko, 2009; Safonov et al., 2020).

This study shows a comparative assessment of the content of Me (Pb, Cd, Cu) and As in the waters and soils of geochemically extreme areas immediately adjacent to the UTP (Sadon polymetallic ore district, Republic of North Ossetia-Alania).

Survey Area, Research Objects and Methods

The survey area covers the channel part of the Ardon river basin stretching from Zintsar village to Kardzhin village (the influx point into the Terek river) at a height of 1740 to 349 m above sea level. The length of the river from its mouth to the most distant point along the river Mamisondon and its tributary the Zymagondon is 108 km. It flows from the glaciers located on the Greater Caucasus Mountain Range and the Side Mountain Range, within the Tual bolson. The basin area is 2700 km^2, the current speed is 3.5 m/s, the average long-term water discharge is 29 m^3/s, the average long-term river flow is 0.815 km^3/year. In the neighbourhood of Zaramag village near the river, the Zaramag hydroelectric power chain and a water-storage reservoir are being constructed (Ministry of Natural Resources and Ecology of the Republic of North Ossetia-Alania 2020). Before reaching the submontane Ossetian plain, the river flows through a deep Alagir Canyon. Near Tamisk resort, the river reaches the submontane zone, and beyond town Alagir it comes to the Ossetian plain. Here the river cuts through alluvial sediments and forms a series of flows. Near town Ardon, the river enters the main channel, and about 1 km before its mouth merging with the water of the Fiagdon and the Gizeddon rivers forming an extensive network of flows on a pebble base. The Transcaucasian Highway runs down Alagir Canyon connecting North Ossetia and South Ossetia through the Roki Pass (Chigoeva et al., 2018).

Unal village is located in the intermontane Unal bolson between the Side and the Skalisty mountain ranges (42º51'36 "N and 44º08'57" E). The village is located in the central part of the Alagir district, on the right bank of the Ardon River where the Unaldon and the Mairamdon rivers inflow, some 22 km from the district center Alagir and 58 km south-west of Vladikavkaz. Near the village is the Unal Tailings Pond (UTP) of the waste coming from the Mizur Ore Mining and Processing Enterprise (OMPE). It was put into operation in 1984 and is located in the flood bed of the Ardon, 500 m below Nizhny Unal village. The Ardon pebbles serve as a bed here. Its right border is separated from the river bed with a concrete dam, and the left one comes close enough to Transcaucasian Highway. During the active period of the Mizur OMPE operation, about 3 million tons of tailings have accumulated in the UTP, and the level of the main ore elements Pb and Zn level there is about 1%, and of the accompanying ones like Cu, Ag, Bi and/or Cd is in the range of $10^{-2} \div 10^{-4}$%. To reduce the aeration process in summer, forced irrigation of the tailings pond was applied, though no more than 50% of its surface was covered with water as a rule. Consequently, the dry pulp is deflated from its open part leading to HM pollution of soil and vegetation on the lower terraces of the Ardon (Pryanichnikova, 2005).

In 2019, within the framework of a regional project "The Clean Country", some works were initiated to eliminate the negative impact of UTP on the environment. In 2020, the UTP area was engineered for protection and a partial recultivation of the polluted land was carried (Ministry of Natural Resources and Ecology of the Republic of North Ossetia-Alania, 2020).

The Ardon trans-sect (profile) included the following survey loops (i.e., areas for biogeochemical material sampling): 1 - Zaramag village meadow in an alluvial bolson, 2 - Buron vil. (edge of a mixed forest, right bank of the Ardon), 3 - Mizur vil. (left bank of the Ardon, the 1st terrace, meadow), 4 - Unal (mountain slope 1.5 km west of UTP, a mountain steppe meadow), 5 - Unal (right bank of the Ardon, near the bridge, a floodplain meadow), 6 - Unal (garden grounds, a cereal and forb meadow), 7 - Unal (a swamp, 0.5 km north of the bridge, a sedge and grass ground), 8 - Unal (right bank of the Unaldon, a forb meadow), 9 - Unal south part, M.V. Lomonosov Moscow State University Camp (steppe and forb meadow), 10 - Unal (right bank, calcareous rock outcrop, a forb ground under the outcrops), 11 - below the Lomonosov MSU Camp, the 2nd above-floodplain terrace, the Ardon right bank, a forb meadow), 12 - below the MSU Camp, the 1st above-floodplain terrace, the Ardon right bank, a meadow area), 13 - southwestern part of the UTP, 14 - northeastern part of the UTP, 15 – Zintsar vil., a mountain steppe meadow), 16 - beyond Zintsar vil., the Ardon left bank, a hydrogen sulfide lake of karst origin, coastal herbaceous plants, 17 - Alagir town, the Ardon left bank, between the flows, a wet meadow, 18 - Ramonovo vil., a meadow between the Ardon flows, a wet meadow, 19 - Ardon town (the Ardon river left bank, a steppe ground near the bridge), 20 - near Karzhin village, the Ardon mouth, the river left bank, a wet floodplain meadow). The transect sampling points are shown in Figure 1.

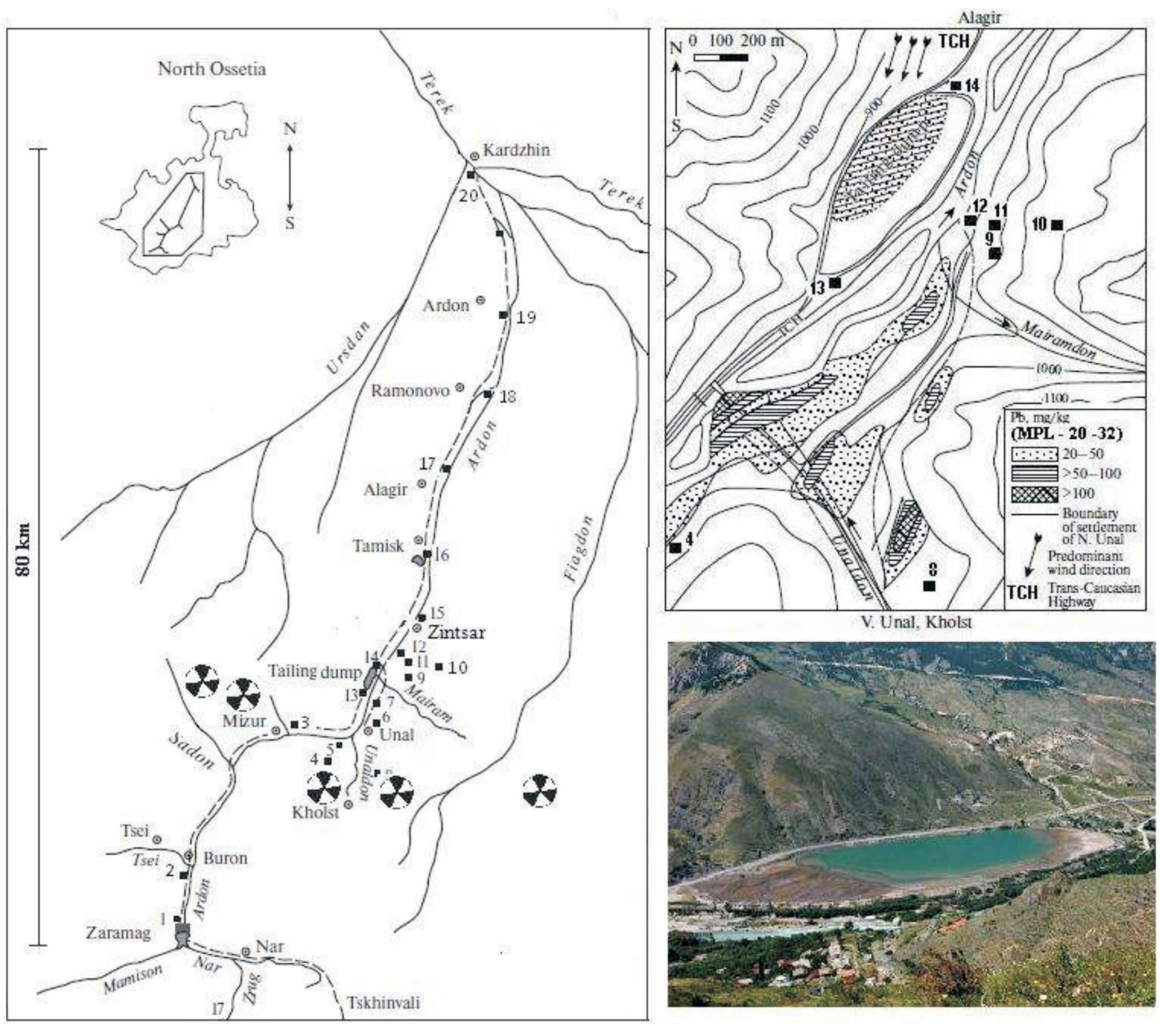

Figure 1: Scheme of soil sampling for the Ardon transect (left), and the sampling in the vicinity of the UTP, and its view (right).

For this study, the upper humus horizon A of various soils was selected. The urban soil and technosol samples were collected from the depth of 15 cm. Also, water samples were taken into 1.5 l polyethylene vessels and 50 ml test tubes. For each sampling point, the geographical latitude and longitude, as well as the height above sea level, were registered.

Analysis Methods

After drying at room temperature, soil and alluvium samples weighing 0.2 g (fraction <1 mm, ground to a grain size of <150 mesh) were decomposed with a mixture of perchloric, nitric and hydrofluoric acids, and diluted to a volume of 15 ml.

Following the collected samples of acid mineralisation, the trace elements were determined using AAS in its flame version with deuterium (Kvant-2A) or flameless version using Kvant-Z.ETA with the Zeeman background corrector. The analyses precision rates were controlled through examination of certified soil samples (standard samples from the PRC, Poland and the Russian Federation, including SP-1, SP-2, SP-3, WEPAL IAE sample 899 (cabbage) and IAEA Soil-7 or NIST 1571 Orchard Leaves). The lower limits for Cu, Zn and Pb were 0.2 mg/kg, for Cd 0.02 mg/kg and for As 0.05 mg/kg of the sample, respectively.

The macro- and micro-components in natural water were determined using unified methods of analysis. To separate the soluble and the suspended Me forms, the water samples were filtered through membrane filters with a pore diameter of 0.45 μm.

When sampling, carbon dioxide and bicarbonate ion levels in the water were determined on site. Total dissolved solids were measured conductometrically using a device DIST 1 (HI 98301) (HANNA, Germany) calibrated against a standard sodium chloride solution. Eh and pH indices were measured using a pH-meter pH-410 (Aquilon). The total $\gamma+\beta$ activity was measured for river alluvium and soils using a radioactivity indicator RADEX RD1706. The locations of the sampling points were determined using a navigator GPS Garmin Oregon 450. For statistical analysis of the research data obtained, Ms-Excel 2013 software was used.

Research Results

Me Migration in the Ardon Water

Disposal of UTP wastewater into the Ardon river and Me supply with its tributaries, especially the Unaldon river water, as well as the dust (pulp) spreading from UTP play a significant role in the Me pollution of the Ardon river basin.

In the filtered wastewater, the following Me concentrations are observed (μg/l): 2.6 to 10.8 (Pb), 0.3 to 95 (Cd), 8.0 to 10.4 (Cu) and 130 to 160 (Zn). The Me contents increase insignificantly after the wastewater discharge (μg/l): Pb 0.2 to 0.6 (before) and 0.8 to 1.6 (after), Cd 0.06 to 0.27 (before) and 0.1 to 0.35 (after), Cu 1.4 to 2.9 (before) and 2.2 to 3.7 (after), and Zn 28 to 50 (before) and 25 to 62 (after). Moreover, after the waste water mixes with the one of the Ardon, the metals first precipitate due to pH and mineralisation levels difference, followed by a gradual increase in their concentrations (Figure 2). A more significant influence is apparently exerted by the UTP pulp which enters the watercourse in the form of dust as a result of deflation. Therefore, the Ardon bottom sediments in the UTP area are characterized by high Me levels, including Pb, which is shown in Figure 2. The Pb concentrations in the alluvium decrease where the Ardon river reaches Ossetian plain though being increased (40 to 50 mg/kg). Figure 2 shows the change in the suspended matter levels as observed in the Ardon water. The sediment load levels in the water samples taken within a stretch from Zaramag village up to Ardon city slightly increase while rising sharply due to the Fiagdon and the Gizeldon rivers falling into it.

The high metal content levels in the Ardon alluvium were determined at a distance of 12 km from the UTP. The alluvium near the tailings pond exposes two significant Pb and Cu anomalies, one being associated with the UTP surface deflation with the highest Pb (645 mg/kg) and Cu 65 (mg/kg) levels. The other anomaly is associated with a clarified water release from the sedimentary reservoir with the highest Pb and Cu levels of 328 and 60 mg/kg, respectively. Both anomalies have a spatial coincidence and affect both the meadow-alluvial soil-forming process and the biogeochemical anomalies formation.

Me Contents in the Soils from the Unal Depression

Table 1 shows the results of determining the total metal levels in the soil. The soils are ranked in descending order of the total pollution degree (∑Me).

The soil analysis has shown high metal levels in the pulp and the anthropogenic soils around the Unal Tailings Pond, which we have repeatedly stated before (Degtyarev and Ermakov, 1998). The technosols represent marginal areas of the UTP where the transformation of the main material, the Mizur OMPE

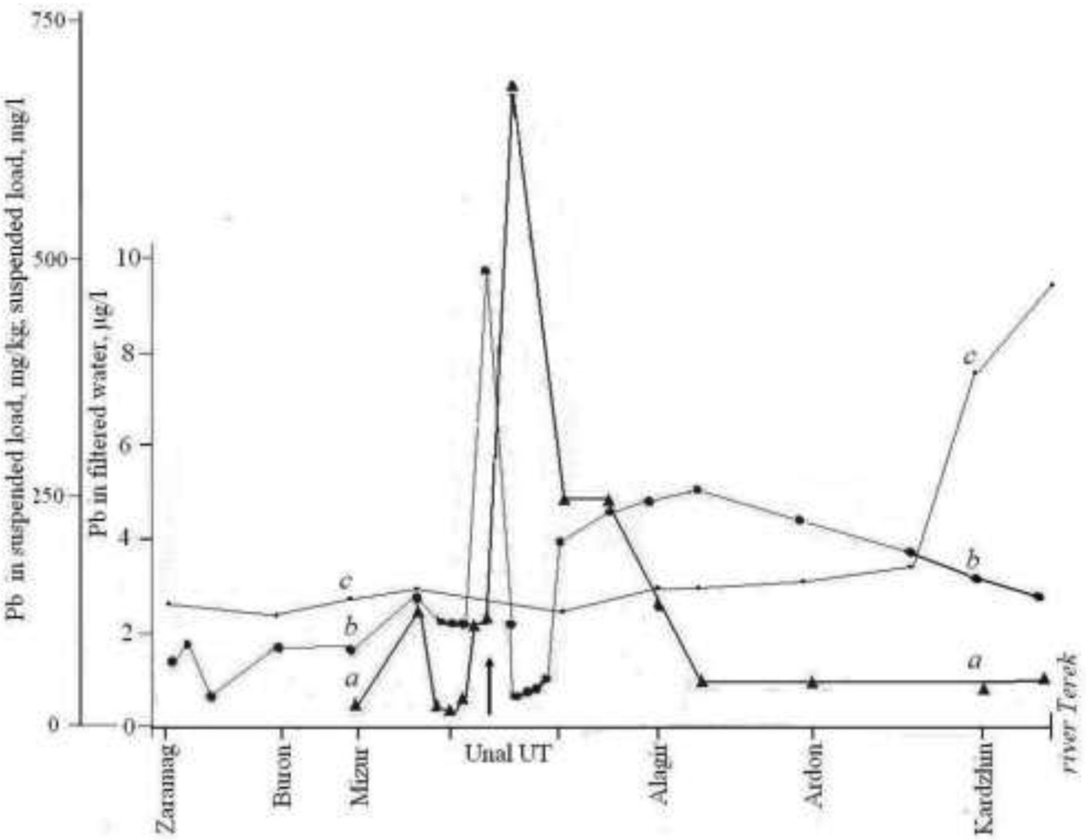

Figure 2: Change in the levels of suspended matter (c) and of lead in filtered water (b) and the suspended matter (a). The arrow shows the lead levels in UTP water disposed into the Ardon.

Table 1: The gross content of Me and As in the soils of the Unal depression collected for sequential fractionation

Point number	*Sampling site*	*Technozem, soil*	*Metal content, mg/kg*					*∑Me, mg/kg*
			Cu	*Zn*	*Pb*	*Cd*	*As*	
	Pulp and tehnoshem of the UTP							
13	SW part of the UTP, H=880 m	Pulp 0-10 cm	275	3800	4500	25.0	66.3	8600
14A	NE part of the UTP, H=878 m	Toxilitostrate 0-10 cm	4400	35400	27300	24.8	71.0	67000
14B	In the same place	Same thing. > 15 cm	306	3200	3000	21.1	52.7	6500
Soils with different degrees of contamination								
12	50 m below point 11, terrace I, H-877 m	Umbric Leptosols Dystric 0-10 cm	68	745	747	5.1	5.9	1560
11	Right bank of the Ardon river, terrace II, H=895 m	Same thing. > 15 cm	54	456	441	3.3	5.1	950
4	1.5 km west of the village Unal, H=931	Mollic Leptosols 0-12 cm	25	304	261	1.7	7.1	590
8A	Unal village, right bank of the river Unaldon, H=962 m	Mollic Fluvisol 0-7 cm	25	271	91	1.4	9.7	390
8B	In the same place	Same thing 8-12 cm	26	445	96	1.0	6.3	570
9	The base of Moscow state University, mountain meadow H=923 m	Umbric Leptosols Dystrict, 0-8 cm	30	195	201	1.3	10.1	430

pulp, takes place. The main transformation factor here is the wind erosion and deflation with the upper horizons of technosols getting Me-enriched, which is shown in Table 1. Thus, in the upper horizon of the technosol sampled in 2019, at point 14 (0-10 cm) the Me concentration was 10 times as higher than the Me level as observed in its lower horizon (> 15 cm). This phenomenon was noted in 2018 (Ermakov et al., 2018). As compared with the earlier data, the metal levels in technosols at points 13 and 14 have increased significantly. It should also be noted that the highest Me levels for all the soils examined were observed in the upper horizons. This phenomenon is presumably connected with the tailings pulp deflation and/or eolian scattering of finely dispersed dust enriched with the ore metals (Figure 3).

Figure 3: Deflation of the Unal Tailings Pond surfaces.

In terms of the Pb, Zn and/or Cu levels in the pulp, the tailings pond under discussion can be attributed to a technogenic deposit. Thus, according to ITS (BAT Bureau, 2016), the commercial contents of lead, zinc and cadmium in ore start from concentrations of 1.12%, 1.24% and 2 g/t, respectively. In the present case, the Pb, Zn and Cd levels in the transformed pulp were determined as 3.54%, 2.73% and 248 g/t. Furthermore, the high As levels in the pulp, soils and grounds as observed around this technogenic formation, which is 10 to 15 times higher than the background values, pose danger as well (Bezuglova and Okolepova, 2012).

The Me concentrations in the UTP soils are interrelated (r = +0.98) indicating there is some uniformity of the pollution. To evaluate the Me technogenic burden on soils in the UTP area, the Zn to Pb concentration ratio in the pulp, being the main source of the pollution, can be used. It amounts to 0.84 to 0.95, i.e. less than 1. For the technosols, the Zn/Pb ratio is 1.06 to 1.30, for soils close to UTP is 0.99 to 1.47, and for soils taken far from UTP - 2.97 to 4.63, the latter value verging towards the Earth's upper crust average composition = 4.41 (Grigoriev, 2009) and soil average elemental composition = 5.0 (Alekseenko and Alekseenko, 2013).

The dust fallout intensity calculations have shown that the parameter values as found in different points of the Ardon lower terraces vary from 74 kg/km^2/day to 304 kg/km^2/day (Pryanichnikova, 2005). On the lower terraces, the average amounts of dust were two times higher than those both on the upper ones and in or around the Loire landslide (1750 m above sea level). At the same time, Zn prevails in dust fallouts throughout the area: the Zn/Pb ratio on the upper terraces is 2.70, in the Loire landslide it is 2.17, and only the lower terraces have shown some increase in Pb ratio among the main ore elements (Zn/Pb = 1.25). On the Ardon lower terraces, the dust macrocomposition is closer to the one for the tailings pulp (quartz > 90%, feldspars> chlorite> glists). The dust in the upper section is characterised by lower amounts of quartz (70%) and chlorites, and higher amounts of clay minerals. In terms of its microcomposition, the dust from the lower terraces is also close to the tailings pond sludge, the main ore elements (Zn/Pb) ratio being 1.05 in there (Pryanichnikova, 2005).

In general, the above ratio of the main ore elements (Zn/Pb) can serve as an indirect parameter for the identification of the airborne technogenic impact of the tailings pond when differentiating pollution sources.

Conclusion

The dust emissions, the waste water coming from the ore mining and processing enterprise, and the water from the tributaries carrying heavy metals from the sulphide deposits of the Sadon group are determined to be the main sources of metal entering the Ardon river. The pulp coming from the Mizur enterprise to the UTP is enriched with Pb (up to 9370 mg/kg) which generally accounts for the pollution of these areas. The analysis of the gross metal content in the slurry and anthropogenic soils of the UTP also indicates high overall metal contamination.

It was found that the discharge of UTP irrigation water into the Ardon River does not create appreciable concentrations of metals in the Ardon River due to the dilution of effluents by river.

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