Water Composition Changes in the Bureiskoe Reservoir after a Landslide and Blasting

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Abstract. Data on changes in the qualitative composition of volatile organic compounds and content of elements in waters of the Bureiskoe Reservoir after a great landslide, which blocked access to the hydroelectric power station, were presented. Blasting with use of trinitrotoluene and hexogen carried out to restore the hydrological regime by creating an artificial channel. Maximum content of methanol and acetone were recorded in water samples taken at the right bank near the landslide, where a lot of disintegrated wood entered the water after river tsunami. After filtering water through a landslide body, the content of Al, Fe, and Pb increased, and content of Mg, Ca, Zn, and Cd decreased. After restoration of the reservoir flow in water samples from the artificial channel, the content of Fe, Mn, Al, Cu, and Zn was at a low level and did not reach the initial values established before the blasting began. However, an increase the content of Pb by 7 times and Hg by 80 times was recorded. Presence of methanol and methylated benzene derivatives in water could stimulate the formation of more toxic bioavailable methylmercury, posing risks to aquatic organisms.

1. Introduction

Usually, landslides cause destructive damages and lead to the death of people around the world [1]. Understanding the mechanisms of destruction of mountain slopes is extremely important for solving socio-economic, geotechnical, and environmental problems [2]. Rapid displacement of rocks is predicted after a change in the water level in the reservoir within 105–130 m and heavy precipitation. On the example of a rock landslide in Chongqing (China, 2014), it was shown that the process of physical weathering became an important cause of the destruction of the slope 16.5 years after the construction works [3]. Water, as a key factor accelerating the weathering process, weakens the mechanical properties of rocks [4]. Studies of the behavior of frozen soils are relevant in connection with climate changes in regions with a wide range of temperature fluctuations and are of great importance for the construction of high-speed roads and the operation of reservoirs [5].

Intense precipitation [6], earthquakes [7], and melting of frozen rocks and glaciers [8] are most often causes the landslides. Biogeochemical processes define the constancy of rock slopes. The disruption effect is often associated with chemical erosion and alternating freeze-thaw cycles [9]. One of the important trigger of landslides is earthquake. For example, in the south-west of China (Sichuan Province), after the earthquake on August 8, 2017, 83 landslides, which increase the volume of sediment load and debris material in waterways, were discovered with use of remote sensing and field research [10]. Studies have shown that the landslide was caused by the combined impact of factors
(steepness of slopes, constant rainfall, flooding, destruction of mountain foothills and human activities) [11].

In addition to the negative consequences on the social sphere, landslides carry risks associated with the disruption of the functioning of terrestrial and aquatic ecosystems. The inflow into the surface waters of a huge amount of fragmented rock particles, organic matters (OM) of various genesis, residues of vegetation and soil cover leads to a change in the qualitative composition of dissolved substances. Undoubtedly, because of landslides, there is a change in the quality of natural waters, which can be confirmed by various indicators.

OMs influence the behavior of some elements in surface waters, determining their transition either to the dissolved state or to the composition of suspended matters. Metals in suspensions bind to surface functional groups, hydroxides, carbonate, sulfide minerals or OM and can be included in biogeochemical processes [12]. The behavior of many metals in the aquatic environment is associated with the biogeochemical cycles of lithogenic elements, such as Fe, Al, and Ca, which are the part of minerals and rocks [13]. Heavy metals can take an active part in the processes of microbiological destruction of natural OM. Metals are involved in the processes of methanogenesis and anaerobic oxidation of methane (AOM) in rocks, mainly located in permafrost zones [14]. Considering that microorganisms can use Fe and Mn ions as electron acceptors in methane oxidation, we hypothesize that, when OMs released from the rock pore space during a landslide, heavy metal reduction/oxidation processes were initiated.

In the Far East of Russia, permafrost areas are associated with watersheds and slopes of northern exposure, including the valleys of the Amur and Bureya rivers basins. Catchment area of the Bureiskoe Reservoir locates in territory with very difficult permafrost-hydrogeological conditions. The migration of metals in coal-bearing and permafrost rocks is affected by the presence of methane. The main volume (85–95%) of hydrocarbon gas resources is associated with deposits of methane in coal seams [15].

Landslide on the Bureiskoe Reservoir occurred on December 11, 2018 at 14:48 local time at an air temperature of 36.2°C below zero. The depth of soil freezing was 0.8 m. According to hydrological and geodetic measurements, the volume of the landslide amounted to 24.5 million m³. The volume of the surface part of the landslide exceeds 4.5 million m³, most of it is under water. The depth of the Bureiskoye Reservoir at the landslide is more than 70 m. The uniqueness of this landslide is that phenomena are usually similar in the Russian Far East occur in the summer, not in the winter. Landslide blocked the former channel of the Bureya River from coast to coast; water access to the Bureiskaya hydroelectric power station was limited. After the landslide, a river tsunami occurred; the wave destroyed a forest on both banks on area of 300 ha [16].

The reasons for the landslide on the Bureiskoe reservoir have not been fully determined, since incident took place in the winter on the back of a calm seismic situation. There are various hypotheses: filling of reservoirs and the influence of groundwater reducing the stability of rocks [16], retreat of regional permafrost and alternation of seasonal processes of thawing/freezing of rocks at the base of steep slope of the reservoir [17].

This work provides information on the change in the qualitative composition of volatile organic compounds (VOCs), discusses their genesis and possible effects on the content of elements in water after a landslide on the Bureiskoe Reservoir in December 2018 and large-scale blasting operations with use of trinitrotoluene and hexogen for creating an artificial channel.

2. Materials and Methods
Filling of the Bureiskoye Reservoir was started in 2003. The width of the flooded channel of the Bureya River is 500–550 m at a depth of 60–80 m. The transverse profile of the valley is asymmetric— the left bank is about 400 m high, steep with a slope of 30°–35°. The riverbed, before flooding, was pressed to the left bank and cut the base of the slope, constantly increasing steepness and reducing its stability. The right slope of the valley is a gently sloping terraced surface of erosive origin with a width of more than one kilometer and a height of up to 50 m above the current water
level. Fluctuations in water levels in the reservoir between the maximum marks in early autumn and the minimum in spring are 20 m. Bedrocks, composing the steep left slope of the Bureya River valley, are presented by Proterozoic igneous rocks. In the fault zones, an increased fracturing of rocks is recorded, which significantly weakened the stability of the slope, having prepared the displacement of huge masses of rocks. Detailed geomorphological description of the landslide location is presented in the work [18].

Researches in the Bureiskoye Reservoir area carried out during short-term flights of helicopters of the Ministry of Emergency Situations of Russia due to the inaccessibility of the region where the landslide occurred. Water samples were taken above and below the landslide body near the left and right banks. After blasting, water samples were taken from the formed channel near the gently sloping left bank (figure 1).

Figure 1. Location of the study area: A—position of the Bureya landslide; B—general view of a landslide from a helicopter (photo by A.N. Makhinov); C—landslide boundaries and points of water sampling: 1—landslide disruption wall, 2—landslide body, 3—channel from the upper part of the reservoir to the lower after blasting, 4—points of water sampling.

The content of elements in natural waters was determined by inductively coupled plasma mass spectrometry, ICP-MS ELAN-9000, Perkin Elmer (USA). The content of volatile organic compounds in water samples was determined by gas chromatography with use of HP-FFAP column (50 m; 0.320 mm; 0.50 micron) at a temperature range of 45–200°C.

3. Results and Discussion
During landsliding, a gigantic volume of fragmentary material of various particle size of disintegrated wood, rock, and soil entered the Bureiskoe Reservoir. It significantly affected the OMs composition and contributed to an increase in the migration activity of many elements.

3.1. Changes in Composition of Volatile Organic Compounds
Qualitative and quantitative composition of VOCs in the water of the Bureiskoye Reservoir before blasting began significantly differed above and below the landslide body (Table 1). This may be due to the slow water drainage through the landslide body and the entering of OM from the soils and pore spaces of rocks, composing it. The dominant component in all water samples was methanol. Its maximum content was found in water sample taken from the right bank below the landslide body, where tsunami was recorded. In water sample above the landslide body at the right bank, the maximum content of acetone was 14 times higher than at the left bank. The main group of components in the water on the left bank, below the landslide body, included \( m \)-xylene (dimethylbenzene).

### Table 1. Composition of volatile organic compounds in the water samples of the Bureiskoe Reservoir in the landslide area: Lb—Left bank; Rb—Right bank; nd—not determined.

| Compound, \( \mu g/L \) | Above the landslide | Below the landslide | After blasting (water from the artificial channel) |
|------------------------|---------------------|---------------------|---------------------------------------------|
|                        | Lb | Rb | Lb | Rb | 14/02/2019 | 03/02/2019 | 17/04/2019 |
| Hexane                 | nd | nd | nd | 7.7 | 58.8 | 5.4 | 7.2 |
| Acetic aldehyde        | 8.9 | 9.3 | nd | nd | 21.1 | 6.6 | nd |
| Acetone                | 9.6 | 140.6 | 30.2 | 40.2 | 33.2 | 5.2 | 24.3 |
| Methanol               | 47.8 | 71.6 | 92.4 | 232.9 | 220.5 | 37.1 | nd |
| Benzene                | 0.9 | nd | 1.2 | 1.1 | nd | nd | nd |
| Toluene                | 1.4 | 0.8 | 1.3 | 0.9 | 428.2 | 1.8 | 1.4 |
| Butyl acetate          | nd | nd | 8.3 | 1.4 | nd | nd | nd |
| \( m \)-xylene         | nd | 13.8 | 95.2 | 1.1 | 0.9 | nd | 1.5 |
| \( o \)-xylene          | nd | 1.3 | 2.5 | 1.0 | nd | 1.1 | 1.8 |
| Isopropylbenzene       | nd | 1.3 | 46.2 | 0.5 | 0.5 | 192.0 | nd |

Water samples taken at different times from the channel, formed after blasting, differed in the composition of VOCs. Samples with a fine suspension from the rocks received on February 14, 2019, after the explosions were especially important. It contained 15 components of VOCs, including the maximum content of hexane (1300 \( \mu g/L \)) and \( m \)-xylene (48.3 \( \mu g/L \)). As shown in the table 1 at this time seven components were found in nature waters, the maximum content was recorded for methanol and toluene. Two weeks later (March 1, 2019), the qualitative composition of water has changed significantly. A decrease in the concentration of many components was recorded, the exception was isopropylbenzene; its content was the highest in comparison with other VOCs. Later, in April, this component was absent.

After blasting, the change in water quality of the Bureiskoe Reservoir could be affected by the influx of OM with various structures and genesis. It can be contained in the pore space of disintegrated rocks and soils, or as a part of the detonation products of trinitrotoluene and hexogen. This is confirmed by the results of the determination of VOCs in water extracts of various substrates from the blasting zone. In a 5-day aqueous extract from charred wood, methanol and acetone dominated. Six components without signs of burning were found in an extract from bedrock after blasting, including hexane, acetone, benzene impurities and its methylated isomers; methanol was absent. The maximum number of components (9) was found in the water extract from bedrocks scorched by a blast. Hexane and methanol dominated in this sample. Additionally, butanol and butyl acetate were also present. Hexane and methanol dominated in the soil extract from the helipad, where fuel and explosives were unloaded, but their concentrations were 2 times lower than in the extraction of rocks with combustion products [19].

In addition, the presence of several VOCs in water can be associated with the processes of degradation of plant residues, including lignin. It was found that because of the conversion (depolymerization) of lignin not only various phenolic compounds can be formed, as well as their methylated derivatives of \( p \)- and \( m \)-xylene [20] and some alcohols, including methanol and butanol [21]. Many of the VOCs identified by us are formed from various high and low molecular weight precursors, including methane by microbiological processes. The VOC spectrum may depend on the
dynamics of methanogenesis/methanotrophy. These processes can occur in wetlands, in the pore space of rocks, and at the bottom of reservoirs. Various volatile compounds are formed as a result of biogeochemical processes of the methane cycle. Therefore, many VOCs could be of natural origin. However, landslide (natural factor) and blasting (anthropogenic factor) acted as triggers, which were accompanied by the inflow of disintegrated rocks, soils, and fragmented wood in the reservoir.

3.2. Content of Elements in Water
Landslide, acting as a biogeochemical barrier, introduced significant changes in the content of many chemical elements. Wood residues after the tsunami, surface runoff with a high OM content of various genesis, erosion of the landslide body, and the entry of natural substances from the pore space of rocks led to intensification of the processes of mineral compounds transformation. Analysis of the content of elements in water samples, taken above and below the landslide body, showed their uneven distribution due to water infiltration through the landslide body (table 2). Below the landslide body the content of such elements as Al, Fe, and Pb increased; the other group consisted of metals which concentration was clearly reduced: Mg, Ca, Zn, and Cd.

Table 2. Content of elements in water of the Bureiskoe Reservoir near the landslide area (January 2019); a—above the landslide; b—below the landslide; Lb—Left bank; Rb—Right bank.

| Location | Fe | Mn | Al | Ca | Mg | Ni | Cu | Zn | Cd | Pb |
|----------|----|----|----|----|----|----|----|----|----|----|
| Lb a     | 207.85 | 11.54 | 164.00 | 4102.51 | 1467.98 | 1.12 | 5.60 | 22.38 | 0.11 | 0.25 |
| Rb a     | 274.20 | 7.73 | 165.75 | 4160.18 | 1457.78 | 0.72 | 3.97 | 14.19 | 0.19 | 0.03 |
| Lb b     | 338.41 | 9.50 | 185.27 | 3907.78 | 1375.48 | 2.90 | 5.11 | 11.27 | 0.03 | 1.38 |
| Rb b     | 344.11 | 9.89 | 181.82 | 3874.44 | 1350.74 | 0.75 | 5.67 | 16.99 | 0.03 | 1.32 |

The most significant increase in concentrations on both banks after passing through a landslide body was recorded for Al and Fe. An increase in the concentration of Ni was recorded near the right bank, after the tsunami and destruction of the vegetation cover, while on the left bank its concentration did not actually change. The content of Cu when passing through the body of a landslide decreased at both coasts. A slight decrease in concentrations was characteristic of lithogenic elements Mg and Ca. Researchers of the Three Gorges Reservoir show that when passing from a hollow slope to a steep one, weathering increases, this affects the content of Al and Fe oxides [22]. We found that above and below the body of the landslide, there were no differences in the Al content, despite the different steepness of the coasts. The Fe content above the landslide body was slightly higher near the hollow right bank. Below the landslide body, these differences in Fe content at different coasts were virtually absent. The increase in the content of individual metals in the water after the landslide may be due to the entering of soil humus (humic and fulvic acids). The portion of organic forms for cations Cu$^{2+}$, Hg$^{2+}$, Fe$^{3+}$, Al$^{3+}$ in their total content can reach 95% [23].

Important changes in the content of many elements in water occurred after blasting. Against the background of high flow rates, an increase in the content of Ni and Hg was recorded in the artificial channel (figure 2). Particular phenomenon was associated with a sharp drop in the concentrations (within the determination method <0.001 μg/L) of metals such as Fe, V, Cu, and Pb. Gradually, the content of these elements increased, but did not reach the previous concentrations. Within two months, there was a decrease in the concentrations of other elements compared to their content in the water taken around the landslide body, including Mg, Al, and Ca. The effect of reducing concentrations of many elements can be associated with their sorption on the surface of fine particles, crushed by rock explosions, or the formation of organo-mineral colloids.

Blasting has affected a sharp increase in the content of priority toxic metals Pb, Cd, and Hg. Moreover, the concentrations of Pb and Hg in the channel exceeded the values established before the explosions (Pb more than 7 times, Hg 80 times). It is known that Hg enters aquatic ecosystems during the destruction of bedrock, leaching from loose sediments and soils, during the decomposition of vegetation, and during precipitation [24]. The risk of mercury pollution depends on many factors,
including the form of this metal in the environment. The most toxic form of Hg, methylmercury \((\text{CH}_3\text{Hg}^+)\), is formed in the presence of methyl radicals in the environment. In our case, the presence of methyl-containing VOCs (methanol, toluene, and xylenes) could affect the mobility of mercury. An additional source for methylation could be the products of transformation of trinitrotoluene and methane.

![Figure 2. Dynamics of the content (Lg C) of lithogenic elements and heavy metals in water in the landslide area before (January 2019) and after blasting (February, March, and April 2019).](image)

**4. Conclusions**

Studies have shown that a landslide resulted in a change in the quantitative volatile organic compounds and elements composition in water of the Bureiskoe Reservoir. The main factors were the entering surface waters of additional sources of OM and chemical elements from rocks, plant debris, and soil. Their interaction with water influenced the increase in the content of organo-mineral complexes, which had a significant effect on the solubility and migration ability of toxic heavy metals.

Analysis of the obtained data shows that the leading factor affecting the water composition was rock disintegration, release of OMs with various structures from the pore space, and the formation of organo-mineral complexes, including with some metals. A group of methylated benzene derivatives may be present among the products of the transformation of humic substances after degradation of plant residues and can enter the water due to drainage of groundwater through the soil and through the body of the landslide. As a result of biogeochemical processes, methyl-containing compounds were a risk factor for the formation of toxic methylmercury in the aquatic environment and a negative effect on aquatic organisms.

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