

# Assessment of the relationships between elements and organic matter in water after a large landslide in the Bureyskoye reservoir (Russia)

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**Abstract.** The article provides information on statistical approaches to identify the dominant factors that influenced the water quality in the Bureyskoye reservoir after a large landslide in December 2018 blocked access to a hydroelectric power plant. To restore the hydrological regime, blasting operations were carried out using trinitrotoluene and hexogen. The main indicators of water quality were volatile organic matters and elemental composition that varied along different banks above and below the landslide body and under the influence of explosives. In water samples from the artificial canal after the restoration of the reservoir flow, the content of Fe, Mn, Al, Cu and Zn remained at a low level and did not reach the initial values established prior to the blasting operations. However, an increase in the content of Pb by 7 times and Hg by 80 times was noted. The presence of methanol and methylated benzene derivatives in water could stimulate the formation of more toxic methylmercury, posing a risk to aquatic organisms. Correlation analysis was used to process the obtained data which made it possible to differentiate the contributions of natural (landslide, river tsunami) and anthropogenic factors (blasting) to the change in the chemical composition of water in the reservoir.

**Keywords:** water quality, landslide, blasting, the Bureyskoye Reservoir, organic matters and elements

## 1 Introduction

Climate change in regions with a wide range of temperature fluctuations has made relevant the study of the behaviour of frozen soils which relate to various objects, including the construction of highways and the operation of reservoirs [1]. Analysis of the consequences of landslides in permafrost zones is of fundamental importance from the standpoint of carbon

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balance management, decision making in land management and prevention of threats to infrastructure in many regions [2].

Landslides are usually devastating and fatal wherever they occur in the world [3]. Understanding the mechanisms of destruction of mountain slopes is extremely important for solving socio-economic, geotechnical and environmental problems [4]. Rapid displacement of rocks is predicted when the water level in reservoirs changes by 105–130 m due to abundant precipitation [5]. For example, an examination of a 2014 landslide of rocks in Chongqing, China showed that the process of physical weathering was an important cause of the destruction of the slope 16.5 years after the construction work. Water, as a key factor accelerating the weathering process, weakened the mechanical properties of rocks [6].

Earthquakes are one of the important triggers of landslides [7]. After the earthquake that occurred on 8 August 2017 in Sichuan in south-western China, 83 landslides were detected with the use of remote sensing and field studies. These landslides significantly increased the volume of sediment and debris in watercourses [8]. Two years later, on 14 August 2019, a giant landslide occurred in the same province of China with the movement of 48 thousand m<sup>3</sup> of soil and stones which blocked an important section of the railway. Studies have shown [9] that the landslide was caused by several factors that led to a combined effect (steep slopes, continuous downpours, floods that erode mountain foundations and human activities).

As a result of a landslide, a huge amount of crushed particles of rocks, minerals, organic matters (OM) of various genesis, remnants of vegetation and soil cover enter the surface waters, leading to a change in the qualitative composition of water. The behaviour of a number of elements in surface waters is influenced by organic matters that determine their migration ability. The toxicity of heavy metals is associated with the processes of their dissolution and precipitation which are determined by the redox conditions of the aquatic environment. The metals in the suspended matter bind with functional groups, hydroxides, carbonate, sulfide minerals or organic ligands, changing the dynamics of biogeochemical processes [10]. In permafrost zones, metals participate in the processes of methanogenesis and anaerobic oxidation of methane which are accompanied by the formation of a wide range of organic matters in the pore space of rocks [11].

In the Russian Far East, permafrost areas are associated with the watersheds and slopes of the northern exposure, including the valleys of the Amur and Bureya river basins. The catchment area of the Bureyskoye reservoir is located in a territory with very difficult permafrost-hydrogeological conditions, most of which are confined to the area of development of insular, discontinuous and continuous permafrost in which the thickness of frozen rocks is tens to hundreds of metres. The migration of metals in coal-bearing and permafrost rocks is influenced by the presence of methane and its conversion products. In the Bureya coal basin, an assessment of coalbed methane resources was carried out at the Urgalskoye field. The main volume (85–95%) of hydrocarbon gas resources is associated with the deposits of methane sorbed in coal seams [12].

This paper presents data on the assessment of possible relationships between the content of volatile organic substances and individual elements in water under the influence of natural (landslide) and anthropogenic factors (blasting operations) using correlation data analysis. This allows us to identify the consequences of the use of explosives (trinitrotoluene and hexogen) to restore the hydrological regime in the Bureyskoye reservoir after a major landslide in December 2018.

## **2 Experimental Research Methodology**

## 2.1 Landslide location

The filling of the Bureyskoye reservoir began 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°. Before flooding, the river bed was pressed against the left bank and cut the base of the slope, constantly increasing the steepness and reducing its stability.

The right slope of the valley is a slightly sloping terraced surface of erosion origin more than one kilometre wide and up to 50 m above the current water level. The mouths of the tributaries are flooded and form narrow and deep bays 1.5–3.0 km long. Fluctuations in water levels in the reservoir between the maximum marks in early autumn and minimum in spring are 20 m.

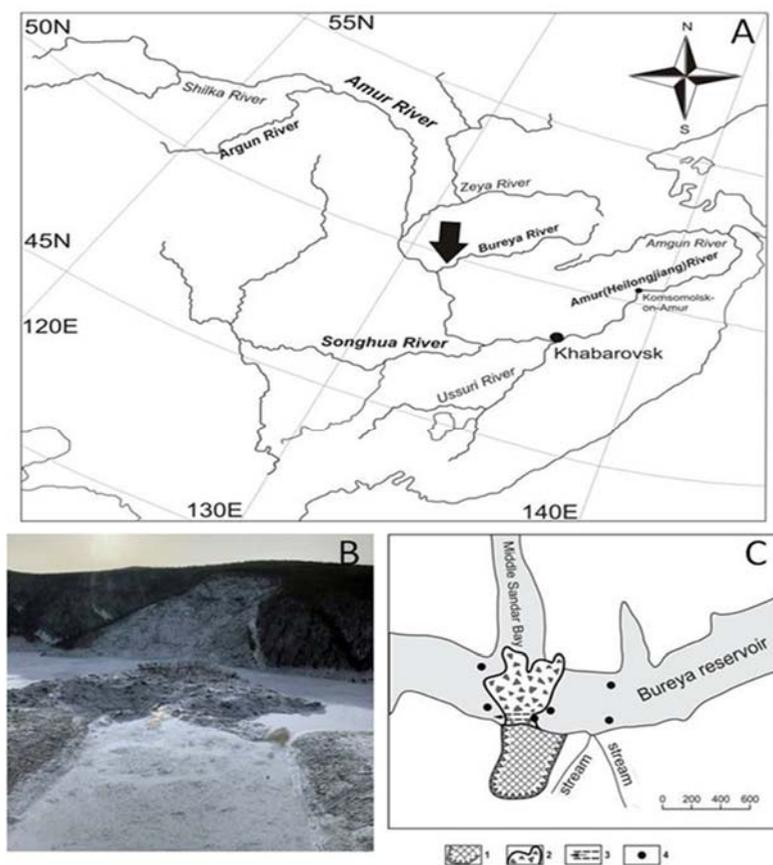
Bedrocks composing the steep left slope of the valley Bureya river are represented by Proterozoic igneous rocks. In the fault zones, an increased fracturing of rocks was noted which significantly weakened the stability of the slope, preparing the displacement of huge masses of rocks [13].

## 2.2 Landslide characteristics

A landslide on the Bureyskoye reservoir occurred on 11 December 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 [14]. According to hydrological and geodetic measurements, the volume of the landslide was 24.5 million m<sup>3</sup>. The volume of the surface part of the landslide exceeded 4.5 million m<sup>3</sup>, the main part of which was under water. The depth of the Bureyskoye reservoir at the site of the landslide was more than 70 m.

Landslide parameters: length of 800 m from edge to edge; height above the reservoir edge from 7.5 to 46 m. The uniqueness of this landslide lies in the fact that similar phenomena in the Russian Far East usually occur in the summer and not in the winter. The landslide blocked the former channel of the Bureya River from coast to coast, thus limiting access to water by the Bureya hydroelectric power station. After the landslide, a river tsunami occurred and its wave destroyed the forest on both banks in an area of 300 hectares [13].

Due to the inaccessibility of the area where the landslide occurred on the Bureyskoye reservoir, research on its water area was carried out by the Ministry of Emergency Situations of Russia during short-term helicopter flights. Water samples were taken above and below the landslide body near the left and right banks. After the blasting operations, water samples were taken from the formed channel from the flat left bank (Fig. 1).



**Fig. 1.** Location of the study area: A— map showing the position of the Bureya landslide; B— general view of a landslide from a helicopter (photo by A. N. Makhinov); C— landslide boundaries and places 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.

### 2.3 Chemicals research

The elemental composition of natural waters was determined by inductively coupled plasma mass spectrometry on an ICP-MS ELAN-9000 from Perkin Elmer (USA). Determination of the content of volatile organic compounds (VOC) in water samples was carried out by gas chromatography using an HP-FFAP column (50 m; 0.320 mm; 0.50 microns) at a temperature range of 45–200 °C.

### 2.4 Statistical analysis

To identify reliable relationships between metals and VOC, the method of correlation analysis was used, taking into account that the correlation coefficients are relatively simple to calculate and easy to interpret. The method of correlation analysis presupposes not only the calculation of correlation coefficients but also a mandatory check of their significance which is based on the principle of testing statistical hypotheses and construction of interval estimates of the correlation coefficients [15, 16]. Due to the small number of observations ( $n = 9$ ), the use of other methods of statistical analysis would have been difficult.

To calculate the correlation coefficient, the following formula was used:

$$r = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}}$$

### 3 Results and discussion

During the descent of the landslide, a huge volume of clastic material of various granulometric composition, crushed wood and soil entered the Bureyskoye reservoir and significantly influenced the VOC composition and contributed to an increase in the migration activity of many chemical elements.

#### 3.1 Change in Composition of Volatile Organic Compounds

The qualitative and quantitative composition of VOCs in the water of the Bureyskoye reservoir before the start of blasting operations significantly differed on different banks above and below the landslide body (Table 1). This may be due to the slow drainage of water through the landslide body and the influx of OM from the soils and pore space of rocks. Methanol was the dominant component in all water samples. Its maximum content was found in water sampled from the right bank below the landslide body where crushed wood came under the influence of the tsunami. Above the landslide body near the right bank, the maximum content of acetone was found in the water, 14 times higher than that near the left bank. The main group of components in the water near the left bank, below the landslide body, included *m*-xylene (dimethylbenzene).

**Table 1.** Composition of volatile organic compound in the water of the Bureiskoe reservoir in the landslide area:

Compound, µg/L	Lb—Left bank; Rb—Right bank; nd—not determined		After blasting (water from the artificial channel)				
	Above the landslide Lb	Above the landslide Rb	Below the landslide Lb	Below the landslide Rb	14.02.2019	1.03.2019	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
<i>m</i> - xylene	nd	13.8	95.2	1.1	0.9	nd	1.5
<i>o</i> - xylene	nd	nd	2.5	1.0	nd	1.1	1.8
propyl benzene	nd	1.3	46.2	0.5	0.5	192.0	nd

Water samples taken at different times from the canal that formed after blasting operations differed in the composition of the VOC. On 14 February 2019, seven components were found in clear waters, with a high content of methanol and toluene. Two weeks later (1 March 2019), the qualitative composition of the water had changed significantly. A decrease in the

concentration of many components was found; the exception was isopropyl benzene with a content that was the highest in comparison with other VOCs. In April, this component was absent.

The change in water quality in the Bureyskoye reservoir after blasting operations could have been largely influenced by the influx of OM of various structures and genesis which were contained in the pore space of crushed rocks and were introduced together with soils or were detonation products of TNT and RDX. It was shown experimentally that six components were found in the extraction of rocks after blasting without signs of burning, including hexane, acetone and benzene impurities along with its methylated isomers, while methanol was absent. The maximum number of components (nine) was found in the water extract of rocks with combustion products. This sample was dominated by hexane and methanol and additionally contained butanol and butyl acetate [17].

The presence of a number of VOCs in water can be associated with the degradation of plant residues. For example, because of the conversion (depolymerization) of lignin, not only can various phenolic compounds be formed but also their methylated derivatives *p*- and *m*-xylenes and some alcohols, including methanol and butanol [18].

Many VOCs are formed as a result of the functioning of the methane cycle (methanogenesis and methanotrophy). These processes can occur in swampy areas, in the pore space of rocks and at the bottom of reservoirs. Based on the foregoing, many VOCs were of natural origin. However, the provoking triggers were landslide (natural factor) and blasting (anthropogenic factor), which were accompanied by the inflow of crushed rocks, soils and crushed wood into the reservoir.

### 3.2 Elemental composition change

Analysis of the content of chemical 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 elements whose concentration was clearly decreasing: Mg, Ca, Zn and Cd.

In the example of the Three Gorges Reservoir, it was shown that during the transition from a gentle slope to a steep one, the weathering increased, which was reflected in the content of Al and Fe oxides [19]. We found that above and below the body of the Bureya's landslide, there were no differences in the Al content, despite the different steepness of the banks. The Fe content above the landslide body was slightly higher near the gently sloping right bank. Below the landslide body, these differences in the Fe content were virtually absent at different shores.

The Cu content during its passage through the landslide body decreased at both banks. A slight decrease in concentrations was characteristic of the lithogenic elements Mg and Ca. Most likely, fine particles that formed in the process of the destruction of rocks, soil and vegetation cover were the main sources of chemical elements.

**Table 2.** The elemental content ( $\mu\text{g/L}$ ) in water from the Bureyskoye 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
	b	344.11	9.89	181.82	3874.44	1350.74	0.75	5.67	16.99	0.03	1.32
Rb	a	274.20	7.73	165.75	4160.18	1457.78	0.72	3.97	14.19	0.19	0.03
	b	338.41	9.50	185.27	3907.78	1375.48	2.90	5.11	11.27	0.03	1.38

The increase in the content of certain metals in the water after the descent of a landslide may be due to the input of soil humus (humic and fulvic acids). The hydroxyl (-OH), methoxyl (-O-CH<sub>3</sub>) and carbonyl (-CO) groups included in these compounds are involved in the formation of organoelement compounds. The proportion of organic forms for the cations Cu<sup>+2</sup>, Hg<sup>+2</sup>, Fe<sup>+3</sup> and Al<sup>+3</sup> in their total content can reach 95% [20].

It is known that after blasting operations, organic intermediates and low molecular weight carbon-, nitrogen-, and sulfur-containing components (CO<sub>2</sub>, CO, O<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, soot; N<sub>2</sub>, NH<sub>3</sub>, C<sub>2</sub>N<sub>2</sub>, HCN, NO, N<sub>2</sub>O; SO<sub>2</sub>, H<sub>2</sub>S), carbonates and bicarbonates, cyanides, sulfates, sulfides, chlorides and metal oxides enter the environment. The most significant changes in the content of many elements in the water occurred after blasting operations. An increase in the content of Ni and Hg was recorded in the artificial channel against the background of high flow rates (Table 3).

**Table 3.** The elemental content in water from artificial channel after blasting (µg/L): nd<0.001 µg/L.

Date	Fe	Mn	Al	Ca	Mg	Ni	Cu	Cd	Hg	Pb
14.02.2019	<0.001	8.74	97.35	2829.43	1027.13	5.24	nd	0.16	0.08	nd
01.03.2019	248.44	4.79	177.35	2635.56	1076.31	0.38	nd	0.02	0.01	0.15
17.04.2019	218.97	9.21	121.52	2130.88	918.90	0.13	0.71	nd	nd	0.17
Max before blasting	344.11	11.54	185.27	4160.18	1467.98	2.9	5.67	0.19	nd	1.38

A special phenomenon was associated with a sharp drop in the concentrations (within the determination method <0.001 µg/L) of elements such as Fe, Cu, Zn and Pb. Gradually, the content of these elements increased, but they did not reach the previous concentrations. Within two months, there was a decrease in the concentrations of other elements compared to their content in water sampled around the landslide body, including Mg, Al and Ca. The effect of reducing the concentration of many elements can be associated with their sorption on the surface of fine particles crushed by explosions of rocks or the formation of organomineral colloids.

Blasting operations influenced a sharp increase in the content of the priority toxic elements Pb, Cd and Hg. Moreover, the concentrations of lead and mercury in the channel exceeded the values established before the explosions (Pb more than 7 times, Hg 80 times).

It is known that mercury enters aquatic ecosystems during the destruction of bedrocks, leaching from loose sediments and soils, during decomposition of vegetation and also during precipitation. The risk of mercury contamination depends on many factors, including how this metal is found in the environment. The most toxic form of mercury, methylmercury (CH<sub>3</sub>Hg<sup>+</sup>), is formed in the presence of methyl radicals in the environment [21]. 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 transformation products of trinitrotoluene and methane.

### 3.3 Statistical research

Correlation analysis data make it possible to reveal the relationship between individual elements and the composition of VOCs before and after blasting operations, including the role of the anthropogenic factor (use of explosives). The strongest dependencies  $0.75 \leq r \leq 0.99$  are presented in Table 4.

**Table 4.** Correlation dependence of elements of VOC ( $0.75 \leq r \leq 0.99$ ,  $p = 0.01$ ) before (January 2019) and after blasting operations (February, March, April 2019).

	Fe	Al	Cu	Mg	Ni	Pb	Hg	Cd
Before the explosion	Acetone, Toluene	Hexane, Acetone, Methanol, Benzene, Toluene	Benzene, Toluene, m- xylene, o-xylene, Butyl acetate	Acetone, Toluene	Hexane, m- xylene, propylbenzene	Hexane	-	-
After the explosion	Hexane, Acetone	Hexane, Acetone	Toluene, m-xylene, o-xylene, propylbenzene	m- xylene, o-xylene, propylbenzene	Methanol, Toluene, o-xylene		Methanol, Toluene, m- xylene, o-xylene	

According to the correlation analysis, a significant change in the dependence on the VOC present was observed for each of the elements before and after blasting. A group of toxic elements Pb, Hg and Cd was distinguished, for which reliable connections with CH<sub>3</sub>-containing compounds were proved after blasting operations. There is reason to believe that the detonation products of trinitrotoluene influenced the behaviour of many elements.

## 4 Conclusions

The studies have shown that as a result of the landslide, the quantitative elemental composition of water in the Bureyskoye reservoir changed. The main factors were the influx of additional sources of OM and chemical elements from rocks, plant residues and soils into the surface waters. Their interaction with water influenced the increase in the content of organomineral complexes, which have a significant effect on the solubility and migration ability of toxic heavy metals.

Attention is drawn to the sharp decrease in the content of Fe and Al after blasting and their partial recovery in March. The Mn content decreased after passing through the landslide body and after blasting, when a large amount of suspended material was present in the channel. In water samples taken in April 2019 from the flow channel, the content of many elements was not restored to the concentrations established after the landslide.

This paper presents data on the assessment of possible relationships between the content of volatile organic substances and individual elements under the influence of natural and anthropogenic factors by means of correlation data analysis. This approach makes it possible to reveal the consequences of the use of explosives (trinitrotoluene and hexogen) during the restoration of the hydrological regime in the Bureyskoye reservoir after a large landslide in December 2018.

As a result of the performed correlation analysis, estimates of the strength of the relationship between random variables (elements and VOC) were obtained, which allow us to conclude that blasting has a significant effect on the content of toxic elements (Pb, Hg and Cd). The leading factor influencing the composition of water was the disintegration of rocks and the release of OM of various structures from the pore space and the formation of organomineral complexes, including those with some metals. A group of methylated benzene derivatives may be present among the transformation products of humic substances formed during the decomposition of plant residues and then enter the water as a result of groundwater drainage through the soil and through the landslide body. The origin of volatile organic compounds in reservoir water samples and water extracts may be associated with the biogeochemical cycle of methane (methanogenesis-methanotrophy), the mechanisms of which are determined by many abiotic and biotic factors. As a result of biogeochemical processes, methane is transformed into methanol. Regardless of their genesis, methyl-

containing compounds were a risk factor for the formation of toxic methylmercury in the aquatic environment and for a negative effect on aquatic organisms.

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