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CHEMICAL COMPOSITION OF THE ATMOSPHERIC INPUT IN THE RESERVE BASTAK IN WINTER

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Abstract

The paper presents the study on main biogenic elements (Fe, Cd, Mn, Ni, Pb, Cu, Zn, Co, Hg), heavy metals and As contained in precipitation (snow) in Bastak natural reserve (winter 2019-2020). Snow samples were selected at 6 stations of the natural reserve having various environmental conditions. The following methods were used: direct potentiometry at pH measurement; titrimetry to determine chlorines content, total hardness and hydrogen carbonates; photometry to determine the content of nitrates, sulfates, nitrites, ammonium ions and phosphates; atomic absorption spectrometry to obtain heavy metal content. The study of snow melt samples discovered hydrogen carbonate ions traces. It confirmed that the natural reserve territory does not have any additional sources of carbon dioxide, in particular, of the human origin. Virtually no samples contained chlorides or phosphates. Sulphate trace amounts were found only in two samples and below detection limit in other snow samples. The winter of 2019-2020 is characterized by nitrogen compounds found in snow melt of fresh precipitation. The detection of Mn, Cd, Ni, Pb, Co, As and Hg content showed that their trace amounts were below detection limit. Iron content in almost all the samples taken in December 2019 was twice and more times lower than in November samples. The zinc content increased twice and more compared with November samples. The chemical test of the snow pack in Bastak natural reserve in the winter season of 2019-2020 showed that the atmosphere above the designated conservation area is not contaminated by pollutants of natural and human origin.

Keywords: Heavy metals, biogenic elements, snow pack, natural reserve

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1. Introduction

Air flows easily transfer pollutants leaking into the urban atmosphere to long distances. Not only large industrial centres but also neighbouring areas are affected by air pollution caused by industrial enterprises and road vehicles (Ershov et al., 2019; Kholodov & Golokhvast, 2020). Therefore, the territory of natural reserves, while having no significant anthropogenic load, may be affected by the chemical pollution due to the atmospheric transport.

Bastak state natural reserve is located on the territory of the Jewish Autonomous Region (JAR). It performs many tasks including environmental monitoring required to assess and forecast the environment condition and its individual components. Atmosphere air monitoring is included into the system of environmental monitoring. The study of the snow pack is made to obtain the data on the atmosphere air pollution in winter.

2. Problem Statement

Atmospheric suspended materials of modern cities, unlike designated conservation areas, contain the great amount of manmade particles. However, due to the growth of the human impact on the Earth atmosphere as a whole, the amount of pollutants grows not only in the urban air but also in the air of natural reserves.

Atmosphere monitoring on the territory of the natural reserves allows not only controlling the level of pollutants in the air basin but also assessing how much the anthropogenic load of the modern city may affect the designated conservation area located in a relative vicinity.

Thus, the study develops the line of the papers dedicated to the research of quantitative and qualitative analysis of atmospheric suspended materials in Bastak natural reserve started in 2011 (Golokhvast et al., 2013; Golokhvast et al., 2016; Kholodov & Golokhvast, 2020).

3. Research Questions

Aerosol compounds leaking into the atmosphere are removed by natural self-purification processes. The main methods used to remove chemical elements from the atmosphere are precipitation scavenging and terrain deposition.

Snow may be used as the integrating indicator of the atmospheric pollution in winter for territories characterized by the presence of stable snow pack (Koroleva et al., 2017; Novorotskaya, 2018; Zhurba et al., 2020). It has a high sorption capacity and absorption of aerosols, dust and soot particles and other atmosphere air components. The snow pack is studied to get the data of pollutants leaked from the atmosphere on the terrain.

The content of pollutants in snow reflect their concentration in the air and indicates the source and the method of aerosol formations near the sampling site. As snowflakes and snow crops fall slower and, while falling, cover the greater area compared with rain drops of the same weight, they are longer affected by pollutants, so they are better indicators of their presence in the atmosphere.

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4. Purpose of the Study

The purpose of the study is to determine the content of main biogenic elements, heavy metals (Fe, Cd, Mn, Ni, Pb, Cu, Zn, Co, Hg) and As in the atmosphere precipitation of Bastak natural reserve in winter 2019-2020.

5. Research Methods

Snow samples were analysed for all elements in the accredited testing laboratory centre FBHI Hygienic and Epidemiological Centre in JAR. Snow was collected on the territory of the natural reserve during snowfalls in winter of 2019-2020. The top layer (5-10 cm) of the new-fallen snow was collected to avoid secondary pollution by human aerosols. It was placed in sterile 3 litre containers. Melted snow samples, once filtered through the white ribbon ash-free filter, were analysed for chemical components.

The methods for the analysis of natural waters may be applied to study the chemical composition of snow melt (Dmitriev et al., 1989). The chemical analysis of snow melt was made using standard methods. The following methods were used during the study: direct potentiometry at pH measurement; titrimetry to define the content of chlorines, total hardness and hydrogen carbonates; photometry to define the content of nitrates, sulfates, nitrites, ammonium ions and phosphates. Potentiometric measurements were made using the pH-meter ANION 4100. Photometric measurements were made using the spectrophotometer PE-5400 VI. All the reagents, used for the analysis, had the qualification of at least CP. Melted snow samples were analysed for heavy metals on the atomic absorption spectrometer Quanta-2 AT.

In total, 12 samples of fresh snow were analysed that is 228 element determinations.

Snow samples were collected on 12.11.2019 and 18.12.2019 at 6 stations located on the territory of Bastak natural reserve and having different environmental conditions.

Snow was selected at the sites described in Table 1.

Table 1. Selection stations and their characteristics

Selection stations	Station characteristics
1	Near Chitinskaya route, a flat land, approximately 100 m from the route, the border of the natural reserve, the right bank of Ikur River. Vegetation: a sedge and reedgrass meadow.
2	Birobidzhan-Kukan route, approximately 15 km from Birobidzhan, a flat land, the left bank of Glinyanka River. Vegetation: a sedge and reedgrass meadow.
3	Birobidzhan-Kukan route, 30 km from Birobidzhan, middle reach of Bastak River, the left bank. Vegetation: a larch marsh.
4	Birobidzhan-Kukan route, 30 km from Birobidzhan, middle reach of Bastak River, the right bank, on the slope exposed to the south (a near-to-summit part). Vegetation: a cedar and oak forest.
5	Chernukha Mountain, the middle part, on the slope exposed to the south west. Vegetation: a cedar and broad-leaved forest, shrinkage of Khingam fir is confirmed (since 2007 ongoing).
6	Birobidzhan-Kukan route, 25 km from Birobidzhan, in Krasnye Sopki District. Vegetation: an oak grove with bush clover.

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The most environmentally stressed site selected is the 1st station near Chita-Khabarovsk route that is the area of the federal motorway with the most active automobile traffic. The 2nd, 3rd, 4th and 6th stations are also located not far from the road. However, Birobidzhan-Kukan route, crossing the territory of the natural reserve and dividing it almost into two equal parts, is quite rarely used, thus, these stations are less environmentally stressed. The 5th station is located 300 m eastwards of Birobidzhan-Kukan motor route, i.e., virtually isolated from its impact.

6. Findings

The results of the snow melt chemical analysis are shown in Table 2.

Table 2. Content of chemical components in snow of Bastak natural reserve, the winter season of 2019-2020

Sampling sites	Concentration, mg/m3							pH, pH Unit Cl-
	SO_4^2	Cl^-		SO_4^2	Cl^-	HCO_3^-	SO_4^2	
				12.11.2019				
1	2.0±0.4	<10	1	2.0±0.4	<10	1	2.0±0.4	<10
2	<2	<10	2	<2	<10	2	<2	<10
3	<2	<10	3	<2	<10	3	<2	<10
4	<2	<10	4	<2	<10	4	<2	<10
5	0.6±0.1	<10	5	0.6±0.1	<10	5	0.6±0.1	<10
6	<2	<10	6	<2	<10	6	<2	<10
				18.12.2019				
1	<2	<10	1	<2	<10	1	<2	<10
2	<2	<10	2	<2	<10	2	<2	<10
3	<2	<10	3	<2	<10	3	<2	<10
4	<2	<10	4	<2	<10	4	<2	<10
5	<2	<10	5	<2	<10	5	<2	<10
6	<2	<10	6	<2	<10	6	<2	<10

According to the obtained data, the pH values of snow melt (snow) measured in the winter were changed from 4.4 to 6.5. The hydrogen ion concentration in air precipitation is usually in the range of 4.6 and 6.1 (Maystrenko et al., 1996).

The concentration of hydrogen carbonates in snow melt for all sampling sites was 12.2 mg/dm3. The amount of these ions in the snow pack is defined by CO2 concentration in the atmosphere, thus, the traces of hydrogen carbonate ions show that the natural reserve has no additional sources of carbon dioxide, in particular, of the human origin.

Chlorine ions in non-polluted atmosphere precipitation have mostly the sea genesis. As the territory of the natural reserve is quite remote from the sea, no chlorides are found in all samples.

A sulphate ion is one of acidic deposition markers as it is the final product of sulphur dioxide transformation in the atmosphere. Sulfate trace amounts are found just in two samples, below detection limit - in other snow samples.

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Unlike the previous winter, when the chemical analysis of the atmospheric suspended matters in the natural reserve was made, the winter of 2019-2020 is characterised by nitrogen compounds found in the snow melt of fresh precipitation.

The content of nitrate ions in the snow pack of the natural reserve ranged between 1.9 mg/dm3 to 4.8 mg/dm3. Its maximum concentration was found in the sample from the 5th station located in the natural reserve at the heart of the forest and far from the motorway.

Nitrite ions were found in all snow samples selected in November 2019 and only in one sample at the 1st station during selection in December 2019. NO2- concentration ranged between 0.003 and 0.018 mg/dm3. The maximum contents of this ion as well as a nitrate ion was also determined in the sample from the 5th station.

Ammonium ion was found in all November samples in the amount ranging from 0.44 to 0.61 mg/dm3. Its maximum concentration (0.61 mg/dm3) was found at 5th and 6th stations. In December 2019 ammonium ion was determined only in two samples, with significantly lower concentrations than in November.

The content of phosphates in all snow samples was below detection limit.

The results of the total hardness determination in snow samples are shown in the Table 3.

Table 3. Total hardness in snow samples selected in Bastak natural reserve during the winter season of 2019-2020

Value	Selection 12.11.2019		
Total hardness, mg-eqv./l	No. of the station		
	1	1	1
	0.20±0.03	0.20±0.03	0.20±0.03
	Selection 18.12.2019		
	0.30±0.05	0.30±0.05	0.30±0.05

Clearly, the total hardness level in samples of the natural reserve was within the range of 0.2-0.3 mg-eqv./dm3. A total hardness of snow melt characterizes the content of calcium and magnesium salts, and, as we see, their concentrations are very low in snow melt of the natural reserve. The hardness of snow melt classifies it into soft waters.

The authors analyzed atmosphere precipitation for 10 elements: Fe, Cd, Mn, Ni, Pb, Cu, Zn, Co, Hg, As (Table 4). As the only traced amounts of Mn, Cd, Ni, Pb, Co, As and Hg were in the samples, as a rule, below detection limit, consider the results for only three metals: Fe, Cu and Zn.

Table 4. Content of heavy metals in snow samples in Bastak natural reserve, the winter season of 2019–2020, mg/dm^3

Date/sampling stations		Fe	Cu	Zn
12.11.2019	1	0.075±0.013	0.011±0.003	12.11.2019
	2	0.041±0.007	0.007±0.002	
	3	0.105±0.018	0.007±0.002	
	4	0.043±0.007	0.011±0.003	
	5	0.051±0.009	0.011±0.002	
	6	0.059±0.011	0.0016±0.0003	
18.12.2019	1	0,.026±0.004	0.031±0.005	18.12.2019

	2	0.017±0.003	0.012±0.002
	3	0.031±0.005	0.012±0.002
	4	0.029±0.005	0.009±0.003
	5	0.027±0.005	0.011±0.002
	6	0.017±0.009	0.011±0.002

The content of iron found in all snow samples from the territory of the natural reserve was ranged from 0.017 mg/dm3 to 0.105 mg/dm3. The maximum concentration of Fe was found in the sample from the 3rd station located at the central part of the natural reserve, not far from Birobidzhan-Kukan motor route. The content of iron in almost all samples selected in December 2019 was twice and more times lower than in the November samples. Perhaps, the first snow cleaned the atmosphere from suspended iron-containing dust particles.

The content of zinc found in all snow samples on the territory of the natural reserve ranged from 0.017 to 0.158 mg/dm3. Its maximum concentration was determined in December 2019 at the 1st station located close to the federal route and being the most environmentally stressed sampling site. The content of zinc in almost all samples selected in December 2019 increased twice and more compared with November samples.

The copper concentration in all snow samples varied from 0.0016 to 0.031 mg/dm3. The greatest amount of copper was found in the sample taken in December 2019 at the most environmentally stressed 1st station.

The Jewish Autonomous Region is the biochemical province characterized by the excessive amount of a number of elements in the environment, including iron and magnesium. It is also characterized by the iodine, fluorine, calcium, magnesium, copper and selenium deficiency (Bondareva, 2009). Therefore, the definition of iron and manganese in snow melt of the natural reserve is the expected situation reflecting the geochemical background of the territory. However, in winter of 2019-2020 Mn was not found in snow samples on the territory of the natural reserve, and the content of zinc in samples taken in December 2019 is 1.5 and more times higher than “excessive” iron levels in some samples. Zinc and copper aerosols in the atmospheric air are mostly submicron particles with the diameter of 0.5-1μm so they are easily transferred to long distances from the source of intake (Maystrenko et al., 1996). As the territory of the region has no expressed anthropogenic zinc sources, its presence in the atmosphere air of the natural reserve is probably explained by the regional transfer from other areas.

7. Conclusion

As a result of the snow melt sample study, low concentrations of hydrogen carbonate ions were found confirming the fact that the territory of the natural reserve has no additional sources of carbon dioxide intake, in particular, of the human origin. No chlorides and phosphates were found in all samples. Trace amounts of sulphates were found only in two samples, below detection limit - in other snow samples. The winter of 2019-2020 was characterised by the presence of nitrogen-containing compounds in snow melt of fresh precipitation.

The determination of Mn, Cd, Ni, Pb, Co, As and Hg content showed that their trace amounts in the samples were below detection limit as a rule. Iron, zinc and copper concentrations were determined. The content of iron in almost all the samples taken in December 2019 were twice and more times lower than in the November samples. The content of zinc, on the contrary, increased twice and more comparing to the November samples.

The chemical analysis of the snow pack in Bastak natural reserve during the winter season of 2019-2020 showed that the atmospheric air above the designated conservation territory is not contaminated by pollutants of natural and anthropogenic origin.

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