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Environmental Performances and Biological Toxicity of Snowpack Water

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Abstract*: This work analyzes the state of snowpack in Nizhny Novgorod on the basis of certain chemical performances and integral biological toxicity. Snow samples were obtained in February 2018 along major highways of Nizhny Novgorod. A snow-covered area in Dubrava forestry was selected as reference. The studies demonstrated that the snowpack was characterized by very high concentrations of chlorides and sulfides: in sampling points of the Lower City, the content of chlorides and sulfates varied in the ranges of 24.67–62.36 mg/l and 30.16–62.09 mg/l, respectively, and in sampling points of the Upper City, this variability was 416.82–988.45 mg/l and 280.11–879.22 mg/l, respectively. The content of lead in snowpack in both the Lower City and the Upper City was approximately the same (0.0053 and 0.0048 mg/l). The minimum content of pollutants in snow samples from reference site was characterized by toxicity (10%, V = 6.0%) which was estimated as allowable (toxicity class 1). Snowpack water from the Lower City was characterized generally by medium toxicity (class 2), and sampled in the Upper City – by acute toxicity (59%, V = 26.5%), with regard to the reference (class 3).

***Keywords*: biological toxicity of snow, criteria of environmental state, snowpack.**

I. INTRODUCTION

Nizhny Novgorod is a megalopolis of Russia with developed industrial infrastructure and high air pollution resulted from automobile emissions. Thus, atmosphere pollution with ecotoxicants in the urban area is a very urgent environmental issue [1-5].

Snow is not a monitored and controlled object of environmental safety, nevertheless, numerous researchers mention its high importance for environmental studies [6-9]. This can be attributed to numerous thermodynamic and physicochemical factors of snow formation, its mass transfer, and polluting processes [10-13]. In particular, during formation of water crystals in air and their precipitation, there occurs wet sedimentation of dissipated pollutants. In addition, air mass transport in atmosphere is very intensive with the consequence that pollutants are deposited in dry form onto snowpack surface. Such natural accumulation of pollutant content in snow is one of the most meaningful evaluation criteria of environmental state [14-17].

This work is aimed at estimation of environmental state of snowpack in Nizhny Novgorod as exemplified by a major highway on the basis of qualitative chemical analysis of thawing water and detection of its integral biological toxicity, including its interconnection with ecotoxicants.

II. METHODS

Snow was sampled manually into polyethylene bags early in February 2018, uniformly along major highways of Nizhny Novgorod: Sormovskoye Shosse (the Lower City) and Prospekt Gagarina (the Upper City). Snow was sampled from visually clean snowpack segments in close vicinity of the roads [10], [18]. Four single samples were taken at equal distances on each highway. Snowpack in Dubrava forestry was selected as reference, it was adjacent to the urban area on the north–east [19]. Four single samples were also taken in the forestry.

Snow samples were delivered to laboratory and placed into containers for natural thawing. Water was analyzed in the environmental laboratory of Minin University for main hydrochemical properties and biological toxicity of matters contained in the snow [20]; the analytical procedures were repeated three times. Acidity in the thawed water was determined by potentiometry using a MARK-903 pH meter and voltmeter, the weight of suspended matters was determined by gravimetry. Content of chlorides in filtrate of these samples was determined by argentometric titration, and content of sulfates – by iodometric titration; total salt content was determined using a DIST-3 (HANNA) conductometer.

Content of heavy metals in snow water was determined by inverse voltammetry using a TA-Lab polarograph according to the procedure for water [21] after preliminary filtration of samples and mineralization of existing organic matters by concentrated formic acid. Integral toxicity of snow samples was determined by bioluminescence based on reaction of *Escherichia coli*

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M-17 gen-engineered bacteria (Ecolum biosensor) using a BIOTOKS 10-M device [20]. The experimental results were processed by variation statistics using Microsoft Office Excel 2007.

III. RESULTS

Variations of snow water properties are summarized in Table I characterizing its generalized chemical state. Acidity of snow water was the most conservative property since its variability was minimum irrespective on sampling sites. In general, the water of all analyzed snowpack samples was in pH neutral range. The snow from both highways was weakly alkaline and the reference snow was weakly acidic.

The content of suspended matters was not homogeneous both by sampling sites and by the analyzed objects in general. For instance, variability of this performance at highways was 72.3% for Prospekt Gagarina and 132.7% for Sormovskoye Shosse. The highest contents of suspended matters were detected in the Upper City equaling to 51.74 g/l of snow water. In the samples from the Lower City, the content of suspended matters was 9.68 g/l. Probably, such values were stipulated by high air pollution due to intensive traffic. The situation was contrary to snowpack state in the forestry selected as reference. Here the content of suspended matters in snow water was minimum and the least varying (V=6.0%).

Sufficiently high contents of chlorides and sulfates in snowpack water were detected along the highways. In this case the Upper City was again characterized by high values of these properties. Thus, if in the samples from Sormovskoye Shosse the content of chlorides and sulfates varied in the ranges of 24.67–62.36 mg/l and 30.16–62.09 mg/l, respectively, then in the samples from Prospekt Gagarina this variability was 416.82–988.45 mg/l and 280.11–879.22 mg/l, respectively.

In the reference samples (Dubrava forestry) total level and variability of these performances were significantly lower: 5.71–6.45 mg/l and 7.76–8.65 mg/l for chlorides and sulfates, respectively. The content of all dissolved salts in samples of snow water determined as total salt content was also sufficiently high and characterized by high variability in urban area. In particular, if at Sormovskoye Shosse, the average value of 333 mg/varied by 32.7%, at Prospekt Gagarina, it was 2678 mg/l with variability of 79.9%. The salt content in snow water sampled at reference site was minimum (20 mg/l, V = 5.9%).

Table I. Chemical performances of snowpack water (M ± m: average ± standard error; V, % – variation coefficient)

Performance	Sampling points				M ± m	V, %
	I	II	III	IV		
Reference (Dubrava forestry)						
pH	6.83	6.22	6.24	6.50	6.45 ± 0.14	4.4
Suspended matters, g/l	1.55	1.72	1.50	1.62	1.60 ± 0.05	6.0
Total salt content, mg/l	21	18	20	21	20 ± 1	5.9
Chlorides (Cl^-), mg/l	5.71	6.37	5.98	6.45	6.13 ± 0.17	5.6
Sulfates (SO_4^{2-}), mg/l	8.65	7.76	8.15	8.45	8.26 ± 0.19	4.7
The Lower City (Sormovskoye Shosse)						
pH	7.13	7.28	6.98	7.04	7.11 ± 0.07	1.8
Suspended matters, g/l	9.68	1.29	1.25	0.74	3.24 ± 2.15	132.7
Total salt content, mg/l	440	410	260	220	333 ± 54	32.7
Chlorides (Cl^-), mg/l	50.49	62.36	51.17	24.67	47.17 ± 7.98	33.8
Sulfates (SO_4^{2-}), mg/l	32.29	62.09	48.80	30.16	43.34 ± 7.51	34.7
The Upper City (Prospekt Gagarina)						
pH	7.27	7.07	6.95	7.05	7.09 ± 0.07	1.9
Suspended matters, g/l	16.36	51.74	10.93	21.87	25.23 ± 9.12	72.3
Total salt content, mg/l	2290	5800	1540	1080	2678 ± 1070	79.9
Chlorides (Cl^-), mg/l	416.82	988.45	660.30	509.71	643.82 ± 125.35	38.9
Sulfates (SO_4^{2-}), mg/l	384.18	879.22	540.49	280.11	521.00 ± 130.85	50.2

In addition to the most occurring chemical substances, the samples of snow water also contained heavy metals (Table II).

While analyzing snowpack, significant content variability of zinc, cadmium, lead, and copper should be mentioned depending on sampling points. For instance, the content of cadmium (up to 104%) and copper (up to 134%) in snow water from Sormovskoye Shosse as well as the content of lead from Prospekt Gagarina (up to 130%) were characterized by the highest statistic heterogeneity.

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Table II. Content of heavy metals in snowpack water
(M ± m: average ± standard error; V, % – variation coefficient)

Performance	Sampling points				M ± m	V, %
	I	II	III	IV		
Reference (Dubrava forestry)						
Zinc (Zn), mg/l	0.0833	0.0192	0.0749	0.0531	0.0576 ± 0.0143	49.6
Cadmium (Cd), mg/l	0.0264	0.0046	0.0032	0.0188	0.0133 ± 0.0056	84.9
Lead (Pb), mg/l	0.0092	0.0047	0.0005	0.0051	0.0049 ± 0.0018	72.9
Copper (Cu), mg/l	BLD*	BLD	BLD	BLD	–	–
The Lower City (Sormovskoye Shosse)						
Zinc (Zn), mg/l	0.0220	0.0094	0.0970	0.0590	0.0469 ± 0.0198	84.3
Cadmium (Cd), mg/l	0.0001	0.0006	0.0053	0.0065	0.0031 ± 0.0016	103.9
Lead (Pb), mg/l	0.0091	0.0035	0.0055	0.0032	0.0053 ± 0.0014	51.0
Copper (Cu), mg/l	0.0096	0.0034	0.0001	0.0002	0.0033 ± 0.0022	134.0
The Upper City (Prospekt Gagarina)						
Zinc (Zn), mg/l	0.0170	0.0750	0.0300	0.0230	0.0363 ± 0.0132	72.8
Cadmium (Cd), mg/l	BLD	BLD	BLD	BLD	–	–
Lead (Pb), mg/l	0.0026	0.0025	0.0002	0.0140	0.0048 ± 0.0031	128.8
Copper (Cu), mg/l	BLD	BLD	BLD	BLD	–	–

* – Below limit of detection according to the applied procedure.

However, the highest pollution with heavy metals was detected in the reference site of the forestry where maximum contents of zinc (in average up to 0.0576 mg/l) and cadmium (in average up to 0.0133 mg/l) were detected. The content of lead in snowpack was approximately the same both for Sormovskoye Shosse and for Prospekt Gagarina (0.0053 and 0.0048 mg/l). Copper as ecotoxicant was detected in snow water only in the Lower City (in average up to 0.0033 mg/l).

Table III shows integral toxicity of snowpack water determined by reaction of Ecolum. It was detected that in general, the thawed water of all samples of the considered snowpack was characterized by toxicity with regard to the selected test object (*Escherichia coli* M-17 gen engineered bacteria).

Table III. Integral biological toxicity of snowpack water (M ± m: average ± standard error; V, % – variation coefficient)

Sampling location	Integral toxicity of snowpack water, % (by sampling points)				M ± m	V, %
	I	II	III	IV		
Reference	9	10	11	11	10 ± 0	6.0
The Lower City	37	54	27	22	35 ± 7	40.3
The Upper City	62	79	53	42	59 ± 8	26.5

It should be mentioned that even minimum content of pollutants in reference snow samples resulted in toxic effect (10%, V = 6.0%) which was estimated as allowable (toxicity class 1). The snow water samples from the highway in the Lower City were characterized by medium toxicity (class 2), and the samples from the highway in the Upper City were characterized by acute toxicity (59%, V = 26.5%) with regard to the test object (class 3).

Since previously analyzed biological toxicity of snowpack water depends on the content of impurities characterized by such toxic effect, the authors evaluated the interrelation between snow pollutants and toxicity (Table IV).

Table IV. Interrelation between chemical state of snowpack water and its biological toxicity
(r ± Sr: coefficient of correlation ± error r)

Performance	Correlation coefficient of chemical composition and integral toxicity (r ± Sr)		
	Reference	the Lower City	the Upper City
Acidity	0.13 ± 0.70	0.94 ± 0.23	0.26 ± 0.68
Salt content	0.98 ± 0.12	0.81 ± 0.41	0.95 ± 0.22
Chlorides	0.60 ± 0.57	0.82 ± 0.40	0.71 ± 0.50
Sulfates	0.98 ± 0.15	0.73 ± 0.49	0.87 ± 0.34

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Zinc	0.99 ± 0.10	0.61 ± 0.56	0.89 ± 0.33
Cadmium	0.85 ± 0.38	0.91 ± 0.29	–
Lead	0.83 ± 0.39	0.45 ± 0.63	0.84 ± 0.39
Copper	–	0.43 ± 0.64	–

It should be mentioned that in technogenic areas, the correlation dependence of performances was more pronounced in comparison with reference values. It was stablished that the content of certain matters in water samples and its integral biological toxicity were directly correlated, in most cases this correlation was strong. For instance, in the samples from Sormovskoye Shosse, the correlation coefficient r was 0.94±0.23 for acidity, 0.82±0.40 – for contents of chlorides, 0.73±0.49 – for contents of sulfates, and 0.81±0.41 – for total salt content.

Concerning the samples from Prospekt Gagarina, these coefficients r were 0.26±0.68, 0.71±0.50, 0.87±0.34, and 0.95±0.22, respectively. It was established that in general the biologic toxicity depended both on the content of dissolved salts and on the content of heavy metal ions in samples, however, no distinct trends were revealed. Sufficiently high error of correlation coefficient should be, probably, attributed to significant variability of absolute values of the performances.

IV. DISCUSSION

It is obvious that the aforementioned difference in concentrations of sulfates, chlorides, and heavy metals should be attributed to high anthropogenic load on urban ecosystem, which can be comprised of existence of fine suspended solids and high contents of technogenic gaseous sulfur dioxide (SO_2) and sulfur trioxide (SO_3) in urban atmosphere which are sufficiently soluble in water, as well as sand salt mixes on surface as a consequence of widely applied deicing procedures, such mixes contain industrial sodium chloride as deicing agent. These aspects are very important in terms of risk of pollution of soil waters with excessive amount of chlorides, sulfates, heavy metals and other ecotoxicants penetrating both through open soil sites and through storm water drainage into soils [15, 16].

V. CONCLUSION

Finally, the importance of snowpack at highways for estimation of environmental state of urban ambient air should be mentioned. Taking into account high content of suspended matters, soluble forms of chemical elements, including heavy metals, during winter season of 2018 the highest environmental impact had the snowpack in the Upper City analyzed on the basis of data for Prospekt Gagarina.

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