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The study of snow pollution levels based on heavy metal concentrations in Arkhangelsk, 2017-2018

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Abstract. Air pollution poses a significant hazard to human health. Snow is able to accumulate pollutants present in the air. Therefore, determination of pollutants levels in the snow is a simple and effective method of environmental monitoring. Heavy metals are among the most hazardous pollutants. Various methods can be used to determine heavy metal concentrations in snow, on being total-reflection X-ray fluorescence spectroscopy (TXRF). TXRF allows for parallel identification of several dozens of metals with concentrations of the order of µg/L. Since quantitative analysis is performed using the internal standard method, calibration for each measured element is not required. An important advantage of this method is the ability to carry out measurements in a mobile laboratory. Performed in 2017 and 2018, this study aims to determine heavy metal contents in the snow in Arkhangelsk using the TXRF method. It is assumed that the contents of heavy metals do not exceed permissible levels. The relative concentrations of Fe, Mn, Ni are the most significant (with respect to MPC). The content of Cu, Zn, Sr, Pb in samples is statistically significant, while the presence of As, Cd, Hg has not be detected.

1. Introduction

Air quality has a significant impact on the state of all ecosystem elements and is of great importance in assessing levels of human health. The list of substances present in the atmosphere is quite extensive and includes solid particles (often of unknown composition); aggressive gases; metal compounds [1]. However, the immediate, direct detection of air pollutants in parallel can be very challenging. Snow cover appears an effective storage of pollutants that come from the air and a convenient indicator for assessing the state of urban areas, reflecting pollution levels in the surface layers of the atmosphere.

Heavy metals are one of the most hazardous environmental pollutants. This is due to the fact that heavy metals are actively involved in physiological processes. Metals form part of many enzymes. They are able to accumulate themselves in soils of various structures, differing in the ability to migrate in environment [2]. Therefore, the study of qualitative composition of snow pollutants constitutes a special focus. Particularly relevant is determination of heavy metal concentration in the snow and in solid particles.

Heavy metals are present in snow in extremely low concentrations; therefore, their determination is a complex analytical task. The methods of analysis must satisfy such requirements as high sensitivity (low limit of detection) and selectivity. At present the problem is solved using methods of stripping voltammetry (SVA), electrothermal atomization atomic absorption spectrometry (ETAAS), and inductively coupled plasma atomic emission spectrometry and mass spectrometry (ICP AES and ICP MS). Total external reflection X-ray fluorescence spectrometry (TXRF), a method gaining wider foothold in highly sensitive elemental analysis [3], can be a state-of-the-art alternative to the above methods. The sensitivity of this method is comparable to that of ICP AES [9] and, in contrast to AAS, it is multi-elemental, ensuring parallel identification of concentrations of several dozens of components in a sample. Among the essential advantages of TXRF that make is especially promising for field research, are small dimensions and weight of the equipment, low energy consumption, and low cost of analysis. The latter is due to the fact that all the operations can be done on very small amounts of test samples (from hundreds of microliters to several milliliters) or chemical agents. Also, no consumables virtually required for equipment to work. The physical basis and the scope of TXRF were considered in detail in review [4]. The application of this method to the analysis of natural waters, including seawaters, is described in [4–7].

Among the cities in the northern regions of European Russia, Arkhangelsk is the largest, with population over 350 thousand people. It is therefore essential that work is conducted to assess pollution levels based on heavy metals occurring in the snow in Arkhangelsk using the TXRF method.

2. Materials and methods

2.1. Sampling and sample preparation

The sampling operations covered the areas of Arkhangelsk outside of influence from motor transport and were performed on 03.03.2017 and on 12.03.2018. In 2017, 26 samples were taken, in 2018 - 9. The location of the sampling points is given in Figures 1 and 2, respectively. Sampling was performed in accordance with the requirements of GOST 17.1.5.05-85 [8]. Sampled snow was placed in pre-cleaned glass vessels (1 liter).

The samples melted at room temperature and the water was filtered through the paper filter. Immediately after the filtration, the samples were preserved by acidification with nitric acid to pH 1–2. Nitric acid was pre-purified by distillation, without boiling, on a DST-1000 apparatus (Savillex, US).

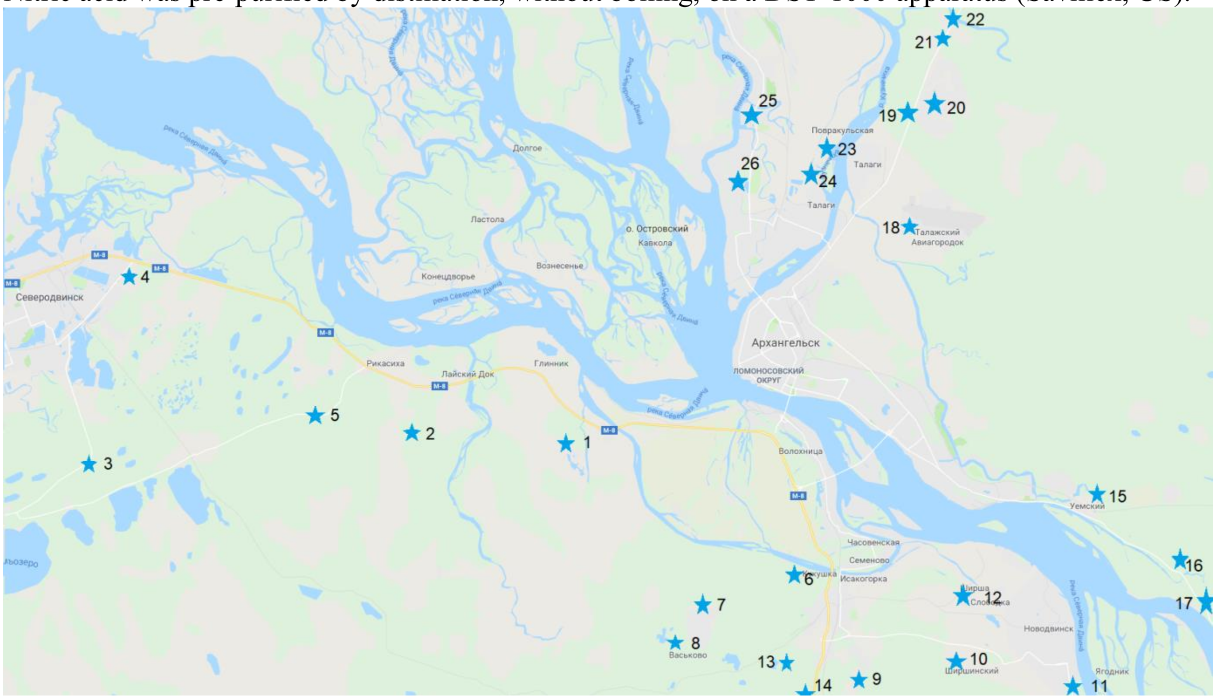

Figure 1. Location of snow sampling points in 2017 (Google Maps).

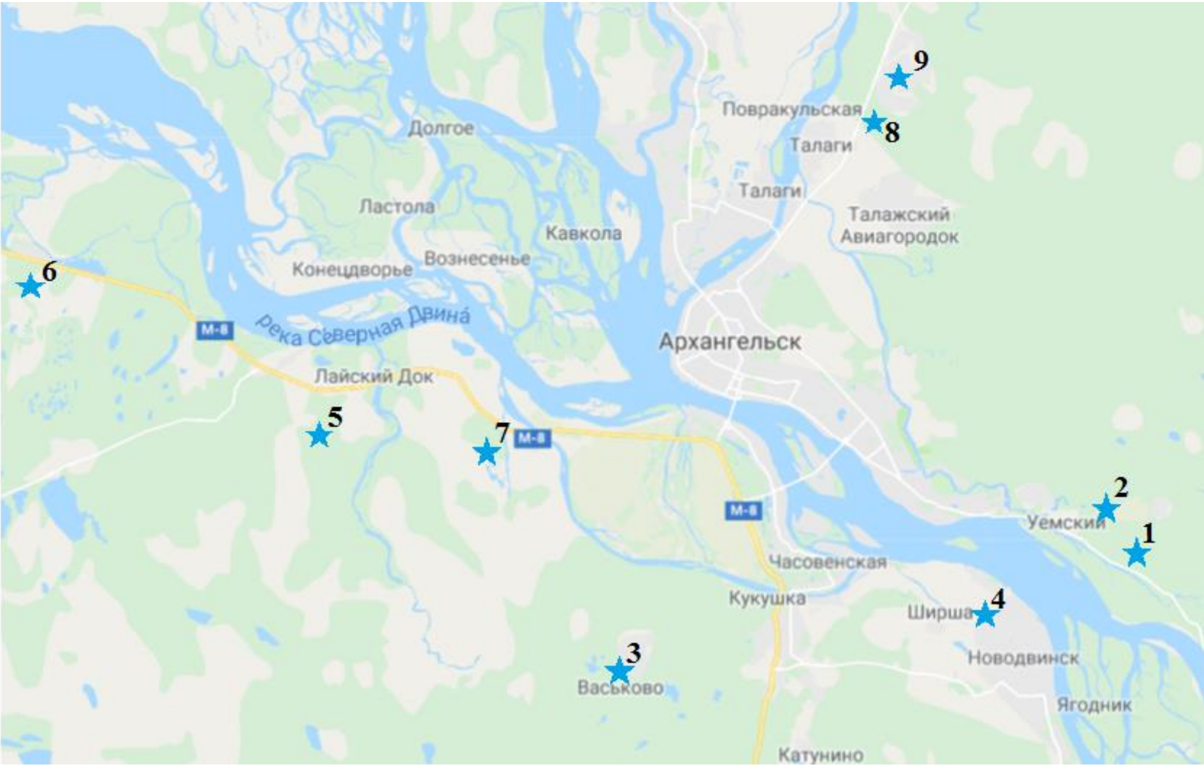

Figure 2. Location of snow sampling points in 2018 (Google Maps).

2.2. *Equipment*

To identity heavy metals concentrations, we used S2 Picofox total reflection X-ray fluorescence spectrometer (Bruker, Germany) installed with a high-efficiency module and automatic sample loading. The X-ray tube with a maximum power of 37 W (50 kV, 750 μA) with a Mo anode, equipped with a multilayered Ni/C monochromator, was an excitation source (energy17.5 keV). A silicon drift detector with thermoelectric cooling and an area of 30 mm2 was used. The maximum counting rate was more than 100,000 pulses/s. The power resolution was <150 eV for MnKα line.

2.3. *Determination of metal concentrations*

Water (100 μL) was mixed with standard Ga solution of 500 μg/L (100 μL) concentration in a polypropylene microcentrifuge tube using a vortex within 60 s. A 10μL solution containing 250 μg/L of the internal standard was placed on a quartz sample holder with a micropipette and dried on a warm plate with a surface temperature of 65 ± 1°C for 300 ± 5 s.

The internal standard was a diluted with Ga standard solution for ICP (Panreac, Reference standards acc. NIST SRM 3119a), 1.000 ± 0.002 g/L concentration. The deionized water that underwent filtering and acidification was used as a blank sample. The deionized water was obtained on Simplicity UV system for preparing ultrapure water (Millipore, Germany)

Fluorescence intensity was measured at 1200 s at X-ray tube voltage 50 kV and current 600 μA. The spectrum obtained was automatically processed by the spectrometer software (Spectra7, Bruker) using the Profile Bayes (normal fit) deconvolution mode. Concentrations of elements in the prepared sample were analyzed using the internal standard calculation method. Metal content in samples was calculated by multiplying the identified concentration (taking into account blank sample) by the dilution coefficient (equaling 2). Each sample was measured twice.

3. Results and discussion

The X-ray fluorescence spectrum of a snow sample is shown in Figure 3. It can be seen that the obtained signal-to-background ratio is indicative of the possibility for achieve reliable quantitative determination of heavy metals under the selected conditions.

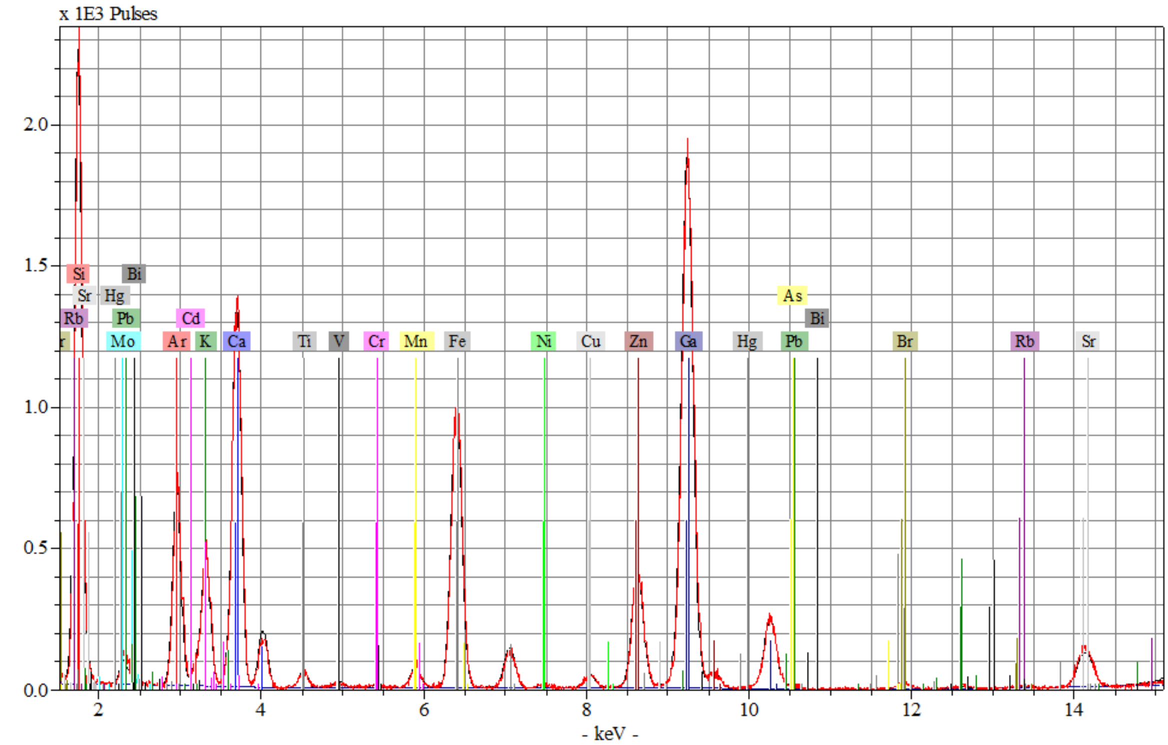

Figure 3. X-ray fluorescence spectrum of snow sample (Ga concentration 250 μg/L).

The following elements were selected for quantification: K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Cd, Ba, Hg, Pb, Tl, Bi. However, during the whole measurements the concentration of Ti, V, Cr, Co, As, Rb, Hg, Tl, Bi were below the spectrometer detection limit. By reason of the inevitability of gross errors in measurements, no calculation of Ba, Br, K, Cd concentrations was performed. This is due to the following reasons: BaLα -line is overlapped by TiKα-line; Br evaporates from the surface of the sample holder in different quantities, so the values of its measured concentrations are unstable; K is a light element, its fluorescent radiation is absorbed by air, which leads to low reproducibility of the results; CdLα-line overlaps with the Ka-line of potassium.

The results of determination of Zn, Ni, Cu, Sr, Mn, Pb, Ca, Fe in the snow samples are presented in Tables 1 and 2. The sample numbers in the tables correspond to markings in Figures 1 and 2. Also, Tables 1 and 2 show the values of maximum permissible concentration (MPC) of metals in water. The average heavy metals content at the selection points for the year is presented in Table 3.

It follows from Tables 1-3 that the triad of atmospheric pollutants within the city of Arkhangelsk outside the areas of influence from motor transport is represented by manganese, iron and nickel. It can be concluded that the most hazardous heavy metals, such as mercury, cadmium, arsenic, have not been found. The concentration of lead is lower than its MPC. Only one metal – Pb – was found close to its MPC in one point (No 26) in 2017. The concentrations of the majority of the remaining metals was either under their MPC or very small.

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Table 1. Measured heavy metal concentrations in snow samples, 2017.

Sample number	Metal concentration, µg/L							
	Ca	Mn	Fe	Ni	Cu	Zn	Sr	Pb
1	3570	18.9	141	0.70	3.97	15.8	18.3	0.32
2	3430	62.6	89.4	1.94	2.90	13.3	19.2	0.00
3	2730	13.4	82.9	0.00	3.48	41.6	16.6	0.00
4	3150	18.2	107	0.79	5.31	15.0	20.3	0.42
5	3000	7.41	77.0	0.00	1.63	11.9	15.5	0.00
6	2490	11.7	106	13.5	1.67	13.8	13.1	1.43
7	3700	16.5	85.7	0.00	17.7	15.1	20.8	0.00
8	2200	9.98	62.2	14.9	2.75	8.21	10.4	0.00
9	3450	34.4	254	0.30	7.38	13.9	22.4	0.23
10	3960	16.4	102	5.62	8.14	25.8	23.5	1.38
11	5740	34.7	145	0.00	3.26	19.2	29.9	0.54
12	5360	28.0	164	0.34	5.21	25.2	28.4	1.72
13	5340	51.7	195	1.70	8.31	23.0	30.1	0.87
14	1820	26.9	49.4	12.6	3.84	7.75	14.0	0.26
15	2630	16.3	67.0	0.00	2.40	8.61	15.5	0.50
16	3310	48.5	82.3	0.00	1.60	7.38	19.4	0.13
17	3350	25.1	108	0.00	4.26	18.6	20.8	0.23
18	3440	29.3	84.6	19.0	4.08	8.49	23.0	0.00
19	4890	42.2	328	7.10	7.68	24.7	27.4	2.30
20	1340	10.5	69.4	5.43	4.83	11.2	8.98	2.22
21	3860	10.8	95.8	5.97	33.0	12.5	24.4	0.00
22	2800	13.3	79.4	2.18	5.97	26.6	17.9	0.16
23	3330	26.3	119	0.09	4.82	40.6	22.1	0.14
24	4120	23.5	115	2.29	3.22	14.2	26.9	1.39
25	3290	19.7	105	3.78	3.75	8.81	20.2	1.64
26	3520	25.3	1291	0.46	7.98	114	22.0	8.58
MPC	-	100	300	20.0	1000	1000	7000	10.0

Table 2. Measured heavy metal concentrations in snow samples, 2018

Sample number	Metal concentration, µg/L							
	Ca	Mn	Fe	Ni	Cu	Zn	Sr	Pb
1	706	5.93	16.8	0.00	0.83	0.00	3.61	0.00
2	891	5.55	27.9	0.70	3.38	0.00	3.67	0.64
3	276	2.88	47.3	0.64	0.65	0.62	0.86	0.00
4	1410	3.30	3.23	0.00	0.00	0.00	3.08	0.00
5	280	1.10	0.00	0.00	0.08	0.00	1.68	0.00
6	509	8.95	23.5	0.26	3.54	3.87	4.02	0.59
7	525	13.6	42.5	14.3	38.1	0.00	4.57	0.00
8	1560	15.6	50.9	0.41	0.00	2.72	8.74	0.00
9	689	3.91	21.7	0.00	0.00	8.21	5.31	0.00
MPC	-	100	300	20.0	1000	1000	7000	10.0

To analyze the spatial distribution of heavy metals, we made use of cartographic information of Google Maps system. Maps were compiled on spatial distribution for each of the 8 investigated elements in snow in Arkhangelsk in 2017 and 2018. The metal distribution on the territory of Arkhangelsk is uneven, and there is often is a big difference between neighboring points. For example, in points 13 and 14 Ni content was measured 1.70 µg/L and 12.6 µg/L respectively.

Table 3. Average metal content at sampling points for the year

Year	Units	Metal concentration							
		Ca	Mn	Fe	Ni	Cu	Zn	Sr	Pb
2017	μg/L	3460	24.7	162	3.80	6.12	20.9	20.4	0.94
	Fraction of MPC	-	0.247	0.539	0.190	0.006	0.021	0.003	0.094
2018	μg/L	760	6.75	26.0	1.81	5.18	1.71	3.95	0.137
	Fraction of MPC	-	0.068	0.087	0.090	0.005	0.002	0.001	0.014

4. Conclusion

The TXRF-based analysis of 35 snow samples, conducted in 2017 and 2018 in Arkhangelsk, has detected a number of statistically significant concentrations of metals – Ca, Mn, Fe, Ni, Cu, Zn, Sr, and Pb. The analysis has not detected any of hazardous elements, such as mercury, cadmium or arsenic. The majority of heavy metals concentrations were found under their MPC.

Calculations targeted the average concentrations of the metals. The triad of atmospheric pollutants within the territory of Arkhangelsk outside of areas of influence from motor transport is represented by iron, manganese and nickel.

The distribution of metals across the territory of Arkhangelsk, outside of the areas of influence from vehicles, is uneven.

Acknowledgments

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