Features of the elemental composition of snow cover in the area of production primary aluminum emissions

N.I. Ianchenko, V.V. Kondratiev, V.V. Verkhoturov

Irkutsk National Research Technical University, Russia, 664074, Irkutsk, Lermontova street, 83
E-mail: fduesn@bk.ru

ABSTRACT

The selection of snow samples was performed in Mongolia (the slope of Mount Munku-Sardyk), Buryatia (ulus Ulbugay), Bratsk (Padun district) and in Irkutsk (Mount «Snow»). Element's content in the samples of snow melt water was determined with the quadrupole ISP-MS mass spectrometer of Agilent 7500 ce. Determination of content of chemical elements (cations) in a filtrate of melted water of snow cover is carried out by a mass spectrometry method with the inductively coupled plasma (ISP-MS). The concentrations of about 70 elements have been defined. Also it has been determined that the side of Mount Munku-Sardyk (Mongolia) and ulus Ulbugay (Buratia) are the clearest ecological areas. The concentrations of some elements in the snow cover in Bratsk exceed the background concentration five times and more. The high coefficients of pair correlation between pairs of elements Al, Li, Be, Tl, V, F and the dependence of change of concentrations from the distance from the smelter has been established. It has been defined, that there is no exceeding in the residential area.

Keywords: background area, marker, fluorine, primary aluminium

1. INTRODUCTION

Atmospheric precipitation of snow [1] and snow cover are efficient stores of gaseous and aerosol substances coming from the atmospheric air [2]. The composition of snow cover depends on the composition of the air. The selection is rather simple [3] and does not demand special equipment.

The relevance of the study is determined by the necessity of comparing the concentrations of elements in snow cover in the area of hazardous emissions stemming from aluminium smelters and in the clean area. This will allow us to make a preliminary environmental estimate of the state of the snow cover and the air.

Clean areas or background areas are areas in which there is an industrial activities or it is minimal in comparison with the study area.

Objective of this study is to investigate the composition of elements in the snow cover in areas with emissions from primary aluminium production and in the clean areas, to determine the dependence of the concentration of elements in

the filtrate of the snow cover on the distance from the plant, to establish correlations between the elements and suggest marker elements.

2. MATERIALS AND METHODS

In 2013 and 2016 samples of the snow cover were taken in the area of industrial emissions of Bratsk, such as the production of primary aluminium (BrAZ), the plant ferroalloy (ferrosilicon production), pulp and paper mill, Galachinskaya thermal electro station (there are several thermal power plants in the city) at a distance of up to 29 BrAZ km from the village Padun (Padunskie district of Bratsk). Many industries in Bratsk (Fig. 1) use hydrocarbon materials (carbon anodes in aluminum production, the reduction of carbon silicon, burning coal in coal power plants).

In 2013 the amount of selected samples was 10, in 2016 – 29 ones. The relief in Bratsk area is largely hilly with height difference from 402 till 670 meters. The average annual wind speed is 1-3 m/s; the wind transfer of air masses [4] is mainly west and pollutions are mainly directed to residential districts. The average annual amount of precipitation in Bratsk is about 369 millimeters, including 25% of them in the cold period of time and 75% - in the warm period of time [4]. Bratsk aluminium plant (BrAZ) is one of the world's largest aluminum producers. In 2015, the Bratsk smelter produced 1,007,002 tonnes of primary aluminum (design capacity is 840,000 tonnes of aluminum per year). The aluminium plant has been working since 1966. The technology of the aluminum producing with electrolytic way included dissolution of alumina (Al2O3) in cryolite (Na3AlF6), being in an electrolytic bath at a temperature of 960 °C, decomposition of alumina with selection of aluminum on the cathode [5]. Except using alumina plants adopt fluoric salts (including AlF_3, due to produce one ton of aluminum 25 kg must be consume) and about 560 kg anode mass flow rate [6]. Irkutsk aluminium plant (IrkAZ), which is situated in Shelekhov, has been working since 1962 and has contemporary efficiency 412,600 tonnes per year (2015). Bratsk and Irkutsk aluminium plants are equipped with electrolytic baths with the self-burning coal anodes (except the smelter's 5th potline at IrkAZ) and top current supply (Soderberg). Bratsk and Irkutsk aluminium plants generally apply a sodo-bicarbonate way of purification of electrolysis gases, except the 5th series on IrkAZ and except 7, 8, 25 potrooms on BrAZ, where "dry" gas purification is applied, effective to reduce the emission of fluorides.

Snow cover sampling was performed in the background area in Tunkinskaya valley (ulus Ulbugai in Buratya) in 2013. In April of 2016 snow cover sampling was performed on the south slope of Mount Munku-Sardyk in Mongolia in the near of Khovsgol Lake (high point is 2024 m). In April of 2016 snow cover sampling was performed on the highway "Irkutsk- Bolshoe Goloustnoe" (Fig. 1) on Mount "Snow" (high point is 943 m).

Snow water samples from snow cover were selected with the 20 ml disposable medical syringes and in number of 10 ml. Samples were filtrated through the disposable polystyrene sterile syringe nozzle Minisart 16555-K (0,45 micrometer, acetate cellulose, Sartorius Stedim Biotech Gmbh) into in beforehand fluidized polypropylene disposable test tubes with the twisting cover (15 milliliter, Greiner bio-one).

Element's content in the samples of snow melt water was determined with the quadrupole ISP-MS mass spectrometer of Agilent 7500 ce. Determination of content of chemical elements (cations) in a filtrate of melted water of snow cover is carried out by a mass spectrometry method with the inductively coupled plasma (ISP-MS). In total 71 elements are defined.

Figure 1. Areas of the sampling of the snow cover.

3. RESULTS AND DISCUSSION

The following statements were defined with comparing of elements concentration in snow cover from four places: Mount Munku-Sardyk, Mount "Snow", ulus Ulbagai and Padun district in Bratsk. The lowest elements concentration is noticed in snow cover on Mount Munku-Sardyk and in ulus Ulbugai. Exceeding concentration of 17 elements in compare with Munku-Sardyk and ulus Ulbugai was marked out in snow cover in Padun (a district in Bratsk is 29 km from BrAZ). Concentration of those elements which in 5 and more times exceeded concentration of elements in these areas is given in table 1. The greatest excess of concentration in snow cover of Bratsk is noted for strontium and cadmium (tab. 1). For comparison, in Irkutsk concentration of strontium makes 58 mgL^{-1} [7], that above, than in Bratsk, in Irkutsk concentration of cadmium makes 0,08 mgL^{-1} [7], that is equal to concentration in the city of Bratsk. The exceeded concentration of Be, Al, V, Tl was noticed in snow cover in Irkutsk, in Brats and on Mount "Snow".

To define markers of emissions of aluminum plant we considered coefficients of pair correlative between elements and distance from BrAZ (tab. 1, 2). According to the following data in 2013 (the number of samples n = 10) and in 2016 (the

number of samples n = 29) the high coefficients of pair correlation between pairs of "element – element" and "element – distance from BrAZ" (Al, F, Li, Be, V, Tl) has been defined. High values of coefficients of pair correlation of these paired elements Li, Be, V, Tl with Al, F allow us to assume that these impurities are mainly contained in the aluminum fluoride (correlation with sodium is low). These elements Li, Be, V, Tl can be the markers of production of primary aluminum in Bratsk now, by the modern element structure of the feed stock (coal anodes, fluorine aluminum, cryolite, alumina) entering from Russia and other countries. The classical scheme of aluminium smelter has been changed and aluminum fluoride is applied in the last decade at the plant instead of cryolite. Fluoride of aluminum is applied to decrease of the cryolite relation and increase production of aluminum. It is known that an efficiency of an aluminium smelter can be increased not only with reducing the cryolite relation, but also with applying additives of salt lithium in electrolyte [10]. Technological additives of compounds of lithium are not applied on Bratsk aluminium smelter, but raw materials content lithium, which has been testified with correlations of lithium with fluorine and aluminum in the filtrate of snow cover (fig. 2).

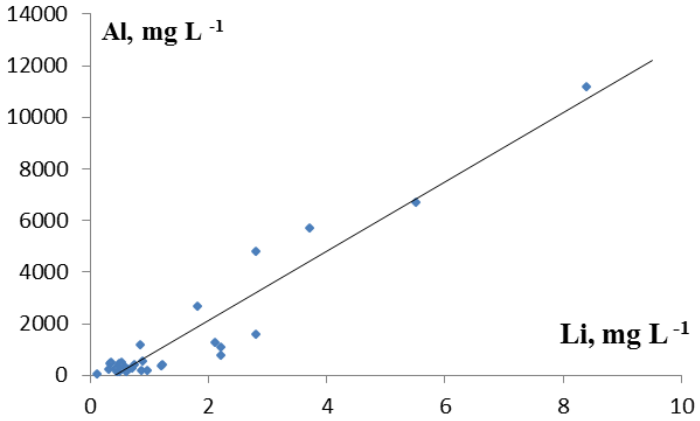

Figure 2. The correlation of concentration of Al and Li in the snow cover in Bratsk

A comparison of the concentration of 17 elements (Table 1) from the maximum allowable concentrations of chemicals in water bodies of fishery [9] has been fulfilled. We can note that there is no exceedances of concentrations for these elements in the snow cover at the distance of 29 km.

4. CONCLUSION

Thus, the selection samples of the snow cover have been made in Mongolia (Mount Munku-Sardyk), Buryatia (Tukinskaya valley, ulus Ulbugay), Bratsk and Irkutsk (Mount "Snow"). The concentrations of about 70 elements have been defined. Also it has been determined that the side of Mount Munku-Sardyk (Mongolia) and ulus Ulbugay (Buratia) are the clearest ecological areas. The concentrations of some elements in the snow cover in Bratsk exceed the background concentration five times and more. The high coefficients of pair correlation between pairs of elements Al, Li, Be, Tl, V, F and the dependence of change of concentrations from the distance from the smelter has been established. The comparison of the actual concentrations in the snow cover of Bratsk with maximum-permissible concentrations of harmful substances in the water of fishery appointment has been carried out. It has been defined, that there is no exceeding in the residential area.

Table 1. The content of elements in the snow cover (mgL^{-1}) of the slope of Mount Munch-Sardyk, ulus Ulbugay, Irkutsk [7, 8] Bratsk. Multiplicity of excess of concentrations of elements concerning to the slope of Mount Munch-Sardyk. Maximum permissible concentration (MPC) of elements in the water fishery

	The slope of Mount Munku-Sardyk	*Ulus Ulbugay*	*Mount Snow*	*Irkutsk [7,8]*	*Bratsk 2013*	*Bratsk 2016*	*The excess of concentration concerning to the slope of Mount Munku-Sardyk* and ulus Ulbugay ***					*[9] Mg L^{-1}*
							*Ulus Ulbugay **	*Mount Snow **	*Bratsk 2013 **	*Bratsk 2016 **	*Bratsk 2016 ***	
Li	0,038	0,41	0,102		0,6	0,302	11	3	16	8	1	80
Be	0,0021	0,0009	0,016	0,27	-	0,019	0	8	13	9	22	0,3
B	0,25	0,88	1,68	8,55	4,9	9,87	4	7	20	21	11	-
Na	260	290	34	571 [8]	1300	890	1	0	5	3	3	120
Mg	63	27	30	304 [8]	310	451	0	0	5	7	17	400
Al	6,8	12,8	67	44 [8],	96	304	2	10	14	20	24	40
V	0,057	0,034	0,42	0,75	0,66	0,907	1	7	12	16	27	10
Ga	0,0037	0,005	0,014		0,027	0,106	1	4	7	24	21	-
Ge	0,0023	0,0028	0,021		0,017	0,022	1	9	7	10	8	-
Br	7,1	10	6,7		39	15	1	1	5	2	2	-
Sr	1,31	1,69	2,4	29[8] 58	39	23	1	2	30	18	14	400
Mo	0,015	0,01	0,028	2,45[8]	0,08	0,12	1	2	5	9	14	1
Cd	0,004	0,006	0,018	0,31[8],	0,09	0,098	2	5	23	25	19	-
Sb	0,007	0,018	0,01	0,35[8],	0,09	0,128	3	1	13	18	8	-
Cs	0,0013	0,0027	0,0056		0,007	0,023	2	4	6	9	9	100
Ba	1,62	0,74	1,69		19	21	0	1	12	13	29	-
Tl	0,0014	0,0018	0,0062	0,04 [7]	0,009	0,006 9	1	4	6	5	4	-

Table 2. The coefficient of pair correlation between Li, Be, Al, V, Tl, F and the distance from BrAZ

	F		*Al*		*The distance from BrAZ. (r, km)*	
	2013 г	*2016 г*	*2013 г*	*2016 г*	*2013 г*	*2016 г*
Li	0,85	0,84	0,82	0,87	- 0,95	- 0,90
Be	0,90	0,90	0,94	0,98	- 0,73	no data
V	0,91	0,82	0,84	0,83	- 0,87	- 0,83
Tl	0,87	0,88	0,88	0,91	- 0,87	- 0,87
Al	0,98	0,97	1	1	- 0,80	- 0,88
F	1	1	0,98	0,97	- 0,88	- 0,93
Cd		0,85		0,9		- 0,80

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