

# Fluorine concentration in snow cover within the impact area of aluminium production plant (Krasnoyarsk city) and coal and gas-fired power plant (Tomsk city)

A V Talovskaya<sup>1</sup>, N A Osipova<sup>1</sup>, E A Filimonenko<sup>1,2</sup>, S A Polikanova<sup>1</sup>,  
N P Samokhina<sup>1</sup>, E G Yazikov<sup>1</sup> and I A Matveenko<sup>1</sup>

<sup>1</sup> National Research Tomsk Polytechnic University, 30 Lenin Ave., Tomsk, 634050, Russia

E-mail: <sup>2</sup> filimonenkoea@mail.ru

**Abstract.** The fluorine contents in snow melt water find in the impact areas of aluminum production plant and coal and gas-fired power plant are compared. In melt water, soluble fluoride is found in the form of fluoride ion, the content of which was determined by the potentiometric method using ion-selective electrode. According to the measurements of 2013-2014, fluoride content in melt water ranges 10.6-15.4 mg/dm<sup>3</sup> at the distance 1-3 km from the borders of Krasnoyarsk aluminum plant with the mean value 13.1 mg/dm<sup>3</sup>. Four-year monitoring from 2012 to 2015 in the impact area of Tomsk coal and gas-fired power plant showed that fluoride content in melt water in vicinity of the thermal power plant is significantly lower than in the samples from the impact area of the aluminum plant. But higher content of fluoride ion (0.2 – 0.3 mg/dm<sup>3</sup>) in snow samples in vicinity of coal and gas-fired power plant was revealed in winter of 2015. Intake of soluble fluoride is mostly explained by dust-aerosol emissions of study plants and deposition of fluorine compounds from air.

## 1. Introduction

Fluoride with its high chemical reactivity occupies a special place among other elements, since its physiologically necessary amount is close to the damaging effect doze. A distinguishing feature of the element is a narrow range of its optimal concentrations in drinking water varying 0.7 – 1.2 mg/L [1-4]. On the one hand, fluoride is included in the group of microelements participating in the processes of growth, development, reproduction, bone tissue metabolism; therefore, it is required for an organism life. On the other hand, even in small concentration it has toxic properties [1-5].

Fluoride clark amounts to 350 g/t for biosphere, 1.3 g/t for hydrosphere [1, 2]. The data on fluoride content in water differs greatly, however, the following common empirical pattern is observed: a positive correlation of fluoride concentrations and Na/Ca ratio [1, 2, 5]. The industrial sources of fluoride and its compounds in the environment are chemical, metallurgical, glass, ceramic, cement plants, coal-fired power plants, and nuclear fuel cycle enterprises.

Fluoride content in the environment is studied in a significant number of works. Conventional natural forms of fluoride in soil are unavailable for plants in contrast to man-made F, water-soluble compounds of which can be absorbed by plants, participate in intensive bioaccumulation, and pass along food chains [1, 2].

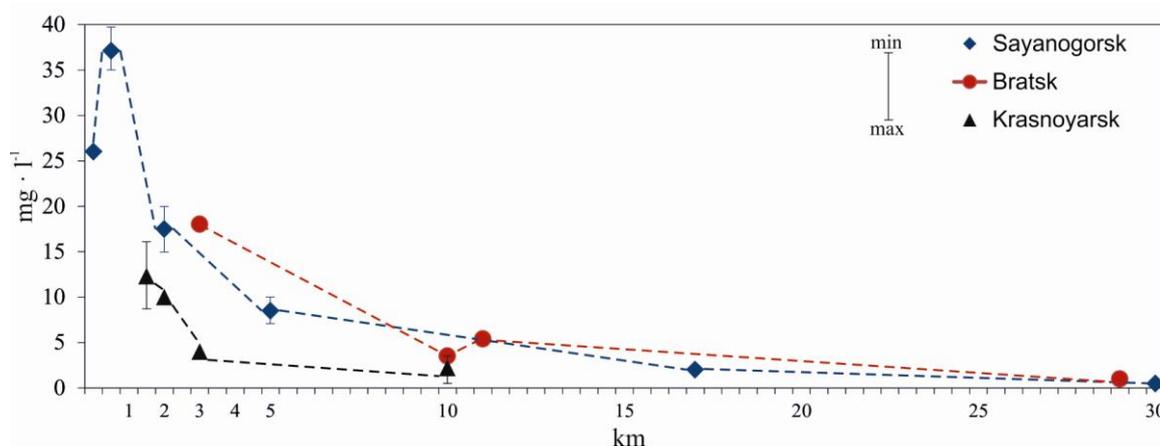


Yanchenko (2013) [6] showed that fluoride content in snow melt water can serve as an site indicator of environmental conditions. Snow is used to study the pollution level of urbanized areas in cold climate conditions, where snow accumulates pollutants for several months [7]. The urgent research in snow is also conditioned by the fact that precipitations are a part of the surface water balance influencing the conditions of soil, plants, and ground waters, as well as ecosystem, in general [7, 8].

Aluminum smelters sufficiently contribute to environmental fluoride pollution. In manufacturing practice, to produce aluminum the initial raw material – cryolit (sodium hexafluoroaluminate) - is added, as a result of which fluoride gaseous compounds and inorganic fluorides are released in the process of electrolysis. In such conditions significant losses of feedstock is observed. In the impact area of Bratsk aluminum plant fluoride content in melt water filtrate amounted to 18 mg/L at a distance of 3 km [6]. In the impact area of aluminum smelters in Canada fluoride content in melt water was determined as up to 13 mg/L [9].

The contribution of thermal power industry in fluoride emissions was studied by the example of some regions [10, 11], however, this involves insufficient information. In the process of coal combustion fluoride-containing compounds can enter the environment in the form of hydrogen fluoride. A certain part of fluorine-containing emissions can be transformed into salts. Depending on wind direction and distance from the thermal power plant (1.7-4.5 km), fluoride concentration ranges from 0.56 to 1.94 mg/L at the mean value of 1.21 mg/L according to [12].

Based on the literature [6, 11, 13-17] fluoride content in snow melt water from the impact areas of aluminum production in Western Siberia was compared (figure 1). These data show that fluoride content in melt water sufficiently exceeds the background values – from 10 to 80 times. But the level of fluoride in filtrated melt water within 1-3 km from site of aluminum plants is 3-7 times higher as compared to fluoride content at the distance of 5-10 km. Fluoride content in melt water at the distance of 29-30 km amounts to 0.5 – 1 mg/L, which is lower than the fluoride content in the samples taken in the vicinity of the plant – 20 – 50 times (figure).



**Figure.** Spatial dynamics of fluoride content in snow melt water at the distances from aluminum plant sites in Western Siberia (according to the data [6, 11, 13-17]).

Spatial dynamics of fluoride content in melt water depends not only on the distance from the source of emission and wind pattern, but also the areal landscape. Moreover, in Krasnoyarsk, according to the data [13], over the last 15 years the wind pattern has changed. It is the result of the major emissions of aluminum production plant fall in Krasnoyarsk [13]. Therefore, the study issue in fluoride content of melt water in the sites of industrial enterprises as an environmental condition indicator of the area, identifying spatial and temporal variability of its content is still topical. This paper is aimed at

studying the content of water-soluble fluoride in filtrated snow melt water in the impact areas of aluminum production plant (Krasnoyarsk) and coal and gas-fired power plant (Tomsk).

## 2. Materials and methods

To determine the fluoride content in snow melt water in the vicinity of Krasnoyarsk aluminum production plant northern-eastern site of the impact area was chosen. In our case, the choice of sample points with regard to landscape, meteorological conditions, and urban development [18] is a special task. Snow sampling was performed in northern-eastern site of aluminum plant as pollutants are transported here in the prevailing wind direction. Besides, there are not any other pollution sources around the plant. In 2013 in the vicinity of Krasnoyarsk aluminum production plant samples were taken at the distance of 1, 2, 3 km to the north-east from the borders of the plant, since the previous research had shown the most intensive accumulation of fluoride in melt water just within the radius 1-3 km from production sites of this aluminum production plant [6, 11, 13-17]. In 2014 snow samples were additionally taken at the distance of 8 and 13 km from the plant. In total, 8 snow samples were taken over the monitoring period.

The previous research in snow pollution of Tomsk territory showed that the dust distribution zone with chemicals from stacks of coal and gas-fired power plant is located in the north-east at the distance of 2 km [19]. Therefore, in the territory of Tomsk, snow sampling (the number of samples is 5) was performed in the northern-eastern impact area of Tomsk coal and gas-fired power plant at the distances of 0.7; 1.0; 1.3; 1.6 and 2.0 km from coal and gas-fired power plant stacks. The thermal power plant operates on Kuznetsk basin coal and natural gas. The main share of coal (up to 80 – 90 %) of the total annual amount is burnt during the winter period – from November till March. The height of stacks is 100 m that contributes to emission distribution over the town territory.

Each sample was taken according to [18] snow in-depth with the exception of 5 cm layer over the soil to avoid sample contamination with soil particles. To take samples plastic bags and non-metal bucket were used. In the course of sampling the width and length of pits were measured, the sampling dates were registered. Then samples were taken to the laboratory, where snow was melted in plastic bowls at room temperature. After melting samples were filtered, separating solids, and content of fluoride ion content in filtered melt water was determined.

Fluoride ion content in the samples of snow melt water was determined by potentiometric technique using the device Anion 4100 with fluoride-selective electrode according to [20]. Satisfactory convergence of fluorescent analysis results is shown. The low detection limit amounts to  $0.05 \text{ mg/dm}^3$ .

## 3. Results and discussion

The data analysis has shown that in 2012 in the impact area of Tomsk coal and gas-fired power plant the maximal value of fluoride ion content was revealed in samples taken 2 km from the stacks of the plant (table 1). In 2013 the values of fluoride ion content in snow melt water did not exceed the detection limit in all sampling points. In the samples taken in 2014 and 2015 fluoride ion content did not sufficiently change with the distance from the plant. Fluoride ion content in the samples taken in 2015 is 2-5 times higher than that of the samples taken in the period from 2012 to 2014. During the whole monitoring period the fluoride ion loading rate in the study area changed from  $0.46$  to  $8.27 \text{ mg/m}^2$  per month, the maximum values being recorded in the samples of 2015. Remarkable changes in fluoride ion content in melt water and fluoride ion loading rate at the distance from the stacks of coal and gas-fired power plant were not observed over the whole monitoring period.

In 2015 the elevated concentrations of fluoride ion content in the samples and fluoride ion loading rate in the study area could be explained by the climatic conditions of that year. The winter of 2015 was characterized by heavy snow falls that could result in more precipitation of fluoride from the air. All values obtained within the four-year period did not exceed maximum permissible concentration in drinking water ( $1.5 \text{ mg/dm}^3$  [21]).

Coal combustion is also one of the principle sources of fluoride in the air [4]. As mentioned above [10], the main part of coal at Tomsk coal and gas-fired power plant is used mostly in winter; hence, water-soluble fluoride compounds in the melt water samples taken in vicinity of the plant are likely to be associated with coal combustion. When coal is burnt, coal can release fluoride compounds which can enter the environment in the form of hydrogen fluoride. The other gaseous compounds, which can be present in the gaseous flow ( $\text{SiF}_4$ ,  $\text{H}_2\text{SiF}_6$ ), are transformed into salts or hydrogen fluoride [4].

**Table 1.** Dynamics of fluoride ion content ( $\text{mg}/\text{dm}^3$ ) in snow melt water and its loading rate ( $\text{mg}/\text{m}^2\text{month}$ ) in the impact area of Tomsk coal and gas-fired power plant between 2012 and 2015.

Distance, km*	2012		2013		2014		2015	
	$C_F^-$	H	$C_F^-$	H	$C_F^-$	H	$C_F^-$	H
0.7	0.03	n.d.	<0.05	0.67	0.09	1.88	0.24	8.27
1.0	0.14	n.d.	<0.05	0.87	0.07	1.22	0.20	7.25
1.3	0.07	n.d.	<0.05	0.59	0.07	1.18	0.26	6.68
1.7	0.08	n.d.	<0.05	0.66	<0.05	0.46	0.24	5.01
2.0	0.20	n.d.	<0.05	0.85	<0.05	0.48	n.d.	n.d.

Note: \* - distance from the stacks of coal and gas-fired power plant to the sampling point;  $C_F^-$  – content of fluoride ion in melt water,  $\text{mg}/\text{dm}^3$ ; H – loading rate of fluoride ion in the territory,  $\text{mg}/\text{m}^2$  per month; n.d. – no data

Table 2 shows fluoride ion content in snow melt water samples from the impact area of Krasnoyarsk aluminum production plant. It was determined that in the samples of 2013 fluoride ion content exceeded maximum permissible concentration in drinking water in 9 times on average. In the samples fluoride ion content exceeded maximum permissible concentration in 5.5 times in 2014. The data on fluoride ion content in melt water are comparable with the previously published data (figure). The results of two-year monitoring show that fluoride ion content in the samples did not sufficiently change at the distance from 1 to 3 km from the borders of aluminum production plant. In 2014 additional study at the distances of 8 and 13 km from the plant borders showed the increase fluoride ion content in 4 times at this distance.

**Table 2.** Dynamics of fluoride ion content in melt water in the impact area of Krasnoyarsk aluminum production plant between 2013 and 2014,  $\text{mg}/\text{dm}^3$ .

Year of sampling	Distance from the plant borders to the sampling point				
	1 km	2 km	3 km	8 km	13 km
2013	13.13	13.76	15.38	n.d.	n.d.
2014	13.83	10.64	11.62	3.88	1.64

Note: n.d. – no data, sampling was not performed

In 2014 the loading rate of fluoride ion in the impact area of aluminum production plant ranges from 13 to 172  $\text{mg}/\text{m}^2$  per month, the maximal loading rate is observed in the sample taken at the distance of 3 km from the plant borders (table 3).

In addition, according to the data obtained it can be stated that water-soluble compounds of fluoride are recorded at significant distances from the emission sources. According to [6, 7, 11, 13-17], the impact radius of large aluminum production plants emissions can reach 30 km.

In snow fluoride content can be conditioned by the peculiarities of water-soluble fluoride compounds transportation in the environment. According to [22] in air gaseous hydrogen fluoride is absorbed by air moisture forming aerosol or smog of hydrofluoric acid solution. Fluoride is removed from the air in the process of wet or dry deposition.

**Table 3.** Loading rate of fluoride ion in the impact area of Krasnoyarsk aluminum production plant, mg/m<sup>2</sup>·per month.

Year of sampling	Distance from the plant borders to the sampling point				
	1 km	2 km	3 km	8 km	13 km
2014	140	58	172	56	13

#### 4. Conclusion

Thus, fluoride contents in melt water and its loading rates in the impact area of Tomsk coal and gas-fired power plant and Krasnoyarsk aluminum production plant are different, which is explained by the plants' specificity. It was shown that the aluminum production plant is a powerful pollution source of snow with fluoride. We have determined that fluoride ion content in snow melt water at the distance of 0.7 to 1 km from the stacks of coal and gas-fired power plant did not change sufficiently over the monitoring period, which can be conditioned by specific air micro-circulation in the city territory because of urban development. In the impact area of Krasnoyarsk aluminum production plant elevated fluoride ion content were identified at the distance of up to 3 km from the plant borders, which could indicate the transportation of fluoride compounds over long distances. The study area is a plain without urban construction that contributes to emission distribution. The data obtained show that fluoride enters the town territory with the study plants emissions with high probability degree. Taking into account high solubility of some fluorides, mainly sodium fluoride, those compounds can pass into soil from snow during snow melt. Therefore, further study should be aimed at the research in content of water-soluble fluoride compounds in soil in the impact area of study plants.

#### Acknowledgment

This work was partly financially supported by the Presidential Grant for young Russian scientists (MK 951.2013.5).

#### References

- [1] Ivanov V V 1994 Ecological geochemistry of elements Book. 2. Main r-elements. Moscow: Nedra, p 303 (in Russian)
- [2] WHO 2002 Fluorides. Environmental Health Criteria **227**. World Health Organization, Geneva
- [3] Lazarev N V 1977 Harmful elements in industry: Reference book. Leningrad: Khimiya. V.III
- [4] Agency for Toxic Substances and Disease Registry (ATSDR) 2003 Toxicological profile for Fluorides, Hydrogen Fluoride, and Fluorine. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service
- [5] Yanin Ye P 1996 Fluoride in drinking water of Saransk town and its hygienic significance. Moscow, IMGRE 51
- [6] Yanchenko N I, Baranov A N and Chebykin E P 2013 Peculiarities and factors influencing distribution of metal, rare-earth elements, hydrogen and fluoride in snow filtrate and solid deposits of Bratsk city *Vestnik of ISTU* **10 (81)** 141–9 (in Russian)
- [7] Bartels-Rausch T et al. 2014 A review of air–ice chemical and physical interactions (AICI): liquids, quasi-liquids, and solids in snow *Atmos. Chem. Phys.* **14** 1587–633
- [8] Zarina L M, Lebedev S V and Nesterov E M 2011 Ecological Geochemical Investigations of the Contents of Heavy Metals in the Snow Cover in the Saint-Petersburg Region with Application of GIS Technologies *Int. J. Chem. Eng. Appl.* **2** 117–20
- [9] Ouellet M 1987 Reduction of airborne fluoride emissions from Canadian aluminium smelters as revealed by snow chemistry *Sci. Total Environ.* **66** 65–72
- [10] Ando M, et al. 2001 Health effects of fluoride pollution caused by coal burning *Sci. Total Environ.* **271** 107–16
- [11] Nikolayeva L A and Turchinova D A 2010 The problem of fluoride pollution of soil in vicinity aluminum production *Yestestvoznaniye i gumanizm* **6** 1 (in Russian)

- [12] Rogovenko E S, Blinnikova N V, Shubin A A and Bondarev LG 2010 Environmental Monitoring of Anthropogenic Pollution of Snow Cover of One of the Industrial Districts of Krasnoyarsk *Journal of Siberian Federal University. Chemistry* **4** (3) 387–94
- [13] Khlebopros R G, Taseyko O V, Ivanova Yu D and Mikhailuta S V 2012 *Krasnoyarsk. Ecological essays* (Krasnoyarsk: SFU) p 130 (in Russian)
- [14] Davydova N V 2014 Problems of environmental pollution in Siberia *Uspekhi sovremennogo yestestvoznaniya* **5**(1) 186–9 (in Russian)
- [15] Znamenskaya T I 2015 Migration and differentiation of pollutants in the steppe landscape in the South of Minusinsk depression Diss. of PhD in Geograph. Sciences Irkutsk p 175
- [16] Tandellov Yu P 2015 Fluoride in soil-plant system Krasnoyarsk 146
- [17] Ecological atlas of Krasnoyarsk city 2012 <http://gis.krasn.ru/blog/ecoatlas/>
- [18] Manual on monitoring of atmosphere pollution 1991 RD 52.04.186 № 2932-83. Moscow Goskomhydromet p 693
- [19] Talovskaya A V, Filimonenko E A, Osipova N A, Lyapina E E, and Yazikov E G 2014 Toxic elements (As, Se, Cd, Hg, Pb) and their mineral and technogenic formations in the snow cover in the vicinity of the industrial enterprises of Tomsk *IOP C. Ser. Earth. Env.* **21** 012042
- [20] Mass concentration of fluoride in water. Methods of measurements using potentiometric technique with ion-selective electrode 2008 RD 54.24.360-2008 Goskomhydromet (in Russian)
- [21] Predelno dopustimye kontsentratsii khimicheskikh veshchestv v vode vodnykh obektov khozyaystvenno-pitevogo i kulturno-bytovogo vodopolzovaniya 2003 GN 2.1.5.1315–03 [Hygienic standards: Maximum permissible concentration of chemicals in water bodies of drinking and domestic cultural water use] (in Russian)
- [22] Arnesen A K M, Abrahamsen G, Sandvik G and Krogstad T 1995 Aluminium-smelters and fluoride pollution of soil and soil solution in Norway *Sci. Total Environ.* **163** 39–53