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Chemical Contamination of Soil on Urban Territories With Aluminum Production in the Baikal Region, Russia

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ABSTRACT: The study was conducted in 2 urbanized areas of the Baikal region of Russia. These are the cities of Shelekhov and Tayshet with their suburbs. Aluminum production has been carried out in Shelekhov for over 60 years and in Tayshet for 5 years. The purpose of the study was to determine the pollution of urban soils with toxic elements—Al, F, Be, Li, as well as Cr, Ni, Pb, and so on under the influence of industrial enterprises (aluminum and cable plants, thermal power plants). Also, the purpose of the research was to determine the effect of increased fluorite (F) in the environment on children's health. Pure aluminum is used much less frequently than in alloys. The addition of various elements (Be, B, Li, Fe, Si, Mg, Mn, Zr, Ag, Pb, Cu, Ni, and others) increases the hardness, density, thermal conductivity, and other properties of the alloys. The area of high F content in urban soil is 15 times higher than the regional context. The maximum content of Na, Be, and Al is 2 to 4 times higher than the regional background. An increased Li content is marked only near aluminum smelters. The F content in urine samples from children living in areas with long-term pollution exposure (Shelekhov) is 1.5 to 2 times higher than in the group of children with a short exposure period (Tayshet).

KEYWORDS: Soil contamination, aluminum smelters, environment pollutants, urban territories, human health

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Introduction

The soil cover is known as the depositing medium capable of accumulating practically all pollutants entering the environment.^{1,2} Therefore, it offers an archive on the geochemical state of the environment. Chemical elements accumulate and migrate in soils due to some factors: type and composition of soils, physicochemical state of the element, forms of occurrence, sorption and migration features, and pH of the liquid phase and soil phase.¹ The urban soils, that is, ground soils, urban earths, and technical earths, represent the soils formed owing to economic activity. In urban territories and suburbs, the anthropogenic contribution to soil formation seems to be critical, so distinct soil horizons are not observed. At present, soils are factually a complicated natural-anthropogenic system due to the long-term inflow of toxicants caused by industrial production.²⁻¹⁰

Aluminum production has been continuously growing worldwide because this element is actually irreplaceable in diverse industries.¹¹ Aluminum is derived from a rock with a complex composition—bauxite. First, alumina (Al₂O₃) is obtained from bauxite. Then from alumina as a result of electrolysis in the melt of fluoride salts at a temperature of about 950°C, the main component of the melt, cryolite, is obtained. Cryolite is Na₃AlF₆ salt.^{7,12,13} Russia is the world leader in aluminum production, with more than 10 factories in different cities (Irkutsk, Bratsk, Krasnoyarsk, Sayansk, Novokuznetsk, Volgograd, Volkhov, Kandalaksha, etc).^{14,15} Many papers have been published on environmental pollution around aluminum

plants in Siberia.^{5,6,8} Most of the aluminum produced in Russia is sent abroad. China, Russia, and India are in the leading positions in aluminum production in the world.^{12,14,16}

In the process of electrolysis, aluminum is deposited in special electrolysis baths. In its pure form, aluminum is used much less frequently than in the form of alloys.¹⁷ The alloys additionally contain various elements that increase their hardness, density, thermal conductivity, and so on.¹⁸ For this purpose, Be, B, Li, Fe, Si, Mg, Mn, Zr, Ag, Pb, Cu, Ni, and other elements are used. All of the above elements, which exceed the regional background content¹⁹ or the city clark²⁰ (Table 1), are to some extent toxic to humans, as evidenced by numerous publications.^{12,21-28} They can accumulate in the human body for a long time and exceed the concentration (dose) necessary for life.²¹ It is known that fluorine and its compounds have a narrow range of physiological optimum, which requires special attention to the problem of health effects.²² Fluoride exposition can have some negative physiological effects, for example, nephrotoxicity,²³ thyroid dysfunction,²⁴ cardiometabolic risk,²⁵ neurodevelopmental disorder in children,^{26,27} and reproductive endocrine disruption.²⁸

Rare articles have reviewed potential health hazards that may also pose health risks²⁹ to some communities because of their proximity to aluminum smelters.^{21,30,31} They pinpoint that there is a potential for materials such as sulfur dioxide, particulate matter, fluorides, and beryllium capable of posing health risks to communities.²¹ Its toxic action is insignificant; however, many water-soluble inorganic compounds, as well as its satellite elements F, Be, and Li, are long-preserved and



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Table 1. Element concentrations in the soil cover of Shelekhov and Tayshet towns.

ELEMENTS	SHELEKHOV AND ITS ENVIRONS	TAYSHET AND ITS ENVIRONS	REGIONAL BACKGROUND OF BAIKAL REGION ¹⁹	CLARKE URBAN SOILS IN CITIES ²⁰
Al, %	$\frac{5.8 - 8.7}{7.2}$	$\frac{4.0 - 8.0}{6.6}$		3.82
K, %	$\frac{1.2 - 1.7}{1.6}$	$\frac{1.0 - 2.8}{1.9}$	1.7	1.34
Na, %	$\frac{1.0 - 1.9}{1.6}$	$\frac{0.8 - 1.9}{1.5}$		0.58
Fe, %	$\frac{4.2 - 6.7}{5.4}$	$\frac{1.4 - 4.4}{3.1}$		2.23
Mg, %	$\frac{1.3 - 1.9}{1.6}$	$\frac{0.5 - 1.2}{0.9}$	1.9	0.79
Ca, %	$\frac{1.5 - 5.4}{2.7}$	$\frac{1.4 - 4.6}{2.1}$	2.2	5.38
Li, mg/kg	$\frac{24 - 54}{32}$	$\frac{10 - 34}{22.5}$		49.5
Be, mg/kg	$\frac{1.5 - 12.0}{2.5}$	$\frac{0.9 - 2.1}{1.5}$	3	3.3
F, mg/kg	$\frac{520 - 2100}{860}$	$\frac{280 - 750}{450}$	140	
Ni, mg/kg	$\frac{23 - 55}{40}$	$\frac{10 - 46}{30}$	44	33
Co, mg/kg	$\frac{6 - 19}{14}$	$\frac{6 - 22}{13}$	17	14.1
Cr, mg/kg	$\frac{42 - 160}{97}$	$\frac{46 - 110}{77}$	100	80
V, mg/kg	$\frac{41 - 130}{84}$	$\frac{58 - 130}{94}$	100	104.9
Mo, mg/kg	$\frac{0.6 - 1.4}{0.9}$	$\frac{0.7 - 1.6}{1.2}$		2.4
Cu, mg/kg	$\frac{14 - 71}{29}$	$\frac{6 - 74}{27}$	51	39
Zn, mg/kg	$\frac{47 - 120}{68}$	$\frac{23 - 180}{69}$	84	158
Pb, mg/kg	$\frac{17 - 110}{31}$	$\frac{10 - 36}{17}$	10	54.5
B, mg/kg	$\frac{5 - 130}{29}$	$\frac{13 - 110}{31}$		45
S, mg/kg	$\frac{100 - 1760}{400}$	$\frac{100 - 400}{150}$		1200
Number of samples	30	38	712	> 8000 (from 300 cities of different countries)

Numerator—minimum-maximum; denominator—average. Bold content above regional background and clark for soils of cities in different countries.

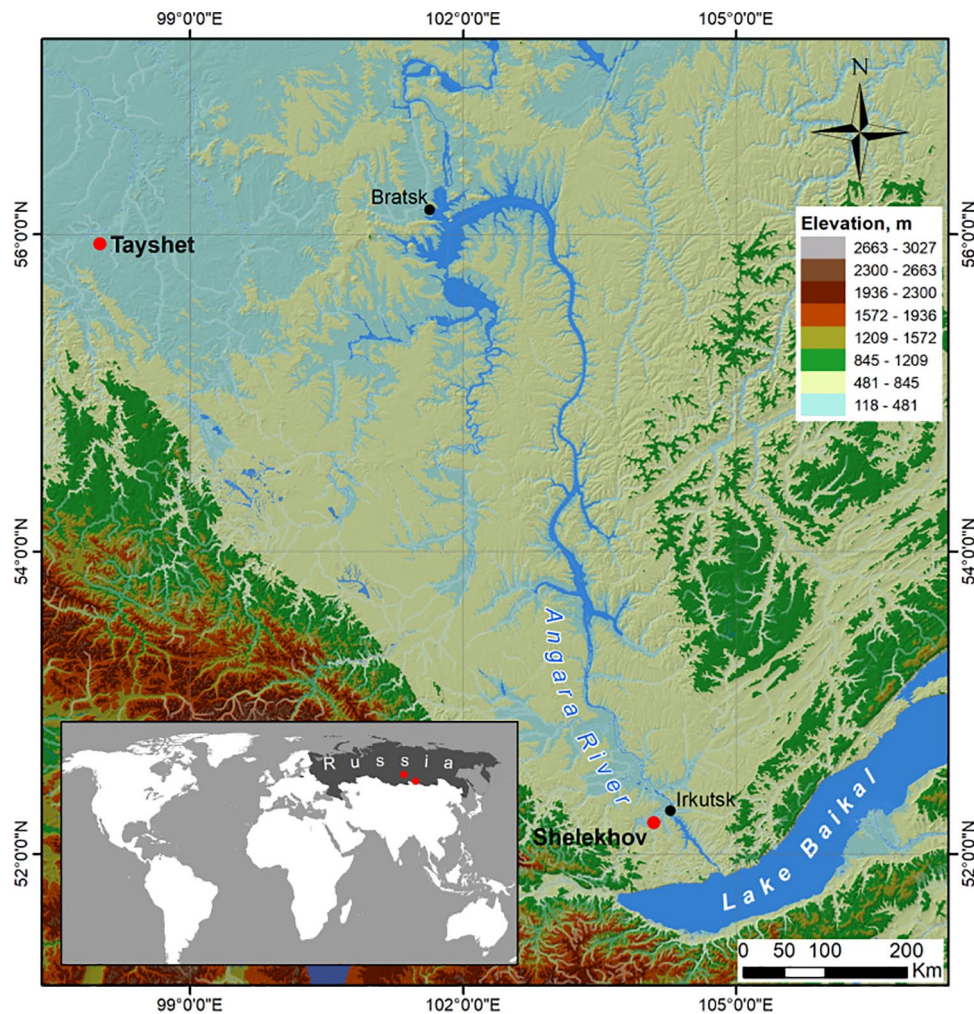


Figure 1. Overview map of the location of cities with aluminum production in the Baikal region (Russia).

might harmfully affect a human being and homoiotherms through drinking water, food, and soil.^{32–38}

Recently, the problem of environment-safe aluminum production has been given serious concern.³⁹ At the Shelekhov aluminum smelter, the production lines have been modernized, up-to-date equipment has been installed, and atmosphere-polluting emissions have been markedly reduced. In the Tayshet region, it was envisaged to employ modern facilities with updated gas purification and minimal release of toxicants into the environment. However, different environment components and the health of the population need to be continuously monitored. Industrial emissions from aluminum electrolysis plants contaminate the environment of adjoining residential areas (particularly where the use of Soderberg anodes continues), demonstrating an association with considerable impairment to the health of newborns.^{40–42}

Thus, the main purpose of this study was to identify additional inflow of toxic elements into the environment, compared with their regional background content, due to the existing and under construction aluminum smelters and providing them with thermal power plants that supply them with electricity. The work aims to identify pollution in areas with aluminum

production: the city of Shelekhov with 60 years of industrial operation and the city of Tayshet with a pilot production.

Materials and Methods

Study area

The study objects are the soils of urban ecological systems of the Baikal region housing operational aluminum plants, for example, at the towns Shelekhov and Tayshet (Figure 1).

Shelekhov is located in the interfluvium of the Irkut and Olkha rivers and is a small industrial town in the Baikal region founded back in 1956 during the construction of the Irkutsk Aluminum Plant (IrkAZ). The city is located 15 km southwest of the Irkutsk regional center (Figure 1). The industrial trends of this town are determined by nonferrous metallurgy, for example, IrkAZ and cable-producing plant, heat power engineering, and construction materials production. The flatlands of the suburbs are basically taken up by agriculture and collective vegetable gardens. Virgin pinery still grows within the town itself.

The operating aluminum smelter and its environment have for a long time been under research monitoring; therefore, extensive information was collected on the chemical state of some

environmental components, for example, snow and surface water.^{19,43} The primary aluminum is produced from imported raw alumina. The capacity of the smelter (annual production capacity of 419 000 tonnes)⁴⁴ is much higher than internationally required standards for environmental protection.⁴⁵

Tayshet is located in the northwest (NW) of Irkutsk Region, 675 km from the Irkutsk regional center, on the right side of the Biryusa River, in the interfluvium of its tributaries Tayshetka and Akulshetka Rivers (Figures 1 and 3). Approximately 10 km NW of Tayshet, there is a small town Biryusinsk. In the northeast (~7 km), the territory between Akulshetka and Baironovka Rivers was picked for a new aluminum smelter and anode-producing factory. The basic enterprises of Tayshet town are railway engine house, a sleeper factory, as well as printing, construction, and forestry industries.

As regards the geological characteristics, in these urban territories can be registered Jurassic rocks, for example, sandstone, siltstone, conglomerate, breccia, and coal deposits, used in power engineering in the Baikal region.⁴⁶ Beyond these towns, the soil cover largely consists of gray woody, sod-carbonate and sod-podzolic soils; the river valleys are covered with meadow-boggy soil.⁴⁷ As it was found out, the urban soil contains a wide range of chemical elements of natural and technogenic origin, as it represents the medium favorable for absorption.⁴⁸ In the towns and beyond, the territories are occupied with coniferous (pine) and mixed forests; in the river valleys, some places are devoid of forest and are mostly occupied by grassland.

On the study territories, the mean annual temperatures of air, water, and soil are commonly low (0°C), dropping to -40°C in winter.^{19,47} Thus, they are marked by the continuous freezing of environmental components, at times for 5 months, which might explain their lowered capacity for self-purification from the anthropogenic effect.⁸ The samples were taken from the urban soils of diversely functioning zones: industrial, residential, natural-recreation, and soils from town suburbs.

Soil mapping techniques

Soil sampling was carried out in 2 towns from 2012 to 2014 at a scale of ~1:100 000 spaced 1 × 1 km and further thickened to 500 × 500 m at mostly problematic sites, such as the location of sludge from production and places of unloading of raw materials. The soil samples were taken by an envelope-like mode from the surface of humus-accumulative layer about 2 to 10 cm thick. Samples are stored and transported in kraft-paper bags. The weight of the sample is 1 kg; after drying, sieving, and quartering, 200 g remains for analysis.

Preparation of soil samples for analysis was carried out according to a standard procedure:⁴⁹ drying in a well-ventilated room at room temperature, sieving through a nylon screen with a 2-mm mesh size, quartering to obtain the main sample and duplicate, taking the quartering samples weighing 150–200 g, abrasion to size 200 mesh in an abrasive with reinforced

alumina ceramics, and taking the samples necessary to transfer to the appropriate types of analysis.

Laboratory analysis

To determine the total content of elements in the soil, a soil sample is transferred to a solution. To do this, a portion of the soil (0.1–1.0 g) is treated with a mixture of acids (hydrofluoric, perchloric and nitric), the resulting solution is evaporated to wet salts, and the residue is dissolved in 5% hydrochloric acid. In the resulting solution, the elemental composition of the soil is determined by atomic absorption spectrometers of model 403 and 503 manufactured by Perkin-Elmer (USA). The study of the forms of finding elements in the soil has been conducted earlier.⁴³

Analysis of soil samples for fluorine was carried out by an individual method of arc atomic emission analysis using injection-dredging. This method is applied for the quantitative chemical analysis of gross content of soils by arc atomic emission spectrometry with photoelectric spectra recording and the introduction of matter into the arc discharge by the method of injection-dredging. The correctness of results was confirmed by an analysis of standard samples of soil,⁵⁰ which are available at the A.P. Vinogradov Institute of Geochemistry SB RAS, Irkutsk. The samples were analyzed with research equipment of the Center for Collective Use “Isotope-geochemical research at IGC SB RAS” at the Irkutsk Science Center.

The study was conducted in accordance with the Helsinki Declaration.⁵¹ The program for child observation was approved by the Ethics Committee of the East-Siberian Institute of Medical and Ecological Research. Besides, formal consent was obtained from the parents of the observed children, who received physical examinations and blood and urine workups. All participants were healthy without urinary tract obstruction and any other systemic and acute diseases. In all, 469 urine samples of children aged 5 to 17 residing in Shelekhov and Tayshet have been analyzed in the range of 2012–2014. Urinary fluoride excretion was assessed by a potentiometric method on a spot morning urine sample, and information on exposure factors was obtained by questionnaire. In accordance with current recommendations as to the permissible level of fluoride in urine, the value of $20.0 \pm 4.9 \mu\text{mol/L}$ was adopted—in hair up to 150 mg/kg.⁵² This was a long-term cohort study of fluoride measured in the urine of Tayshet-inhabiting children (as the indicators of an individual pre-exposed and exposed to fluoride, respectively) in the age groups 5–7, 8–10, and 11–17 years (Table 2).

Statistical analysis

Statistical analysis distribution pattern was verified using the Shapiro-Wilk method. They were tested statistically by analysis of variance (ANOVA) to compare the means of the outcome or

Table 2. Fluorine content in urine of children from industrial centers of Baikal region, $\mu\text{mol/L}$.

TOWN, GROUP OF CHILDREN	N	AVERAGE VALUE	MEAN VALUE ERROR	MODE	MINIMUM	95TH PERCENTILE
5-6 years						
Shelekhov	97	68* $P=--000$	3.0	58	15	135
Tayshet	133	30	2.9	51	15	121
7-10 years						
Shelekhov	66	63* $P=--000$	2.8	59	14	118
Tayshet	55	31	3.2	49	15	139
11-17 years						
Shelekhov	75	45* $P=--152$	2.5	35	26	66
Tayshet	43	40	2.4	22	20	60

Abbreviation: n, number of observations.

* P : statistical significance of differences after the Student test.

exposure within the groups defined according to the distribution of each covariate. The Spearman correlation coefficients (r_{xy}) were referred to when measuring the correlation between soil and urinal fluoride in the cohorts. The regression models were assigned to assess binding between pre-exposed and exposed fluoride. The statistical significance between groups was evaluated through the Student t test on P level of .05. Acquired results were processed with the software package Statistica.v.8.

Results and Discussion

Elements—toxicants in the soil of the cities with aluminum production

In the soil cover of Shelekhov and Tayshet towns, the contents of the main macrocomponents Ca, Mg, Fe, K, Na, and Al are fairly similar (Table 1), showing they belong to the same structural zone of the Baikal region and occur within the same formation of Jurassic soil-forming rocks. The concentrations in soils of S, Pb, and other items and satellite elements of aluminum production (F, Li, Be, etc) reveal contrasting differences. Maximum values are recorded in the soils of Shelekhov town, being in excess of the regional background values of Baikal region¹⁹ and clarkes of urban territories.^{19,20,53} The contents of the other toxic elements like B, Cr, Ni, Co, V, Mo, and Zn are common for the clarkes of urban soils, sometimes exceeding them and regional background values (Table 1).

Cities with aluminum production in the Irkutsk region

Now we look upon the areal distribution of some element concentrations within soils of the towns and suburbs considered herein.

Shelekhov. This region is distinguished by the presence of high Al, Li, Be, and F concentrations in soils (Table 1), that is,

chemical elements indicating the presence of the aluminum industry located close to the town territory. The high content haloes of toxic elements generally coincide; they merely differ in some detail in their configuration (Figures 1 and 2). The latter is the case due to the varying migration abilities of elements. The chemical elements penetrate the soil cover through wind transfer of the primary raw material from discharge sources, accumulation of the industrial products in snow cover, snow melting, accumulation of snow in solid sediment,^{43,48} and further entry into soil. High Al, Be, Li, F, and Na abundances and some other elements (from 2 to 20 times in excess of background ones and RPC and MPC_{soil}) are recorded at the entry to the plant territory, around it, and in the zone suitable for the wind rose of this territory (Figure 2). The impact of the aluminum plant may spread pollution of soil for 15 to 25 km, depending on wind direction and force. As a result, the halo of Al, Be, and F contamination around Shelekhov is NW- to SE-directed within the interfluvium of Olha and Irkut Rivers. The halo of high F contents in the urban soil is 15 times more than the regional background of soils (Table 1); maximum values are measured for the haloes of Na and Be; Al is 2 to 4 times higher than the regional background and clarkes of urban soils. The Li contents are not much in excess; they are, however, higher, closer to the aluminum plant area.

In addition to the enumerated elements for soils of Shelekhov territory and its suburbs, high concentrations of some toxic elements were measured: for example, B, S, Cr, Ni, Co, Cu, Pb, and Zn, as well as U and Th. They might be due to the effect of effluents of thermal power plant^{54,55} and cable plant because there are no other large industrial enterprises in the city. The abundances of some toxicants exceed the clarkes of urban territories (Table 1). The total area of the geochemical halo of elevated contents of toxicant elements can reach 200 to 400 km² (Figure 2).

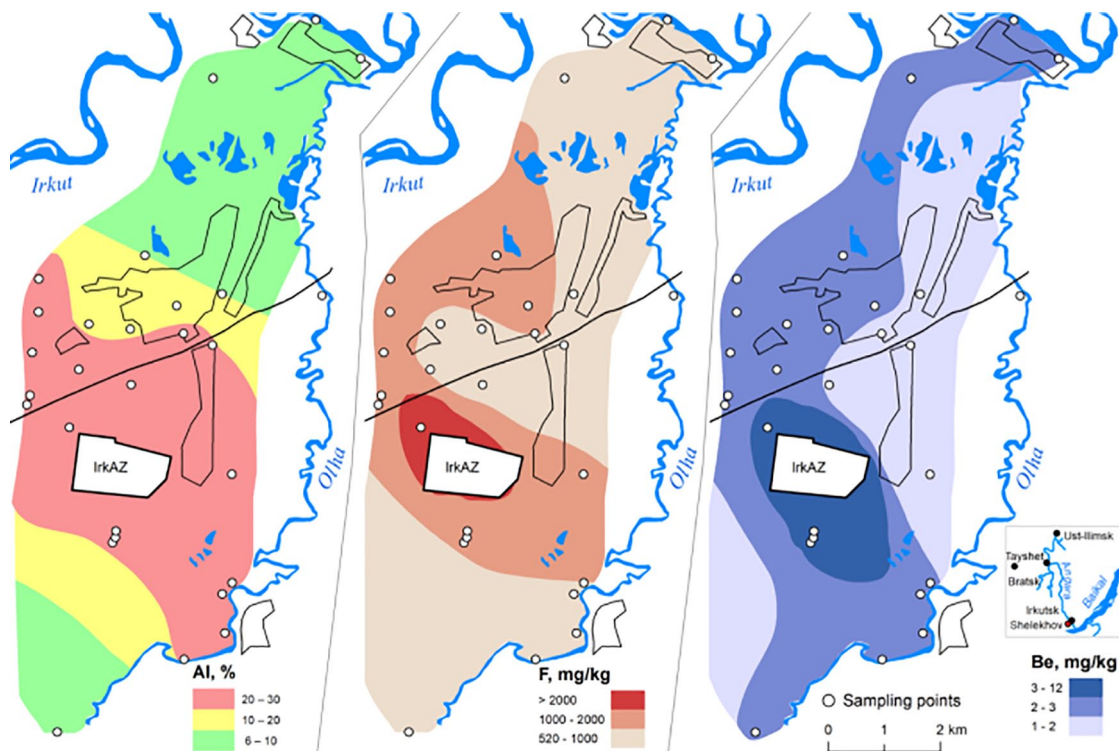


Figure 2. Distribution of Al, F, and Be contents in the soil cover of Shelekhov and its environs.

The obtained data of element contents in the soil of Shelekhov are confirmed by the work of other researchers in Russia^{5,7,26,27} and in other regions of the world.^{10,32–34} The soil cover survey shows the presence of contaminating chemical elements in its composition, which might result in their accumulation in the adjacent areas, in the composition of agricultural crops, biological substrate, that of the human one inclusive as noted by other researchers.^{34,56,57} The minimum and maximum contents of some toxic elements in soils around aluminum and anode plants being built close to Tayshet town are markedly similar to those of Shelekhov (Table 1). But the content of F is lower because it takes longer to accumulate in the soil.

Tayshet. The construction of a plant near Tayshet began in 2008. The pilot smelter was operating for 3 years; later its work was stopped and recently recommenced again. The evidence of its effect on the chemical composition of soil cover is already noted. The abundances of Al and Na in soils seem to be nearly the same as in Shelekhov. The minimal values of the metals Cr, Ni, Co, V, Cu, and Mo occur at the same level of values. In Tayshet, when compared with the Shelekhov area, the maximum values of heavy metal concentrations are noticeably higher than the clarkes for urban soils.²⁰ The Pb and S contents are measured as essentially lower.

In the Tayshet region, the plant under construction is placed in the interfluvium between the Biryusa, Akulshetka and Baironovka Rivers; the wind rose blows in the NW-SE direction. Around the plants under construction, the haloes of increased Al and its satellite elements F, Be, and Li look

elongated; they are found between the Akulshetka and Baironovka Rivers (Figures 3 to 5). However, their maximum values are determined as minimal values marked in the soils of Shelekhov town and its suburbs, which could indicate the initial stage of territory pollution. It should be noted that the increased contents of the elements, being satellites of aluminum production, were measured in the soil cover of Tayshet town, where the raw materials for Al production had been supplied to.

Relatively increased contents of the elements such as B, S, Zn, and Pb and those of metal Cr, Ni, Co, and V are typical of the soils of the urban territories of Tayshet and Biryusinsk, which typify towns with developed railway and motor-car transport, heat stations, coal boilers, and treating enterprise. In the Tayshet region, these element contents are higher than the regional background values, but they are closer to the soil clarkes of urban territories (Table 1).

From yearly observations on admixture contents in soils at the towns housing operational aluminum industries, the F compounds are priority pollutants.^{58–60} Maximum fluorine concentrations enter the human body through foodstuff and water, but in the zones of man-made pollution an important route of impact is atmospheric air, and in child groups it is soil.^{37,38,61,62} The study of the relationship between the F compound contents in the surface soil horizon and snow cover (Figure 5) points to a direct and strong relation ($r_{xy} = 0.76$, $P < .05$) (Figure 6). The coefficient summation ratio of the content in the atmosphere of solid fluorides and hydrofluoride to their MPC (K_{sum}) was calculated in the study.³⁶ Between F content in soil and calculated values of

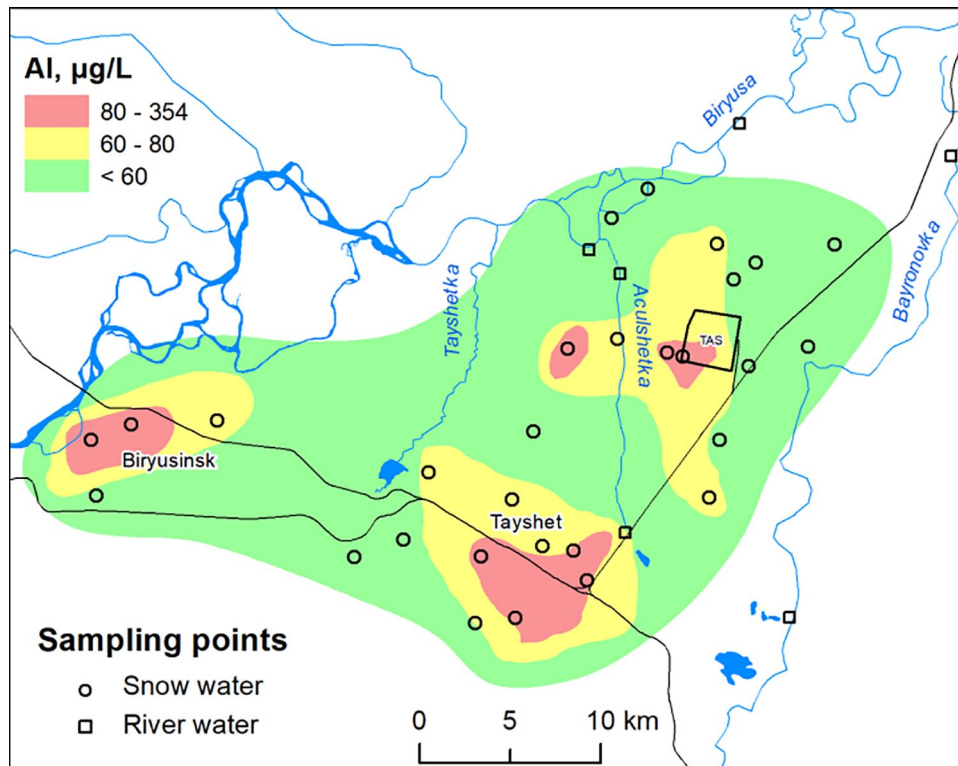


Figure 3. Distribution of Al contents in the soil cover of Tayshet and its environs.

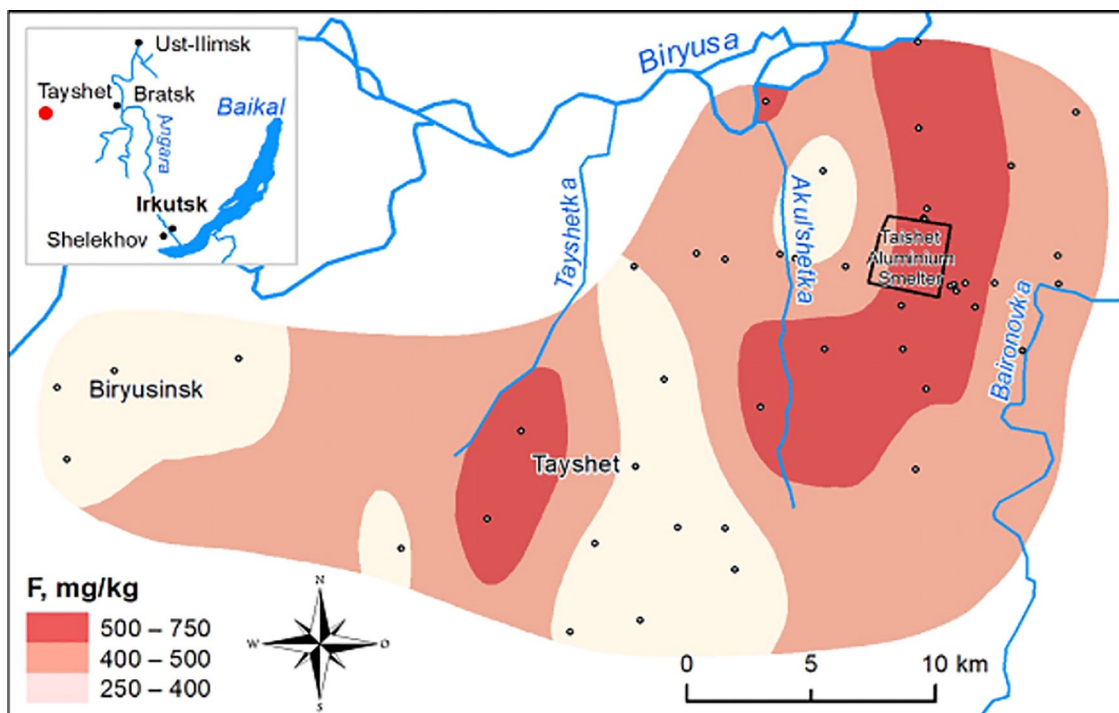


Figure 4. Distribution of F contents in the soil cover of Tayshet and its environs.

air pollution, the correlation coefficients display the relations of medium force with K_{sum} ($r_{xy}=0.49$, $P<.05$; solid fluorides $r_{xy}=0.52$, $P<.05$; hydrofluoride $r_{xy}=0.47$, $P<.05$). The relationship between fluorine accumulation in deep soil and surface layers is presently featured by the tendency ($r_{xy}=0.37$, $P<.1$).

Acquired data indicate that the soil cover around the aluminum smelter in Tayshet shows geochemical specifics and already experiences anthropogenic impact. Having defined the genesis of sites of enhanced pollutant abundances, either natural or technogenous one might employ the obtained data for recognizing ecologically unfavorable zones and priority toxicants in

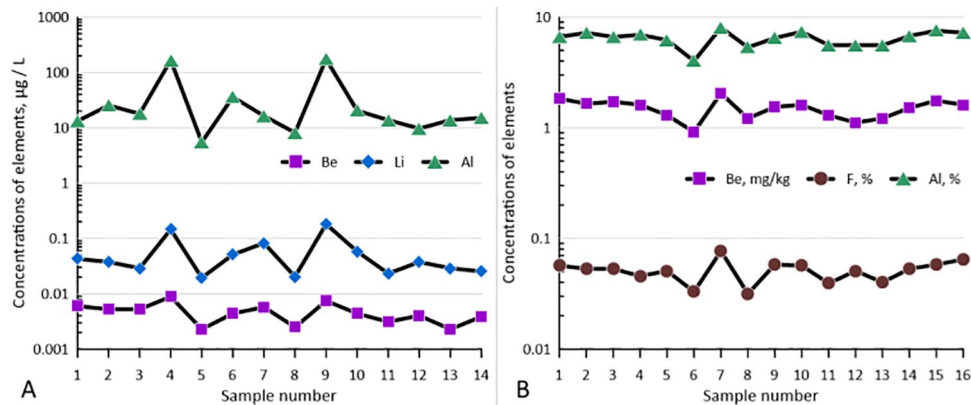


Figure 5. Correlation of element contents in the environmental components around the Tayshet aluminum smelter: (A) in snow water ($\mu\text{g/L}$) and (B) in soil (mg/kg) cover.

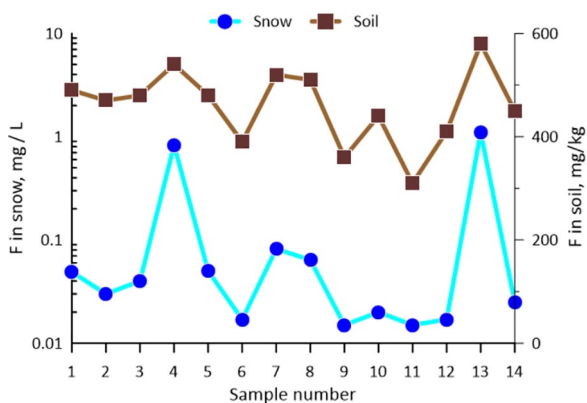


Figure 6. Correlation of F content in snow water (mg/L) and in soil (mg/kg) around the Tayshet aluminum smelter.

the urban territory; substantiation and realization of the measures focused on health preservation. The excess of the content of elements (above MPCs) is characteristic not only of soils in the environment of smelters but also affect nearby residential areas of cities, for example, in Norway,⁵⁸ Spain,⁶³ and Russia.^{36,56}

Fluorine (F) contamination of urban child populations

Contamination of soil at the residential zones may cause penetration of toxic admixture into the human body. In Shelekhov, in a 10-year period, the daily intake of fluorine and its compounds from soil for adults is on average 0.4 mg/kg , that is, 20% of the required average daily dose of fluorine; for children, it is 1 mg/kg per day, that is, 67% of the required average daily dose of fluorine. In Tayshet, these values were not in excess of 5.5% and 25% of the daily rates (Table 2).

The average F-ion content in the children of Shelekhov at the age of 5 to 7 years was 68 ± 3.0 and at the age of 7 to 10 years was $63 \pm 2.8 \mu\text{mol/L}$ ($P > .05$) (Table 2). In groups of children of Tayshet, the concentrations were 30 ± 2.9 and $31 \pm 3.2 \mu\text{mol/L}$ ($P > .05$). When comparing the levels of fluorine excretion in children at Shelekhov and Tayshet, it was revealed that in groups

with prolonged exposure the excretion of F-ions is significantly higher than in children residing in the territory of recently located emission sources ($P = .000$). The World Health Organization (WHO) suggests a reference value of 1 mg/L for healthy adults when monitoring renal fluoride excretion in community preventive programs.⁶² It should be noted that at Shelekhov children show the 95th percentile of fluoride excretion above the level recommended by the WHO as safe. The average values are lower than in the regions of high natural fluoride content in water, such as Pakistan,⁶⁴ China,^{61,65} Sri Lanka,³² and Ethiopia.⁶⁶ Remarkably, on the territories of smelter placement, the researchers identified significant differences in the level of child and youth sickness rate: for example, increase in the rate of bone-and-muscle sickness in children by 5.6 times and in adolescents by 12 times compared with unexposed groups.⁵⁶

In comparing the groups of adolescents, no statistically important differences were recognized. This is possibly due to the lower significance of the channel of toxicant transfer to adolescents because no direct contact was the case.

With the cohort study, the researchers evaluated the dynamics of fluorine excretion in urine in the residents from a formerly unexposed territory, and it was established that, prior to launching pilot smelter in Tayshet, the primary observation of children assessed showed an average concentration of $15.9 \mu\text{mol/L}$. After commissioning the enterprise, the concentration increased to $38.1 \mu\text{mol/L}$; in 89% of children, the F abundance in urine was much in excess of the regional background level. Maximally high values (over 95 percentile) varied from 97.8 to $140.2 \mu\text{mol/L}$ (Table 2). Dynamics of F-ion excretion, following from the data of linked samples, shows nonlinear dependence and is described by the equation $y = -0.03x^2 + 0.314x + 0.045$ (approximation coefficient $R = 0.87$, $P < .05$). Interestingly, after stopping raw aluminum production, fluorine is being eliminated from the human body during 2 years at a level having no statistically important differences with the indices at low exposure. The obtained results point to the possible capacity of fluorine to

accumulate in the body and then gradually move away. In comparing the average-group levels of F-ion excretion in urine in children, some differences were observed depending on the distance of residence from the source of F-compound emission. In the groups of exposed people, the median of F-ion excretion is higher than in contemporaries and the residents of a conventionally clean region—1.2 times in preschool children and 1.6 times in schoolchildren ($P < .05$). It should be noted that significant differences in the level and structure of certain situations among children and adolescents, such as an increase of 5.6 times in the incidence of musculoskeletal ailments in children and 12 times in adolescents compared with unexposed groups, have been found in the territories housing aluminum plants.⁵⁶

Different studies have shown that the aluminum industry discharges fluoride into the air, and several studies have shown a slight but significant contribution to the intake of fluoride by children living around aluminum smelters.^{30,31} The research³⁰ found that fluoride excretion decreases with age in children ($r = 0.31$), but the authors do not discuss any interfering factors, for example, dental treatment with fluoride-containing drugs or the use of bottled water with fluoride. In a different country, total fluoride intake, urinary excretion, and consequently fluoride retention no longer reflect residence in a community with a nonfluoridated or fluoridated water supply^{67,68} because of fluoride toothpaste of 57%, 35%, and 47% for children receiving low, suboptimally, and optimally fluoridated water, respectively.⁶⁹ Considering the wide variations in the F concentrations of different foods and drinks, it is important to assess differences in F intake and consequently fractional urinary F excretion in children.⁷⁰

Thus, the nonspecific changes revealed in the health of children and the data on biological monitoring necessitate further monitoring of the situation from individual and population (statistic) data. To optimize preventive measures, it is reasonable to develop prognosis of health measurements regarding the data acquired through perennial observations in the territories where similar industrial enterprises operate.

Conclusions

The chemical survey of soils conducted in the urban territories housing aluminum industries identified contamination and degradation of soil cover. The comparison reveals similarities and differences in the content of Al, F, Be, and Li around aluminum plants. Other toxic elements (Pb, Zn, Cu, Cr, Ni, V, etc) accumulate in the soil due to the impact of thermal power plants that serve the aluminum smelter and city and can be fixed at a distance of 25 km from the emission source. The geochemical halo of pollutants in the city of Shelekhov can reach 200 to 400 km². Maximal elevation of element contents (above MPC_{soils}) is common for the soils occurring close to plants and neighboring residential areas.

The fluorine content in the urine samples of children living in areas with long-term pollution by emissions from an aluminum smelter is 2 times higher than in the group of children from the territory of the new development. In the exposed children, the median of F-ion excretion is higher than in the residents of the unexposed territory—1.2 times in preschool children and 1.6 times in schoolchildren. Although urinary fluorides may be used for exposure surveillance, additional details on individual exposure agents and patterns of exposure over time are required for a complete assessment.

Toxic substances from industrial pipes can travel up to 25 km and have long-term effects on environmental components such as soil, air, water, and food. It is harmful to public health due to the inhalation and ingestion of toxins by humans. The location of industrial sources in urban areas creates zones of soil pollution, oriented along the wind rose.

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REFERENCES

1. Brevik E, Slaughter L, Singh B, et al. Soil and human health: current status and future needs. *Air Soil Water Res.* 2020;13:1-23. doi:10.1177/1178622120934441.
2. Naprasnikova EV. Biochemical features of soil of industrial city under the conditions of Eastern Siberia. *Chem Sustain Dev.* 2014;22:483-488.
3. McIlwaine R, Doherty R, Cox SF, Cave M. The relationship between historical development and potentially toxic element concentrations in urban soils. *Environ Pollut.* 2017;220:1036-1049. doi:10.1016/j.envpol.2016.11.040.
4. Butakov E, Kuznetsov P, Kholodova M, Grebenshchikova V. Mercury in soils of the agro-industrial zone of Zima city (Irkutsk oblast). *Eurasian Soil Sci.* 2017;50:1354-1361.
5. Makukhin V, Yanchenko N, Baranov A. Study of the processes of distribution, transformation and deposition of fluorine and sulfur compounds in the region of the city of Bratsk [in Russian]. *Atmos Ocean Opt.* 2010;23:525.
6. Yanchenko N, Baranov A, Koroleva G, Makukhin V. Atmospheric deposition in the area of influence of aluminum plants in Priikalye [in Russian]. *Life Saf.* 2010;46-52.
7. Anshits AG, Polyakov PV, Kucherenko AV, Kryukovsky VA, Safarova LA. Environmental aspects of aluminum production by electrolysis. Analytical review [in Russian]. Novosib GPGTB SB USSR. Published 1991.
8. Naprasnikova EV, Istomina EA. Investigation and mapping of the ecologico-biochemical properties of soils in the city of Sayanogorsk [in Russian]. *News Irkutsk State Univ Ser Sci Earth.* 2016;18. <http://izvestiageo.isu.ru/en/article?id=304>.
9. Rodrigo-Comino J, López-Vicente M, Kumar V, et al. Soil science challenges in a new era: a transdisciplinary overview of relevant topics. *Air Soil Water Res.* 2020;13:1178622120977491. doi:10.1177/1178622120977491.

10. Rodriguez J, Heo J, Park J, Lee S-S, Miranda K. Inorganic pollutants in the water of Midland and Odessa, Permian Basin, west Texas. *Air Soil Water Res.* 2019;12:1178622119861089. doi:10.1177/1178622119861089.
11. Brown T, Idoine N, Raycraft E, et al. World mineral production 2012-16. <http://nora.nerc.ac.uk/id/eprint/519784/>. Published 2018.
12. Brough D, Jouhara H. The aluminium industry: a review on state-of-the-art technologies, environmental impacts and possibilities for waste heat recovery. *Int J Thermofluids.* 2020;1-2:100007. doi:10.1016/j.ijft.2019.100007.
13. Vas K. Using technology and automation for enhanced returns in aluminium scrap processing. Paper presented at: Proceedings of the 21st International Recycled Aluminium Conference; November 3-5, 2013. <https://www.metalbulletin.com/events/download.ashx/document/speaker/6614/a0ID000000X0joZMAR/Presentation>.
14. RUSAL. Geography. <https://rusal.ru/about/geography/>. Accessed December 8, 2020.
15. Portnov AM. Aluminium is everywhere. .where? *Nature.* 2020;7:57-65. doi:10.7868/S0032874X20070078.
16. UC RUSAL. The history of aluminium industry. All about aluminium. https://www.aluminiumleader.com/history/industry_history/
17. Davis JR, ed. *Aluminium and Aluminum Alloys*. Materials Park, OH: ASM International; 1993.
18. Rambabu P, Prasad NE, Kutumbarao V, Wanhill R. Aluminium alloys for aerospace applications. In: Prasad NE, Wanhill R, eds. *Aerospace Materials and Material Technologies*. Singapore: Springer; 2017:29-52. doi:10.1007/978-981-10-2134-3_2.
19. Grebenshchikova V, Lustenberg E, Kitayev N, Lomonosov I. *Geochemistry of the Environment of the Baikal Region (Baikal Geocological Polygon)*. Novosibirsk, Russia: Academic Publishing House "GEO"; 2008.
20. Alekseenko VA, Alekseenko AV. The abundances of chemical elements in urban soils. *J Geochem Explor.* 2014;147:245-249.
21. Martin SC, Larivière C. Community health risk assessment of primary aluminium smelter emissions. *J Occup Environ Med.* 2014;56:S33-S39. doi:10.1097/JOM.000000000000135.
22. O'Mullane DM. Fluoride and oral health. *Community Dent Hlth.* 2016;33:69-99. doi:10.1922/CDH_3707O'Mullane31.
23. Choi AL, Sun G, Zhang Y, Grandjean P. Developmental fluoride neurotoxicity: a systematic review and meta-analysis. *Environ Health Perspect.* 2012;120:1362-1368. doi:10.1289/ehp.1104912.
24. Sachdeva S, Ahmed J, Singh B. Thyroid dysfunction associated with excess fluoride intakes: scope for primary prevention. *Thyroid Res Pract.* 2015;12:50. doi:10.4103/0973-0354.156726.
25. Nabavi SM, Nabavi SF, Moghaddam AH, Setzer WN, Mirzaei M. Effect of silymarin on sodium fluoride-induced toxicity and oxidative stress in rat cardiac tissues. *An Acad Bras Cienc.* 2012;84:1121-1126. doi:10.1590/S0001-37652012005000056.
26. Malin AJ, Till C. Exposure to fluoridated water and attention deficit hyperactivity disorder prevalence among children and adolescents in the United States: an ecological association. *Environ Health.* 2015;14:17. doi:10.1186/s12940-015-0003-1.
27. Ha Rahim Z, M Bakri M, Hm Z, Ia A, Na Z. High fluoride and low pH level have been detected in popular flavoured beverages in Malaysia. *Pak J Med Sci.* 2014;30:404-408.
28. Spittle B. Halting the inertia of indifference: fluoride and fertility revisited. *Fluoride.* 2009;42:159-161.
29. Donoghue AM, Frisch N, Olney D. Bauxite mining and alumina refining: process description and occupational health risks. *J Occup Environ Med.* 2014;56:S12-S17.
30. Declercq C, Ponti P, Warembourg D, Tronet V, Rousselle JF. [Urinary excretion of fluorides in children living around an aluminum smelter]. *Rev Epidemiol Sante Publique.* 1995;43:504-509.
31. Seixas NS, Cohen M, Zevenbergen B, Cotey M, Carter S, Kaufman J. Urinary fluoride as an exposure index in aluminum smelting. *AIHAJ.* 2000;61:89-94. doi:10.1080/15298660008984520.
32. Young SM, Pitawala A, Ishiga H. Factors controlling fluoride contents of groundwater in north-central and northwestern Sri Lanka. *Environ Earth Sci.* 2011;63:1333-1342. doi:10.1007/s12665-010-0804-z.
33. Vikas C, Kushwaha R, Ahmad V, Prasannakumar V, Reghunath R. Genesis and geochemistry of high fluoride bearing groundwater from a semi-arid terrain of NW India. *Environ Earth Sci.* 2013;68:289-305. doi:10.1007/s12665-012-1739-3.
34. Perezhogin AN, Safronov NP. Hygienic assessment of environmental quality in Shelekhov town in Irkutsk region [in Russian]. *Bull East Sib Sci Cent SB RAMS.* 2013;3:109-113.
35. Wesdock JC, Arnold IMF. Occupational and environmental health in the aluminium industry: key points for health practitioners. *J Occup Environ Med.* 2014;56:S5-11. doi:10.1097/JOM.0000000000000071.
36. Efimova NV, Mylnikova IV, Paramonov VV, Kuzmina MV, Grebenshchikova VI. Assessment of chemical contamination and risk to public health of the Irkutsk region [in Russian]. *Geogr Nat Resour.* 2016;S6:99-104.
37. Lisetskaya LG, Efimova NV. Regional indices of trace element levels in hair in children of the population of the Irkutsk region. *Gig Sanit.* 2016;95:266-269. doi:10.18821/0016-9900-2016-95-3-266-269.
38. Rukavishnikov VS, Efimova NV, Gornov AY, et al. Evaluation of environment and population health in the area of aluminium production in East Siberia, exemplified by Shelekhov town [in Russian]. *Geogr Nat Resour.* 2016;S6:104-108.
39. Kvande H, Drabløs PA. The aluminum smelting process and innovative alternative technologies. *J Occup Environ Med.* 2014;56:S23-S32. doi:10.1097/JOM.0000000000000062.
40. Den Hond R, Hiralal I, Rijkeboer A. Alumina yield in the Bayer process past, present and prospects. In: Donaldson D, Raahauge BE, eds. *Essential Readings in Light Metals*. Cham, Switzerland: Springer; 2016:528-533.
41. Dai X, Jolly M. Potential energy savings by application of the novel CRIMSON aluminium casting process. *Appl Energy.* 2012;89:111-116. doi:10.1016/j.apenergy.2010.12.029.
42. Henning B, Jasper R. MultiMelter®—the new generation of aluminium melting furnaces. *Heat Process.* 2004;2:1-4.
43. Filimonova LM, Parshin AV, Bychinskii VA. Air pollution assessment in the area of aluminum production by snow geochemical survey. *Russ Meteorol Hydrol.* 2015;40:691-698. doi:10.3103/S1068373915100076.
44. Irkutsk Aluminium Smelter. <https://rusal.ru/en/about/geography/irkutskiy-alyuminievyy-zavod/>. Accessed February 2, 2021.
45. Belozertseva IA. Monitoring of environmental pollution in the impact zone of the Irkutsk aluminum plant [in Russian]. *Water Chem Ecol.* 2013;10:33-38.
46. Atlas lake Baikal. *Past, Present, Future*. Frankfurt am Main, Germany: Federal Agency for Cartography and Geodesy; 2005.
47. Korytny LM, ed. *Geographical Encyclopedia of Irkutsk Region. A General Overview*. Irkutsk, Russia: V.B. Sochava Institute of Geography; 2017.
48. Grebenshchikova VI, Kuzmin M. Comparative analysis of chemical composition of snow melt water and river water from areas with aluminum production (Russia, Baikal region). *Integr J Environ Earth Sci.* 2020;1:16-20.
49. Gromovik AI, Yonko OA. *Modern Instrumental Methods in Soil Science. Theory and Practice* [in Russian]. Voronezh; 2010.
50. Vasil'eva IE, Shabanova EV. Certified reference materials of geological and environmental objects: problems and solutions. *J Anal Chem.* 2017;72:129-146. doi:10.1134/S1061934817020149.
51. Assembly WG, Seoul O. Declaration of Helsinki. Paper presented at: Proceedings 64th WMA General Assembly; October 2013:11-14; Fortaleza, Brazil.
52. World Health Organization. *Hazardous Chemicals in Human and Environmental Health*. Geneva, Switzerland: World Health Organization; 2002.
53. Isaev L. *Control of Chemical and Biological Parameters of the Environment*. St. Petersburg, Russia: RF Publishing House; 1998.
54. Grebenshchikova VI, Gritsko PP, Kuznetsov PV, Doroshkov AA. Uranium and thorium in soil cover of the Irkutsk-Angarsk industrial zone (Baikal region). *Bull TOMSK Polytech Univ-GEO ASSETS Eng.* 2017;328:93-104.
55. Broström M, Enestam S, Backman R, Mäkelä K. Condensation in the KCl-NaCl system. *Fuel Process Technol.* 2013;105:142-148. doi:10.1016/j.fuproc.2011.08.006.
56. Shalina TI, Nikolaeva LA, Savchenkov MF, Bykov YN, Manueva RS. [Environmental pollution with fluoride compounds and their influence on children health]. *Gig Sanit.* 2016;95:1133-1137.
57. Mold M, Umar D, King A, Exley C. Aluminium in brain tissue in autism. *J Trace Elem Med Biol.* 2018;46:76-82. doi:10.1016/j.jtemb.2017.11.012.
58. Arnesen AKM, Krogstad T. Sorption and desorption of fluoride in soil polluted from the aluminum smelter at Ardal in Western Norway. *Water Air Soil Pollut.* 1998;103:357-373. doi:10.1023/A:1004900415952.
59. Kozlova A, Lopatovskaya O, Granina N, Chipanina E, Kuchmenko E, Bobrov A. Fluoride contamination of gray forest soils from Irkutsk Aluminum Smelter (IrkAZ). *Izv Irkutsk Gos Univ Seriya Biol Ecol.* 2011;4:87-94.
60. Pollution of soil of the Russian Federation by toxicants of industrial production in 2015. Yearbook. http://www.typhoon.obninsk.ru/upload/medialibrary/827/ezheg_tpp_2015.pdf. Published 2015.
61. Qin R, Wu Y, Xu Z, Xie D, Zhang C. Assessing the impact of natural and anthropogenic activities on groundwater quality in coastal alluvial aquifers of the lower Liaohe River Plain, NE China. *Appl Geochem.* 2013;31:142-158. doi:10.1016/j.apgeochem.2013.01.001.
62. Baez RJ, Petersen PE, Marthaler TM. *Basic Methods for Assessment of Renal Fluoride Excretion in Community Prevention Programmes for Oral Health*. Geneva, Switzerland: World Health Organization; 2014.
63. Gago C, Romar A, Fernández-Marcos ML, Álvarez E. Fluorine sorption by soils developed from various parent materials in Galicia (NW Spain). *J Colloid Interface Sci.* 2012;374:232-236. doi:10.1016/j.jcis.2012.01.047.

64. Khan SD, Mahmood K, Sultan MI, Khan AS, Xiong Y, Sagintayev Z. Trace element geochemistry of groundwater from Quetta Valley, western Pakistan. *Environ Earth Sci*. 2010;60:573-582. doi:10.1007/s12665-009-0197-z.
65. Zhang L, Huang D, Yang J, et al. Probabilistic risk assessment of Chinese residents' exposure to fluoride in improved drinking water in endemic fluorosis areas. *Environ Pollut*. 2017;222:118-125. doi:10.1016/j.envpol.2016.12.074.
66. Kebede A, Retta N, Abuye C, et al. Dietary fluoride intake and associated skeletal and dental fluorosis in school age children in rural Ethiopian rift valley. *Int J Environ Res Public Health*. 2016;13:756. doi:10.3390/ijerph13080756.
67. Zohoori FV, Walls R, Teasdale L, et al. Fractional urinary fluoride excretion of 6-7-year-old children attending schools in low-fluoride and naturally fluoridated areas in the UK. *Br J Nutr*. 2013;109:1903-1909. doi:10.1017/S0007114512003583.
68. Ibiyemi O, Zohoori FV, Valentine RA, Maguire A. Fluoride intake and urinary fluoride excretion in 4- and 8-year-old children living in urban and rural areas of Southwest Nigeria. *Community Dent Oral Epidemiol*. 2018;46:482-491. doi:10.1111/cdoe.12396.
69. Maguire A, Zohoori FV, Hindmarch PN, Hatts J, Moynihan PJ. Fluoride intake and urinary excretion in 6- to 7-year-old children living in optimally, sub-optimally and non-fluoridated areas. *Community Dent Oral Epidemiol*. 2007;35:479-488. doi:10.1111/j.1600-0528.2006.00366.x.
70. Omid N, Maguire A, O'Hare WT, Zohoori FV. Total daily fluoride intake and fractional urinary fluoride excretion in 4- to 6-year-old children living in a fluoridated area: weekly variation? *Community Dent Oral Epidemiol*. 2016;45:12-19. doi:10.1111/cdoe.12254.