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Chapter II/44: ECOLOGICAL RATIONING OF TECHNOGENIC LOADS OF SOILS IN THE INFLUENCE AREA OF AN ALUMINUM SMELTER IN SIBERIA

Глава II/44: Экологическое нормирование техногенной нагрузки на почвы в зоне влияния алюминиевого завода в Сибири

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DOI 10.25680/1341.2018.24.79.141

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ABSTRACT. Detailed studies of snow and soil contamination within the influence zone of the Irkutsk Aluminum Plant were carried out in 1996 - 2014. The main atmospheric and soil pollution and their amounts and distribution area were described. According to researches of the author it is revealed that within the territory of up to 1 km from IrkAZ, the maximum fluorine concentration in snowmelt water reaches 66 mg/dm^3. The interrelation of technogenous contaminators in the soil and snow was assessed, and their influence on some soil parameters was found. The standard setting for technogenous loads with respect to the most significant and sensitive soil parameters was carried out. The values of the "dose - effect" relationship can be used to determine the maximum permissible and maximum impermissible concentrations of elements in soils. For example, according to the total form, they are in g/kg, respectively: 0.66 and 0.84 for fluorine, 82 and 93 for aluminum, and 24 and 26 for sodium.

Резюме. В 1996 - 2014 гг. было проведено детальное изучение загрязнения снежного и почвенного покрова в зоне воздействия Иркутского алюминиевого завода. Установлены основные загрязнители атмосферы и почв, объем выбросов и площадь их распространения. Согласно исследованиям автора выявлено, что на территории до 1 км от IrkAZ, максимальная концентрация фтора в снеговой воде достигает 66 мг/дм^3. Прослежена взаимосвязь содержания техногенных загрязнителей в снеге и в почве. Выявлено их влияние на некоторые показатели состояния почв. Проведено нормирование техногенных нагрузок по наиболее значимым и чувствительным параметрам почв. В результате анализа графиков зависимости “доза-эффект” по различным почвенным параметрам выявлены максимальные допустимые и максимальные недопустимые концентрации химических элементов в почвах. Например, максимально допустимые и недопустимые концентрации фтора, алюминия и натрия в почвах составляют соответственно: 0.66 и 0.84, 82 и 93, 24 и 26 г/кг (валовое содержание).

KEYWORDS: snow, soil, pollution, influence of the Irkutsk Aluminum Smelter, ecological standard setting

Ключевые слова: снег, почвы, загрязнение, Иркутский алюминиевый завод, экологическое нормирование

INTRODUCTION

The production capacity of the aluminum smelters in southern Siberia varies from 450 (Irkutsk Aluminum Smelter (IrkAZ)) to more than 1000 thousand tons per year (Bratsk Aluminum Smelter (BrAZ)). The production of primary aluminum by the electrolysis method, as used at IrkAZ, is responsible for the pollution of the environment by fluorine compounds, carbon and sulfur oxides, as well as hazard class 1 substances: vanadium, chromium and nickel compounds, polycyclic aromatic hydrocarbons, such as benzo(a)pyrene, some of which are characterized by mutagenic and carcinogenic activity. The city of Shelekhov is situated within the lowland broad valley of the Irkut River and its right tributary, the Olkha River; accumulation and stagnation of pollutants in the urban atmosphere is aided by the unfavorable meteorological conditions, which are characterized by a high recurrence frequency of ground air temperature inversions and weak winds.

METHODS

The system of ecological observations of the state of soils and earth materials was designed around the landscape-geochemical differentiation having regard for the geochemical barriers and the most likely routes of superficial and ground (subsoil) migration of pollutants, in 0.5, 1, 2, 6, 20 and 70 km from a factory. A total of more than 60 main soil cross sections were prepared, with more than 192 samples taken for physicochemical analyses. A total of 64 snow samples were collected in late February – March with weighting-type snow sampler VC-43 (NPO Taifun, Russia) to determine its depth and density. At the time of sampling, the period of accumulation was 131–140 days. Analytical work was done in the V.B. Sochava Institute of Geography SB RAS (IG SB RAS) under laboratory conditions using standardized techniques and modern equipment. Concentrations of basic ions and cations in snowmelt were determined by standard chemical methods with due regard for GOST requirements. The pH-value for suspension was determined by the potentiometric method using combined electrodes, with the soil: solution ratio equal to 1:2.5. Fluorine concentration was measured on ionomer N-120 with a fluorine-selective electrode. Gross contents of metals were inferred using the quantitative spectral technique with spectrograph DFS (distributed file system)-8, the atomic emission spectroscopy method with the optima 2000 DV (optical emission spectrometer) instrument, and by standard chemical methods, with regard to the requirements of the Russian state standards. Humus content was characterized by quantifying carbon of organic compounds using Tyurin’s method (TsINAO version). The structure of a humus was determined by a pyrophosphatic method of Tyurin in V.V. Ponomareva and T.A. Plotnikova's Modification. Speed of destruction of cellulose was determined by A.F. Zakharchenko's method. Determination of biochemical activity is carried out by the express method developed by T.V. Aristovska and M.V. Chugunova. The toxicity of soils was determined by viability and length of sprouts of test plants in soils.

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RESULTS AND DISCUSSION

According to researches of the author it is revealed that within the territory of up to 1 km from IrkAZ, the maximum fluorine concentration in snowmelt water reaches 66 mg/dm^3, or 2.6 t/km^2. Here, the concentration coefficients (K_k) for the snow cover in the range from 40 to 60 are characteristic for Sr, V, Mg, Cr, Ni, Fe, and Co; K_k from 60 to 100 are typical of Pb, Ca, and Cu; K_k in excess of более 100 are characteristic for F, Al, Na, Mn, and Ba (Table 1). The area of the most severe pollution occupies about 14 km^2, including the southern part of Shelekhov and the northern half of the Olkha. Accumulation of solids in the snow cover within the city's industrial district exceeds 20 mg/m^2, reaching 18 in the sanitary-protective zone of IrkAZ, 1−13 in the residential districts, and 2−5 mg/m^2 in horticultural and agricultural suburban areas.

As a result of modernization of the production process (by introducing the technique of baked anodes and the advanced equipment for purification of gaseous emissions), and a concurrent decrease in the output of primary aluminum, the emissions from the smelter reduced dramatically by the year 2004 (that is coordinated with researches of the author; Table 2), involving a significant decrease of solids (suspended material) and dissolved matter (dry residue) in the snow cover. However, in connection with the commissioning of the fifth series of electrolysis production and an increase in the output of primary aluminum, the pollution indices for the snow cover in 2008 returned to their levels for the time interval 2000−2002. The data in the table are also indicative of the large contribution from the wind direction to pollution of the snow cover. Pollutants from IrkAZ are transported by air flows predominantly along a north-westward direction (Fig. 1).

Table 1 - Maximum exceedances of background content, and concentration of elements in the liquid snow phase nearby IrkAZ (in 0.5 km on the northeast from plant)

Element	1996		2002		2010	
	Content, mg/L	Exceedance of background, times	Content, mg/L	Exceedance of background	Content, mg/L	Exceedance of background
F	55.00	208	50.00	189	43.00	159
Al	7.60	54	10.81	77	11.12	79
Si	6.27	31	3.81	19	1.51	8
Mn	0.80	52	0.18	12	0.11	7
Ba	0.50	49	0.10	10	0.01	1
Pb	0.07	27	0.02	8	0.01	4
Ca	7.00	23	2.32	7	9.30	28
Na	67.5	123	18.0	33	35.29	64
K	5.1	15	0.98	3	2.36	7
Cu	0.06	32	0.02	11	0.01	6
Sr	0.12	17	0.03	4	0.06	2
Cr	0.04	16	0.01	4	0.00	1
Mg	5.90	26	1.62	7	1.61	7
V	0.04	20	0.01	5	0.02	10
Ni	0.09	45	0.02	10	0.01	5
Fe	27.1	27	5.67	6	0.04	1
Ti	1.10	13	0.23	3	0.00	1
Co	0.01	20	0.00	16	0.00	15
S	7.10	10	1.70	2	10.00	12
Cl	0.31	3	0.28	3	3.55	30

a b The bulk of material in technogenic emissions is deposited on the soil surface, which is an important component of the urban environment. As a result of the conducted researches in the zone of IrkAZ, the chemical elements according to their distribution in the snow–soil system are categorized by the author into three groups. The first group (F, Al, Na, Mn, and Ba) is characterized by an excess of concentrations in the snow over the respective background values by a factor of 50 or more, and in the snow the exceedance is by a factor of five or more. The second group (Ca, and Cu) exhibits exceedances over the snow and soil background by factors of 25–50 and 3–5, respectively; the third group (Co, Ni, Sr, Mg, Fe, Ti, V, and Cr) shows exceedances over background concentrations in the snow and soil by factors of less than 25 and less than three, respectively. In the topsoil layer, for most elements K_k <5; it is 5–7 for Al, Na, Mn, Ba, and 20 for F.
The most ecologically hazardous pollutant in the soil environment of the city of Shelekhov is fluorine; it accumulates to a maximum extent in the zone of IrkAZ, reaching 10–14 MPC (maximum permissible concentration); in the sanitary-protective zone of the smelter and in its residential districts, it reaches 3–6 and 1–2 MPC, respectively, exceeding the background regional level. With a decrease in the amount of solid pollutants with a distance from the smelter, the amount of water-soluble fluorine remains at a relatively high level; at 6 km from the source it decreases only to MPC in the topsoil layer. There is a decrease for different forms of fluorine by the end of the growing period, which is caused by the soil self-cleaning processes, and by the involvement of the element in the bioproduction process.
Researches of the author into the susceptibility of the soil environment to the effects from IrkAZ revealed a number of properties highly responsive to pollution. Among such indicator properties are the destruction rate of cellulose, urease activity characterizing destruction of organic compounds of nitrogen, soil toxicity, and the availability in the soils of mobile forms of nitrogen, phosphorus, potassium, and organic matter. The quantitative parameters of the aforementioned properties at a distance of up to 0.5 km from the smelter are more than an order of magnitude below the background values, and they approach them with the distance from the source of pollution.

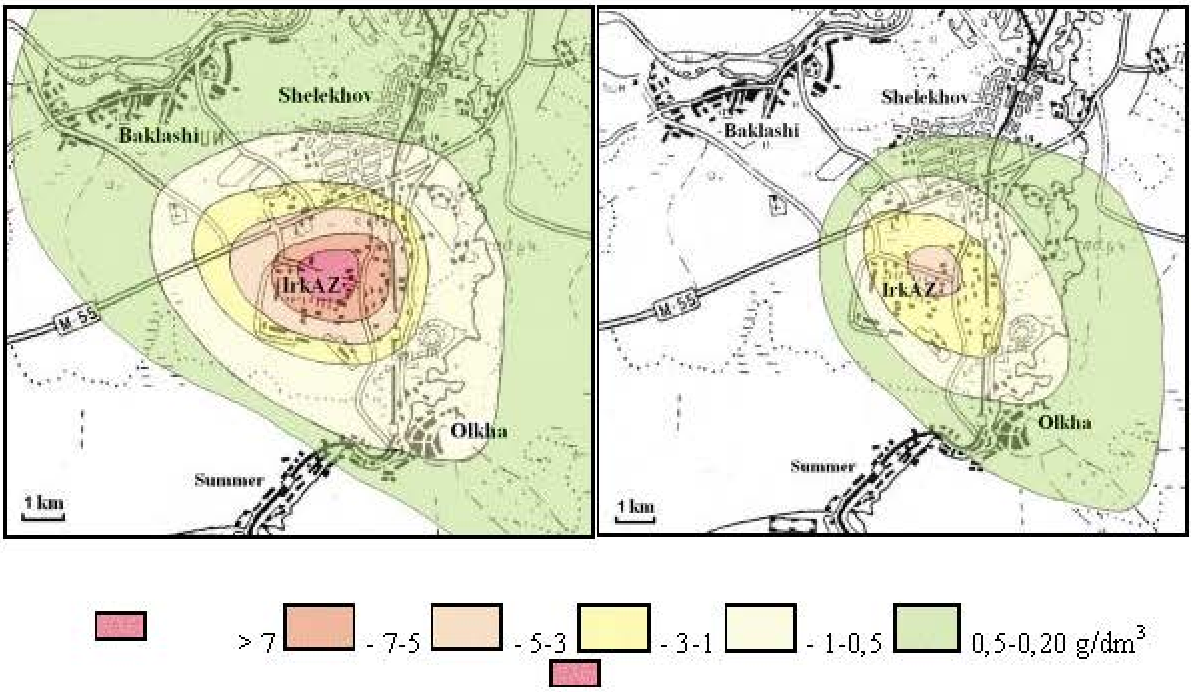
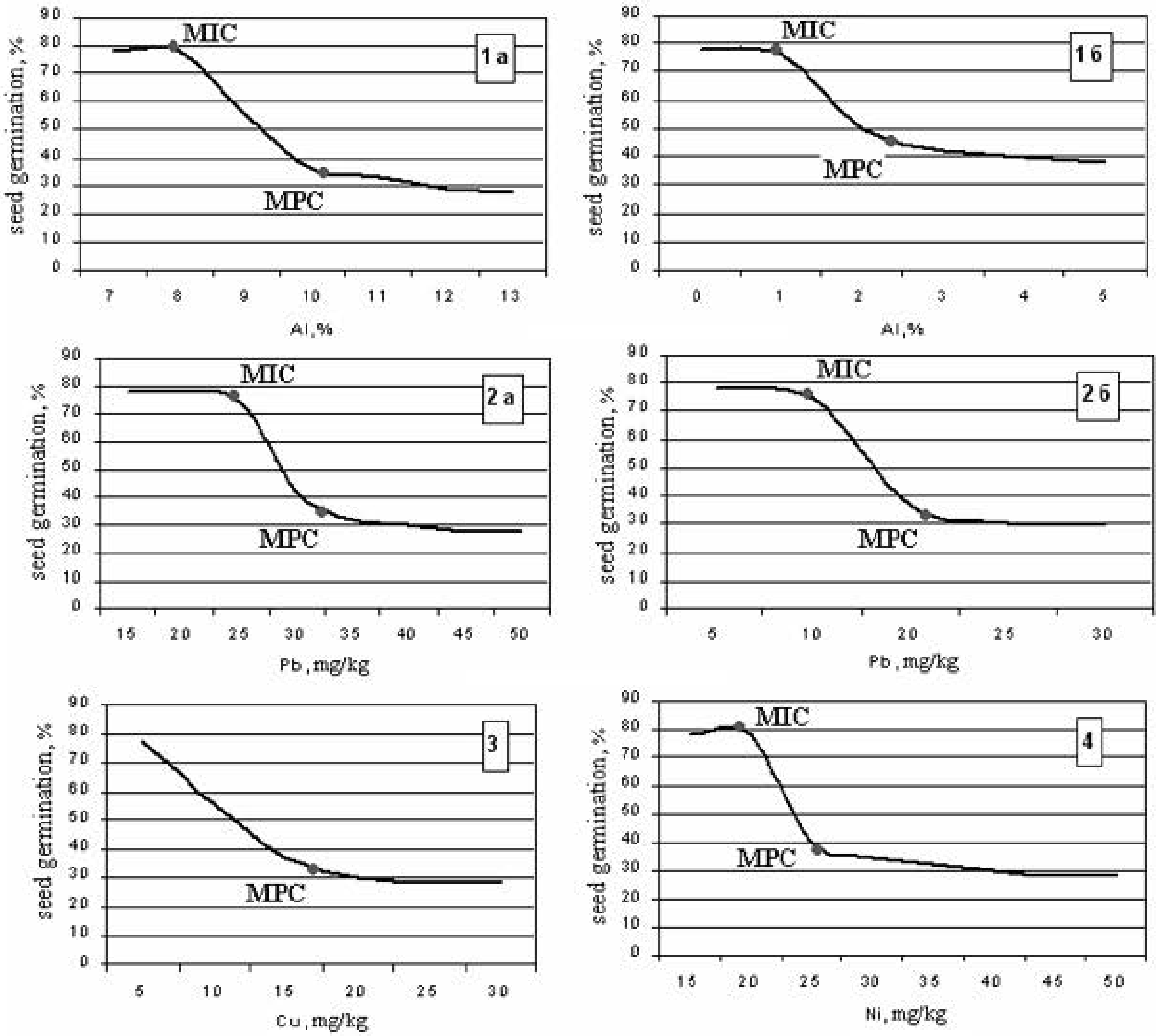


Figure 1 - The content of strong substance (the rest on the filter or dust) in snow for the winter period of 1996. (A) and 2010 (B) in a zone of influence of IrkAZ, g/dm3

Urease activity of soils at the distance of 0.5 – 1 – 2 – 6 km from the smelter decreases, respectively, by factors of 11 – 6 – 7 – 3, the content of mobile P_2O_5 and NO_3 drops from 16 mg/100 g to zero and from 8 to 1 mg/100 g, respectively. In the zone of up to within 0.5 km, soil toxicity that is determined from seed germination and from the length of germs of test plants (pine and lettuce) is 30% below the control, which is caused by the high content of the polluting substances (Fig. 2). The soil humus composition revealed a two-fold decrease in its mobile fraction, i.e. fulvoacids, and a two to three-fold increase in the contribution of fractions bound with calcium and iron oxides. The destruction indicators of organic matter are, to a greater extent, correlated with F and Pb, while contents of mineral nutrients are more correlated with Al, Na, Ba, Pb, and Cu.

As a result of the conducted researches by the author, it is revealed that under conditions differing in the degree of pollution showed that the response of the aforementioned properties (the "dose–effect" principle) was clearly pronounced with regard to an increase in concentrations of F, Al, Na, Ba, Pb, Cu, and Ni in soils. As far as the other elements are concerned, no "dose–effect" relationship was revealed. The ultimate load levels were inferred by identifying critical points on the "load vs. effect" curve that was constructed from sensitive parameters varying in a regular fashion from the content of polluting substances. A critical point is considered to mean the start of the most rapid change in the parameter. The lower critical point on the plot is regarded as the maximum permissible concentration (MPC) of chemical element at which there are taking place changes in the meaningful indices of the soil but they are still reversible. Admissible concentration of chemical elements is indicated by the upper critical point where the changes in the soil parameters that have occurred are no longer reversible. The maximum permissible ecological load implies the lowest of the high loads on the various natural components.



MPC - maximum permissible concentration (lower critical point)

MIC - maximum impermissible concentrations (upper critical point)

Figure 2 - Average seed germination versus A1 total (1, *a*), acidsoluble in 0.1 HCl (1, *b*), %; Pb total (2, *a*), acidsoluble (2, *b*), Cu acidsoluble (3), Ni acidsoluble (4), mg/kg

The values of the "dose–effect" relationship can be used to determine the maximum permissible and maximum impermissible concentrations of elements in soils (the upper and lower critical points on plots, such as shown in Fig. 2). According to the total form, they are in g/kg, respectively: 0.66 and 0.84 for fluorine, 82 and 93 for aluminum, and 24 and 26 for sodium; according to the acid-soluble form in mg/kg: 220 and 580 for fluorine, 9 and 24 for aluminum, and 250 and и 480 for sodium. A conversion of the parameters of this relationship determined the maximum permissible and impermissible loads of pollutants in t/km^2 · year, respectively: 2.2 and 10.2 for solids, 2.4 and 5.2 for fluorine, 19.0 and 42.0 for aluminum, 0.8 and 4.0 for sodium, and 0.04 and 0.84 for barium; in kg/km^2 · year: 7 and 26 for lead, 5 and 20 for copper, and 2 and 17 for nickel. In view of the existing emissions, the necessary multiplicity of their decrease is as high as a factor of two and 13 for maximum permissible and impermissible loads, respectively.

CONCLUSIONS

1. The values of the "dose - effect" relationship can be used to determine the maximum permissible and maximum impermissible concentrations of elements in soils. For example, according to the total form, they are in g/kg, respectively: 0.66 and 0.84 for fluorine, 82 and 93 for aluminum, and 24 and 26 for sodium.
2. Properties of soils highly responsive to pollution (indicator proper-ties are) are revealed: the destruction rate of cellulose, urease activity characterizing destruction of organic com-pounds of nitrogen, soil toxicity, and the availability in the soils of mobile forms of nitrogen, phospho-rus, potassium, and organic matter.
3. According to the existing number of technogenic emissions at the plant (IrkAZ), it is necessary to reduce emissions of the polluting substances (on the maximum permissible concentrations (MPC) for various elements) in 0-3.7 times, (on the maximum inadmissible concentrations for various elements) in 1.2 – 26.2 times.

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