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Vertical migration of pollutants in the soils of the Orenburg technogenic biogeochemical province.

Aleksandr S. Frid, Tatiana I. Borisochkina

V.V. Dokuchaev Soil Science Institute

119017 Moscow, Pyzhevskiy s., 7, b. 2, Russia

e-mail: asfrid@mail.ru

Abstract

The parameters of migration models of Cr, Ni, Cu, Pb, F in the soils of the Eastern Orenburg technogenic biogeochemical province are estimated. The enterprises of ferrous metallurgy, non-ferrous metallurgy, chemical industry are concentrated in this region, and there are many-year soil pollution. The results of field surveys of the 1980 s. Diffusion and convection-diffusion models were used. These models met the criteria of adequacy in most cases. The values of the diffusion parameters found are compared with the previously published values. The "apparent" diffusion coefficients are in the range (0.2-27) 10^{-8} cm^2 /s. Soil contamination forecast for 2020 is calculated. Calculated forecast values can be compared with the results of the next monitoring survey.

Keywords: Chrome Nickel Copper Lead Fluoride Migration by soil profile Parameters of migration models Forecast for 2020.

1 Introduction

The eastern part of the Orenburg region of the Russian Federation belongs to the natural biogeochemical province (Vazhenin, 1989). In this area there are exits to the earth's surface of ores of Fe, Cu, Zn, Ni,Co. Powerful enterprises of ferrous and nonferrous metallurgy operate on this territory for a long time. Industrial emissions of industrial enterprises have turned the natural geochemical province into a man-made province.

Few studies have been devoted to the experimental study of vertical mitigation. (Labanowski et al. 2008; Doronsoro et al. 2002; Ruan et al.2008; Frid, Borisochkina 2010; Goma Botchina Saad 2011 et al.). The methodological difficulties of soil sampling and the lack of sensitivity of analytical methods are the reason for the small amount of experimental work. We do not consider in the article the migration of radionuclides, which is studied better.

The use of dynamic mathematical models for describing the vertical migration of polluting technogenic elements is practically absent. The available semi-imperial models help to understand the real processes in the soils and to predict the migration of polluting elements to different depths.

The purpose of our work is to estimate the parameters of vertical migration of chemical contaminants in the soils of the territory of the Orenburg technogenic province.

Using semi-empirical migration models requires some simplifying assumptions. The models used have few parameters and this simplifies verification.

2 Objects and Methods

We used the results of soil surveys of the Orenburg region, conducted in the eighties of the last century. We chose soil ranges in which there are significant exceedances of background contents and gradients of total concentrations can be traced well.

In the city of Novotroitsk there are several large enterprises, including the Orsk-Khalilovsky Metallurgical Plant (currently “Ural steel”). This plant has been operating since 1955 (Table 1). At the sites located in the zone of the plant, the soil is dark chestnut (Vazhenin, 1989) and southern black loamy soil.

Copper-sulfur plant operates in the city of Mednogorsk since 1939. Surrounding landscapes were severely affected by acidification of the top layer of soil by acidic emissions (table 2).

Here are the soils: low-powered gravel black chernozems, ordinary chernozems light-loamy and southern chernozems.

The South Ural Cryolite Plant has been operating in the city of Kuvandyk since 1954. Soils in the vicinity of the plant are contaminated with fluorine and other chemicals (Table 3). The soil is mostly gravelly. Here two series of soil sampling were carried out (Vazhenin, 1991, Golovkova, Sivolobova, 1992). In 2012, the main production was mothballed.

The total content of heavy metals and macronutrients in soils was determined by the X-ray fluorescence method. Total fluorine content in soils was determined by the spectral emission method with a sample spillage in an arc of variable current. Water-soluble fluoride in soils was determined by potentiometric method using Tisab buffer (pH 6.5) (Golovkova, Sivolobova, 1992). Soil agrochemical properties were determined according to generally accepted methods (Agrochemical methods for studying soils, 1975)

As a control (background) in relation to the levels of soil contamination with heavy metals (Vazhenin 1989, Vazhenin 1991), a soil profile was taken on a virgin lands near the Sara railway station. The soil is located 25 km east of the city of Mednogorsk and 50 km west of the city of Orsk. The soil of this soil profile is southern chernozem. The characteristics of this soil are presented in table 4. In the study of fluorine pollution, as a control, a site was taken 30 km from the cryolite plant, the soil is ordinary chernozem (Golovkova, Sivolobova, 1992).

When analyzing the distribution of concentrations of pollutant elements, two dynamic models for a semi-infinite medium were used. 1) A diffusion model with a boundary condition on the soil surface as a constant flow of the incoming element averaged over many years of pollution. 2) Convective-diffusion model with a boundary condition on the soil surface in the form of mass exchange of the element between aerogenic fallout and soil (averaged over many years). The initial content of pollutants over the depth of the soil (before pollution) was assumed to be constant (as well as the density of the soil). According to the available data there was no reason to take into account the biological accumulation of elements in the upper layers of the soil.

The parameters of migration models were assumed to be constant in depth and time as the result of many years of averaging the real variations in soil conditions and rates of soil processes. The initial (background) content was considered as the desired parameter. Parameers found in this way are called “apparent”

Diffusion model: $\partial P/\partial t = D \cdot \partial^2 P/\partial x^2$, at $x = 0$ flow= f_0, at $t=0$ $P=P(0)$. $P=P(x,t)$ total pollutant content in soil, D - apparent diffusion coefficient in soil, x – depth, t – time from the start of pollution. Required parameters – D, f_0, P(0). The solution of the differential equation for the given boundary and initial conditions is given in Malkovich, Polyanin et al. (1998).

Convective diffusion model: $\partial P/\partial t = D_k \cdot \partial^2 P/\partial x^2 - V \cdot \partial P/\partial x$, at $x =0$ $-D_k \cdot dP/dx + V \cdot P = V \cdot P_{in}$, at $t=0$ $P=P(0)$. D_k – apparent convective diffusion coefficient, V – the apparent rate of directional transfer of the element in the soil with different streams (including moisture), P_{in} – conditional concentration of the element coming from streams through the soil surface. Required parameters - D_k, V, P_{in}, P(0). The solution of the differential equation for the given boundary and initial conditions is given in van Genuchten, Alves (1982).

The procedure for finding estimates of the parameters of migration models was as follows. For each depth, the concentration range was determined on the basis of a measurement error, or by setting it as 10% relative error, thus obtaining a concentration range in depth. We set different combinations of parameter values and calculate the values of P (x, t). At the same time, we selected such combinations so that the calculated concentrations fit into the established range of values. In order to recognize the model and parameter estimates as adequate to the experimental data, we compared the content of the pollutant in the soil (minus the background content) with the estimated input of the pollutant into the soil over a certain time.

3 Results and Discussion

The upper layers of the soil near the Orsk-Khalilovsky plant are contaminated with Cr and Ni (table 1). The nickel content in the soil was several times higher than the standards adopted in the Russian Federation. For gross chromium content in the soil there is no approved standard. The applied models of chromium migration in soil turned out to be adequate for describing chromium migration in soil sections at a distance of 0.5 and 2 km from the plant and insufficiently adequate for describing migration in a soil section in the floodplain of the Ural River (Table 5). The reasons for this result were not clarified. For a soil section located at a distance of 0.5 km from the plant, two different adequate sets of parameters of the convection-diffusion model were obtained, while set (A) showed the direction of flow Cr up (parameter V). Both models showed a wide variation in the values of such a parameter as the initial (background) content. These values do not contradict the chromium content in the background soil cut (table 4). For Ni, adequate models and parameter sets were obtained for all three distances from the plant. For the floodplain of the Ural River, two adequate sets of parameters of the convection-diffusion model were obtained.

Finally, the ranking of elements according to the values of parameters D and Dk. It is clear that it is possible only taking into account the distance from the source of pollution (numbers in brackets), as mentioned above. The result is a series

Cr ≥ F (1.5) ≈ Ni (0.5 and 2)> Cu (0.5) ≈ Pb (0.5)> F (0.5 and 3) ≈ Ni (8)> Pb (7) ≈ F (2)> Cu (7).

The range of D values - from $0.23 \cdot 10^{-8}$ to $27 \cdot 10^{-8}$ cm^2 / s - was two orders of magnitude, and for Dk - from 0.06 .06 10^{-8} to 16.5 10^{-8} cm^2 / s, that is, almost 300 time.

Let us now compare our estimates of diffusion parameters with the few literature data, where the migration rate was measured experimentally (Table 9). For Cr and F such data is not found. For Ni, Cu, Pb, the data obtained by us previously prevail.

If for Ni the estimates for the soils of Egypt were close to the estimates for the aqueous solution, for the soils of Orenburg they are much smaller and are close to the estimates obtained during the migration of elements from the pyrite tailings to the soil.

For Cu, there are still the results of laboratory experiments with water-saturated clay minerals. Estimates decrease in the following order: water solution - kaolinite and irrigated soils of Egypt - montmorillonite - loess soils of southern China and mountainous Orenburgia acidified with chernozem - migration from pyrite tails in Spain and into acidified chernozem of southern Orenburgia.

For Pb, we get the following descending series of estimates: water solution - sod-podzolic loamy soil (RF) and Egypt's irrigated soil - leached sod-calcareous soil (RF), migration from pyrite tails (Spain), loess soils of southern China and acidified black soil of mountainous soil rubble

For Pb, we get the following descending series of estimates: water solution - sod-podzolic loamy soil (RF) and Egypt's irrigated soil - leached sod-calcareous soil (RF), migration from pyrite tails (Spain), loess soils of southern China and acidified black soil of mountainous soil - britty Orenburg - acidified chernozem southern Orenburg.

Since the experimental measurements analyzed in this work were carried out in the 1980s, the forecast of the profile pollution of the studied elements, for example, for 2020, was of interest.

It was assumed that the average intensity of aerogenic pollution has not changed significantly. The forecast results are presented in tables 1-3. They are quite unexpected. First, the convective-diffusion model with mass transfer on the soil surface in all cases showed less total pollution of soil profiles than the diffusion model with a constant flow through the soil surface. Secondly, according to the diffusion model, contamination of soil profiles in all cases should increase by 2020, except for Pb at a distance of 7 km from the Mednogorsk Copper-Sulfur Combine. The latter is probably related to the lowest input flux into the soil in this work - (4.5-6.5) 10^{-7} mg / (cm^2/ s). In addition, the practical absence of additional contamination of soil profiles is expected from the convection-diffusion model for Ni (2 km south of the Orsk-Khalilovsky plant) and for Cu (7 km from the Mednogorsk plant).

Thus, it follows from the forecast that we can expect a noticeable increase in the danger of soil contamination for all elements according to the diffusion model (except for one case for Pb) and a somewhat smaller growth according to the convective-diffusion model. Therefore, the next monitoring in this region would allow assessing the quality of this forecast and the adequacy of the migration models used here.

4 Conclusion

1. It is shown that the diffusion and convective-diffusion models with averaged over time and soil depth parameters adequately described the distribution of heavy metals and fluorine over the soil depth in most cases of technogenic soil pollution of Eastern Orenburg region.
2. The “apparent” diffusion coefficients for Cr, Ni, Cu, Pb, F found on these models in local soils are in the range (0.2–2.7) · 10^{-8} cm^2 / s and are close to the lower limit of the values obtained earlier.
3. The forecast of pollution of the profiles of these soils for 2020 was calculated, which can be compared with the data of the next monitoring.

Tables

Table 1 The total content of chromium and nickel in the soils in the zone of impact of the Orsk-Khalilovsk metallurgical plant, mg/kg (Vazhenin, 1991)

Depth (cm)	Cr		Ni	
	Found	Forecast for 2020	Found	Forecast for 2020
0.5 km from the plant to the east, virgin lands				
0 – 1	718	954/986(711)	448	582/415
1 – 5	556	857/816(638)	332	519/385
5 – 10	403	702/616(514)	226	419/329
10 – 20	280	498/432(349)	178	289/237
20 – 30	-	316/292(223)	-	176/136
30 – 40	-	213/205(178)	-	115/73
40 - 50	-	161/156(167)	-	86/43
Total over background	>4960	13500/11900(6750)	>3750	8060/7140
2 km from the plant to the south, virgin lands				
0 – 1	680	967/695	460	535/442
1 – 5	530	874/635	330	480/376
5 – 10	480	724/528	206	394/273
10 – 20	290	523/374	180	278/157
20 – 30	-	339/245	-	173/94
30 – 40	-	229/192	-	112/82
40 – 50	-	171/178	-	81/80
Total over background	>5100	14500/7020	>3210	8020/3440
8 km from the plant to the west, virgin lands, meadow chernozem in the flood land of the Ural River				
0 – 1	427	-	665	932/699(734)
1 – 5	467	-	459	656/509(595)
5 – 10	278	-	178	352/277(309)

10 – 20	159	-	204	190/148(164)
20 – 30	-	-	-	170/135(160)
Total over background	Background unclear	-	>2390	3820/3480(3100)
Estimated concentrations	-		80	

Note Topsoil (20 cm), 2 km from the plant to the south, pH_{H2O} 8.3-7.8.

Dash - no data. Forecast for: above the line — by the diffusion model, under the line - by convective-diffusion model, in brackets - according to the second variant of the parameter values for the corresponding model. The same explanations apply to tables 2 and 3

Table 2 Total content of copper and lead in the soil, agrochemical properties of soils in the zone of impact of Mednogorsky sulfur copper plant (Vazhenin, 1991)

Depth (cm)	Cu		Pb		CaO total	humus	pH_{H2O}	pH_{KCI}	H_h	Exchangeable		Available		
	Found	Forecast for 2020	Found	Forecast for 2020	%					Ca	Mg	P_2O_5	K_2O	Na_2O
	mg / kg								mg-eqv. /kg			mg / kg		
0.5 km from the plant to the east, lee side, the upper part of the slope of the hill, mountainous chernozem rubble, virgin land														
0 – 10	3900	6410/4800	1350	2080/1540	3.15	7.2	4.28	3.88	186	324	26	19	241	40
10 – 20	465	1410/1160	127	445/406	4.44	6.4	7.05	6.10	17	575	54	62	144	74
20 – 27	73	320/274	59	98/85	5.00	5.9	7.32	6.90	8.7	790	49	36	154	94
30 – 40	100	110/106	20	33/30	6.34	4.8	7.56	6.05	6.1	1000	46	29	137	94
50 – 65	102	-	20	30/29	7.41	3.7	7.72	6.91	5.8	1700	45	27	113	101
Total over background	41700	77900/58900	14400	25100/19200										
0 – 1	758	1070/851	292	375/309	1.81	-	4.10	3.73	215	114	20	218	469	27
1 – 5	187	406/368	114	214/185	1.79	-	5.29	4.38	139	212	34	146	469	40

5 – 10	132	55/78	42	71/51	1.92	-	5.60	4.70	108	210	46	200	261	81
10 – 20	80	28/76	33	28/30	8.26	-	6.12	4.67	86	206	26	442	154	693
20 – 35	60	28/76	22	27/30	7.72	-	8.17	6.90	6.6	406	37	478	197	819
35 – 50	30	28/76	15	27/30	4.75	-	-	-	-	-	-	-	-	-
50 – 60	20	28/76	91	27/30	2.43	-	-	-	-	-	-	-	-	-
60 – 70	20	28/76	18	27/30	2.87	-	-	-	-	-	-	-	-	-
Total over background	2080	2760/2020	1300	1290/1000										
Estimated concentrations	66		65											

Table 3 Total content of fluorine in the zone of impact of the South Ural cryolite plant, mg / kg.

1 series of sampling (Vazhenin, 1991)			2 series of sampling (Golovkova, Sivolobova, 1992)			
Depth, cm	Total content of fluorine		Depth, cm	Total content of fluorine		F water-solvable
	Found	Forecast for 2020		Found	Forecast for 2020	
2 km from the plant to the northwest, upper third part of the hill, chernozem ordinary loam, virgin land			0.5 km from the plant, plain between hills, litter - 0-3cm, horizon A -3-20(22) cm, heavy loam (area 1)			
0 – 1	1400	1970/1500	0 – 3	1800	2580/1970	-
1 – 5	560	1010/850	3 – 10	820	1520/1260	46
5 – 10	300	384/333	10 – 25	520	627/561	20
10 - 20	300	300/300	25 – 40	540	506/525	2.1
			40 - 50	540	504/525	1.1
Total over background	2140	4930/3570		6690	15200/10000	
addition	pH_{H2O}	Ca exchangeable mg-eqv./ kg				
0 – 5	5.8	260				
5 - 10	6.3	300				
3 km from the plant to the east, virgin land (woodland belt) at the base of the hill			1.5 km from the plant to the northwest, lower third of the hill, horizon A (0-12(14) cm - sod with rubble inclusions up to 1-2 cm, horizon BC – heavy loam effervescent with the inclusion of rubble (area 2)			
0 – 1	1820	2320/1710	0 – 2	1400	1960/1550	-
1 – 5	830	1630/1190	2 – 13	1300	1540/1240	27
5 – 10	510	839/593	13 – 25	540	1000/799	15
10 - 20	380	387/351	25 – 38	410	649/524	0
			38 – 50	-	470/411	
			50 - 80	-	369/372	

Total over background	>4890	>10500/6150		>15200	30100/19600	
			7 km from the plant to the northwest, horizon A(0-15(18) cm)- loamy with the inclusion of rubble; horizon BC 35(37) cm– loamy with the inclusion of rubble (area 3)			
			0 – 3	390	-	3.0
			3 – 18	540	-	3.0
			18 – 28	390	-	0
			28 - 35	290	-	0
Estimated concentrations	-			-		10

Note On the control (background) site in the upper soil horizons, the total content of F - 290 mg/kg, water soluble F – 1.1 mg/kg (Golovkova, Sivolobova, 1992).

Table 4 Total composition and agrochemical properties of the control (background) soil profile, long-term deposit, southern chernozem heavy loamy (Vazhenin, 1991)

Depth (cm)	Cr	Ni	Cu	Pb	CaO	Humus	pH_{H2O}	pH_{KCl}	H_h	Exchangeable				Available		
										Ca		Mg		P_2O_5	K_2O	Na_2O
	mg/kg				%					A	B	A	B	mg / kg		
									mg-eqv. /kg							
0 – 1	151	43	29	14	-	7.9	7.1	6.2	17.5	500	-	57	-	159	960	32
1 – 5	118	40	24	19	2.40	6.1-7.1	7.7	6.8	8.5	650	210	45	36	55	790	48
5 – 10	108	41	26	18	2.46	5.9-6.8	7.65	6.6	8.7	630	240	56	31	77	310	43
10 – 20	118	41	27	17	2.28	5.8-6.7	7.8	6.8	5.5	770	250	60	35	52	230	54
20 – 27	96	40	27	18	3.45	3.5-4.9	7.9	6.9	4.4	1340	230	70	45	49	200	74
27 – 43	100	41	27	19	2.05	2.3	7.9	6.9	5.5	1050	240	62	38	49	200	74

Notes: 1. The humus content is different in different articles (Vazhenin, 1991), therefore, a range of values was taken. 2. Exchange Ca and Mg were measure by two methods: A –in ammonium acetate extract, B - according to Pfeifer (extract of ammonium chloride in 70% alcohol to remove easily soluble salts and suppress the dissolution of carbonates).

Table 5 Parameters of Cr and Ni migration models in soils in the impact zone of the Orsk-Khalilovsk Metallurgical Plant. The impact of the plant-30 years

Diffusion model					Convective diffusion model					
Background, мг/кг	$D \cdot 10^8$, cm^2/s	$f_0 \cdot 10^7$, $mg/(cm^2 \cdot s)$	Input to the soil by model	Found in soil above background	Background, mg/kg	$D_k \cdot 10^8$, cm^2/s	$V \cdot 10^9$, cm/s	C_{in}, mg/kg	Input to the soil by model	Found in soil above background
			mg/cm^2						mg/cm^2	
Cr, 0.5 km from the plant to the east, virgin lands										
50-200	13-20	50-85	6390	3760-6760	A) 0-250	5-16.5	-11 …-9	440-470	4260	2760-7760
					B) 110-220	3.7-8.0	-1 …+0.8	680-760	4620	3360-5560
Cr, 0.5 km from the plant to the east, virgin lands										
0-250	10-27	40-105	6860	3100-8100	100-250	3-9	0-0.6	650-730	4430	3100-6100
Cr, 8 km from the plant to the west, virgin lands, meadow chernozem in the flood land of the Ural River										
60-100	17-25	48-55	4870	3280-4080 (*)	130-190	1.4-1.45	2.80-2.95	290-310	1250	1790-2680 (*)
Ni, 0.5 km from the plant to the east, virgin lands										
60-75	10-20	35-45	3780	3190-3490	5-50	8-11	0.5-1.3	370-410	3920	3690-4590
Ni, 2 km from the plant to the south, virgin lands										

35-80	10-25	35-45	3780	3010-3910	A) 40-120	2.5-5	-1 …0	410-450	2310	2210-4210
					B) 30-60	2.5-4	1.6	350-370	2130	3410-4010 (*)
Ni, 8 km from the plant to the west, virgin lands, meadow chernozem in the flood land of the Ural River										
A) 60-100	2.5-3.0	27-33	2840	3430-4230 (*)	A) 120-200	0.3-0.7	0.4-0.7	580-680	1280	1540-2630
B) 170	1.2-1.7	17-22	1850	1990	B) 100-170	0.9-1.3	-1 …+0.2	630-730	1950	1990-3430

Note (A) and (B) – different combinations of estimates of the parameters of migration models that satisfy the condition that the concentration values fall into the corridor. The same explanations apply to tables 6 and 7. (*) – The model is not sufficiently adequate when comparing the amount of an element found in the soil and entered the soil according to the model.

Table 6 Parameters of Cu and Pb migration models in soils in the impact zone of the Mednogorsk copper-sulfur plant. The impact of the plant-46 years

Diffusion model					Convective diffusion model					
Background, mg/kg	$D \cdot 10^8$, cm^2/s	$f_0 \cdot 10^7$, $mg/(cm^2 \cdot s)$	Input to the soil by model	Found in soil above background	Background, mg/kg	$D_k \cdot 10^8$, cm^2/s	$V \cdot 10^9$, cm/s	C_{in}, mg/kg	Input to the soil by model	Found in soil above background
			mg/cm^2						mg/cm^2	
Cu, 0.5 km from the plant to the west, mountainous chernozem rubble, virgin land										
100	2.4-2.8	310-340	47200	41600	A) 100	1.45-1.65	0.6-0.75	5450-5950	30800	41600 (*)
					B) 100	2.1-2.25	-1 … +0.05	6900-7500	45300	41600
Cu, 7 km from the plant to the south-east, table land, southern chernozem, virgin land										
0-55	0.23-0.33	10.5-12.5	1670	1640-4520	40-110	0.06-0.12	0.15-0.25	680-820	925	1070-2470
Pb, 0.5 km from the plant to the west, mountainous chernozem rubble, virgin land										
10-50	2-3.1	100-110	15200	13900-14900	18-40	1.5-2.1	0.25-0.43	1800-2400	12000	14100-14700
Pb, 7 km from the plant to the south-east, table land, southern chernozem, virgin land										
17-37	0.4-0.9	4.5-6.5	798	588-1010	20-40	0.15-0.37	0.01-0.3	260-350	614	558-918

Table 7 Parameters of Cu and Pb migration models in soils in the impact zone of the South Ural Cryolite Plant.The impact of the plant 32 years (1 sampling) and 30 years (2 sampling).

Diffusion model					Convective diffusion model					
Background, mg/kg	$D \cdot 10^8$, cm^2/s	$f_0 \cdot 10^7$, $mg/(cm^2 \cdot s)$	Input to the soil by model, mg/cm^2	Found in soil above background, mg/cm^2	Background, mg/kg	$D_k \cdot 10^8$, cm^2/s	$V \cdot 10^9$, cm/s	C_{in}, mg/kg	Input to the soil by model, mg/cm^2	Found in soil above background, mg/cm^2
1 sampling. 2 km from the plant to the northwest, upper third part of the hill, chernozem ordinary loam, virgin land										
270-330	0.3-0.6	21-29	2520	1990-2740	270-330	0.15-0.28	0.01-0.3	1300-1700	2050	1990-2740
1 sampling. 3 km from the plant to the east, virgin land (woodland belt) at the base of the hill										
290-350	1.5-1.6	52	5250	4490-5690	320-360	0.7-0.85	-0.5 … +0.01	1680-1750	4270	4290-5090
2 sampling. 0.5 km from the plant, plain between hills (area 1)										
468-540	1.5-3.7	70-85	7330	5740-8360	450-600	0.8-1.4	-0.03 … +0.8	1800-2200	5600	5140-9040
2 sampling, 1.5 km from the plant to the northwest, lower third of the hill, soil heavy loam with rubble inclusions (area 2)										
300-400	15-25	130-160	13700	13700-17500	290-450	8-13	-2 … +1	1400-1700	13100	12300-17900

2 sampling, 1.5 km from the plant to the northwest, lower third of the hill, soil heavy loam with rubble inclusions (area 2)										
-	-	-	-	-	280-295	1.9-2.4	7	310-315	3190	4910-5400 (*)

Note The value of D (F^-) for an infinitely diluted solution of fluoride, calculated from the maximum equivalent electrical conductivity at 25 º C (reference data) is $1.5 \cdot 10^{-5}$ cm^2/s ($1500 \cdot 10^{-8}$ cm^2/s).

Table 8 Summary of the diffusion parameters that we obtained for adequate migration models

Element	Removal from intended source of contamination, km	$D \cdot 10^8$, cm^2/s	$D_k \cdot 10^8$, cm^2/s
Cr	0.5 2	13-20 10-27	A) 5-16.5; B) 3.7-8.0 3-9
Ni	0.5 2 8	10-20 10-25 1.2-1.7	8-11 2.5-5 A) 0,3-0,7; B) 0.9-1.3
Cu	0.5 7	2.4-2.8 0.23-0.33	2.1-2.25 0.06-0.12
Pb	0.5 7	2-3.1 0.4-0.9	1.5-2.1 0.15-0.37
F	0.5 1.5	1.5-3.7 15-25	0.8-1.4 8-13
	2 3	0.3-0.6 1.5-1.6	0.15-0.28 0.7-0.85

Table 9 Comparison of literature and obtained in this work estimates of "apparent" diffusion coefficients (D) and convective diffusion (D_k) of polluting elements in soils

Element	Environ	Measurement conditions	$D \cdot 10^8$, cm^2/s	$D_k \cdot 10^8$, cm^2/s	Reference
Cr	Почвы Оренбуржья	Perennial aerogenic pollution	12-24	4-11	-
Ni	Water solution 8.8 mm $Ni(NO_3)_2$	-	670	-	(Reference 1964; ; tables 1976)
	Pyrite tails on carbonate sand. Spain	2 months of exposure	-	0.2-1.5	(Frid, Borisochkina 2018)
	Soils of Egypt	Perennial irrigation with natural waters and wastewater	85-110 600-700	35-60 400-700	(Frid et al. 2016a)
	Soils of Orenburg region	Perennial aerogenic pollution	10-22	5-8	-
			1.2-1.7 (meadow chernozem)	0.6-1.0	-
Cu	Water solution	-	700-800	-	(Reference 1964)
	Water-saturated kaolinite, water-saturated montmorillonite	Laboratory experience	420 27-95	-	(Shackelford 1991)
	Pyrite tails on carbonate sand. Spain	2 months of exposure	-	0.13-0.27	(Frid, Borisochkina 2018a)
	Soils on loess under	Perennial	2.5-6.3	2.0-3.2	(Frid,

	deciduous forest. South China	aerogenic pollution			Borisochkina 2018b)
	Soils of Egypt	Perennial irrigation with - natural water - wastewater	150-330 260-400	42-540 140-350	(Frid et al. 2014; Frid et al. 2016b)
	Soils of Orenburg region strongly acidified - gravelly mountain chernozem - southern chernozem	Perennial aerogenic pollution	2.4-2.8 0.23-0.33	2.1-2.3 0.06-0.12	-
Pb	Water solution	-	820-950	-	(Reference 1964)
	Leached sod-calcareous soils	Perennial aerogenic pollution	1.0-2.0	0.65-0.90	(Frid, Borisochkina 2011)
	Sod-podzolic loamy soil	Field experience 2.5 years	-	210	(Blinov, Vertinskaya 1980)
	Pyrite tails on carbonate sand. Spain	2 months of exposure	0.6-1.2	0.7-1.3	(Frid, Borisochkina 2018a)
	Soils on loess under deciduous forest. South China	Perennial aerogenic pollution	0.4-1.6	0.3-1.1	(Frid, Borisochkina 2018b)

	Soils of Egypt	Perennial irrigation with - natural water - wastewater	125-135 510-630	90-150 370-525	(Frid et al. 2016b)
	Soils of Orenburg region strongly acidified - gravelly mountain chernozem - southern chernozem	Perennial aerogenic pollution	2-3.1 0.4-0.9	1.5-2.1 0.15-0.37	-
F	Soils of Orenburg region - unknown soil - ordinary chernozem -medium loamy -heavy loamy - heavy loamy gravelly	Perennial aerogenic pollution	1.5-1.6 0.3-0.6 1.5-3.7 15-25	0.7-0.85 0.15-0.28 0.8-1.4 8-13	

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