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PARAMETERS OF MATHEMATICAL MODELS FOR VERTICAL MIGRATION OF HEAVY METALS IN SOILS IN THE AREA OF LEAD AND ANTIMONY PLANT

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The data on distribution of heavy metals in the soil profile (Yuan et al., 2017) of the province Guangxi in southern China in the zone influenced by lead and antimony plant were analyzed. The soil is sod-calcareous and rich in humus. The averaged over the years and depth ("apparent") parameters of diffusion and convective-diffusion models of migration in the area of combined soil pollution (only soil aerogenic pollution and in combination with the sewage waters) are estimated. The largest values of the diffusion parameters were obtained for Zn and Cd ($n \cdot 10^{-7}$ cm^2/sec), the smallest values were obtained for Pb and Sb ($n \cdot 10^{-8}$ cm^2/sec). When soil was flooded by waste waters, a reliable convective component of migration for Zn and Sb was noted. At the same time the peak of Zn concentration moved to the depth of 40–60 cm. Under these conditions there was no clear inverse correlation between the migration mobility and the amount of sorption of elements by the soil.

Keywords: sod-calcareous soil, heavy metals, vertical migration in soils, migration models and their parameters, south China.

INTRODUCTION

This work continues the series of similar studies on the analysis of experimental data obtained in different regions of the world on the vertical migration of heavy metals and other elements in soil in the areas of intensive pollution (Frid, Borisochkina, 2010; Frid, 2016; Frid et al., 2016; Frid, Borisochkina, 2018 a, b, c, d). These experimental data are scarce and their analysis with the use of mathematical migration models has not virtually been carried out, in contrast to the similar data for radionuclides at radiation accidents and for global drop-outs (Prokhorov, 1981; Frid, 1999).

The urgency of the issue is related to the forecasting evaluation of contamination depth of various soil with different elements at different pollution sources. The other side of the issue is the estimation of self-purification rate of soil upper layer which degree of contamination is usually associated with all environmental characteristics.

The work aims to estimate the parameters of mathematical models of Pb, Sb, Cd, Zn vertical migration in soils at pollution with aerogenic emissions and the subsequent waterlogging with metallurgical plant sewage waters. It should be noted that migration model parameters characterize migration mobility of the substances, unlike the chemical mobility, which is determined by the content of fractions extracted from soil by various reagents.

MATERIALS AND METHODS

The description of the objects is based on the original source (Yuan et al., 2017). Lead and antimony factory was located in the south of the People's Republic of China – the north-west of Guangxi province in the suburbs of Hechi City.

The production started in 1992, the processed ores are: stibnite (Sb_2S_3), antimony ($FeSb_2S_4$), plaglonit ($Pb_5Sb_8S_{17}$). Plant waste waters had a high content of heavy metals. In 2008 the area surrounding the plant was flooded with these sewage waters and factory ceased operations.

Soil samples were collected in about 2014, that is, 6 years after the plant closed down. They were taken at three sites: A) a gully that was once flooded with sewage waters; B) a non-flooded foot of a neighboring hill; C) a control area in 8.4 km from the plant.

Soil type is a rich in humus sod-calcareous one (terra fusca). Climate type is a humid subtropical one, the average annual temperature is 20.4 ºC, annual precipitation is 1470 mm with the domination of south-west winds.

The authors analyzed more in detail the upper soil layer samples (0–10 cm) – Table 1 and Table 2. The total content of pollutants in soil samples were determined after samples decomposition HNO_3 + HF (final detection on ICP-MS); the total content of macroelements – by X-ray-fluorescence method. The samples were collected from the layers of 10–20 cm along the soil depth, were determined on the gross content of Pb, Sb, As, Zn, Cu, Cd, on their concentration in the pore solution and Kd distribution coefficients (the ratio of the gross concentration to the concentration in the pore solution). Unfortunately, the authors (Yuan et al., 2017) demonstrated the profile data in the graphs in logarithmic scale of concentration.

Table 1. Composition and properties of the upper soil layer (mean and standard deviation)

Indicator	**Location of sampling selection, in parenthesis - the number of repeated samples**			
	A (10)	**B (8)**	**C (3)**	**The upper part of the continental crust** *
pH_{H2O}	5.86 ± 0.58	6.03 ± 0.50	7.05 ± 0.19	-
Organic matter,%	2.96 ± 0.30	1.05 ± 0.42	1.77 ± 0.16	-
Total macronutrient content, %				
Al_2O_3	11.0 ± 2.3	10.5 ± 2.8	10.7 ± 2.1	14.9
Fe_2O_3	4.90 ± 0.94	5.0 ± 1.3	5.18 ± 0.69	4.68
CaO	1.04 ± 0.66	0.89 ± 0.60	0.88 ± 0.17	3.55
Mn	0.18 ± 0.02	0.15 ± 0.04	0.09 ± 0.03	-
Ti	0.72 ± 0.20	0.69 ± 0.09	0.40 ± 0.05	-
MgO	0.51 ± 0.16	0.48 ± 0.19	0.43 ± 0.11	2.46
Granulometric texture, %				
Clay (mud)	21.3 ± 4.1	19.8 ± 3.4	17.9 ± 1.6	-
sand	76 ± 7.1	78 ± 4.3	81 ± 3.2	66.3
dust	2.8 ± 1.3	2.2 ± 2.3	1.02 ± 0.68	-

Note. A dash (-) indicates the absence of data, an asterix (*) – data from Condie, 1993.

Therefore, for our calculations we had to take data from the charts, which made the data less accurate.

Table 2. Contaminants content (mg/kg) in the upper soil layer (mean and standard deviation)

Element	**Location of sampling selection, in parenthesis - the number of repeated samples**					
	A (10)	**B (8)**	**C (3)**	**sewage waters (8)**	**dust from the pipes (9)**	**Province background**
Sb	3100 ± 1600	290 ± 170	21	13300 ± 6500	15200 ± 9000	2.12
As	410 ± 260	32 ± 14	39	5200 ± 2200	4000 ± 1600	20
Pb	6400 ± 2900	440 ± 360	76	940 ± 320	2300 ± 1700	18.8
Zn	920 ± 420	290 ± 130	26	4800 ± 2000	1030 ± 590	46
Cu	192 ± 58	59 ± 38	10	580 ± 240	790 ± 360	21
Cd	34 ± 15	12 ± 6	2	47 ± 59	42 ± 31	0.062

For mathematical analysis at the migration patterns we used the contaminant concentration profiles where there were noticeable gradients along the depth over several layers. The information thus obtained (from the graphs) is presented in Table 3.

Table 3. Total contaminants content and distribution along the soil profile (taken from the charts of Yuan et al., 2017), mg/kg

Soil layer, cm	**Location of sampling selection**					
	(B) non-flooded foot of the hill		**(A) gully flooded with sewage waters**			
	Cd	**Zn**	**Pb**	**Sb**	**Cd**	**Zn**
0–10	19	840	2 440	2 680	25	1 060
10–20	6.1	620	289	336	14	1 000
20–30	3.5	580	189	190	6.4	1 000
30–40	2.5	540	182	190	5.1	1 060
40–60	2.2	535	165		4.7	4 005
60–80	1.75	535	158		3.1	2 700
80–90	1.65	465	154		2.3	1 060

Two types of migration patterns were used with evaluation of their parameters: diffusion and convection-diffusion. The parameters were considered constant over the migration time and the soil depth, considering that they reflect the average actual vibrations of various processes accompanying the migration. Such an assumption, on the one hand, greatly simplifies the mathematical models and work with them, and on the other hand, it is justified itself in our and other studies presented earlier. Relevant parameter values are called “apparent”.

The migration time before the sample selection consisted of two segments: the first 16 years the surface of the soil plots A and B received aerogenic drop-out from the plant, the next 6 years there was no drop-out, however, the plot A underwent immediate flooding with waste waters. These circumstances are reflected in the choice of the boundary conditions on the soil surface. The corresponding exact solutions to migration differential equations were taken from the publications (Ryzhinskii et al., 1971; Polyanin et al., 1998; Malkovich, 1999).

The selection procedure for model parameters was the following. First, a possible range of gross concentrations was calculated in the form of ± 15 % to ones indicated in Table 3. It was considered that the migration of the contaminating elements is evaluated with gross content, since, on the one hand, contaminating they often significantly exceed background ones and, on the other hand, background gross content in the calculations either set or subtracted. Deviation of 15 % exceeds analytical errors indicated in Yuan et al., 2017 as 10 %, however, natural variation and errors in reading data from graphs are partly considered. Further, the concentration values were calculated at different combinations of the specific model parameter values until they entered the predetermined corridor (± 15 %) of experimental values. The corridor can also simultaneously measure a possible range of the parameters. An additional control was the proximity of the measured values of the profile content (over the background) and those calculated by the input pattern of the polluting element. Under these conditions the model and its parameters were supposed reasonable.

RESULTS AND DISCUSSION

The upper soil layer at the plot A (flooded with waste waters), as it follows from Table 2, is obviously contaminated with all six elements; at the plot B (without flooding) there is no obvious contamination with the exception for As. The contamination is confirmed by the profile examination (Table 3). Peculiarity of Zn distribution over the depth on the plot A is visible, unlike for other elements, its maximum concentration is in the layer of 40–60 cm rather than at the surface, which clearly demonstrates the convective transfer of zinc under sewage water flooding.

Table 4–6 shows the estimated apparent parameters of migration models, Table 7 – their summary. At the plot A (flooding) a convective transfer into the soil depth was recorded (except for Zn) only for Sb, whereas the average rate for Zn for 6 years had a very big value – about 10 cm/year.

Table 4. Apparent parameters of diffusion model – plot B, termination of aerogenic drop-out from the plant after cessation of its16 year-long work

Background mg/kg $D \cdot 10^8$ cm^2/s	**Flow on the soil surface during the plant operation (q), mg/(cm^2·s)**	**$D \cdot 10^8$, cm^2/s**	**Found in profile above the background, mg/cm^2**	**Entered soil according to the model, mg/cm^2**
Zinc				
500	35	40	7200	7020
Cadmium				
1.2	The range of values from (D = 6.8, q = 8) to (D = 11, q = 5); middle one – D = 8, q = 6.5		272	For the whole range – 274–278

The diffusion migration parameters (D and D_k) for all the elements demonstrated a considerable variation both between plots A and B and between the models (diffusion and convection-diffusion). The estimation differences between the models for Pb and Sb are difficult to explain. In general, it can be noted that the parameters of Zn and Cd diffusion migration were higher than of Pb and Sb.

Table 5. Apparent parameters of diffusion model – plot A, termination of aerogenic drop-out from the plant after cessation of its16 year-long work and one-time waste waters (containing Zn, Cd) flooding

Diffusion model, the diffusion layer of 0–10 cm after flooding				
Background, mg/kg	The initial concentration in 0–10 cm layer, mg/kg	$D \cdot 10^8$, cm^2/s	Found in the profile over the background, mg/cm^2	Entered soil according to the model, mg/cm^2
Zink				
-	-	-	-	-
Cadmium				
2.0	40–49	80–100	428–580	442

Convection-diffusion model, impulse source at the time of the flooding					
Background, mg/kg	The number of elements in impulse mg/cm^2	$D_k \cdot 10^8$, cm^2/s	$V \cdot 10^8$, cm/s	Found in the profile over the background, mg/cm^2	Entered soil according to the model, mg/cm^2
Zink					
1000	56 500–76 000	21–27	31.5–32.8	81 500–110 300	98 450
Cadmium					
2.0	300–530	40–95	-5 … +2	428–580	412

Let us compare the evaluations obtained in this study D (D_k) with those obtained for the other field conditions. For Zn and Cd they are close to the values found for Egypt carbonate saline soils irrigated by natural (river and artesian) waters (Frid et al, 2016); for Pb they are closest to the leached sod-calcareous soil of Vologda Region (Frid, Borisochkina, 2010) and to one soil type (Hapli-Udic Argosols) of south China (Frid, Borisochkina, 2018b); for Sb there is while only a single estimate for heavily-leached by pyrite waste calcareous sandy soil (Frid, Borisochkina, 2018a), which is lower than obtained in this work.

Table 6. Apparent parameters of diffusion model – plot A, termination of aerogenic drop-out from the plant after cessation of its16 year-long work and one-time waste waters (containing Pb, Sb) flooding

Diffusion model, the diffusion layer of 0-10 cm after flooding					
Back-ground, mg/kg	Initial concentration in the layer 0–10 cm, mg/kg	$D \cdot 10^8$, cm^2/s	Found in the profile over the background, mg/cm^2		Entered soil according to the model, mg/cm^2
Lead					
150	2 600– 3 000	1.9–3.0	25 500		28 000
Antimony					
190	2 000– 3 450	1.85–3.0	26 360		27 250
Convective-diffusion model, impulse source at the moment of flooding					
Back-ground, mg/kg	The number of elements in impulse mg/cm^2	$D_k \cdot 10^8$, cm^2/s	$V \cdot 10^8$, cm/s	Found in the profile over the background, mg/cm^2	Entered soil according to the model, mg/cm^2
Lead					
150	18 000– 30 000	8.5–9.7	-0.4 … +0.8	25 500	24 310
Antimony					
190	18 000– 32 500	7–9	0.3–0.7	26 360	26 220

Table 7. Summary table of the found apparent migration parameters

Element	**Plot B**	**Plot A**		
	$D \cdot 10^8$, cm^2/s	**$D \cdot 10^8$, cm^2/s**	**$D_k \cdot 10^8$, cm^2/s**	**$V \cdot 10^8$, cm/s**
Zn	40	-	21–27	31.5–32.8 (9.9–10.3 cm/year)
Cd	8	80–100	40–95	-
Pb	-	1.9–3.0	8.5–9.7	-
Sb	-	1.85-3.0	7–9	0.3–0.7 (0.10–0.22 cm/year)

Note. Only the values that differ from zero are shown for V.

The properties of the upper soil layers at the plot A and B are quite similar (Table 1) except for the content of organic substances, which amount is substantially more at the plot A, which one would associate with a larger diffusion Cd lability and high convective Zn lability.

However, there may be other circumstances, for example, different Zn and Cd forms in aerogenic drop-out and waste waters. So that a clear answer on the available information is difficult.

Mechanical migration models in porous media (Prokhorov, 1981; Prokhorov, Frid, 1971; Ryzhinskii, Frid, 1973) show us that parameter values of migration models D (Dk) and V depend on sorption of migrating substance. In the case of linear isotherms and two-phase medium, one of which is a sorbent (liquid and solids), can be written simplistically as:

$$D = \frac{D_1 (l_0/l_1)^2 \Theta_1 + D_2 (l_0/l_2)^2 \Theta_2 K}{\Theta_1 + \Theta_2 K}, \quad V = (l_0/l_1) \Theta_1 V_1/K,$$

where D_1 и D_2 – diffusion coefficient in liquid and solid phases (more precisely, over the solid phase surface), $(l_0/l_1)^2$ and $(l_0/l_2)^2$ – tortuosity coefficients of the same phases, Θ_1 and Θ_2 – volume fractions of these phases in medium, K – volume (dimensionless) coefficient of the distribution between solid and liquid phases ($K = K_d d_0$), K_d – normal distribution coefficient (ml/g), d_0 – specific mass of the solid phase, V_1 – substance flow rate (e.g., water) causing convective transfer of the element under study.

Since in this paper we are dealing with the elements heavily-sorbed by soil, then Θ_1 value in the denominator of the relation for D can be neglected and thus we obtain:

$$D = D_1 (l_0/l_1)^2 \Theta_1/\Theta_2 K + D_2 (l_0/l_2)^2.$$

Consequently, both for D and for V one can expect the reverse dependence on the distribution coefficient.

In the work (Yuan et al., 2017) Figure 4 shows the K_d values for various elements over the soil depth for plot A. The K_d values were calculated as the ratio of the element total contents in the soil samples to their concentration in the pore solution. The figure shows that for all elements K_d value significantly increased from the depth of 5 cm to 10 cm, and deeper growing trend slowed down. This trend contradicts our assumption of the constancy of average parameters over the soil depth but it does not deny adequate values of migration patterns according to the criteria described above. This contradiction can be explained as a low calculation accuracy for K_d and as unknown prerecord of K_d changes for 22 years since the time the pollution started.

However, it seems interesting to compare element differences in K_d values and migration parameters (Table 7). K_d depth charts are in the following order: Pb >> Zn ≥ Sb >> Cd. As noted above, the diffusion parameters for Pb are related to the minimum ones, and for the Cd – to the maximum ones, which is consistent with K_d number. At the same time, Zn and Sb are the extreme parameters on diffusion values, and they are the average values on K_d. The similar situation can be observed for Zn and Sb on convective parameter V (Table 7). Thus, during continuous migration of contaminating elements in the field conditions the dependence between the parameters of migration model into the soil depth and adsorption indicator (at one-off measurement) is ambiguous.

Maintaining or familiar changing of boundary conditions on the soil surface the migration pattern with the found parameter estimates can be used to forecast profile contamination.

CONCLUSIONS

We estimated average by year and depth (“apparent”) migration models parameters (diffusion and convection-diffusion) in the area of technogenic soil pollution (only aerogenic together with waste waters of metallurgical plant). Bigger values of diffusion parameters were obtained for Zn and Cd ($n \cdot 10^{-7}$ cm^2/s), lower – for Pb and Sb ($n \cdot 10^{-8}$ cm^2/s). In the case of waste waters flooding a reliable convective component of migration for Zn and Sb was marked, wherein zink peak concentration moved to the depth of 40–60 cm. At the same time under these conditions there was no expected clear inverse correlation between the migration mobility and the value of the element sorption by soil.

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