



## MIGRATION FORMS OF CHEMICAL ELEMENTS IN SHALLOW GROUNDWATER IN LITHUANIA

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**Abstract.** The migration forms of basic (Ca, Mg, Na, K) and polyvalent (Fe, Mn) chemical elements, heavy metals (Cd, Cu, Ni, Pb, Zn), and water saturation with minerals under natural and polluted conditions in shallow groundwater of Lithuania were calculated using a computer program WATEQ4F. Change of metals migration forms with increase of their concentration and alkalinity of environment has been well described by logarithmic functions, which can also be used for the forecasting. The migration forms of chemical compounds enable to identify the pollution sources and intensity of their influence.

**Key words:** groundwater, thermodynamic modelling, chemical elements, migration forms.

**Abstrakt.** Wykorzystując program komputerowy WATEQ4F, określono możliwe formy migracji pierwiastków chemicznych o stałej wartościowości (Ca, Mg, Na i K) i o różnych wartościowościach (Fe, Mn) oraz metali ciężkich (Cd, Cu, Ni, Pb i Zn) w czystych i zanieczyszczonych płytkich wodach podziemnych Litwy. Zmiany mobilnych form metali wraz ze wzrostem ich koncentracji i zasadowości środowiska dobrze opisują funkcje logarytmiczne, wykorzystywane również do prognoz pogody. Mobilne formy związków chemicznych umożliwiają identyfikację źródeł zanieczyszczenia oraz intensywność ich wpływu na środowisko.

**Słowa kluczowe:** wody podziemne, modelowanie termodynamiczne, pierwiastki chemiczne, specjacje.

### INTRODUCTION

Types of chemical elements forms in groundwater and their impact on migration processes were investigated by method of thermodynamic modelling. The modelling based on a computer program WATEQ4F (with thermodynamic data BASIC), which was designed for calculation of the forms of the main, trace and oxidation–reduction elements in groundwater and water saturated with minerals (Ball, Nordstrom, 1992).

Shallow groundwater in Lithuania occur in alluvial, fluvioglacial, limnoglacial, glacial, and organogenic sediments (Table 1).

#### GROUNDWATER CHEMISTRY FACTORS

The major factors controlling chemical composition of groundwater under natural conditions are: atmospheric precipitation, lithological and chemical structure of rocks in the aeration and saturation zones, and also thermodynamic conditions of underground environment (temperature, pressure, and struc-

ture of gases). Dissolving solid matter of the aquifers is the main process of formation of the water chemical composition. A water solution may be over and under saturated or in balance with carbonate minerals, calcium or iron (such as apatite, calcite, basalumnite and aragonite).

In the sum of cations and anions of groundwater, calcium and magnesium bicarbonates prevail: 75–80 and 60–30 meq/l accordingly. Under such conditions, water chemistry is formed by  $\text{HCO}_3\text{--Ca--Mg}$ , in which the basic anions and cations are mainly in the ion forms (up to 90–100%) (Table 2).

Concentrations of organic matter and biogenic elements determine processes of dissolution and leaching from the soil. Atmosphere plays an important role in the nitrogen formation, e.g. the atmospheric precipitation contains up to 8–9 — fold concentrations of ammonium salts compared with their values in natural water of the sediments in consideration. Concentrations of polyvalent elements — iron and manganese being the most important ones — are controlled by two factors: dissolution and thermodynamic environment (pH, Eh).

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**Table 1**  
**Background values of groundwater chemical composition in Lithuania**

Aquifer	Sampleset	Statistical index*	General chemical components										Biogenic components						Metals						pH	Eh mV
			Cl mg/l	SO <sub>4</sub> mg/l	HCO <sub>3</sub> mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Hard- ness meq/l	TDS mg/l	NH <sub>4</sub> mg/l	NO <sub>2</sub> mg/l	NO <sub>3</sub> mg/l	COD <sub>Mn</sub> mgO <sub>2</sub> /l	Pb mg/l	Cd mg/l	Cu mg/l	Ni mg/l	Zn mg/l	Mn mg/l	Fe mg/l				
Alluvial sediments	473	min	13.9	32.7	250	7.8	2.0	60.5	21.0	4.7	431	0.18	0.01	1.21	2.80	0.0002	0.006	0.007	0.024	0.08	0.13	7.00	162			
		max	24.1	47.1	364	16.0	4.5	87.0	38.0	6.2	546	0.35	0.04	3.66	4.00	0.0030	0.036	0.012	0.083	0.17	0.18	8.10	303			
		average	19.1	38.8	293	11.0	3.5	74.5	29.5	5.3	479	0.23	0.03	2.04	3.42	0.0012	0.015	0.008	0.052	0.14	0.15	7.58	211			
Fluvioglacial sediments	212	min	10.0	11.0	117	4.3	0.9	30.6	10.3	2.4	220	0.10	0.01	1.38	1.20	0.0002	0.006	0.002	0.020	0.03	0.13	6.85	160			
		max	26.5	38.0	321	11.6	2.7	74.0	24.0	5.5	478	0.26	0.04	4.00	4.35	0.0006	0.010	0.004	0.050	0.05	0.29	8.15	335			
		average	14.8	24.8	210	7.0	1.6	60.9	19.6	4.4	378	0.14	0.03	2.69	2.58	0.0005	0.009	0.003	0.031	0.04	0.23	7.54	245			
Limmoglacial sediments	128	min	5.1	30.8	159	8.3	2.0	35.5	12.2	3.8	246	0.05	0.04	2.60	2.00	0.0005	0.010	0.001	0.080	0.05	0.05	7.23	40			
		max	17.7	44.7	169	17.1	4.2	46.6	30.0	4.3	319	0.31	0.05	3.31	3.50	0.0030	0.032	0.002	0.330	0.12	1.0	7.57	160			
		average	11.4	37.8	164	8.5	3.3	41.0	24.5	4.1	283	0.18	0.05	2.96	2.90	0.0015	0.021	0.002	0.205	0.06	0.40	7.38	120			
Organogenic sediments	112	min	2.8	26.0	218	1.4	0.6	34.0	12.0	3.2	290	0.95	0.01	0.30	10.0	0.0003	0.010	0.001	0.010	0.16	0.70	6.00	90			
		max	14.7	42.2	332	3.6	5.7	56.5	21.1	4.5	428	2.70	0.04	3.90	18.1	0.0030	0.018	0.009	0.100	0.60	6.40	7.20	150			
		average	5.8	29.2	240	2.4	2.4	43.6	16.5	3.7	370	2.50	0.02	1.80	12.1	0.0016	0.014	0.006	0.046	0.25	3.10	6.80	110			
Glacial sediments	257	min	17.5	16.1	234	9.5	2.0	31.2	21.2	3.3	451	0.29	0.01	0.88	0.75	0.0002	0.004	0.001	0.003	0.04	0.40	6.80	113			
		max	28.5	44.1	485	34.0	4.3	105.0	50.0	9.4	680	1.56	0.04	6.30	5.10	0.0030	0.080	0.018	0.137	0.14	1.42	7.33	230			
		average	23.0	31.5	375	17.4	4.1	69.0	34.8	6.2	563	0.88	0.03	2.77	3.05	0.0012	0.028	0.010	0.060	0.08	1.00	6.94	205			

Table 2

**Migration forms of general chemical components (% of total element amount) in the natural groundwater  
(calculated by average concentration values)**

Aquifer	Ca			Mg			Na	K	HCO <sub>3</sub>		SO <sub>4</sub>			Cl
	Ca <sup>2+</sup>	CaCO <sub>3</sub> CaHCO <sub>3</sub> <sup>+</sup>	CaSO <sub>4</sub>	Mg <sup>2+</sup>	MgCO <sub>3</sub> MgHCO <sub>3</sub> <sup>+</sup>	MgSO <sub>4</sub>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> CO <sub>3</sub>	SO <sub>4</sub> <sup>2-</sup>	CaSO <sub>4</sub>	MgSO <sub>4</sub>	Cl <sup>-</sup>
Alluvial sediments	94.8	1.9	3.1	94.8	2.3	2.8	99.8	99.8	91.5	6.5	83.9	10.3	5.6	100.0
Fluvioglacial sediments	95.6	2.6	1.7	95.3	3.1	1.6	99.8	99.9	90.8	7.4	84.5	11.0	4.3	100.0
Organogenic sediments	95.3	2.3	2.4	95.0	2.8	2.1	99.7	99.9	69.0	30.1	88.4	8.6	2.6	100.0
Glacial sediments	94.5	3.6	2.0	93.9	4.3	1.7	99.6	99.9	75.2	23.2	81.7	10.2	7.5	100.0

### MIGRATION FORMS OF METALS

Fe<sup>2+</sup> and Fe(OH)<sub>3</sub> are the main migration forms of iron compounds. In the oxidizing environment iron compounds slowly dissolve in the water. Therefore, they usually migrate in the form of water-suspended oxides. In the reducing environment the solubility of iron compounds increases. In the silt layer of surface water bodies, iron transforms into a ion form and infiltrates under the ground with surface water. Similar processes — reduction being even more intensive — take place during the transformation of manganese compounds. Manganese is more oxidation-resistant element. Entering the aquifer it stabilizes causing the increase of background concentration.

Fulvic acids are the regulating factors of iron concentrations. The concentration of fulvic acids in water sometimes reaches 0.5 (average value is 0.25) mg/l. Alluvial sediments contain rather high concentrations of manganese compounds — 500–600 mg/kg. Hydrophosphates (MnHPO<sub>4</sub>) are, presumably, the main cause of such concentrations. The bulk of manganese is dissolved in hydrocarbonate sediments, in the MnCO<sub>3</sub> and MnHCO<sub>3</sub> forms. The elementary bivalent manga-

nese ions (Mn<sup>2+</sup>), which account for 68 % of this element compounds in the groundwater, represent the main migration form of manganese (Diliunas, Jurevicius, 1997; Diliunas *et al.*, 2000; Diliunas, Jurevicius *et al.*, 2002).

Chemically stable elements — heavy metals in the first place — are more widely dispersed in groundwater. Changes of migration forms, formation of new compounds, sorption and desorption, dispersion etc., are the main processes which hinder or intensify that dispersion of metals. Forms and compounds of metals and their change, which depend on the concentration of metals, on hydrogeological and thermodynamic conditions, and on the level of anthropogenic impact on the environment, play an important role in heavy metals migration in groundwater.

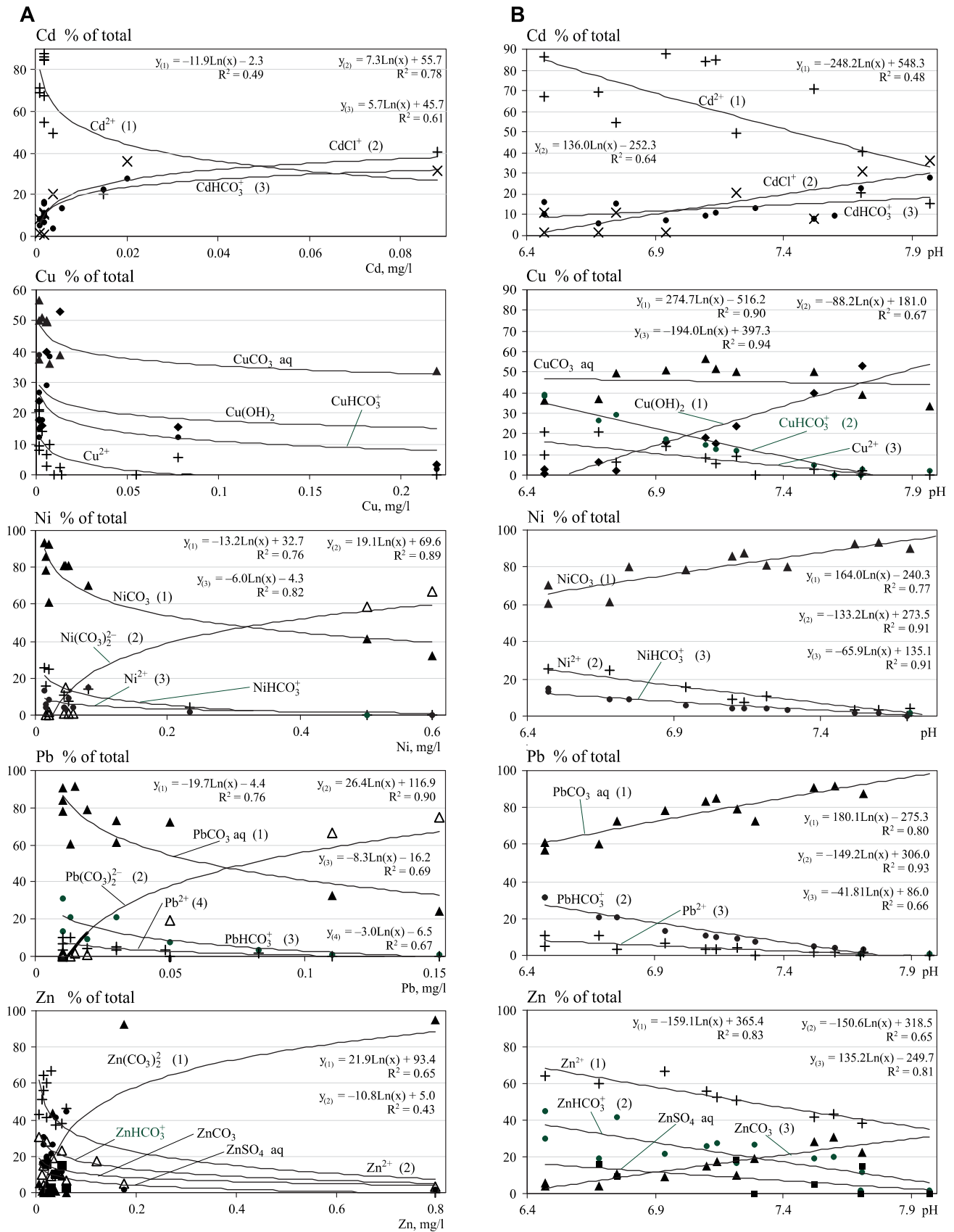
Metals, which migration forms were analysed in groundwater, could be divided into 3 groups:

- 1) mainly in carbonate complexes (?90%) (Pb, Ni);
- 2) composite ion form and carbonate complexes (Zn, Mn) and ion form and carbonate and hydroxyl complexes (Cu, Fe);
- 3) mainly in ion form (Cd); migration forms of metals influence their ability of sorption; the most active metals for sorption are in hydroxyl and carbonate complexes, the least — in ion forms (Table 3).

Table 3

**Migration forms of metals (% of total element amount) in the natural groundwater  
(calculated by average concentration values)**

Aquifer	Cd		Cu				Ni		Pb		Zn		Mn		Fe	
	Cd <sup>2+</sup>	CdHCO <sub>3</sub> <sup>+</sup>	Cu(OH) <sub>2</sub> CuOH <sup>+</sup>	CuCO <sub>3</sub> CuHCO <sub>3</sub> <sup>+</sup> Cu(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	Cu <sup>2+</sup> Cu <sup>+</sup>	NiCO <sub>3</sub> NiHCO <sub>3</sub> <sup>+</sup> Ni(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	Ni <sup>2+</sup>	PbCO <sub>3</sub> PbHCO <sub>3</sub> <sup>+</sup> Pb(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	ZnCO <sub>3</sub> ZnHCO <sub>3</sub> <sup>+</sup> Zn(CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	Mn <sup>2+</sup>	MnHCO <sub>3</sub> <sup>+</sup> MnCO <sub>3</sub>	Fe <sup>2+</sup>	Fe(OH) <sub>3</sub> Fe(OH) <sub>2</sub> <sup>+</sup>	FeHCO <sub>3</sub> <sup>+</sup> FeCO <sub>3</sub>
Alluvial sediments	85.3	7.8	65.1	31.2	3.2	90.9	8.8	95.0	3.1	57.6	38.3	77.9	19.7	47.7	37.5	12.7
Fluvioglacial sediments	87.6	7.4	52.2	44.5	3.1	95.1	4.8	96.8	2.0	50.6	47.1	68.2	30.8	51.6	30.4	16.7
Organogenic sediments	88.0	7.2	5.7	33.6	42.0	79.2	20.2	89.8	8.6	68.3	29.2	77.6	21.0	57.9	25.1	15.7
Glacial sediments	88.0	7.1	16.8	68.8	14.0	84.0	15.6	91.9	6.6	66.8	30.7	76.8	21.5	71.3	7.5	19.3



**Fig. 1. Dynamic of metal migration forms**

**A** — dependence on the concentration; **B** — dependence on the acidity of filtration environment

Transformation of migration forms and complex compounds are influenced mostly by the change of pH value. Increase of pH value causes the increase of Ni, Pb, and Zn in carbonate form complexes. In the alkaline environment ( $\text{pH} > 7.5$ ), ion forms of metals decline by 2–3 times, sometimes disappear at all. Increasing alkalinity ( $\text{pH} > 7.8\text{--}8.0$ ) converts almost all Cu into hydroxyl form, and its migration is very slow. Increase of metal concentrations and alkaline environment influences the activation of chemical compounds formation (in case under consideration — mostly with carbonates) and decreases the metal migration activity. Logarithmic functions make the best description model of migration forms change that depends on different processes, and could be used for prognostic evaluation (Fig. 1).

#### MAIN FACTORS CONTROLLING CHEMICAL ELEMENTS MIGRATION IN GROUNDWATER

The anthropogenic factor is reflected by higher concentrations of chemicals in groundwater, intensification of settlement, crystallization, sorption, ion exchange, and other chemical processes, and even in the change of the character of these processes. The migration capacity of chemical elements in groundwater technogenic metamorphisation process is controlled by spectrum of their geochemically significant migration forms (not smaller than 10–20% of the total concentration of element).

Chemical component concentration in the groundwater of polluted territories depends mainly on pollution type, concentration of pollutants, zone of aeration, lithogenic composition of

aquifer, and thermodynamic environment which influence the activity of physical–chemical processes. Metals are sensitive to change of groundwater thermodynamic environment and mineralisation. Usually hen pollution of groundwater increases the amount of Zn, Mn, and Fe (mainly with carbonates). Yet, the ion forms decrease and quantitative changes of carbonate complexes (Ni, Pb) occur. Cd and Cu chlorinate complex compounds could form in highly polluted groundwater.

In case of highly concentrated pollution, 3 hydrochemically polluted zones appear:

I — intensively polluted zone, which is near the pollution source, in 100–150 m radius;

II — affected by direct impact zone (200–300 m radius);

III — disturbed zone (500 and more metres from the pollution source).

Concentration of metals in the intensively polluted groundwater exceeds the background values by 10–20 times, and rapidly decreases away from the centre of pollution. Metal concentrations in a zone affected by direct impact are 2–6 times lower than in the intensively polluted zone, and 1.5–2.5 times lower in the disturbed zone than in the direct impact zone.

Changes of migration forms in the polluted groundwater are controlled by concentrations of pollutants and thermodynamic environment. Distinctive changes metals migration forms occur in groundwater around the landfills. The metals migration form, typical for various pollution zones and calculated using average concentrations, are given in Table 4.

With increasing pollution, the metals forms change in the following sequence:

— carbonate forms of Pb and Ni slightly increase at the expense of ion forms of these elements;

Table 4

Migration forms of metals in the groundwater of landfill impact area (average value, % of the total of elements)

	Cd				Cu				Ni	
	$\text{Cd}^{2+}$	$\text{CdHCO}_3^+$ $\text{Cd}(\text{CO}_3)_2^{2-}$	$\text{CdCl}^+$ $\text{CdCl}_2$	$\text{CdSO}_4$ $\text{Cd}(\text{SO}_4)_2^{2-}$	$\text{CuCO}_3$ $\text{CuHCO}_3^+$ $\text{Cu}(\text{CO}_3)_2^{2-}$	$\text{CuCl}_2^-$ $\text{CuCl}_3^{2-}$	$\text{Cu}(\text{OH})_2$ $\text{CuOH}^+$	$\text{Cu}^{2+}$ $\text{Cu}^+$	$\text{NiCO}_3$ $\text{NiHCO}_3^+$ $\text{Ni}(\text{CO}_3)_2^{2-}$	$\text{Ni}^{2+}$
Intensively polluted	18.2	24.4	54.0	2.8	29.1	69.8	1.1	0.1	99.6	0.4
Affected by direct impact	61.0	16.0	11.0	11.8	77.0	8.8	1.9	11.2	88.0	10.8
Disturbed	71.1	8.6	8.5	11.6	66.2	0.3	29.9	3.0	96.0	3.7

	Pb		Zn			Mn			Fe		
	$\text{PbCO}_3$ $\text{PbHCO}_3^+$ $\text{Pb}(\text{CO}_3)_2^{2-}$	$\text{Pb}^{2+}$	$\text{ZnCO}_3$ $\text{ZnHCO}_3^+$ $\text{Zn}(\text{CO}_3)_2^{2-}$	$\text{Zn}^{2+}$	$\text{ZnSO}_4$ $\text{Zn}(\text{SO}_4)_2^{2-}$	$\text{MnHCO}_3^-$ $\text{MnCO}_3$	$\text{Mn}^{2+}$	$\text{MnSO}_4$	$\text{FeHCO}_3^+$ $\text{FeCO}_3$	$\text{Fe}^{2+}$	$\text{Fe}(\text{OH})_3$ $\text{Fe}(\text{OH})_2^+$ $\text{Fe}(\text{OH})_4^-$
Intensively polluted	99.7	0.2	96.3	3.4	0.1	83.4	14.3	0.6	70.5	16.6	10.9
Affected by direct impact	94.0	4.1	52.1	41.4	6.3	42.5	52.0	5.0	43.6	51.3	0.0
Disturbed	97.2	1.5	52.6	41.4	5.3	35.8	59.2	4.6	28.0	61.4	5.7

— the content of Fe and Mn carbonate forms increases considerably whereas the content of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  decreases;

— a considerable increase of carbonate forms of Zn is almost equivalent to the decrease of ion forms;

— the content of Cd carbonate forms also increases considerably whereas significant chloride forms appear in the most intensively polluted zone. Their formation is predetermined probably by chlorinated hydrocarbon compounds getting into the groundwater with the landfill filtrate.

When the concentrations of elements increase and the environment becomes highly alkaline, the formation of chemical compounds (mostly carbonate) accelerates whereas the migration activity of metals slows down. The most actively sorbed are metals contained in hydroxyl and carbonate compounds, and the most slowly — the ion forms of metals. The migration forms of chemical compounds enable to identify the sources of pollution and intensity of their impact.

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