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Migration forms of main chemical elements in the groundwater of the Quaternary deposits of Lithuania

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Abstract The article deals with the potential background forms of main chemical elements—cationgenic, aniongenic and complexing—in fresh groundwater of the Quaternary deposits in Lithuania. The forms of chemical elements in water and their impact on migration have been studied applying the thermodynamical calculation (modelling) method and the WATEQ4 software. Major chemical elements were found to be migrating in Quaternary groundwater mainly as ions and carbonates; while migration of metals was different: Pb and Ni as carbonate complexes, Cu and Fe as mixed carbonate and hydroxyl complexes, Zn and Mn as ions and carbonate complexes, and Cd as ions, mainly.

Keywords *Chemical elements, concentration, migration forms, aquifers, thermodynamic modelling, software WATEQ4F, saturation.*

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INTRODUCTION

Assessment of chemical element forms in groundwater and their migration peculiarities is one of the most important fields of hydrogeochemical research. Different compounds of the same chemical element are known to possess different thermodynamical, physico–chemical and hydrogeochemical parameters and indices (free energy, diffusion, sorption etc.) determining their distribution and migration. The presence of a chemical element in the water in different state is reflected in ion exchange, as well as sorption and settling processes, since not only common cations and anions, but also the compounds charged differently (in size and sign) participate in the exchange and sorption processes. Therefore, in order to understand the formation of chemical composition of groundwater and distribution of chemical elements in the water–deposit system and prognosticate the changes caused by natural and man–made factors, it is necessary to know their complex compounds. The present article is devoted to solve such a problem for the Quaternary fresh groundwater (up to 1 g/l solids) taken to drink in Lithuania (Fig. 1).

The fresh groundwater chemistry in Lithuania is rather well studied (Diliūnas, Jurevičius 1998; Diliūnas *et al.* 1998; Juodkazis *et al.* 2003, 2003a; Klimas 1994, 2005). However, the mechanism how groundwater chemistry is being formed and their peculiarities are not enough revealed yet. To study them, up to now, physical and chemical methods and general chemistry postulates following from quantitative relations and ratios of elements had been used as a rule.

Chemical thermodynamic methods have been rarely applied yet they are especially helpful in determining element forms and compounds, as well as their balance and distribution. The results presented in the paper largely fill the gap in the knowledge about the fresh groundwater chemistry in Lithuania and adjacent areas; they also provide new data for investigation of hydrochemical conditions and assessment of groundwater quality.

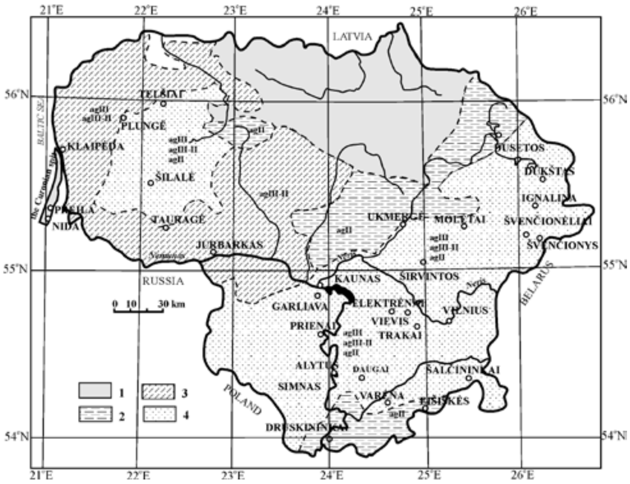

Fig. 1. Quaternary intermorainic aquifers occurrence: 1–no intermorainic aquifers, 2–Middle Pleistocene (agII), 3–Middle-Upper and Upper Pleistocene (ag II-III, agIII), 4–Middle and Upper Pleistocene (agII, agIII-II, agIII).

METHODS

Only the potential forms of the main cationgenic (Na, K, Ca, Mg), aniongenic (CO_3, Cl, SO_4, PO_4, F) and complexing (Fe, Mn, Ni, Cu, Zn, Cd) elements in fresh Quaternary groundwater were studied focussing on fully dissolved compounds being the basic migration forms of these chemical elements. Those occurring in suspension and colloid state were not analysed due to their secondary role in migration processes (Krainov *et al.* 2004).

Occurrence of chemical elements in groundwater and their impact on migration processes were studied by applying the thermodynamic calculation (modelling) method. The software WATEQ4F (with thermodynamic database BASL) was applied to calculate the macro, micro and oxidation–reduction forms of elements in the nature water and their saturation with mineral matter (Appelo, Postma 1993). The software WATEQ4F solves non–linear mass balance equations by the mathematical continued fraction method (Ball, Nordstrom 1991). The calculation is based on a combined solution of the mass balance equations for the element studied and all present complex particles. Using WATEQ4F it is possible to calculate the molar and percentage composition of the element migration forms, ionic activity and indices of mineral saturation in water. These indices show which mineral compounds saturate or almost saturate water; i.e. they indicate the ability of water to dissolve or settle certain minerals. The saturation index is expressed as follows:

$$SI = \lg IAP/K, (1),$$

were IAP is the product of a corresponding ion activity, and K is the solubility constant.

If the saturation index (SI) is close to zero, the water and the mineral analysed is in equilibrium; if SI exceeds zero, water is oversaturated with this mineral and the latter tends to settle; if SI is below zero, water is not saturated with the mineral analysed and the latter tends to be dissolved.

The calculations were done for the key components of groundwater chemistry: SO_4, Cl, HCO_3, Ca, Mg, Na, K, CO_2, O_2, pH, Eh, electric conductivity, hardness, nutrients and indices, such as NH_4, NO_3, NO_2, BOD, COD_{Mn} , and metals Cd, Cr, Ni, Pb, Cu, Zn, Fe, Mn. About 13 000 water sample analyses have been performed in the study of migration forms of chemical elements and their compounds. The calculation results reflect the average values. Elements concentration is expressed in mg/l; content of free ions and compounds is given in percentage of corresponding element content.

Performing the investigations on migration of chemical element forms in groundwater, the long–term water chemistry analyses done at different laboratories for the samples taken in different time have been used. The average content of chemical components is estimated by statistical methods after extreme values were discarded.

RESULTS AND DISCUSSION

Hydrogeological and hydrogeochemical conditions

The Quaternary thickness in Lithuania reaches 200 m. These deposits had been formed under conditions of the continental ice sheet and, later, by the water and the weathering processes. The Quaternary in Lithuania contains only up to 4–5 aquifers and their system (several hydraulically interacting aquifers), which, according to their type of contact with the atmosphere, can be grouped as unconfined (water table), semi–confined and confined (Fig. 2).

Formation of groundwater chemistry in Lithuania is determined by petrographical and mineralogical composition of water bearing and aquitard deposits, as well as the type of connection of aquifers with the surface water and atmosphere (i.e., their confinement degree). The Quaternary deposits are compound from aggregates of crys-

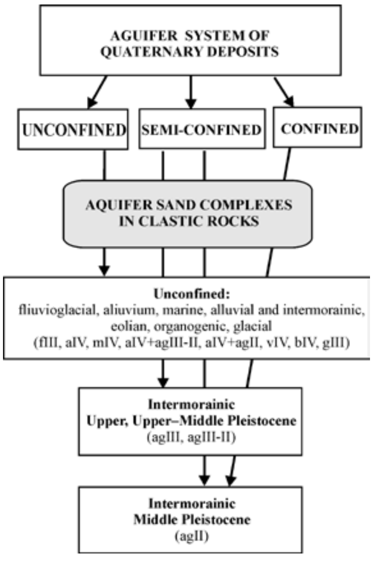

Fig. 2. Classification of the aquifer systems of Quaternary deposits in Lithuania.

Table 1. Migration forms of major chemical elements in groundwater of unconfined Quaternary aquifer system.

Aquifers and their complex (geological index)	Ca	Ca^{2+}	$CaSO_4$	$CaHCO_3^+$	Mg	Mg^{2+}	$MgHCO_3^+$	Na	Na^+	K	K^+	Minerals*	
	mg/l	%			mg/l	%		mg/l	%	mg/l	%	saturated	in equilibrium
Glacifluvial deposits (fIII)	60.9	95.6	1.7	2.3	19.6	95.3	2.9	14.7	99.8	2.7	99.9	1)	3)
Alluvium (aIV)	60.8	94.8	3.1	1.5	21.0	94.8	2.1	14.0	99.8	4.5	99.8		
Marine deposits (mIV)	71.6	94.8	2.5	2.2	15.0	94.9	2.8	21.0	99.7	3.4	99.9	2)	
Alluvium & Middle Pleistocene (aIV+agII)	66.8	94.1	3.3	2.3	20.9	94.0	2.9	15.2	99.7	2.7	99.8		
Alluvium & Upper-Middle Pleistocene (aIV+agIII-II)	58.1	94.8	2.4	2.4	21.0	94.6	2.8	13.3	99.7	2.9	99.9	2)	
Aeolian & marine deposits (vIV+mIV) (Juodkrantė)	27.4	95.4	3.2	1.1	8.0	95.5	1.4	10.4	99.8	1.4	99.9		
Aeolian & marine deposits (vIV+mIV) (Nida, Preila)	31.6	95.3	2.3	1.6	10.0	95.1	1.7	10.2	99.8	2.9	99.9		
Glacial deposits (gIII)	135.0	86.8	9.8	3.0	59.0	87.0	3.6	62.5	99.2	11.4	99.4	▨	4), 5)
Organogenic deposits (bIV)	43.6	95.3	2.4	2.3	9.0	95.0	2.8	2.7	99.7	1.4	99.9	▨	6), 7)

Aquifers and their complex (geological index)	CO_3	HCO_3^-	H_2CO_3	$CaHCO_3^+$	SO_4	SO_4^{2-}	$MgSO_4$	Cl	Cl^-	Minerals*	
	mg/l	%			mg/l	%		mg/l	%	saturated	in equilibrium
Glacifluvial deposits (fIII)	255	90.8	7.4	0.9	23.0	84.5	4.3	14.8	100	1), 9)	3) 11)
Alluvium (aIV)	220	91.5	6.5	0.9	41.6	83.9	5.6	22.6	100		12)
Marine deposits (mIV)	250	91.4	6.8	1.0	38.1	84.2	3.4	40.0	100		11)
Alluvium & Middle Pleistocene (aIV+agII)	262	89.4	8.7	0.9	40.6	83.7	4.9	17.9	100	10)	
Alluvium & Upper-Middle Pleistocene (aIV+agIII-II)	256	91.5	6.6	0.9	35.4	84.7	4.7	22.1	100		
Aeolian & marine deposits (vIV+mIV) (Juodkrantė)	116	84.5	14.6	0.4	23.0	91.6	2.1	22.9	100		
Aeolian & marine deposits (vIV+mIV) (Nida, Preila)	162	80.4	18.0	0.6	13.7	88.8	2.9	11.3	100	11)	12)
Glacial deposits (gIII)	426	86.9	9.9	1.4	240.0	77.5	8.8	210.0	100	8)	4), 5)
Organogenic deposits (bIV)	307	69.0	30.1	0.5	29.2	88.4	2.6	5.8	100		11) 6), 7)

Aquifers and their complex (geological index)	PO_4	HPO_4^{2-}	$H_2PO_4^-$	$CaHPO_4$	$MgHPO_4$	$FeHPO_4$	$CaPO_4^-$	F	F^-	MgF^+	CaF^+	Minerals*	
	mg/l	%						mg/l	%			saturated	in equilibrium
Glacifluvial deposits (fIII)	0.06	52.1	20.5	15.6	9.1	0.3	1.1	0.30	97.0	2.3	0.6	1),13)	14)
Alluvium (aIV)	0.02	52.2	17.8	15.0	12.0	0.2	1.2	0.26	96.5	2.9	0.6		
Marine deposits (mIV)	0.07	52.7	17.5	18.2	8.6	0.3	1.4	0.21	97.2	2.0	0.7	2)	
Alluvium & Middle Pleistocene (aIV+agII)	0.04	48.6	23.4	15.2	10.0	0.5	0.8	0.17	96.6	2.6	0.6	10)	15)
Alluvium & Upper-Middle Pleistocene (aIV+agIII-II)	0.27	52.1	20.0	14.2	10.8	0.5	1.0	0.26	96.8	2.6	0.6	2), 14),15)	▨
Aeolian & marine deposits (vIV+mIV) (Juodkrantė)	1.69	46.9	39.1	8.4	2.9	1.5	0.3	0.32	98.9	0.7	0.3	16)	▨
Aeolian & marine deposits (vIV+mIV) (Nida, Preila)	1.81	41.3	37.0	8.2	3.9	7.4	0.3	0.66	98.4	1.0	0.4		▨
Glacial deposits (gIII)	0.09	41.0	22.0	16.8	16.6	0.6	0.8						14), 15)
Organogenic deposits (bIV)	0.15	27.0	60.2	6.1	2.8	1.9	0.1					14), 15)	▨

*Minerals: *(1)* FCO_3 Apatite; *(2)* Fluorapatite $Ca_5(PO_4)_3F$; *(3)* Aragonite & Calcite $CaCO_3$; *(4)* Dolomite $CaMg(CO_3)_2$; *(5)* Magnesite $MgCO_3$; *(6)* Jarosite K $KFe_3(SO_4)_2(OH)_6$; *(7)* Jarosite ss $[K_{0,77}Na_{0,03}(H_3O)_{0,2}]Fe_3(SO_4)_2$; *(8)* $Fe(OH)_{2,7}Cl_{0,3}$; *(9)* Basaluminite $Al_4(OH)_{10}SO_4$; *(10)* Clpyromorphite $Pb_5(PO_4)_3Cl$; *(11)* Siderite $FeCO_3$; (*12)* Rhodochrosite $MnCO_3$; *(13)* Plumbogummite $PbAl_3(PO_4)_2(OH)_5*H_2O$; *(14)* $MnHPO_4$; *(15)* Strengite $FePO_4*2H_2O$; and *(16)* Vivianite $Fe_3(PO_4)_2*8H_2O$.

talline (~30% in average) and sedimentary rocks with particles of limestone (~40%) and dolomite prevailing. These rocks determine the hydrocarbonate type of shallow groundwater with calcium and magnesium cations reaching, respectively, about 55–63 and 20–30 mg-eq.%, sulphate and sodium ions do not exceed 20 mg-eq.%, the rest components making 1–5 mg-eq.%.

Aquifer system contains water of the prevailing hydrocarbonate–calcium–magnesium type, and more confined aquifers are notable for higher mineralisation of groundwater and higher content of many chemical components (except for organic matter) (Tables 1, 2). Content of dissolved oxygen is lower there, as well as redox potential, thus causing the deterioration of oxidation conditions in the aquifers and, hence, higher conditions of chemical elements in more confined aquifer system. Against the background of the major typical aquifer system, there are anomalous zones where concentration of chemical elements, their migration forms and stability in groundwater are determined by specific chemical components. Such zones are the areas at the surface water bodies being the main groundwater recharge (safe yield) source (for instance, Curonian sand spit, Kauno Marios coasts, etc.), as well as the areas with occurrence of organogenic and morainic deposits.

The highest concentration of dissolved salts is detected in the water occurring in the confined (intermorainic) beds (Tables 2, 4). Here the content of solids depends rather significantly on thermodynamical indices of the environment. The groundwater of the aquifer complexes distinguished in this regard is uniform in hydrogen ion concentration: pH values ranging in 6.8–8.1 prevail. On the contrary, the redox potential (Eh) value differs significantly–decreasing with the depth of aquifers from 100–360 mV in unconfined beds to negative value in confined ones.

Content of organic matter and nutrients depends also on processes of their solution and taking out from the soil, whereas nitrogen compounds are formed under the atmosphere impact. Hence, atmospheric precipitation often contains 8–9 times higher ammonium salt concentration than those in the shallow groundwater of the deposits discussed here.

Peculiarities in formation of unconfined groundwater chemistry. According to the chemical composition of shallow groundwater water is formed, the following main groups of water are distinguished (see Fig. 2): (1) glaciofluvial, alluvial, marine, alluvial and intermorainic deposits (fIII, aIV, mIV, aIV+agIII-II, aIV+agII), (2) marine and aeolian deposits (in Curonian Spit) (vIV+mIV), (3) organogenic deposits (bIV), and (4) glacial deposits (gIII).

The Group 1 of shallow groundwater is notable for rather high content of dissolved oxygen (1–3 mg/l) and rather high redox potential (Eh up to 200–250 mV).

Table 2. Migration forms of major chemical elements in groundwater of Quaternary confined and semi-confined aquifers.

Aquifers and their complex (geological index)	Ca	Ca^{2+}	$CaHCO_3^+$	$CaSO_4$	$CaCO_3$	Mg	Mg^{2+}	$MgHCO_3^+$	$MgSO_4$	$MgCO_3$	Na	Na^+	K	K^+	Minerals*		
	mg/l	%				mg/l	%				mg/l	%	mg/l	%	sat	equ	
Upper & Upper-Middle Pleistocene semi-confined systems (agIII. ag III–II)	69.0	94.4	2.5	2.4	0.4	19.3	94.4	3.1	2.2	0.2	9.1	99.7	2.3	99.8	*1)*	*3), 4)*	*2)*
Middle Pleistocene confined systems (agII)	86.0	94.2	3.8	1.4	0.4	25.5	93.7	4.8	1.2	0.2	18.4	99.6	2.9	99.9			*6)*

Aquifers and their complex (geological index)	CO_3	HCO_3^-	H_2CO_3	$CaHCO_3^+$	$MgHCO_3^+$	SO_4	SO_4^{2-}	$CaSO_4$	$MgSO_4$	Cl	Cl^-	Minerals*		
	mg/l	%				mg/l	%			mg/l	%	sat	equ	
Upper & Upper-Middle Pleistocene semi-confined systems (agIII. ag III–II)	290	90.8	7.0	0.9	0.6	41.5	83.7	11.3	4.8	*17.8*	100	*1),8),9)*	*3), 4)*	*11)*
Middle Pleistocene confined systems (agII)	458	88.5	9.2	1.1	0.7	23.2	81.7	12.4	5.4	*16.7*	100	*11)*		*6)*

Aquifers and their complex (geological index)	PO_4	HPO_4^{2-}	$H_2PO_4^-$	$CaHPO_4$	$MgHPO_4$	$CaPO_4^-$	$FeHPO_4$	$MgPO_4^-$	F	F^-	MgF^+	CaF^+	Minerals*			
	mg/l	%							mg/l	%			sat		equ	
Upper & Upper-Middle Pleistocene semi-confined systems (agIII. ag III–II)	*0.10*	51.3	20.4	15.8	9.7	1.0	0.8	0.6	*0.16*	96.6	2.6	0.6	*1* *13*	*14)*	*2)*	*15)*
Middle Pleistocene confined systems (agII)	*0.09*	45.8	22.3	16.1	10.6	0.8	2.6	0.6	*0.28*	96.0	3.0	0.7		*15)*		*14)*

*Minerals: sat–saturated, equ–in equilibrium; *(1)* FCO_3 Apatite; *(2)* Fluorapatite $Ca_5(PO_4)_3F$; *(3)* Aragonite & Calcite $CaCO_3$; *(4)* Dolomite $CaMg(CO_3)_2$; *(6)* Jarosite K $KFe_3(SO_4)_2(OH)_6$; *(8)* $Fe(OH)_{2.7}Cl_{0.3}$; *(9)* Basaluminite $Al_4(OH)_{10}SO_4$; *(11)* Siderite $FeCO_3$; *(13)* Plumbogummite $PbAl_3(PO_4)_2(OH)_5*H_2O$; *(14)* $MnHPO_4$; *(15)* Strengite $FePO_4*2H_2O$.

Specific hydrogeological conditions are detected in some lengths of the Neris and Nemunas river valleys (Vilnius and Kaunas environs), where the alluvial and intermorainic aquifers are merging directly. The chemistry of shallow groundwater in the cases of Group 2 and Group 3 is determined by organic matter occurring between the aquifers and lower pH values (less than 7), while that in Group 4 is affected by concentration of clay minerals and increased content of some metals (Mn, Fe, Ni, Pb).

Peculiarities in formation of confined groundwater. The setup and spreading of the Quaternary confined aquifers are given in Fig. 3. The aquifers of the glacial deposit complex are, as a rule, hydraulically related due to rather intensive water exchange, both vertical and horizontal, that causes rather uniform chemistry of the groundwater. The Quaternary glacial beds are conditionally divided into two parts with several interrelated aquifers in each part. In accordance to the hydrogeodynamical features, two water–bearing complexes are distinguished in the Quaternary glacial deposits: Upper–Middle Pleistocene in the upper part, and Middle Pleistocene in the lower part. The Quaternary confined aquifers contain, with rare exceptions, the groundwater of hydrocarbonate–calcium–magnesium type (Table 2).

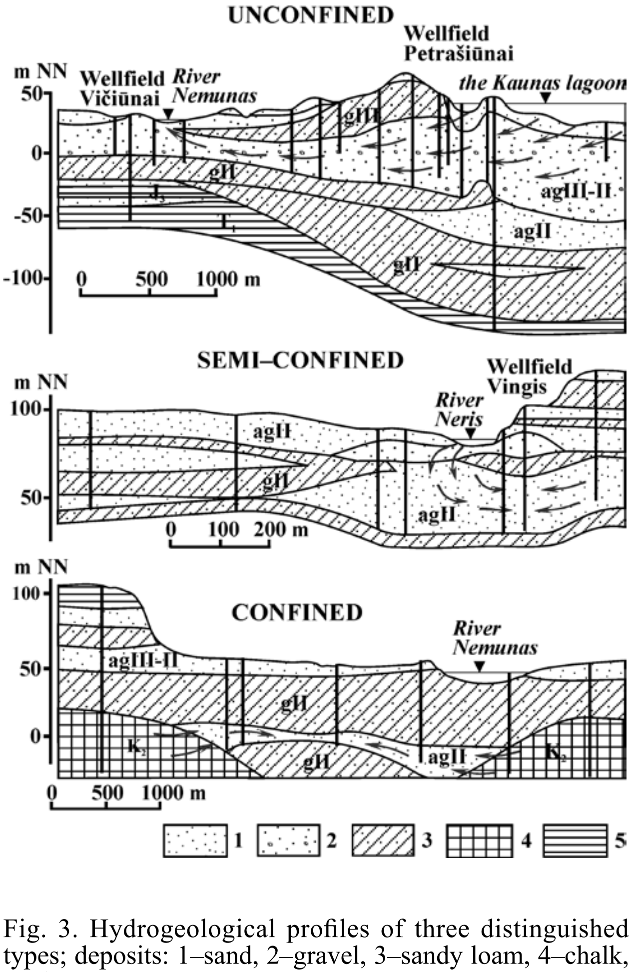

Fig. 3. Hydrogeological profiles of three distinguished types; deposits: 1–sand, 2–gravel, 3–sandy loam, 4–chalk, 5–clay.

Forms of chemical elements in groundwater

Migration capacity of chemical elements in groundwater is determined by the spectrum of their important migration forms. The important migration forms of chemical elements are those the content of which makes at least 10–20% of the total content of a certain element. The most important inorganic state of macroelements in the natural water is presented by the elementary cations (Ca^{2+}, Mg^{2+}, Na^{+}, H^{+}) and anions (Cl^{-}, F^{-}); the anions in compounds with oxygen and hydrogen (SO_4^{2-}, CO_3^{2-}, HCO_3^{-} etc.), as well as the ionic and molecular associates – in complex (coordination) compounds ($CaSO_4^0$, $CaHCO_3^+$, $CaCO_3^0$, $CaCl^+$, $CaCl_2^0$, $MgSO_4^0$ $MgHCO_3^+$, $MgCO_3^0$, $MgCl^+$, $MgCl_2^0$, $NaCl^0$, $NaSO_4^-$, $NaHCO_3^0$ etc.). Microelements migrate in groundwater in a form of even more complicated complex compounds (Tables 3, 4).

Cationgenic elements. Water of Quaternary aquifers is saturated with sodium, magnesium and calcium carbonates, or they are in equilibrium state (calcite, aragonite) (see Tables 1, 2).

Sodium and potassium migrate in Quaternary groundwater only in ionic form.

Calcium in groundwater is observed mainly as a Ca^{2+} ion (87–95%), and only a very small part of calcium is detected in sulphates $CaSO_4$ and hydrogen carbonates $CaHCO_3^-$ (1–3%). Only groundwater in glacial beds contains lower amount of calcium migrating in ionic form (87%) and a bit higher its migration in sulphate compounds (up to 10%). General concentration of calcium in groundwater grows due to the increase in sulphate forms and less in carbonate forms. Changes in thermodynamical environment (pH, Eh) have no basic impact on variation of calcium forms.

Magnesium in fresh groundwater, with its ion form prevailing, occurs in sulphates $MgSO_4$ (2–9 %) and carbonates $MgCO_3$, $MgHCO_3^-$ (1–6 %). The major part of $CaSO_4$ is detected in groundwater of glacial beds.

Aniongenic elements. Chlorine in fresh water migrates only as a Cl^- ion.

Carbonates migrate mainly as a HCO_3^- ion (69–92%), less as H_2CO_3 (6–30%), and even less as $CaHCO_3^-$ and $MgHCO_3^-$ (see Table 1). Differently, in organogenic beds a large part of carbonates migrate as H_2CO_3 (30%). For groundwater in confined intermorainic aquifers, the higher confinement degree is linked to a slightly lower content of HCO_3^- and higher H_2CO_3.

Sulphates in Quaternary groundwater migrate mainly as a SO_4^{2-} ion (78–92%), a small part is in Ca_2SO_4 (6–13%) and $MgSO_4$ (2–9%), and a very small one (less 1%) in $NaSO_4^-$ compounds. The high content of the SO_4^{2-} ionic form is observed in groundwater of aeolian and marine (88–92%), as well as organogenic deposits (6–9% in a form of Ca_2SO_4). Groundwater of glacial deposits contains less sulphates than that of

Table 3. Migration forms of key metals in groundwater of unconfined Quaternary deposits aquifer system.

Aquifers and their complex (geological index)	Fe	Fe^{2+}	$Fe(OH)_3$	$FeHCO_3^+$	$Fe(OH)_2^+$	$FeCO_3$	$FeSO_4$	Mn	Mn^{2+}	$MnCO_3$	$MnHCO_3^+$	$MnSO_4$	Minerals*	
	mg/l	%						mg/l	%				saturated	in equilibrium
Glacifluvial deposits (fIII)	0.29	51.6	19.9	13.4	10.5	3.3	0.7	0.04	68.2	14.6	16.2	0.9	8), 17), 18)	11) 14)
Alluvium (aIV)	0.18	47.7	27.9	9.9	9.6	2.8	1.2	0.14	77.9	10.7	9.0	1.7		12)
Marine deposits (mIV)	0.22	65.0	7.4	16.8	3.6	4.5	1.3	0.09	67.7	14.9	15.8	1.4		11)
Alluvium & Middle Pleistocene (aIV+agII)	0.52	42.0	19.9	13.4	12.9	3.1	1.5	0.14	66.6	13.5	17.7	2.0		15)
Alluvium & Upper-Middle Pleistocene (aIV+agIII-II)	0.61	57.7	14.4	15.8	6.4	4.1	1.1	0.36	66.4	16.0	16.2	1.3	14), 15)	
Aeolian & marine deposits (vIV+mIV) (Juodkrantė)	1.10	71.4	7.8	8.9	7.2	1.6	1.7	0.05	80.0	9.0	8.9	2.0	16),19)	
Aeolian & marine deposits (vIV+mIV) (Nida, Preila)	5.93	64.9	5.6	14.5	6.8	1.8	1.4	0.23	77.6	6.4	14.4	1.5	11)	12)
Glacial deposits (gIII)	1.23	49.8	14.1	17.7	10.9	2.7	4.3	0.08	62.8	11.1	19.8	5.4		14), 15) 6), 7),11)
Organogenic deposits (bIV)	3.10	57.9	6.6	15.0	18.5	0.7	1.1	0.25	77.6	3.0	18.0	1.5	14), 15)	

Aquifers and their complex (geological index)	Pb	$PbCO_3$	$PbHCO_3^+$	Pb^{2+}	$PbOH^+$	Ni	$NiCO_3$	Ni^{2+}	$NiHCO_3^+$	Cd	Cd^{2+}	$CdHCO_3^+$	$CdSO_4$	$CdCl^+$	Minerals*
	µg/l	%				µg/l	%			µg/l	%				sat
Glacifluvial deposits (fIII)	6	91.1	4.4	2.0	1.1	2	92.4	4.8	1.8	0.6	87.6	7.4	2.4	2.2	13)
Alluvium (aIV)	3	89.9	4.0	3.1	1.6	8	88.9	8.8	1.6	0.2	85.3	7.8	3.6	2.9	
Marine deposits (mIV)	5	92.2	3.4	1.7	1.0	2	93.4	4.0	1.4	0.2	83.5	6.8	3.4	5.9	
Alluvium & Middle Pleistocene (aIV+agII)	5	91.1	4.2	1.8	0.9	3	92.7	4.2	1.6	0.9	81.5	8.2	5.5	4.3	10)
Alluvium & Upper-Middle Pleistocene (aIV+agIII-II)	3	91.7	4.0	1.8	1.0	10	93.2	4.2	1.6	1.2	85.9	7.4	2.0	3.3	
Aeolian & marine deposits (vIV+mIV) (Juodkrantė)	7	80.2	8.9	8.1	1.8	2	81.0	15.6	2.9	2.0	89.1	3.8	3.0	3.9	
Aeolian & marine deposits (vIV+mIV) (Nida, Preila)	8	84.5	7.9	5.5	1.4	5	83.6	12.8	3.2	1.1	90.0	5.4	1.7	2.2	
Glacial deposits (gIII)	25	88.2	6.4	2.3	0.6	22	90.2	5.5	2.7	5.0	62.5	7.0	10.5	19.2	
Organogenic deposits (bIV)	7	71.8	17.8	8.6	0.8	6	71.8	20.2	7.3	0.3	88.0	7.2	3.4	1.0	

Aquifers and their complex (geological index)	Cu	$Cu(OH)_2$	$CuCO_3$	Cu^{2+}	$CuHCO_3^+$	Cu^+	$CuCl_2^-$	Zn	Zn^{2+}	$ZnCO_3$	$ZnHCO_3^+$	$Zn(CO_3)_2^{2-}$	$ZnSO_4$	Minerals*	
	mg/l	%						mg/l	%					sat	equ
Glacifluvial deposits (fIII)	0.009	51.5	40.0	3.0	4.2	0.06	0.00	0.024	50.6	26.9	16.9	3.3	1.1	17)	▨
Alluvium (aIV)	0.036	64.4	28.6	3.1	2.5	0.1	0.02	0.024	57.6	23.8	11.9	2.6	2.4		▨
Marine deposits (mIV)	0.046	53.5	40.0	2.3	3.0	0.01	0.00	0.025	47.4	30.1	15.4	4.3	1.5		▨
Alluvium & Middle Pleistocene (aIV+agII)	0.009	44.6	44.2	2.7	4.2	0.5	0.2	0.017	45.9	28.1	17.9	3.2	2.3		▨
Alluvium & Upper-Middle Pleistocene (aIV+agIII-II)	0.060	51.0	41.0	2.7	3.6	0.3	0.03	0.026	48.7	28.2	16.8	3.6	1.5		▨
Aeolian & marine deposits (vIV+mIV) (Juodkrantė)	0.053	24.3	23.1	7.6	5.3	32.7	3.3	0.025	75.5	8.8	13.0	0.2	1.9	21) 20)	▨
Aeolian & marine deposits (vIV+mIV) (Nida, Preila)	0.022	13.4	15.4	3.0	2.7	53.5	2.2	0.006	68.8	12.9	16.2	0.5	1.0		▨
Glacial deposits (gIII)	0.080	10.9	24.0	2.0	3.6	6.0	52.2	0.060	47.4	21.1	21.2	3.1	6.3		20)
Organogenic deposits (bIV)	0.010	5.3	22.3	8.6	11.3	33.4	0.2	0.010	68.3	6.6	22.5	0.1	2.1		

*Minerals: sat–saturated, equ–in equilibrium; *(6)* Jarosite K $KFe_3(SO_4)_2(OH)_6$; *(7)* Jarosite ss $[K_{0,77}Na_{0,03}(H_3O)_{0,2}]Fe_3(SO_4)_2$; *(8)* $Fe(OH)_{2,7}Cl_{0,3}$; *(10)* Clpyromorph $Pb_5(PO_4)_3Cl$; *(11)* Siderite $FeCO_3$; *(12)* Rhodochrosite $MnCO_3$; *(13)* Plumbogummite $PbAl_3(PO_4)_2(OH)_5{*}H_2O$; *(14)* $MnHPO_4$, *(15)* Strengite $FePO_4{*}2H_2O$; *(16)* Vivianite $Fe_3(PO_4)_2{*}8H_2O$; *(17)* Cupric Ferrite $CuFe_2O_4$, Cuprous Ferrite $CuFeO_2$; *(18)* $Fe_3(OH)_8$, Ferrihydrite $Fe(OH)_3$, Goethite $FeO(OH)$, Hematite Fe_2O_3, Maghemite Fe_2O_3, Magnetite Fe_3O_4; *(19)* Chalcopyrite $CuFeS_2$, Greigite Fe_3S_4, Mackinawite FeS, Pyrite FeS_2; *(20)* Cu metal; *(21)* Cuprite Cu_2O.

Table 4. Migration forms of key metals in groundwater of the Quaternary confined and semi-confined aquifers.

Aquifers and their complex (geological index)	Fe	Fe^{2+}	$FeHCO_3^+$	$Fe(OH)_3$	$Fe(OH)_2^+$	$FeCO_3$	$FeSO_4$	Mn	Mn^{2+}	$MnHCO_3^+$	$MnCO_3$	$MnSO_4$	Minerals*		
	mg/l	%						mg/l	%				sat		equ
Upper & Upper-Middle Pleistocene semi-confined systems (agIII, ag III–II)	0.89	56.2	16.5	13.9	6.8	3.9	1.3	0.12	65.7	17.2	15.3	1.4	*8), 17), 18), 19)*	*14)*	*11), 15)*
Middle Pleistocene confined systems (agII)	3.98	48.3	21.6	15.1	10.2	3.8	0.4	0.13	59.7	23.8	15.8	0.6		*11), 15)*	*6), 14)*

Aquifers and their complex (geological index)	Pb	$PbCO_3$	$PbHCO_3^+$	Pb^{2+}	$PbOH^+$	Ni	$NiCO_3$	Ni^{2+}	$NiHCO_3^+$	Cd	Cd^{2+}	$CdHCO_3^+$	$CdSO_4$	$CdCl^+$	Mine-rals*
	µg/l	%				µg/l	%			µg/l	%				sat
Upper & Upper-Middle Pleistocene semi-confined systems (agIII, ag III–II)	8	91.1	4.3	1.8	0.9	4	92.9	4.3	1.7	1.2	85.1	8.0	3.9	2.2	13), 22)
Middle Pleistocene confined systems (agII)	2	90.3	5.7	1.6	0.6	1	92.5	3.8	2.3	0.1	83.6	11.9	1.5	2.7	

Aquifers and their complex (geological index)	Cu	$Cu(OH)_2$	$CuCO_3$	$CuHCO_3^+$	Cu^{2+}	Cu^+	$CuCl_2^-$	Zn	Zn^{2+}	$ZnCO_3$	$ZnHCO_3^+$	$Zn(CO_3)_2^{2-}$	$ZnSO_4$	Mine-rals*
	mg/l	%						mg/l	%					sat
Upper & Upper-Middle Pleistocene semi-confined systems (agIII, ag III–II)	0.006	50.1	42.1	3.7	2.9	0.7	0.03	0.020	47.7	29.1	16.9	3.6	1.5	*17)*
Middle Pleistocene confined systems (agII)	0.002	25.6	52.8	6.0	2.7	8.0	0.9	0.037	42.1	28.2	23.8	4.7	0.6	

*Minerals: sat–saturated, equ –in equilibrium; *(6)* Jarosite K $KFe_3(SO_4)_2(OH)_6$; *(8)* $Fe(OH)_{2,7}Cl_{0,3}$; *(11)* Siderite $FeCO_3$; *(13)* Plumbogummite $PbAl_3(PO_4)_2(OH)_5{*}H_2O$; *(14)* $MnHPO_4$; *(15)* Strengite $FePO_4{*}2H_2O$; *(17)* Cupric Ferrite $CuFe_2O_4$, Cuprous Ferrite $CuFeO_2$; *(18)* $Fe_3(OH)_8$, Ferrihydrite $Fe(OH)_3$, Goethite $FeO(OH)$, Hematite Fe_2O_3, Maghemite Fe_2O_3, Magnetite Fe_3O_4; *(19)* Chalcopyrite $CuFeS_2$, Greigite Fe_3S_4, Mackinawite FeS, Pyrite FeS_2; and *(22)* Millerite NiS.

other beds, and migration in a form of SO_4^{2-} prevails (ca. 78%); there is also a relative increase in Ca_2SO_4 (13%) and $MgSO_4$ (9%) compounds, the content of which is observed to be higher at the higher confinement degree of intermorainic aquifers.

Phosphates. Spreading of phosphorus in groundwater is limited by geochemical barriers, the impact of which is expressed in formation of low soluble calcium and iron phosphates, as well as settling of phosphate anions together with iron and aluminium hydroxides and calcium carbonates. When the calcium and iron concentration in the Quaternary groundwater often exceeds 30–50 and 0.5–1.0 mg/l, correspondingly, the phosphate content is most often observed ranging 0.01–0.1 mg/l. The higher phosphate content is detected in groundwater of organogenic deposits in Kaunas Petrašiūnai well field (to 0.3 mg/l) being recharged by Kauno Marios lake water.

However, the highest phosphate concentration (1.7–1.8 mg/l) is determined in the shallow groundwater of marine and aeolian sediments in the Kuršių Nerija sand spit (see Table 1). Here, the aquifer on the Kuršių Marios lagoon coast is formed of marine sand rich in organic matter (environs of Nida, Preila, etc.), where maximum COD_{Mn} value reaches 12–15 mgO_2/l, and concentration of fulvic and humic acids is up to 1.9 mg/l. Due to excessive organic matter, the carbonic acid content increases (to 15–18%). The H_2S ion form (or sulphide form in other genetic types) and hydrophosphates prevail. Differently than in other deposits, the major part of phosphates in groundwater of Kuršių Nerija aeolian and marine sediments is observed as a $H_2PO_4^-$ ion (37–39%). It is a solution may saturate with siderite, aragonite, chalcopyrite, vivianite, apatite and other minerals (see Tables 1, 2).

The higher is the confinement degree, the slightly lower is content of phosphates in a form of HPO_4^{2-} (from 51 to 46%), and also a slightly higher $H_2PO_4^-$ (from 20 to 22%) is observed in the intermorainic groundwater. Deeper aquifer beds contain less phosphorus, since there is more Ca^{2+} and Fe^{2+}, which settle phosphates. Since Fe^{2+} concentration grows with redox potential decrease in groundwater, phosphates are also lower at the lower Eh value. If positive Eh value is low, phosphorus anions should be settled by Fe^{2+} cations and form the mineral vivianite $Fe_3(PO_4)_2\ 8H_2O$. This mineral is stable at Eh<200mV and pH 5–9. Therefore the iron in groundwater with low redox potential should be a geochemical barrier for phosphorus (Krainov *et al.* 2004).

Anions of orthophosphoric acid form low soluble compounds with calcium, magnesium and iron (II, III); therefore they are settled by these elements and form such minerals as brushite, monetite, hydroxylapatite, strengite, vivianite etc. If groundwater contains several mg/l of calcium, magnesium or iron, there is a minimum content of phosphorus; and if water contains low amount of Ca^{2+} ir Fe^{2+}, but high sodium, there is an increased content of phosphorus. The basic phosphorus–containing mineral is apatite that saturates fresh water in all aquifers; and water of shallow aquifers with higher amount of organic matter and fluorides contains also strengite, vivianite and fluorapatite (see Tables 1, 2).

Fluorides. Fluorine is known to be a typical carrier of aniongenic elements and a universal addend for eight electronic elements determining their migration in water (Alekin 1970). Therefore the fluorine content is rather important for geochemistry of groundwater. Maximum fluoride concentration (to 0.7 mg/l) is observed in shallow groundwater of Curonian Spit marine and aeolian sediments, while that in groundwater of other Quaternary beds did not exceed 0.2–0.3 mg/l.

The groundwater fluorides in a medium close to neutral (pH about 7.5) migrate mainly as F^- ions (96–99%) with the rest going to MgF^- (0.7–3%) and CaF^- (less than 1 %) compounds (see Table 1). Migration of fluorides in ionic form is slightly better expressed in groundwater of shallow Quaternary aquifers than in the intermorainic ones (about 2%). In general, percentage of fluorine compounds in fresh groundwater depends little on fluorine content. The groundwater of all aquifers analysed was found to be saturated with fluorine carbonates (apatite) with fluorapatite detected in equilibrium state (see Tables 1, 2). Accumulation of fluorine in groundwater is known to be indicated by the Na/Ca ratio (Krainov, Shvets 1992). In our case, low value of Na/Ca (0.1–0.4) corresponds to fluoride concentration in groundwater (0.3–0.4 mg/l).

Complexing elements (elements-hydrolysers). The concentrations of multivalent elements, iron and manganese of which being most important, are determined by two factors: solving, and thermodynamical environment (pH, Eh). According to migration forms, metals can be grouped as follows: (1) those migrating mainly ($\geq$ 90 %) as carbonate complexes (Pb, Ni), (2) as mixed carbonate and hydroxyl complexes (Cu, Fe) or as ions and carbonate complexes (Zn, Mn), and (3) mainly as ions (Cd) (Fig. 4).

Iron content in the Quaternary groundwater ranges from 0.1 to 6.0 mg/l. Its maximum value has been observed in the shallow groundwater of Curonian Spit sand spit marine and aeolian sediments. Iron content in the groundwater of the intermorainic aquifers grows from 0.9 to 4 mg/l the increase in degree of confinement of the aquifers. The lowest iron content (0.2–0.3 mg/l) is observed in groundwater of alluvial and glacifluvial deposits in the Quaternary shallow hydrogeological systems, where iron compounds are formed in oxidative medium (Diliūnas, Jurevičius 1998). If the water contains no organic matter, all iron would be oxidised when dissolved oxygen content exceeds 1.2 mg/l. Fulvic acids play the role of regulating agents as their content in water reaches 0.5 mg/l in some periods (average 0.25 mg/l). Iron migrates in groundwater as a Fe^{2+} ion (42–71%), hydroxides $Fe(OH)_3$, $Fe(OH)_2^-$ (11–38%), carbonates $FeHCO_3^-$, $FeCO_3$ (10–29%), and (a small part) as sulphate complexes $FeSO_4$ (0.2–4.0%).

Shallow groundwater in the Curonian Spit aeolian and marine deposits as well as Litorina Sea terrace sediments (if compare to other Quaternary aquifers) contains iron migrating mainly as a Fe^{2+} ion (65–71 %) with its lower part migrating as hydroxides and carbonates (see Table 3). Groundwater in intermorainic aquifers, when their confinement degree increasing, shows a slightly higher share of iron migrating as hydroxides and carbonates (from 20 to 25%) with a slight decrease of iron as ions (from 56 to 48%) and sulphates (see Table 4).

Manganese**.** The highest content of manganese is observed in groundwater of marine and aeolian deposits, organogenic sediments as well as alluvium and intermorainic beds (0.12–0.14 mg/l) (Diliūnas *et al.* 2002). Manganese migrates in groundwater mainly as a Mn^{2+} ion (50–80%), also as carbonates $MnHCO_3^-$ and $MnCO_3$ (18–50 %), with a smallest part as sulphates. Due to chemical erosion, dissolved manganese is taken away, mainly, from hydrocarbonate deposits as $MnCO_3$ and $MnHCO_3$. When confinement conditions strengthen in the intermorainic aquifers, the share of manganese migrating as carbonates increases (from 32 to 40%), while its ionic and sulphate shares decrease, respectively, from 66 to 60% and from 1.4 to 0.6% (see Table 4).

Manganese concentration, if compared to those of iron, is low: Mn/Fe ≈ 0.3. This is determined by low water alkalinity 1.7 mg-eq./l ($HCO_3^- \approx 115$ mg/l); moreover, it is difficult for manganese, contrary to iron, to form complexes with organic matter, therefore, it is transferred to water. High content of iron and manganese is also determined by the excessive amount of organic matter. Humic and fulvic acids (HR, FR) limit oxidation and hydrolysis of iron. The kinetics of hydrolysis is known to be inversely proportional to FR/Fe^{3+}, ratio, i.e., FR increasing the hydrolysis slows down and more iron remains in solution. A setback of iron oxidation is also favoured by other organic compounds, for instance, when COD_{Mn} reaches 6–10 mgO_2/l.

Lead content in groundwater of Quaternary deposits ranges within 0.002–0.008 mg/l, except for glacial deposits, where lead in groundwater reaches 0.025 mg/l. The lead migrates mainly as carbonates of $PbCO_3$, $PbHCO_3^+$, $Pb(CO_3)_2^{2-}$ (89–99 %) with a small part migrating as ion Pb^{2+} (1–9%) and hydroxyl (0.6–1.8%).

Groundwater in alluvium as well as in Curonian Spit aeolian, marine and organogenic sediments con-

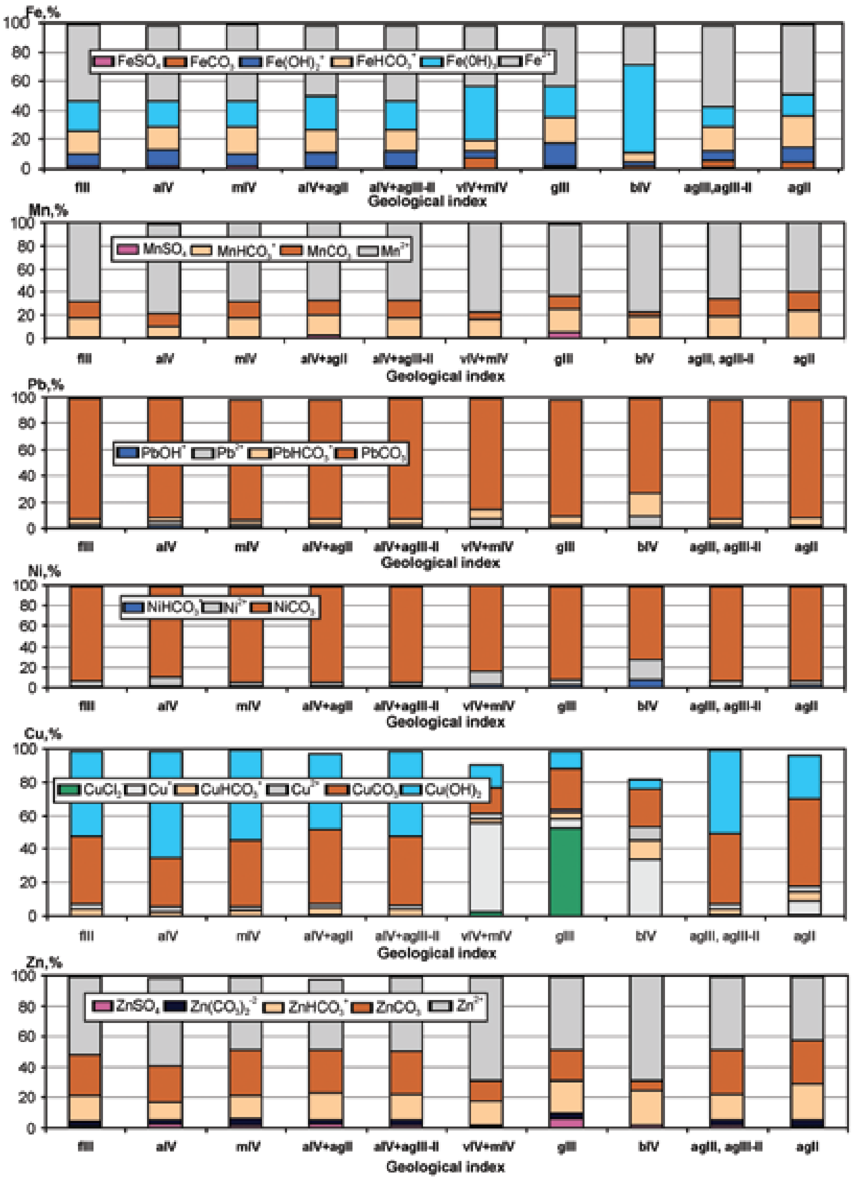

Fig 4. The main forms of metal in the groundwater of Quaternary deposits. Age indexes see Fig. 1.

tains less lead migrating as carbonates and higher as ionic and hydroxyl form than in other aquifers (see Table 3). Groundwater of intermorainic aquifers, with their confinement degree increasing, contains a slightly increasing lead migrating as carbonates and decreasing amount in ion and hydroxyl forms.

Nickel content in groundwater of alluvium and Petrašiūnai well field alluvium and intermorainic complex, Curonian Spit marine and aeolian, as well as organogenic sediments reaches 0.008–0.01 mg/l, and that in glacial deposits groundwater is 0.02 mg/l. Nickel content in groundwater of Quaternary intermorainic beds decreases from 0.004 to 0.001 mg/l with the increase in aquifer confinement degree.

Major part of nickel migrates as carbonates $NiCO_3$, $NiHCO_3^+$, $Ni(CO_3)_2^{2-}$ (79–98 %), its minor part is migrating as a Ni^{2+} ion (2–20%). The lowest percentage of nickel migrating as carbonates is observed in groundwater of organogenic, Curonian Spit aeolian and marine sediments. Nickel migrating in groundwater of intermorainic aquifers, when their confinement degree increasing, slightly increases in a carbonate form and slightly decreases in an ionic form (see Table 4).

Copper content in groundwater ranges within 0.001–0.06 mg/l, but it is higher in glacial beds groundwater 0.08 mg/l. The higher copper concentration is observed in groundwater of alluvium, Curonian Spit marine and aeolian sediments, and Petrašiūnai well field (0.02–0.06 mg/l). Copper content in Quaternary intermorainic groundwater decreases with increasing confinement degree of aquifers (from 0.006 to 0.002 mg/l).

Copper migrates in groundwater in it different forms: as hydroxides $Cu(OH)_2$, $CuOH^+$ (6–65%), carbonates $CuCO_3$, $CuHCO_3^+$, $Cu(CO_3)_2^{2+}$ (18–61%) and ions Cu^{2+}, Cu^+ (1–56%). The lowest amount of copper migrates as chlorides $CuCl_2^+$ (0–4 %), but this form is anomalously high in groundwater of glacigenic deposits. There is more copper migrating as carbonates in groundwater of Quaternary intermorainic beds than in Quaternary shallow aquifer (44–61% and 18–49%, correspondingly). The main part of copper in groundwater of Curonian Spit aeolian and marine sediments, as well as organogenic beds, migrates mainly as an ion (40–56%), but copper chloride migration prevails in water of glacigenic beds. Major part of copper in groundwater of alluvium migrates as hydroxyl (65 %), and here copper carbonates content is lower (31%) than in other aquifers. The increase in confinement degree of the intermorainic beds, copper amount increases in the form of carbonates (from 46 to 59%) and ions (from 3 to 11 %), but it decreases in hydroxide form (from 51 to 27%).

Zinc content in groundwater ranges in 0.006–0.06 mg/l. Its maximum observed in groundwater of glacial deposits and the minimum in that of Curonian Spit marine and aeolian, as well as organogenic sediments. With the aquifer confinement degree increasing, the content of zinc slightly increases from 0.02 to 0.04 mg/l.

Zinc migrates in groundwater mainly as a Zn^{2+} ion (47–76%) or its carbonates $ZnCO_3$, $ZnHCO_3^+$ and $Zn(CO_3)_2^{2+}$, a small part as sulphate $ZnSO_4$ (0.2–6.3%) and hydroxyl compounds: $Zn(OH)_2$ and $ZnOH^+$

(0.4–1.3%). Major part of zinc migrating in the form of ions is observed in groundwater of Curonian Spit aeolian and marine, as well as organogenic sediments (68–76%). The carbonate form of zinc is being the lowest (22–30 %). As confinement of aquifers increases in the intermorainic beds, the part of zinc in the form of carbonate compounds increases (from 50 to 57%), but there is a decrease in ionic (from 48 to 42%) and sulphate (from 1.5 to 0.6%) forms.

If groundwater contains high amount of fulvic acids, a large part (80–95%) of complex–forming elements (e.g., Fe^{3+}, Cu^{2+}) is bound by these acids. Fulvic and humic acids protect many elements hydrolysers from total hydrolysis, inhibits formation of hydroxides and hold these elements in groundwater under neutral or even alkaline conditions (Krainov, Shvets 1992).

Cadmium content in groundwater, as a rule, does not exceed 0.0001–0.002 mg/l, except for glacial deposits where it reaches 0.005 mg/l. Major part of cadmium in groundwater migrates as a Cd^{2+} ion (75–90%) and its minor part in the form of carbonates $CdHCO_3^-$ (2–20%), sulphates $CdSO_4$ (0.6–11%) and chlorides $CdCl^+$ (0.9–8.5%). Anomalous distribution of cadmium compounds is observed in groundwater of glacial deposits: 62.5% in ionic form, 7% as carbonates, 10.5% as sulphates, and 19% as chlorides. The groundwater of Quaternary water table aquifers contains higher amounts of cadmium migrating in the form of ions than that of Quaternary confined water bearing beds (respectively, 84–90 and 75–86%), but the cadmium migration in the form of carbonate compounds is lower (respectively, 4–8% and 7–12%). With the confinement of aquifers increasing, the content of cadmium in Quaternary intermorainic (confined) aquifers decreases from 0.001 to 0.0001 mg/l with a slight decrease of cadmium in ionic (from 85.1 to 83.6%) and sulphate (from 4 to 1.5 %) forms.

CONCLUSIONS

There are three hydrodynamical types of Quaternary deposits in the water–bearing complex distinguished: unconfined (shallow), semi–confined and confined (intermorainic). Shallow groundwater is divided according to peculiarities of chemical composition formation into four main groups: (1) glaciofluvial, alluvial, marine, as well as alluvial and intermorainic deposits, (2) marine and aeolian deposits, (3) organogenic deposits, and (4) glacial deposits. The Quaternary glacial deposit beds contain two intermorainic aquifers. Mineralogical and petrographical composition of the Quaternary deposits is similar—fragments of crystalline rocks as well as limestone and dolomite prevail, thus, determining mainly the hydrocarbonate–calcium–magnesium type of water. With confinement of aquifers increasing, the oxidative conditions worsen and concentration of chemical elements in the intermorainic beds (confined aquifers) increases.

Cationgenic and aniongenic elements migrate mainly as ions with a very small part of Ca and Mg (to 10%) observed in carbonate and sulphate complexes. Three groups of metals are distinguished according to migration forms: (1) those migrating mainly ($\geq$ 90 %) as carbonate complexes (Pb, Ni), (2) as mixed carbonate and hydroxyl complexes (Cu, Fe) or as ions and carbonate complexes (Zn, Mn), and (3) mainly as ions (Cd).

The background migration forms of chemical elements analysed in fresh groundwater of the Quaternary deposits make the basis for prognostication and interpretation of migration of chemical elements and their distribution due to interaction of water with rocks as well as assessment of changes going in these compounds under the technogenic impact.

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