Hidrogeologija • *Hydrogeology* • *Ãèäðî ãåî ëî ãèÿ*

Water geochemistry in the Šventoji–Aruküla aquifer system, Lithuania

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The concentration of dissolved solids in the groundwater of the Šventoji-Aruküla aquifer system is less than 300 mg/l in the Baltic Highland and increases downgradient towards the West Lithuanian coast. The other major anions and cations show the same trend as the dissolved solids. The sulfate concentration increase in West Lithuania is caused mostly by leakage from the overlying Frasnian aquifer system. The values of hydrogen activity decrease with increasing the content of dissolved solids from 7.5–8 in the recharge area to less than 7.0 downgradient. The hydrochemical facies vary from alkali-earth carbonates at the eastern highlands plot to alkali-earth carbonate-sulfate and chloride facies at the discharge area in West Lithuania. The meteoric water percolating through the recharge area regulates the thermodynamic state of carbonates and aluminosilicates; the groundwater approaches the calcite and dolomite saturation and also belongs to the stability field of kaolinite. With an increase in the depth, more active is the saturation with sulfates and chlorides, and during the hydrolysis transformation of aluminosilicates to kaolinite and illite is intensified. The calcium–magnesium sulfate groundwater type is replaced by the transitional water facies from carbonate to chloride, mostly in the western part of Lithuania. The regional fresh groundwater flow is generally directed westward from a large, topographically high area of the Baltic Highland. However the deep groundwater flow is mostly directed upgradient from the Kaliningrad District toward the fresh groundwater discharge area on the Baltic Sea coast. At the interface of the two oppositely directed flows, the hydrochemical trap has formed a large groundwater mixing zone of the transitional hydrochemical facies types.

Key words: groundwater chemistry, hydrochemical facies, calcite and dolomite saturation, chloride and bromide ratio, stable isotopes, clay mineral transformation

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INTRODUCTION

The occurrence area of the Šventoji–Arukŭla aquifer system occupies more than 50 thousand km² in the Lithuanian territory and is a groundwater body very important for potable water supply for municipal and domestic use. The long-term and large-scale water needs will require a more intensive exploitation of productive bedrock aquifers and quality control. Without knowledge of the groundwater flow and resources, the characteristics of the aquifer system, of its hydrochemical quality cannot be defined efficiently. The proper use of groundwater resources can be achieved through understanding the regional hydrogeologic and geologic framework and its relation to the response of the topographic and hydrologic system to water-supply development. Progress in regional hydrogeology of the Šventoji–Arukŭla aquifer system in Lithuania has been made owing to investigations of the Baltic States researchers: in general groundwater chemistry – Gatalsky (1954), Kondratas (1969), Perens and Paltanavièius (1989), Mokrik (2003); with respect to hydraulic properties as the hydrogeological parameters, groundwater resources and chemical discharge – Zektser (1968), Klimas (1974), Juodkazis and Mokrik (1981), Gregorauskas et al. (1984, 1987), Mokrik (2003); in paleohydrogeology – Mokrik and Petkevièius (2002), Mokrik (2003).

This paper encompasses the geochemical aspects of the Šventoji–Arukŭla aquifer system in Lithuania. The hydrogeochemical data used in this study were compiled from the database of the Lithuanian Geological Survey and available commercial data files. The entire hydrogeochemical database contains more than 1000 entries in a computer-readable form.

METHODS AND PURPOSE

The basic objectives of the study were to use the new interpretative data on groundwater chemistry for defining its formation. All of these resulting data were incorporated into water chemistry database analysis to draw a more comprehensive conception of groundwater formation and to provide an improved estimate to qualitative analysis within the aquifers and between the flow system boundaries. The objectives of the Šventoji–Arukŭla aquifer system study were (1) to delineate the extent of fresh to saline water in various hydrochemical facies units, (2) to analyze the thermodynamic state of minerals in the groundwater chemistry and in the flow system, (3) to assess the current groundwater hydrochemical facies distribution and to identify the trends of these changes.

The equilibrium thermodynamics of groundwater was interpreted using the computer code PHREEQE Interactive 2,8 program which calculates mineral saturation states for an aqueous solution by the chemical analysis and physical parameters relative to car-

bonate, sulfate, chloride and clay minerals. In conjunction with this investigation of the regional Šventoji–Arukŭla aquifer system, there was delineated the potentiometric topography according to the hydrogeological map (Hydrogeological Map …, 1982), and a numerical simulation model of the confined groundwater flow in natural steady-state conditions was constructed (Mokrik, 2003). The potentiometric maps were used as the information on groundwater discharge direction that provided interpretation of the facies geochemistry.

DISCUSSION

Hydrochemical zonality and formation of groundwater chemical composition

The fresh groundwater downgradient flow of the Šventoji–Arukŭla aquifer system is directed westward from the Baltic Highland toward the discharge area in the Baltic Sea. The lithological and mineral composition, hydraulic parameters and depth of aquifer rocks, their physical-geographical situation, orographic system, etc. determine the velocity of groundwater filtration, the distribution of hydrochemical facies and their peculiarities. The alternation of the hydrochemical facies from infiltration to discharge area represents the hydrochemical zonality of the aquifer system (Fig. 1). The hydrochemical map is grounded on the hydrochemical classification of the Baltic artesian basin, which is based on metamorphization degree – $(rNa^+ + rCl^-)/rHCO_3^-$ (Jurgaitis, Mokrik, 1990) and location of boreholes (Fig. 2). The values of groundwater metamorphization degree reflect the ratio of dissolved sodium and chloride concentrations of a deep and bicarbonate concentration of shallow groundwater, which changes toward the flow path in appropriate diapasons perfectly. Consequently, the intervals of continuous range of metamrphization degree modify the particular hydrochemical facies of groundwater.

There are three lateral hydrochemical facies in the Šventoji–Arukŭla aquifer system. The first corresponds to the carbonate class groundwater – Ca-HCO$_3$ (C$_1$a), Mg-Ca-HCO$_3$ (C$_1$b-c), Na-HCO$_3$ (C$_2$) hydrochemical facies. It is prevalent in the eastside, central and northwest parts of Lithuania. The body thickness is irregular, sometimes slenderizes and even disappears. It depends on the impact of meteoric water. Metamorphization degree reaches up to 2.3 and mineralization varies in the range of 0.2–1.2 g/l. The fourth facies is transitional from carbonate to chloride class, where HCO$_3$-Cl (C-Cl). The fifth, Ca-Na-Cl (Cl$_1$), and the sixth, Mg-Na-Cl (Cl$_2$), hydrochemical facies belong to the chloride class of groundwater. The influence of sulfates is appreciable in the groundwater of the 2nd–5th facies zones. The values of groundwater metamorphization degree increased from 2.3 to 300 in chloride class facies. At least the Na-Cl (Cl$_3$) hydrochemi-
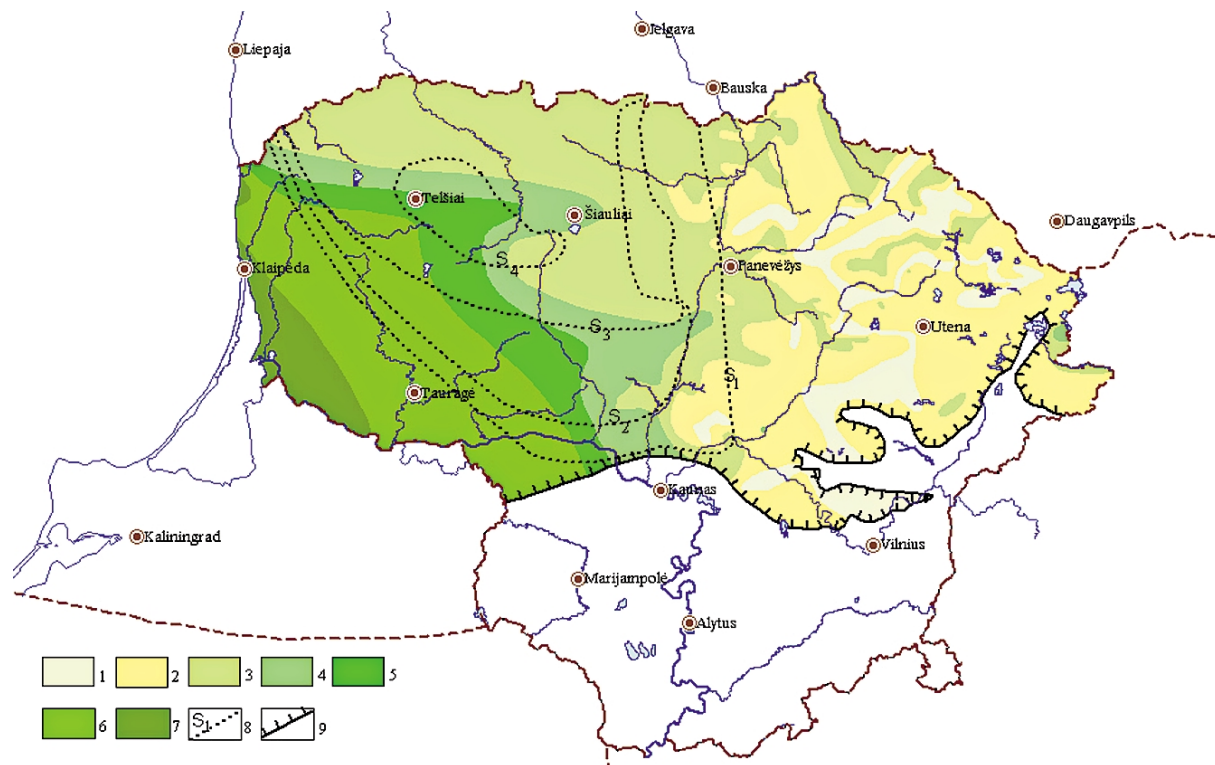
Fig. 1. Hydrochemical map of the Šventoji–Arukūla aquifer system.
1–7 – distribution of groundwater hydrochemical facies: *1* – calcium bicarbonate – C_1a (Ca-HCO$_3$); *2* – calcium-magnesium bicarbonate or magnesium-calcium bicarbonate – C_1b-c (Ca-Mg-HCO$_3$ or Mg-Ca-HCO$_3$); *3* – sodium bicarbonate – C_2 (Na-HCO$_3$); *4* – bicarbonate-chloride – C-Cl (HCO$_3$-Cl); *5* – calcium-sodium chloride – Cl_1 (Ca-Na-Cl); *6* – magnesium-sodium chloride – Cl_2 (Mg-Na-Cl); *7* – sodium chloride – Cl_3 (Na-Cl); *8* – sulfate saturation degree isoline (S_1 – 20–40; S_2 – 40–60; S_3 – 60–80; S_4 – >80%-eq/l correspondingly); *9* – boundary of the aquifer system
**1 pav.** Ðventosios-Arukiulos vandeningø komplekso hidrocheminis þemëlapis.
1–7 – poþeminio vandens hidrocheminiø tipø paplitimas: *1* – kalcio hidrokarbonatinis – C_1a (Ca-HCO$_3$); *2* – kalcio-magnio hidrokarbonatinis arba magnio-kalcio hidrokarbonatinis – C_1b-c (Ca-Mg-HCO$_3$ arba Mg-Ca-HCO$_3$); *3* – natrio hidrokarbonatinis – C_2 (Na-HCO$_3$); *4* – hidrokarbonatinis chloridinis C-Cl (HCO$_3$-Cl); *5* – kalcio-natrio chloridinis – Cl_1 (Ca-Na-Cl); *6* – magnio natrio chloridinis – Cl_2 (Mg-Na-Cl); *7* – natrio chloridinis – Cl_3 (Na-Cl); *8* – sulfatø prisotinimo laipsnio izolinija (atitinkamai: S_1 – 20–40; S_2 – 40–60; S_3 – 60–80; S_4>80%-eq/l); *9* – vandeningo komplekso paplitimo riba

cal facies belongs to the deep saline hydrochemical zone which is prevalent only on the area of the Baltic Sea coast, where the degree of mineralization and metamorphization is the highest, reaching 34.4 g/l and 2900, respectively.

Carbonate cement dissolution
Groundwater chemistry particularly depends on the type of rocks through which groundwater flows. Carbonate minerals are found in the cement of the Devonian Šventoji–Arukūla aquifer system sandstones and mostly prevail in the Quaternary aquifer system. Such minerals are well soluble in the CO$_2$-rich groundwater, so they form a carbonate type chemical composition of groundwater rapidly and signally. Meteoric water has a great influence and intense impact on the soil and sediments in the active groundwater exchange zone. During filtration through the soil, it saturates with CO$_2$ because of the degra-

dation of organic matter and becomes aggressive to calcite substances:

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-. \quad (1)$$
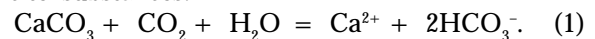
Groundwater becomes high in Ca^{2+} and HCO$_3^-$ ions. When groundwater mineralization is higher, partial pressure of carbon dioxide increases from the meteoric average ($10^{-3,5}$) to 10^{-2} atm. As a result, Ca-HCO$_3$ groundwater is formed. Increasing further (from 10^{-2} to $10^{-1,5}$ and more), groundwater composition comes closer to the equilibrium with calcite and dolomite. Carbon dioxide affects rocks intensively, and Ca-HCO$_3$ groundwater leaches the dolomite cement, resulting in dedolomitization. In this way, the Šventoji–Arukūla aquifer system groundwater receives higher calcium, magnesium and bicarbonate concentrations (Mokrik, Petkevièius, 2002):

$$Ca^{2+} + HCO_3^- + CaMg(CO_3)_2 + H_2O = Ca^{2+} + Mg^{2+} + CaCO_3 + 2HCO_3^- + OH^-. \quad (2)$$
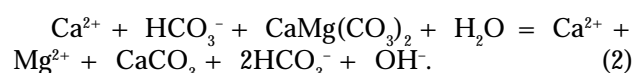
Fig. 2. Location map of boreholes with chemical database:
1 – borehole number; *2* – boundary of the aquifer system
2 pav. Faktiniø duomenø þemëlapis:
1 – græþinio numeris, *2* – vandeningo komplekso paplitimo riba
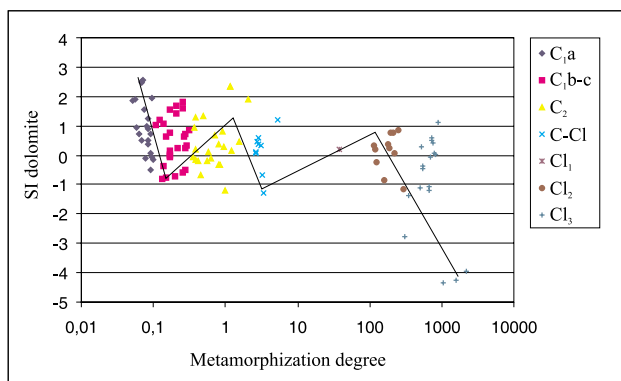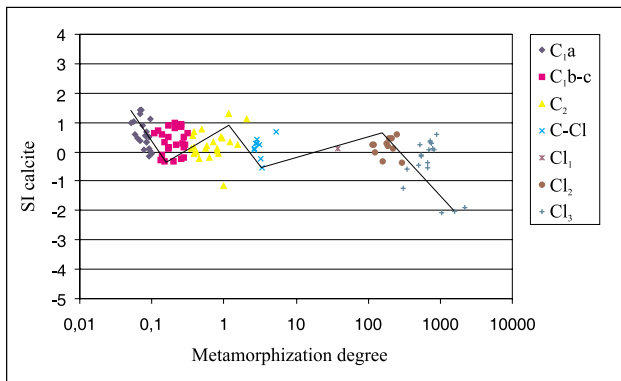
Dedolomitization is also conditioned by Ca–SO$_4$ groundwater type in the western part of Lithuania. For example, in borehole 26418 groundwater is of calcium–magnesium bicarbonate–sulfate hydrochemical composition, where SO$_4^{2-}$ concentration varies in the range of 84–87%-eq/l, and is onward of saturation and slightly supersaturated for calcite. The saturation index (SI) with dolomite is somewhat higher, but still differs by ± 0.5 from the equilibrium. The ratio of [aMg^{2+}] / [aCa^{2+}] fluctuates from 0.7 to 0.8. In that case,

$$1.8 \ CaSO_4 + 0.8 \ CaMg(CO_3)_2 = 1.6 \ CaCO_3 + Ca^{2+} + 0.8 \ Mg^{2+} + 1.8 \ SO_4^{2-}. \qquad (3)$$
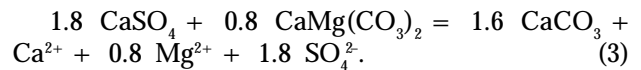
The reaction indicates that SO$_4^{2-}$ concentration rises with the concentrations of Ca^{2+} and Mg^{2+}. Consequently, the activity of hydrogen plunges and CO$_2$ partial pressure grows.

The above described processes determine the spread of Ca–Mg–HCO$_3$ (C$_1$b-c) groundwater facies in

Fig. 3. Groundwater saturation indices (SI) with calcite and dolomite depending on metamorphization degree diagrams (symbols demonstrate hydrochemical facies of groundwater)

3 pav. Kalcito ir dolomito prisotinimo indeksø (SI) priklausomybës nuo metamorfizacijos laipsnio (sutartiniai þenklai nurodo poþeminio vandens hidrocheminius tipus)

Bor.Nr	An. Nr	Depth, m	Hydroch.facies (met.degree)	TDS, g/l	pH	SiO₂(ppm)	Log $\frac{aCa}{(aH)^2}$	Log $\frac{aMg}{(aH)^2}$	Log $\frac{aNa}{aH}$	Log $\frac{aK}{aH}$
4266	53776	128.5-133	C₁b-c (0.31)	0.43	7.6	24.30	12.39	12.07	4.88	3.36
4294	53818	115-120	C₂ (0.98)	0.39	7.2	15.50	10.40	11.54	4.62	
6790	52132	86-96	C₂ (1.17)	1.24	8	6.75	13.37	13.23	5.70	
233	52036	55-102	C-Cl (2.69)	0.89	7.4	6.00	11.87	11.80	5.22	
4pe	22	487.46-502,2	Cl₁ (113.23)	11.02	7.2	5.60	12.08	11.85	6.24	4.47
	11	-.-	Cl₂ (182.14)	-.-	7.25	-.-	12.18	11.95	6.29	4.53
1pe	44	666-680.4	Cl₃ (716.17)	22.80	7.25	8.60	12.38	12.15	6.62	4.70
	12	-.-	Cl₃ (730.86)	-.-	7.2	-.-	12.29	12.04	6.57	4.70
	33	-.-	Cl₃ (778.47)	-.-	7	-.-	11.87	11.66	6.37	4.46

Fig. 4. Stability diagrams of silica and clay minerals (*1* – number of borehole and chemical analysis)

4 pav. Poþeminio vandens pusiausvyros su siliciu ir molio mineralais diagramos (*1* – græþinio ir cheminës analizës numeris)

the Šventoji–Arukūla aquifer system. Ca^{2+} may amount to 66, Mg^{2+} to 48, and HCO_3^- ion concentration may reach even a milliequivalent percentage in such type of groundwater. Since these cations have almost equal concentrations, one may come to a conclusion that they are formed during the dolomite cement dissolution.

After designing the stability diagram of calcite and dolomite depending on the hydrogen and carbon dioxide partial pressure, and calculating the saturation indices with calcite and dolomite, we observed that groundwater with negative SI values was located before the calcite equilibrium line. The distribution of dots below zero in the diagrams of saturation indices dependence of metamorphization degree modifies groundwater subsaturation with the above mentioned minerals (Fig. 3.). Consequently, an intensive dissolution of carbonate cement takes place. On drawing an equilibrium line, the saturation index with calcite becomes positive and with dolomite remains negative. It means that in this zone, on the one hand precipitation of calcite begins and, on the other hand, saturation with dolomite continues. On overpassing the dolomite equilibrium line, both these indices are positive and groundwater turns into metastable state when saturated with Ca^{2+} and Mg^{2+}, but there is no precipitation because of the other ions' hydratation.

As the reaction (1) shows, CO_2 is used when dissolution of carbonate cement takes place. Groundwater with a larger degree of metamorphization is formed in the deeper areas, and the closed system is far away from the equilibrium with carbonates in the calcite and dolomite stability diagram (Figs. 3 and 4). In such circumstances, the velocities of exchange are distinctly lower. Because there is no CO_2 production and the partial pressure varies from $10^{-1,5}$ to 10^{-3} atm. and lower, the dissolution of carbonates is not intensive or doesn't proceed at all. Then the HCO_3^- concentration decreases apace: from 39%-eq/l in the bicarbonate-chloride to 0.1%-eq/l in the sodium chloride hydrochemical facies. If dissolution processes of evaporate minerals take place, groundwater tends to reach an equilibrium with sulfates. The equilibrium diagrams of dolomite-calcite and clay minerals show that in groundwater with a higher metamorphization degree without dolomite cement dissolution, aluminosilicate weathering is active and the samples of groundwater sites lie in Mg-montmorillonite (smectite) and kaolinite stability fields (see Fig. 4).

It was noted that with an increase in depth and metamorphization degree from the Ca–Mg–HCO₃ to Na–Cl hydrochemical type of facies, groundwater is saturated with calcite and dolomite several times (see Fig. 3). When the secondary formation of carbonate
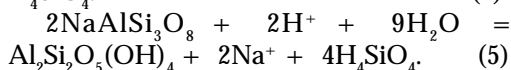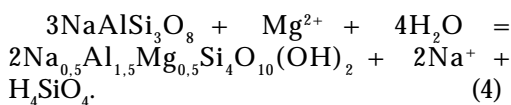
cement proceeds, the concentration of Ca^{2+} and Mg^{2+} ions drops in groundwater. Then Na^+ ion is trying to aggregate with HCO_3^-. As a result, groundwater with a higher concentration of sodium is formed. Besides, aluminosilicates and clayey rocks can be a source of sodium. When Ca-Mg-HCO_3 groundwater is percolating through them, the weathering of feldspars and cation exchange reactions follow on the clayey rock surface. This means that Ca^{2+} interacting with clay particles enters their composition and Na^+ is hustled into a solution. Such increment of Na^+ concentration is observed in the C_2 and C–Cl hydrochemical facies. Furthermore, in the range of the latter, the transitional area of the Šventoji–Arukūla aquifer system extends; there carbonate and chloride hydrochemical facies are mixed, Ca^{2+} being replaced by Na^+ and HCO_3^- by Cl^-.

In the chloride facies, groundwater saturation with calcite and dolomite is also observed, since there is no additional CO_2 production in a closed system; during dissolution of carbonate cement groundwater consumes it, and CO_2 content is rapidly used up. In the stability diagram of calcite and dolomite, depending on hydrogen and carbon dioxide partial pressure, the groundwater receding from the equilibrium with calcite and dolomite becomes increasingly negative. As a result, in the solution Ca^{2+} and Mg^{2+} are replaced by Na^+ while HCO_3^- by Cl^- and SO_4^{2-}.

Clay minerals as aluminosilicate weathering products

Clay mineral as an insoluble remnant can be formed during an incongruent dissolution of aluminosilicates. The stability diagrams of anorthite, albite, potassium feldspar and biotite provide a better understanding of stability relation between minerals and groundwater in a complicated thermodynamic system. In this instance, the stock of silica is important to measure, because the effect of silicate weathering on water chemistry is primarily expressed as addition of cations (Na^+, Ca^{2+}, Mg^{2+}, K^+) and silica.

Using albite as an example, the transformation into different weathering products can be described by the following equations (Appelo, Postma, 1993):

$$3NaAlSi_3O_8 + Mg^{2+} + 4H_2O = 2Na_{0.5}Al_{1.5}Mg_{0.5}Si_4O_{10}(OH)_2 + 2Na^+ + H_4SiO_4. \qquad (4)$$

$$2NaAlSi_3O_8 + 2H^+ + 9H_2O = Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4. \qquad (5)$$

The change of albite into kaolinite and monmorillonite clay minerals represents an increasing removal intensity of silica and sodium cations from the weathering product. When albite transforms into montmorillonite, groundwater leaches 89% and if into kaolinite – 33% of silica (Appelo, Postma, 1993). Which clay mineral will form depends also on groundwater exchange intension.

Thermodynamic analysis demonstrates that when albite, anorthite and biotite are hydrolized, all data points locate in the stability plot of kaolinite (see Fig. 4). The main reactions of aluminosilicate transformation into kaolinite are (Appelo, Postma, 1993):

$$2NaAlSi_3O_8 + 2H^+ + 9H_2O = Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4. \qquad (6)$$

$$2KAlSi_3O_8 + 2H^+ + 9H_2O = Al_2Si_2O_5(OH)_4 + 2K^+ + 4H_4SiO_4. \qquad (7)$$
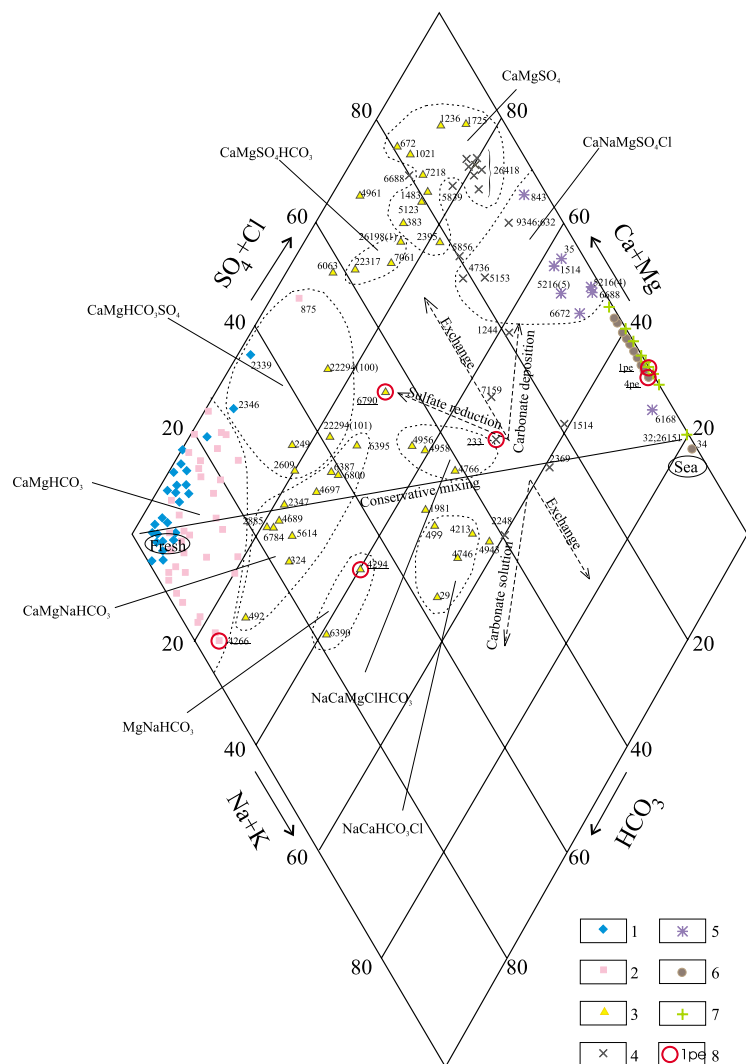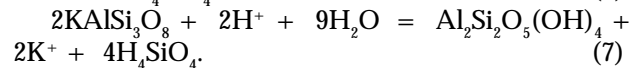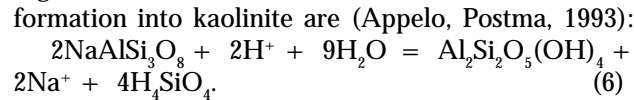
Fig. 5. Piper diagram showing groundwater composition. *1–7* – hydrochemical facies of groundwater: *1* – C_1a, *2* – C_1b-c, *3* – C_2, *4* – C-Cl, *5* – Cl_1, *6* – Cl_2, *7* – Cl_3; *8* – borehole with measured SiO_2 content in groundwater

5 pav. Poþeminio vandens cheminës sudëties pokytis pagal Piperio diagramà. *1–7* – poþeminio vandens hidrocheminiai tipai: *1* – C_1a, *2* – C_1b-c, *3* – C_2, *4* – C-Cl, *5* – Cl_1, *6* – Cl_2, *7* – Cl_3; *8* – græþinys, kurio poþeminiame vandenyje analitiðkai nustatytas SiO_2 kiekis
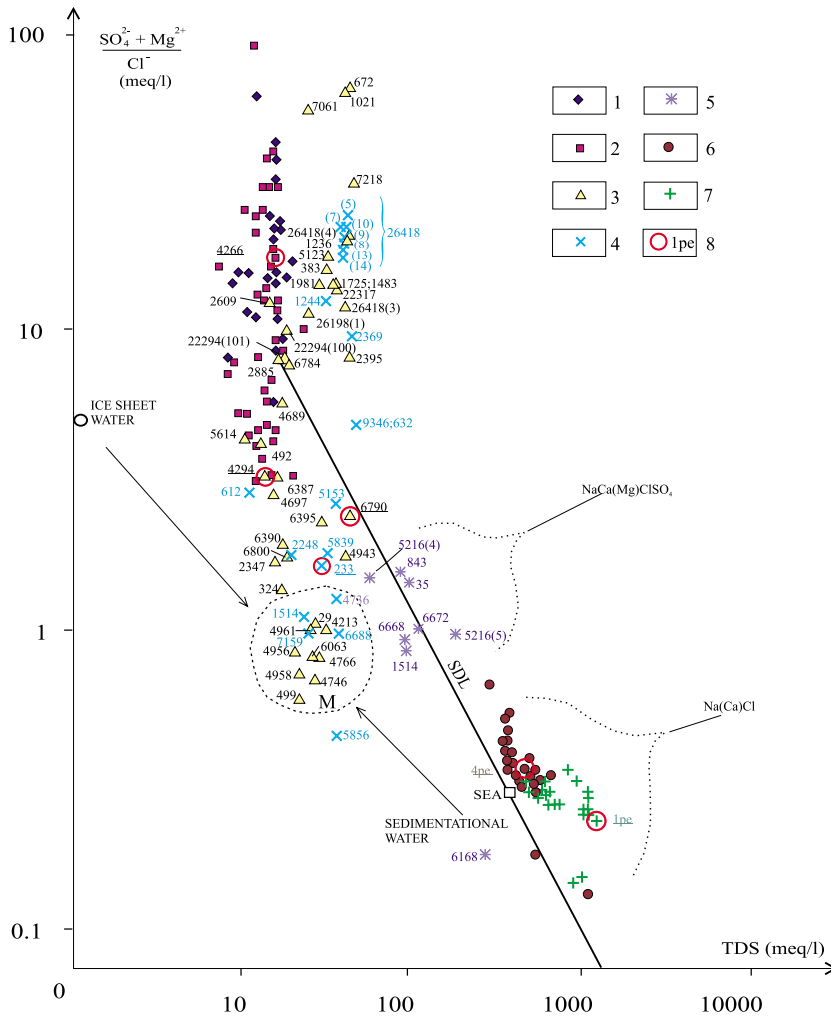
Fig. 6. Characteristic coefficient $(SO_4^{2-}+ Mg^{2+})$ / Cl^- versus TDS diagram. *1–7* – hydrochemical facies of groundwater: *1* – C_1a, *2* – C_1b-c, *3* – C_2, *4* – C-Cl, *5* – Cl_1, *6* – Cl_2, *7* – Cl_3; *8* – borehole with measured SiO_2 content in groundwater

6 pav. Koeficiento $(SO_4^{2-} + Mg^{2+})$ / Cl^- priklausomybës nuo TDS diagrama. *1–7* – poþeminio vandens hidrocheminiai tipai: *1* – C_1a, *2* – C_1b-c, *3* – C_2, *4* – C-Cl, *5* – Cl_1, *6* – Cl_2, *7* – Cl_3; *8* – græþinys, kurio poþeminiame vandenyje analitiðkai nustatytas SiO_2 kiekis

$$CaAl_2Si_2O_8 + 2H^+ + H_2O = Al_2Si_2O_5(OH)_4 + Ca^{2+}. \qquad (8)$$

$$2K[Mg_2Fe][AlSi_3]O_{10}(OH)_2 + 10H^+ + 0,5O_2 + 7H_2O =$$
$$Al_2Si_2O_5(OH)_4 + 2K^+ + 4Mg^{2+} + 2Fe(OH)_3 + 4H_4SiO_4. \qquad (9)$$
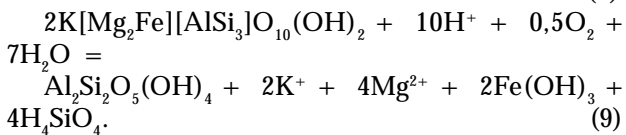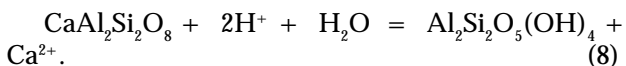
In the stability diagram with silica and clay minerals, when K-feldspar is hydrolyzing, the data points of the 4pe and 1pe boreholes locate in the stabil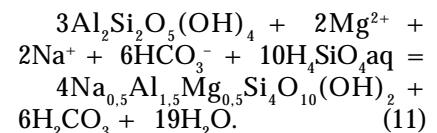ity plot of muscovite (or seawater) and of 4266 on the precipitation line of illite. In the Šventoji–Arukūla aquifer system, kaolinite amounts to 35% and illite from 65 to 99% of clay minerals in the terrigenous formation. Hydrated muscovite particles are also present here (Narbutas, Uginèius, 2001). Thus, the obtained results do not contradict the distribution of clay minerals in the aquifer system and show that

during metamorphization groundwater is able to produce these minerals. It should be emphasized that aluminosilicate weathering and the formation of clay minerals is a very slow process and does not have such a distinct and rapid effect on groundwater chemical composition as dissolution of carbonates. Groundwater of almost all borehole sites in the stability plot of dolomite in the diagram of dolomite–calcite and clay minerals shows an equilibrium, because this diagram is applied to analyze the processes in the carbonate system. Thus, it means that alongside aluminosilicate weathering, the dissolution of dolomite cement also proceeds in groundwater. Besides, in some cases even carbonate precipitation can be a result of silicate weathering (Appelo, Postma, 1993). The point of borehole 4294 lies in the stability field of Mg-montmorillonite, and in the stability diagram with silica and clay minerals it is removed from the zone of carbonate equilibrium. Plausible formation of montmorillonite could be related here to the larger concentrations of bicarbonates formed during kaolinite hydrolization (Garrels, Mackenzie, 1997):

$$3Al_2Si_2O_5(OH)_4 + 2Mg^{2+} + 2Na^+ + 6HCO_3^- + 10H_4SiO_4aq =$$
$$4Na_{0,5}Al_{1,5}Mg_{0,5}Si_4O_{10}(OH)_2 + 6H_2CO_3 + 19H_2O. \qquad (11)$$

Formation of groundwater chemistry

The Ca-HCO_3 (C_1a) and Ca-Mg-HCO_3 (C_1b-c) hydrochemical types of groundwater (mineralization does not reach 0.7 g/l) have the lowest metamorphization degree (up to 0.33) and are formed in the active groundwater exchange zone where the aquifer system is covered only by the Quaternary sediments and has a close hydraulic interaction with its water, especially in river valleys. These hydrochemical facies of groundwater are located in the left corner of the Piper diagram where the percentage of calcium, magnesium and bicarbonate ions is the utmost, and are formed under the intensive infiltration of meteoric water which conditions an active dissolution of the carbonate cement of Quaternary and Devonian sediments in the Baltic Highland area (Fig. 5). Carbon dioxide is added to the percolation water at the recharge area along its flowpath, followed by its in-

teraction with carbonate compounds. In a diagram of the characteristic coefficient $(SO_4^{2-} + Mg^{2+})$ / Cl^- *versus* TDS (total dissolved solids), this groundwater is shifted from the SDL (sea dilution line) to the left, because it has the highest values of the mentioned coefficient (3–34 meq/l) and the lowest TDS values (9–19, sometimes 24 meq/l) (Fig. 6).

Hydrochemical type sulfates are prevalent in both active and delayed groundwater exchange zones in the western part of Lithuania. The maximum content of sulfate ions is characteristic of sodium bicarbonate (C_2), bicarbonate-chloride (C-Cl) and calcium sodium chloride (Cl_1) hydrochemical facies, and is coherent mostly with the leakage process from the overlying Frasnian aquifer system and may amount up to 87%-eq/l. In this type of groundwater, sulfate production processes are proceded by the dissolution of Frasnian gypsum:

$$CaSO_4 \cdot 2H_2O = SO_4^{2-} + Ca^{2+} + 2H_2O. \quad (12)$$
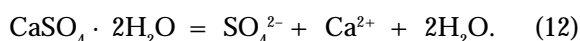
This reaction moves the groundwater chemical composition from the conservative mixing line with a parallel shift towards the $SO_4^{2-} + Cl^-$ side in the Piper diagram. The rise of SO_4^{2-} ions results in higher TDS (to 48%-eq/l) and a shift from the SDL to the upward right, though southwest down toward the Baltic Sea coast the concentration of sulfate ions decreases, while hydrochemical type sulfates disappeared because of a rise of mineralization and Cl^- content.

Sodium bicarbonate (C_2) and bicarbonate–chloride (C–Cl) hydrochemical facies are fored during an intensive mixing of the active and the delayed exchange zones in the transitional area. In the northwest of Lithuania, fresh groundwater declining down from the Þemaitija Highland to the depth of 400 m still belongs to the C_2 hydrochemical facies because, on account of a good permeability, the internal (transmissivity is still 100–300 m²/d), mineralization does not exceed 1 g/l and the metamorphization degree is not higher than 2.3. In the transitional area, cation exchange processes may enrich Ca-Mg-HCO_3 hydrochemical groundwater facies with sodium ions. Indeed, sodium amounts to 58%-eq/l in C_2 and 61%-eq/l – in C-Cl hydrochemical facies. However, the sodium ion is dominant in the bicarbonate hydrochemical class at the very rare intervals. Groundwater chemical composition is moved to the $SO_4^{2-} + Cl^-$ and $Na^+ + K^+$ corner in the Piper diagram, indicating that due to carbonate cement dissolution the concentration of HCO_3^-, Mg^{2+}, Ca^{2+} ions increases.

Westward, due to the growth or metamorphization degree from 12 to 2900, the hydrochemical facies of the chloride class gradually change from calcium sodium chloride, magnesium sodium chloride to sodium chloride. Such chemical composition of

groundwater is located parallel to the $Ca^{2+} + Mg^{2+}$ side in the upper part of the Piper diagram, implying an exchange of cations when the exchanger takes up sodium and Ca^{2+} is released into groundwater:

$$NaCl + 2Ca^{2+}(solid) = CaCl_2 + Na(solid). \quad (13)$$
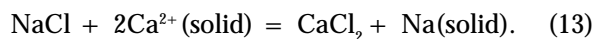
However, the calcium chloride facies does not form in the Šventoji–Aruküla aquifer system and is characteristic only of an extra isolated environment with an intensive metamorphism and diagenesis. However, the stock of Ca^{2+} ions is lower than 20%-eq/l only in rare places. The reason for its relative decrease could be precipitation of carbonate cement.

Groundwater of Cl_2 and Cl_3 hydrochemical facies is situated above the SDL and is close to the seawater point. The Cl/Br ratio, which identifies the genesis of salt water, was calculated for the 4pe (depth 488–502 m) and 1pe (depth 666–680 m) boreholes (Palanga). The mineralization reached 14.2 and 34.3 g/l, the concentration of Br^- ions being 44 and 115.3 mg/l and of Cl^- 7151 and 19259 mg/l, respectively. The value of the average estimated Cl/Br ratio is 161. Since the ratio of the seawater is ~280, the implication is that this mineralized groundwater is diluted with the fresh one.

In Fig. 6, the groundwater composition of some boreholes in the southern part of the aquifer system shifts into plot M. The value of the scharacteristic coefficient $(SO_4^{2-} + Mg^{2+})$ / Cl^- lowers to 0.7 because of a considerable growth of Cl^- ion concentration, though mineralization doesn't exceed 0.9 g/l (except for boreholes 4736 and 6688, where due to an increase of SO_4^{2-} ions the concentration grows to 1.2 and 1.3 g/l respectively). Such a composite Na-Ca-(Mg)-HCO_3, rarer Ca-Mg-(Na)-HCO_3-Cl or Cl-HCO_3 hydrochemical type could result from groundwater mixing with water of glacial origin in the Pleistocene. Besides, as data show, because of a slower vertical groundwater exchange there is a noticeable difference in metamorphization, mineralization and chemical composition between the upper and the lower parts of the aquifer system. For example, at a depth of 247 m (borehole 1514), Na-Cl-SO_4 hydrochemical groundwater type with a 0.7 g/l mineralization (metamorphization degree 5.7) occurs (where Na^+ ions amount to 59, Ca^{2+} 22, Mg^{2+} 19, Cl^- 48, SO_4^{2-} 33, HCO_3^- 19 %-eq/l, respectively). At a depth of about 318 m mineralization grows to 2.89 g/l (metamorphization degree reaches up to 17.8) and groundwater of hydrochemical type turns into Na-Ca-Cl-SO_4 (Na^+ ion concentration equals to 43, Ca^{2+} 38, Mg^{2+} 19, Cl^- 61, SO_4^{2-} 33, HCO_3^- 6 %-eq/l, respectively). Thus, in the deeper part of the aquifer system, more mineralized and metamorphozed groundwater with higher concentrations of Ca^{2+} and Cl^- and lower levels of Na^+ and HCO_3^- ions occurs and shifts closer to

the SDL line. Such differences in groundwater chemical composition reflect the mixing effect of mineralized and fresh water. The deeper part of groundwater is located in the cation exchange zone and of the upper part is not so far from the conservative mixing line in the Piper diagram. The concentration of stable isotopes should be measured for a more precise identification of this groundwater formation. The deep groundwater flow is directed upgradient from the Kaliningrad District toward the fresh groundwater discharge area on the Baltic Sea coast. At the interface of the two opposite flows the hydrochemical trap boundary is formed, reflecting a large groundwater mixing zone with transitional hydrochemical facies types.

CONCLUSION

Groundwater chemistry data of the Šventoji–Arukůla aquifer system were classified and grouped into seven hydrochemical facies throughout fresh and saline water. The data were also evaluated with regard to the equilibrium groundwater thermodynamics using a computer code program which calculates saturation states for an aqueous solution relative to carbonate, sulfate, chloride and clay minerals. On the highlands, dissolution of carbonate minerals by fresh water is the main source of calcium, magnesium and bicarbonates, and water has a low content of dissolved solids. The calcium bicarbonate and magnesium calcium bicarbonate compositions have TDS less than 450–600 mg/l and pH less than 7.5. Downgradient the active water exchange zone, sodium bicarbonate becomes dominant and groundwater has TDS of 550–800 mg/l. The sulfate concentration is high in West Lithuania where groundwater recharge occurs through the overlying Frasnian aquifer which contains chemical components of gypsum. Most aluminosilicate minerals do not react to the equilibrium but can still have an effect on groundwater chemistry through cations. On the groundwater stability diagrams, the dominant clay mineral is kaolinite. Groundwater in the deepest part is saline and of sodium chloride type. The regional fresh groundwater flow is generally westward from a large, topographically high area of the Baltic Highland. The deep groundwater flow is directed upgradient from the Kaliningrad District towards the fresh groundwater discharge area on the Baltic Sea coast. At the interface of the two opposite flows, the hydrochemical trap boundary has formed a large groundwater mixing zone with the transitional hydrochemical types of facies.

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LIETUVOS ŠVENTOSIOS-ARUKIULOS VANDENINGO KOMPLEKSO POÞEMINIO VANDENS GEOCHEMIJA

S a n t r a u k a
Sistemoje „dolomitas – kalcitas ir molio mineralai“, atsiþvelgus á vandenilio rodiklá ir CO_2 parcialiná slëgá, kalcito bei dolomito prisotinimo indeksø (SI) priklausomybës nuo metamorfizacijos laipsnio diagramas ir sudarius pusiausvyros su kalcitu bei dolomitu grafikus nustatyta, kad atmosferinis vanduo dirvoþemyje ir kvartero komplekse, praturtëjæs anglies dvideginiu, tampa agresyvus karbonatiniam vandeningo komplekso uolienø cementui. Já tirpindamas poþeminis vanduo praturtëja Ca^{2+}, Mg^{2+}, HCO_{3-} jonais – taigi didëja poþeminio vandens mineralizacija. Ðiuo atveju daugiausia

formuojasi kalcio-magnio hidrokarbonatinio tipo poþeminis vanduo. Þá dedolomitizacijos procesà lemia ir kalcio sulfatinio tipo poþeminis vanduo. Didëjant metamorfizacijos laipsniui ir gyliui, keièiasi poþeminio vandens hidrocheminis tipas – nuo kalcio-magnio hidrokarbonatinio iki natrio chloridinio. Atviros sistemos sàlygomis poþeminis vanduo kelis kartus prisisotina antriniu kalcitu ir dolomitu. Taèiau chloridinio tipo poþeminis vanduo formuojasi uþdaroje sistemoje, kurioje praktiðkai nëra anglies dvideginio prieaugio, o já sunaudojus karbonatinis cementas nebetirpsta.

Poþeminio vandens pusiausvyros su silicio ir molio mineralais analize nustatyta, kad vykstant aliumosilikatø iðplovimui ðie netapaèiai transformuojasi á molio mineralus. Poþeminis vanduo praturtinamas natrio, kalcio, magnio ir kalio jonais bei siliciu. Termodinaminës diagramos rodo, kad hidrolizuojantis albitui, anortitui ir biotitui, poþeminio vandens ëminiø analizës iðsidësto kaolinito stabilumo lauke, o hidrolizuojantis kalio lauko ðpatui – muskovito arba jûrinio vandens ir ilito.

Piperio diagramoje poþeminio vandens tipø iðsidëstymas vaizduoja vandeningame komplekse vykstanèius procesus. Nustatyta, kad: 1) aktyvios apykaitos zonoje plaèiausiai paplitæs kalcio-magnio hidrokarbonatinis poþeminis vanduo formuojasi intensyviai tirpinant karbonatiná cementà; 2) sulfatinio tipo poþeminis vanduo formuojasi dël sulfatø prietakos ið aukðèiau slûgsanèio franio komplekso ir yra lydimas sulfatø redukcijos; 3) natrio hidrokarbonatinio tipo poþeminis vanduo Ðventosios-Arukiulos vandeningame komplekse praktiðkai nesiformuoja, nes dël karbonatinio cemento tirpinimo poþeminiame vandenyje padaugëja kalcio ir magnio jonø, kurie daþniausiai virðija natrio koncentracijà; 4) pereinant ið aktyvios apykaitos zonos á sulëtëjusià, dël kalcito

ir dolomito antrinio iðkritimo á nuosëdas ir sumaþëjusio CO$_2$ parcialinio slëgio maþëja kalcio, magnio bei hidrokarbonato jonø ir poþeminis vanduo pereina á chloridiná tipà.

Ðîáåðò Ì îêðèê, Àóðåëèÿ Áàóáëèòà

ÃÅÎ ÕÈÌ È ß Ï Î ÄÇÅÌ Í ÛÕ ÂÎ Ä Ø ÂßÍ ÒÎ ÑÊÎ - ÀÐÓÊÞ ËßÑÊÎ ÃÎ ÊÎ Ì Ï ËÅÊÑÀ ËÈÒÂÛ

Ðàçþ ì å
Ðàññì îòðàíî ðàñï ðàäàëàí èà ãèäðîõèì è÷åñêèõ Ôàöèé ï î äçàì í ûõ âî ä Ø âÿí òî éñêî -Àðóêþëàñêî ãî êî ì ï ëàêñà Ëèòâû. Â âîäîî ñîî êî ì ï ëàêñà Ôî ðì èðóþòñÿ êàðáî í àòí ûé, ñóëüôàòí ûé è õëî ðèäí ûé òèï û ï î äçàì í ûõ âî ä çà ñ÷àò ï ðî öàññî â ñîì âø áí èÿ ï ðàñí ûõ è ñî ëàí ûõ âî ä, êàòî í í î àî îáì áí à è ñóëüôàòðàäóêöèè. Â âîä í î ñî î êî ì ï ëàêñà ï ðàî áëàäàþò âûùàëà÷èâàí èà êàðáî í àòî â ñ î áðàçî âàí èàì âîä èòèà Ca-Ì g-HCO$_3$, à òàêæà èõ âûâäàëà è â î ñàäî ê ï î ì àðà ï î äôóæàí èÿ êî ì ï ëàêñà â î áëàñòè ðòàì çèòà. Áî ëäà ñî ëàí ûe âîäû î áðàçî âàâëèñü â ñî í âîí î çà ñ÷àò ï ðî öàññî â êàòèî í í î î î îáì áí à, âûùàëà÷èâàè ñóëüôàòî â è õëî ðèäî â, à òàêæà àëþ î ñèëèêàòî â. Ôàöèè õèì ÷åñêî ãî ñî ñòàâà ðàñï ðàäàëàí û ñëàäóþùèí î áðàçî : í à âî ñòîê Ëèòâû ðàñï ðî ñòðàí àí û Ca-HCO$_3$, Ca-Mg-HCO$_3$, Na-HCO$_3$ è HCO$_3$-Cl, à í à çàï àäà – ñî î òàòñòâóàí í î Ca-Na-Cl, Mg-Na-Cl è Na-Cl òèï û ï î äçàì í ûõ âî ä. Ñòàï àí ü í àñùùàí í îñòè ï î äçàì í ûõ âî ä îï ðàäàëÿàíü ñ èíï î ëüçî âàí èàì êî ì ï üþòàðî é ï ðî ãðàì ì û PHREEQE Interactive 2.8.