

# Boron, fluoride, strontium and lithium anomalies in fresh groundwater of Lithuania

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Anomalies of certain trace elements most typical of salt water sometimes occur in fresh groundwater aquifers. For example, it is a well-known fact that Permian–Devonian aquifers contain increased concentrations of fluoride in West Lithuania. In the recent years, increased concentrations of boron and strontium have also been found there. An analysis of available data shows that natural anomalies of B, F, Sr and perhaps Li interrelate with fresh–salt water transit zones where groundwater circulates in fine-grained clayey sand or in fissured beds of limestone, dolomite or gypsum deposited in marginal parts of high salinity basins.

**Key words:** trace elements, groundwater, anomalies, Lithuania

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## INTRODUCTION

Fresh groundwater is the main source of drinking water in many countries. Lithuania entirely relies on aquifers for drinking water supply. World Health Organization (WHO) recommends (Guidelines..., 2006) and Lithuanian Hygiene Norms HN 24:2003, HN 48:2001 require (Lietuvos..., 2003; 2001) that the concentrations of certain trace elements in drinking and raw water should not exceed a particular limit (MAC, maximum acceptable concentration). Technogenic toxic substances and trace elements in drinking and groundwater should be minded first of all. However, results of recent investigations show that some of these trace elements in groundwater are of natural origin. If the concentration of these trace elements in groundwater increases against the MAC, we should know where such anomalies exist and should take measures to reduce these concentrations or to find alternative sources of drinking water.

Anomalies of fluoride (F) in fresh water aquifers of Lithuania are old-established: as far back as in 1968, hygienists organized extensive investigations of fluoride in dug- and drill-wells (Štarkas et al., 1968). After a while, some regularities of fluoride occurrence in fresh groundwater were ascertained (Климаc, 1985; 1988). Recently Lithuanian Geological Survey has demonstrated an initiative to survey fluoride occurrence in West Lithuanian aquifers, relating it with caries prophylaxis (Balčiūnienė ir kt., 2001).

Quite a long time ago it was known that the concentrations of boron (B), strontium (Sr) and, perhaps, lithium (Li) in some fresh water aquifers of West Lithuania are also raised up (Климаc, Брейве, 1981; Климаc, 1988). But more extensive studies of those trace elements started only after the incorporation of boron into the HN 24:2003 (Lietuvos..., 2003) and of strontium, lithium into

the HN 48:2001 (Lietuvos..., 2001). New data enable us to understand better and to reveal the regularities of the formation of B, F, Sr, Li anomalies in fresh groundwater of Lithuania. Some data on the occurrence of these trace elements in fresh water aquifers have been already published (Klimas, Mališauskas, 2007; 2007a). This paper presents not just deeper studies of B, F, Sr occurrence in these aquifers, but also contains results of calculations of their migration species and correlations of their content with other characteristics of groundwater chemistry.

## HYGIENIC ASPECTS

Recommendations of WHO include boron and fluoride (F-ion in water) into the list of inorganic constituents of health significance in drinking water (Guidelines..., 2006). Both these toxic chemical elements are also included into the Lithuanian Hygiene Norm of drinking water, HN 24:2003 (Lietuvos..., 2003). Strontium and lithium, as mentioned above, are inscribed into the Lithuanian Hygiene Norm HN 48:2001 of raw water (Lietuvos..., 2001) (Table 1).

The main source of all these trace elements is water-bearing rocks and soils. Nevertheless, B and F can enter groundwater

Table 1. MAC of B, F, Sr, Li in drinking and groundwater  
1 lentelė. B, F, Sr, Li DLK geriamajame ir požeminiame vandenyje

Trace element	MAC, mg/l		
	HN 24:2003	HN 48:2001	WHO
Boron, B	1.0	1.0	0.5
Fluoride, F	1.5	1.5	1.5
Strontium, Sr	–	7.0	–
Lithium, Li	–	0.03	–

together with other contaminants, because boron is a component of many washing powders and fluoride is present in certain mineral fertilizers, e. g., superphosphate.

Hygienists state that the concentrations of boron exceeding 1–5 mg per day lead to gastrointestinal irritation. Because boron and its compounds (borates, boric acid) are highly soluble in water, B is rapidly and almost completely absorbed from the gastrointestinal tract. Boron excretions occur mainly through the kidney. Long-term animal studies did not show a mutagenic or carcinogenic effect of boron or its compounds, but large amounts of boron have a negative impact on the reproductive organs of animals (Guidelines..., 2006). Therefore, the WHO guideline value of B is 0.5 mg/l. The MAC of B in the European Drinking Water Directive (Council..., 1998) and in the Lithuanian Hygiene Norm (Lietuvos..., 2003) is 1 mg/l.

The effect of fluoride and its compounds on the human organism is known better than the effect of boron. The reason is that F is more common in nature and human products; e. g., the average content of F in rocks and soils is 0.3 g/kg, in fertilizers (superphosphate) more than 4% (Крайнов и др., 2004). But there are certain problems with the F normative in drinking water, because this trace element is not only harmful: everybody knows that fluoride protects teeth from caries. Moreover, certain and sometimes not small levels of F are present not only in water, but also in tea, toothpaste. Nevertheless, special studies show that higher than 1.5 mg/l concentrations of F in drinking water may cause dental fluorosis (Guidelines..., 2006). Much higher concentrations of F lead to skeletal fluorosis. No cancerogenic effect of fluoride was declared. Therefore, it is universally accepted that the optimal concentration of F in drinking water is 1.5 mg/l. However, it is also known that fluorosis does not occur at even high concentrations of F, if the concentration of Ca in water is high. For example, studies in Russia show that fluorosis is not evident if the ratio of F and Ca is  $rF/rCa < 0.25$ ; here  $r$  is a molar concentration of ions (Крайнов и др., 2004). Therefore, the WHO suggests to take into account local geological, climatic conditions and even nutrition traditions when elaborating a national normative of F.

Strontium (Sr) is an earth alkaline metal, chemically more active than Ca, therefore Sr may easily substitute Ca in human bones. But Sr constituents are not strong, therefore such bones become fragile. Moreover, even three isotopes of Sr (of the four available) are radioactive. Therefore substitution of Ca by Sr can be very hazardous. However, Sr is not classified as a very dangerous chemical trace element. Therefore its MAC in raw water is 7 mg/l (Lietuvos..., 2001); in the drinking water normative of Lithuania Sr is absent.

The MAC of another trace element, lithium (Li), in raw water is 0.03 mg/l (Lietuvos..., 2001). But this really rare toxic chemical element is absent in WHO recommendations (Guidelines..., 2006), its biological influence is not properly known. However, it is an established fact, that high concentrations of Li salts are dangerous for man: Li is toxic for the human nervous system, kidney, gall (Brazauskienė, Pukelienė, 1989).

## THEORY

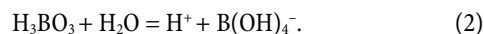
From the chemical viewpoint, B, F, Sr and Li are quite different elements of the famous Mendeleev Table: B is a metalloid of the IVA group, similar to Al; F is a gas of the VIIA group, close to Cl

and other halogens (Br, I); Sr is an alkaline earth metal of the IIA group, similar to the other metals of this group – Ca and K; lithium is a metal of the IA group, close to the other members of this group – sodium (Na) and potassium (K) (Brazauskienė, Pukelienė, 1989). Therefore, the occurrence and spread of these trace elements in the sediments, rocks and groundwater, their forms / types of migration and concentrations in water considerably vary.

There are known two forms of boron – an amorphous brownish powder and slate-grey crystals. The main minerals of B are sodium tetraborate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (borax) and kernite ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ ). Borax and kernite are fairly soluble in water: the solubility of those minerals in 20 °C water reaches 25 g/kg (Крайнов и др., 2004):



Therefore, we can find a weak B-acid  $\text{H}_3\text{BO}_3$  or its anions in groundwater, e. g.,  $\text{H}_2\text{BO}_3^-$ . It is also known that in neutral water (pH 7) even 99% of boron is in the form of B-acid. In slightly alkaline water, certain anions of B-acid happen; e. g., at pH 8 water may contain 6% of  $\text{H}_2\text{BO}_3^-$ , at pH 10 water may contain about 1% of  $\text{BO}_3^{3-}$  (Крайнов и др., 2004). In alkaline water, due to the hydrolysis of B-acid, B-hydrates may be produced and survive (Крайнов и др., 2004):

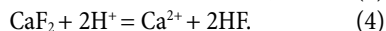
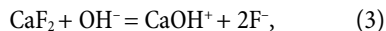


The concentration of boron in groundwater is regulated by two factors: 1) the availability of this trace element in water-bearing rocks and soils, 2) geochemical conditions inside the aquifers.

Because B compounds are fairly soluble, its minerals are present only in certain rocks and in certain beds. Large volumes of B are found in fine-grained, clayey sediments of saline basins (Крайнов и др., 2004). In Lithuania, such sediments are present in certain Cretaceous, Jurassic and Devonian beds. Groundwater circulating in those beds may cause boron anomalies. Because fairly soluble compounds of B survive in brine till the end of its evaporation, boron can be buried together with brine. Certain volumes of B precipitate together with limestone, dolomite or gypsum. We shall see later that for this reason we have B-anomalies in carbonate rocks of the Upper Permian and Upper Devonian ages.

A favourable milieu for B accumulation and migration in aquifers should be alkaline (pH  $\gg 7$ ). In a fresh groundwater zone, an alkaline milieu is characteristic of Na- $\text{HCO}_3^-$ -type of water (Klimas, 2003). Many facts show that if the ratio  $[\text{Na}] / [\text{Ca}]$  (concentrations in meq/l) in groundwater exceeds 0.5–1, the concentration of B in these aquifers nearly always exceeds the MAC (Закутин, 2005). And vice versa: the concentration of B decreases proportionally to the increase of Ca concentration in groundwater (Крайнов и др., 2004).

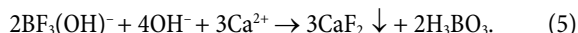
The chemical element fluorine (F) is a yellowish-green gas with a strong smell. F is very active chemically and fairly toxic. The main minerals of F are fluor spar  $\text{CaF}_2$ , fluorapatite  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$  and cryolite  $\text{Na}_3\text{AlF}_6$ . Fluor spar and fluorapatite are only slightly soluble in water: at 20 °C water dissolves only 14.7–22 mg/l of  $\text{CaF}_2$  (Крайнов и др., 2004). Even such a poor solubility of these minerals depends upon the reaction of water – fluor spar is better soluble in alkaline water, although it is also slightly more soluble in acid water:



These minerals are also even less soluble in water rich in Ca. And, on the contrary, these minerals, especially fluor spar, are fairly soluble in water rich in Na (Apello, Postma, 1993). Reaction of such water, like in the case of B, should be alkaline ( $\text{pH} \gg 7$ ).

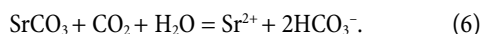
Yet Ca does not allow the concentration of F to increase even in very alkaline water: e. g., the concentration of Ca more than 25 mg/l, which is typical of fresh groundwater, does not allow F concentration to exceed 4–5 mg/l (Крайнов и др., 2004).

It was noticed that increased concentrations of F are sometimes characterized by increased concentrations of B, because these two ions may form rather stable boron–fluoride–ortho-oxo-compounds, e. g.,  $\text{BF}_3(\text{OH})^-$  (Крайнов и др., 2004). When such water mixes with alkaline water rich in Ca, fluor spar is precipitated, but B (boric acid) remains in water:



Fluoride may make stable complexes with aluminium (e. g.,  $\text{AlF}_n^{3-n}$ ), iron (bivalent –  $\text{FeF}^+$ , trivalent –  $\text{FeF}_2^+$ ), certain organic complexes (Apello, Postma, 1993). All this increases the possibilities of F migration in the subsurface. However, the main form of F migration (95–99%) is the F ion.

Strontium is a silver-white metal, very active in chemical reactions. Sr often substitutes Ca in minerals and rocks. Therefore, carbonate rocks (e. g., limestone) often contain Sr-carbonate – strontianite  $\text{SrCO}_3$ , sulphate rocks (e. g., gypsum) – Sr-sulphate – celestite  $\text{SrSO}_4$ . Like Ca and Mg carbonates, Sr-carbonate is fairly soluble in water, especially in acid water, e. g., containing  $\text{CO}_2$  (Крайнов и др., 2004):



Therefore fresh groundwater of Ca, Mg- $\text{HCO}_3^-$ -type often contains increased concentrations of Sr. Similarly groundwater rich in Ca, Mg- $\text{SO}_4$  (circulating in sulphate-rocks) may be enriched with Sr ions, because sulphate rocks (gypsum) fairly often stock strontianite or celestite:



The degree of groundwater saturation by Ca, Mg sulphates regulates the concentration of Sr in such water. Therefore, carbonate or sulphate species of Sr in groundwater usually do not exceed 5–10%, and 90–95% of this element in water make  $\text{Sr}^{2+}$  ions.

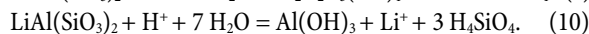
Lithium is a soft metal of silvery tint. Differently from other earth alkaline metals (Na, K), Li is only weakly soluble in water (Фримантл, 1991). This author notices one more difference of Li from Na, K: lithium is fairly similar to Mg, a metal of another, IIA group. Consequently, the solubility of Li-carbonate  $\text{Li}_2\text{CO}_3$  is similar to that of  $\text{MgCO}_3$  and is low:



This circumstance may indicate possible anomalies of Li: it is reliable that increased concentrations of Li can be detected in aquifers rich in Mg- $\text{HCO}_3^-$ .

However, the main source of Li in groundwater is the mineral spodumene, Li, Al-silicate  $\text{LiAl}(\text{SiO}_3)_2$ . Like other silicates,

spodumene is only weakly soluble in groundwater. Nevertheless, in acid water spodumene, like other Al-silicates, is weathered and transformed into gadolinite  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  or completely destructed, releasing Li (Apello, Postma, 1993):



This means that increased concentrations of Li, like B concentrations, may be present in groundwater circulating in terrigenous, clayey rocks and soils. The main species of migration are  $\text{Li}^+$  ions.

Because large concentrations of B, Li and other trace elements are found in brines, it is true to say that increased concentrations of B, Li may also be present in salt-water discharge areas.

## ACTUAL DATA

Only fluoride anomalies in fresh groundwater of Lithuania were formerly known. The possibilities to detect and to delineate similar anomalies of other trace elements described in this paper fairly depend upon the presence or absence of those elements in water-bearing sediments or in the brine of deep aquifers.

**Trace elements B, F, Sr, Li in rocks.** Data on the content of mentioned trace elements in sediments / rocks are not numerous. Moreover, there is completely no information about the fluor spar content in the geological strata of Lithuania. Only very scarce data are available on B content in those sediments.

However, every year such data become more and more abundant. In any case, there are possibilities to size up these potential sources of trace elements. For example, there are statistically approved background concentrations of certain trace elements in the main types of rocks and soils of various geological strata of Lithuania (Table 2).

Even from this scarce data it follows that the highest concentrations of B are present in Paleogene clay and sand and in Devonian clay. Highest contents of B differ from the lowest ones

Table 2. Highest background values of B, Li, Sr in the main types of sediments of various age (Kadūnas ir kt., 2004)

2 lentelė. Maksimalūs B, Li, Sr foniniai kiekiai svarbesniuose įvairiaus amžiaus uolienu tipuose (Kadūnas ir kt., 2004)

Rock, soil	Age of beds	Background values* of trace elements, mg/kg		
		B	Li	Sr
Sandstone	Lower Paleogene, P <sub>1</sub>	<b>245</b>	9.3	290
	Middle Paleogene, P <sub>2</sub>	80.6	14.8	78
	Upper Paleogene, P <sub>3</sub>	290	12.2	95
Clay	Middle Devonian, D <sub>2</sub>	<b>140</b>	30	56
	Middle Paleogene, P <sub>2</sub>	<b>245</b>	<b>35</b>	45
	Upper Paleogene, P <sub>3</sub>	<b>290</b>	12.2	95
Marl	Middle Jurassic, J <sub>2</sub>	–	<b>40</b>	335
	Upper Jurassic, J <sub>3</sub>	–	8.8	<b>460</b>
	Upper Cretaceous, K <sub>2</sub>	–	7.5	<b>535</b>
Limestone	Middle Jurassic, J <sub>2</sub>	–	8.8	<b>400</b>
Chalk	Upper Cretaceous, K <sub>2</sub>	–	7.5	<b>560</b>
Gypsum	Upper Permian, P <sub>2</sub>	–	–	<b>1510</b>

\* Highest contents are balled.

Table 3. Maximal values of B, Sr in certain rocks of Lithuania (Kadūnas et al., 2004)  
3 lentelė. Maksimalūs B, Sr kiekiai kai kuriose Lietuvos uolienose (Kadūnas ir kt., 2004)

Trace element	Age of bed	Depth, m	Rock	Value, mg/kg
Boron, B	Vendian, V <sub>2j</sub>	418.9	sandstone	900
	Vendian, V <sub>2j</sub>	480.5	–“–	800
	Cambrian, C <sub>1,bl</sub>	435.4	–“–	700
Strontium, Sr	Triassic, T <sub>1</sub>	745	clay	33000
	Triassic, T <sub>1</sub>	607.8	marl	30000
	Permian, P <sub>2</sub>	280.3	anhidrite	25000

Table 5. Mineral constituents in the brine of Lithuanian territory (Klimas, Zuzevičius, 2004)

5 lentelė. Naudingi komponentai Lietuvos teritorijos sūrymuose (Klimas, Zuzevičius, 2004)

Trace element	Unit	Required concentration	Actual concentration
Boron, HBO <sub>2</sub> <sup>-</sup>	mg/l	200	30–117 (7.4–28.9 B)
Strontium, Sr	–“–	300	36–400
Lithium, Li	–“–	10–20	49

Table 4. Concentrations of boron in the brine of deep aquifers of Lithuania (Кондратас, 1969)

4 lentelė. Boro koncentracija giliųjų sluoksnių sūrymuose (Кондратас, 1969)

Bore	Aquifer	Tested interval	Concentration of B, mg/l		Dry residual, g/l
			HBO <sub>2</sub> <sup>-</sup>	B	
Stoniškės	Cambrian, C <sub>2+1</sub>	2012–2112	116.6	28.8	193.9
	Ordovician, O <sub>2+1</sub>	1975–1990	86.8	21.4	74.8
	Devonian, D <sub>3st</sub>	1072–1077	35.7	8.8	58.7

Table 6. Concentrations of B, F, Sr, Li and other constituents in bottled groundwater with mineralisation >1 g/l

6 lentelė. B, F, Sr, Li koncentracijos padidėjusios mineralizacijos (>1 g/l) vandenyje

Parameters, constituents	Name of water source, aquifer			
	Telšiai, "Žemaitijos pienas", Upper-Middle Devonian, D <sub>3šv</sub> + D <sub>2up</sub>	Druskininkai, "Rasa", Upper Cretaceous, K <sub>2</sub>	Lapės, "Rasa", Lower Cretaceous, K <sub>1</sub>	Druskininkai, "Elmenhorster", Upper Cretaceous, K <sub>2</sub>
B, mg/l	0.37	0.10	0.71	0.12
F, mg/l	0.43	0.29	0.53	0.21
Sr, mg/l	2.88	5.03	3.18	0.52
Li, mg/l	0.036	0.047	0.076	0.021
pH	7.49	7.42	7.42	7.40
Mineralisation, g/l	1.317	2.06	1.518	1.363
Cl <sup>-</sup> , mg/l	37	1140	244	417
SO <sub>4</sub> <sup>2-</sup> , mg/l	835	36	600	15
HCO <sub>3</sub> <sup>-</sup> , mg/l	141	230	372	420

10 times. This enables us to speak about certain anomalies of B in those beds. Unfortunately we have almost no data on the content of B in Cretaceous, Jurassic and Permian beds which, as we shall see later, are especially interesting and important for us, hydrogeologists.

Much more data are available on the Li content in the above geological strata (but not in groundwater, as we shall see later). As was expected, highest levels of Li are present in clay and marl of Permian, Jurassic and Paleogene beds. The ratio of highest / lowest content of Li in those beds is the same as in the case of B, i. e. about 10.

From the theoretical part of this paper it follows that the largest quantities of Sr should be present in carbonate rocks (limestone, dolomite, chalk) and gypsum. From Table 2 we see that it is really so: rich in Sr are gypsum strata of the Permian age, Jurassic limestones and Cretaceous chalk. Largest and smallest quantities of Sr in these rocks differ significantly: the above-mentioned ratio of these quantities is almost 50.

We have some data on the highest contents of B and Sr in even deeper beds (Table 3).

It is evident that the highest contents of boron in the old Vendian and Cambrian sandstones are 2–3 times higher than the highest contents of B in younger strata. Besides, highest contents of Sr in Permian and Triassic beds rich in these trace elements are rather impressive.

**Trace elements B, F, Sr, Li in brine (>30 or 50 g/l) and salt water (>1 g/l).** Unfortunately, only very few data are available on the content of these trace elements in brine of deep aquifers of Lithuania, although these brines were specially studied as a potential source of certain chemical elements for industrial needs (Tables 4, 5).

Even the first look at these Tables shows that the concentrations of B, Sr, Li in brines, compared with the above-mentioned MAC in drinking and raw water (remind them: B – 1 mg/l, Sr – 7 mg/l, Li – 0.03 mg/l) are very high. We see that the highest concentrations of Sr and Li are close to the required values needed for industrial needs or even exceed those values. However, publications show, that the highest concentrations of B, Sr, Li in brines can be even higher and reach 20 g/l for B and F, 1.3 g/l for Sr and 0.7 g/l for Li (Крайнов и др., 2004).

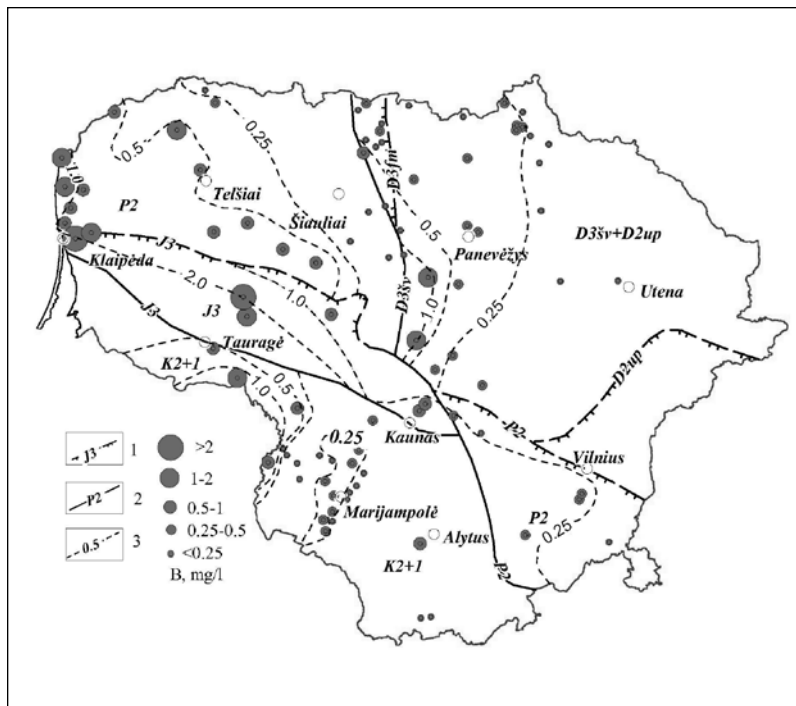
Among the dozen of chemical elements and constituents listed in the requirements to bottled water, B, F, Sr and Li are also present. In Table 6 we presented some data on such water.

Table 6 shows that the levels of these trace elements in bottled water occupy an interim position between fresh and salt water and are considerably lower than in brine, but higher than in fresh water, but not always. Besides, the concentration of Li in bottled water of three types (among the four presented) exceeds MAC for raw water (0.03 mg/l).

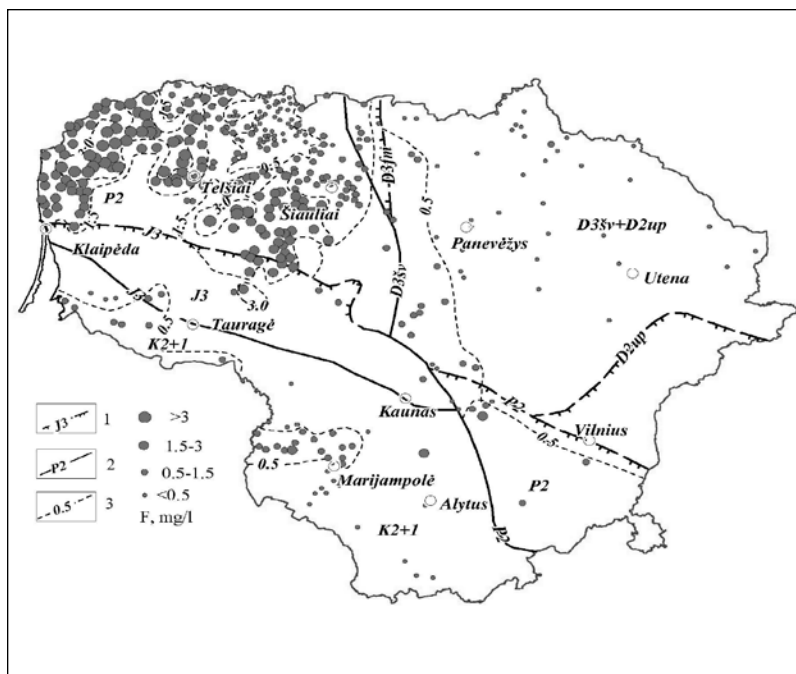
**Trace elements B, F, Sr, Li in fresh groundwater and drinking water.** In Introduction we have mentioned that only the history of F-studies in fresh groundwater of Lithuania is fairly long. Therefore, we have an impressive amount of data about the occurrence and spread of this toxic chemical element in the aquifers and groundwater systems of Lithuania. As far back as in 1962–1967, in the course of special studies of F occurrence in fresh groundwater, almost 4000 samples were taken from the different sources of drinking water supply wells and wellfields (Štarkas et al., 1968). Actually, attention was focused on shallow, dug wells, but plenty of data on F concentration in deeper aquifers were also obtained.

Almost 20 year later, new data on F and B occurrence in fresh water (respectively 435 and 254 analyses) were studied and interpreted (Климас, 1988). Once more extended studies of F occurrence in drinking water were organized in West Lithuania in 1999 (Balčiūnienė et al., 2001). These data were summarized in a special study which describes groundwater quality from Lithuanian wellfields (Klimas, 2006). Data on Sr and especially on Li content in groundwater / drinking water are scarce: in the chemical data, we have 430 analyses of Sr and only 10 analyses of Li. The reason is that Sr and Li are not included into the drinking water hygiene norm (Lietuvos..., 2003) and are present only in the raw water hygiene norm (Lietuvos..., 2001).

From previous investigations it has been known that the average concentration of B in fresh groundwater of Lithuania is 0.16 mg/l, the highest concentrations reaching 2.57 mg/l (Klimas, 1988; Климас, 1988). The same statistics for F show 0.38 mg/l (average) and 3.44 mg/l (maximum). Also, it has been known that the main anomaly of F is attributed to the Permian–Devonian (P<sub>2</sub> + D<sub>3</sub>žg) groundwater system of West Lithuania, where in fissured limestone and dolomite circulates groundwater of sodium (Na-HCO<sub>3</sub>) type



**Fig. 1.** Boron concentration in fresh groundwater systems and aquifers. 1 – boundaries of occurrence; 2 – fresh water boundaries; 3 – isocones of boron, mg/l; K<sub>1</sub> + K<sub>2</sub> – Upper and Lower Cretaceous, J<sub>3</sub> – Upper Jurassic, P<sub>2</sub> – Upper Permian, D<sub>3</sub>šv – Upper Devonian – Frasnian and Šventoji (note of editors: in the recent stratigraphical subdivision they belong to Middle Devonian (D<sub>3</sub>šv) – Givetian), D<sub>2</sub>up – Middle Devonian, Upninkai 1 pav. Boro koncentracija požeminio vandens sluoksniuose. 1 – sluoksnių paplitimo ribos; 2 – gėlo vandens paplitimo ribos; 3 – boro izokonos mg/l (K<sub>1</sub> + K<sub>2</sub> – viršutinė ir apatinė kreida, J<sub>3</sub> – viršutinė jura, P<sub>2</sub> – viršutinis permias, D<sub>3</sub>šv – viršutinis devonas – franis ir Šventoji (redaktorių pastaba: D<sub>2</sub>up – vidurinis devonas, Upninkai)



**Fig. 2.** Fluoride concentration in groundwater systems and aquifers. 1 – boundaries of occurrence; 2 – fresh water boundaries; 3 – isocones of fluoride, mg/l. Stratigraphical indexes see under fig. 1 2 pav. Fluorido koncentracijos požeminio vandens sluoksniuose. 1 – sluoksnių paplitimo ribos; 2 – gėlo vandens paplitimo ribos; 3 – fluorido izokonos, mg/l. Stratigrafiniai indeksai po 1 pav.

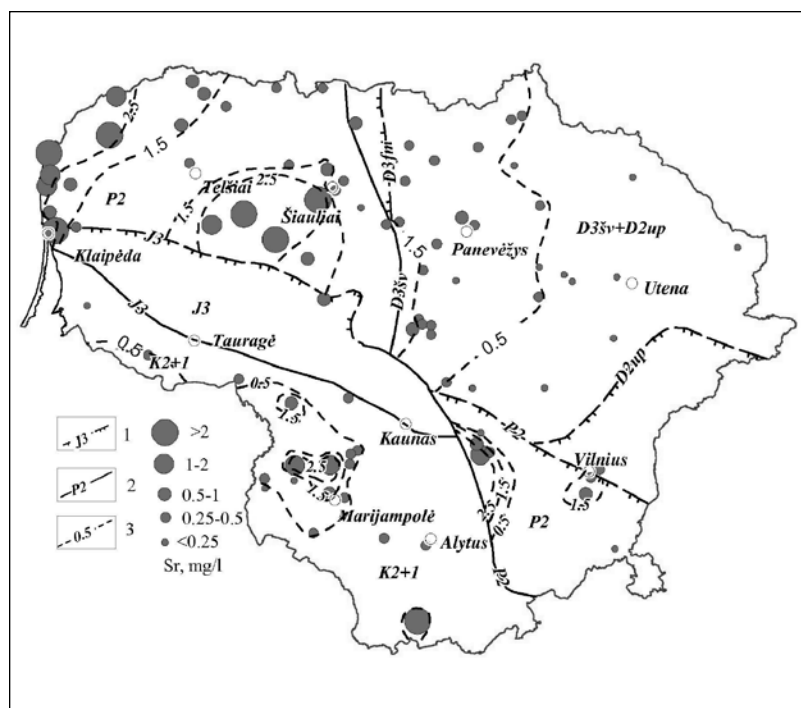


Fig. 3. Strontium concentration in groundwater systems and aquifers. 1 – boundaries of occurrence; 2 – fresh water boundaries; 3 – isocones of strontium, mg/l. Stratigraphical indexes see under fig. 1

3 pav. Stroncio koncentracijos požeminio vandens sluoksniuose. 1 – sluoksnių paplitimo ribos; 2 – gėlo vandens paplitimo ribos; 3 – stroncio izokonos, mg/l. Stratigrafiniai indeksai po 1 pav.

(Климаc, 1985). New data show that the highest concentrations of F within the limits of this anomaly reach 6.52 mg/l, i. e. exceed the MAC more than four times (Balčiūnienė ir kt., 2001). Besides, this water also contains the highest concentrations of Sr: e. g., water from the Šventoji (Palanga) wellfield contains 6.73 mg/l of Sr. This figure is quite close to the MAC of Sr in raw water (7 mg/l). Among the few analyses of Li in fresh groundwater, the highest concentrations of this trace element (0.022–0.033 mg/l) were detected in the Elektrėnai wellfields No 1 and 2.

For the delineation of the anomalies of selected trace elements in fresh groundwater, only data on B, F and Sr were sufficient (Figs. 1–3). These figures show the main aquifers and groundwater systems of Lithuania, used for drinking water supply, and the highest concentrations of these trace elements in samples taken from the wells and wellfields pumping those aquifers.

From Fig. 1 it follows that the lowest concentration of B occurs in marginal parts of aquifers located in groundwater recharge areas (East, South East Lithuania). These concentrations increase with the distance from the recharge areas. Besides, here we suppose that the term “anomalies” may be attributed to the areas where B concentration exceeds 0.5–1.0 mgB/l. A number of facts show that such anomalies of B are related to the fresh / salt water transit areas and are also distinctly seen in salt-water discharge zones – valleys of the Nemunas and the Šešupė rivers (Климаc, 1975; 1987).

Increased concentrations of F in fresh water aquifers, especially in West Lithuania, have been long since and well known (Štarkas ir kt., 1968; Klimas, 1987). Quite big anomalies of this trace element have been determined in the Upper Permian aquifer

in Kretinga, Skuodas, Telšiai and Kelmė regions (Fig. 2). Differently from B, F anomalies often are not related to groundwater mineralization. However, in the central and SW parts of Lithuania, increased concentrations of F, similarly like B contents, are observed in the above-named fresh / salt water transit zones where groundwater of Na-Cl, HCO<sub>3</sub> type circulates in carbonate and sand / clay beds of the Cretaceous and Jurassic age (Климаc, 2006).

Although studies of Sr concentrations in fresh groundwater of Lithuania started almost 20 year ago, at that time anomalies of Sr and other trace elements were only preliminary investigated and delineated (Климаc, 1988). Besides, at that time certain relations of Sr anomalies with carbonate rocks were also noted. Likewise, a new map (Fig. 3) shows that the highest concentrations of Sr are present in West Lithuania, in groundwater circulating in limestone, dolomite, marl and chalk of various age. But we can see again that certain anomalies of Sr, similarly like those of B, are somehow related to the areas of increased groundwater mineralization.

From the above and from the theoretical part of this paper it follows that the main source of described trace elements (B, F, Sr, Li) is water-bearing rocks, but the concentration

of these chemical elements in groundwater fairly depends upon the geochemical environment (e. g., alkaline or neutral) in the aquifer and the type of water (e. g., carbonaceous, sulphate, etc.). Some examples of such dependence are given in Table 7.

Even from this Table we can see that the highest concentrations of B, F, Sr, as was shown above, relates to the fresh / salt water transit areas characterized by increased concentrations of major ions, but not always. The point is that the concentration of these trace elements even more depends on the specific conditions of sedimentation of water-bearing beds than on groundwater mineralization (Крайнов и др., 2004). Therefore, water rich in B circulates in the marginal zones of these ancient basins of sedimentation, attributed to the clayey sand deposits of the Cretaceous (Kazikėnai, Jurbarkas region), Jurassic (Dumpliai, Klaipėda region) and Devonian (Kėdainiai) age. Similarly, F and Sr are related to the carbonaceous sediments of these old saline basins (Šventoji, Palanga). Another important factor is that this water is always fairly alkaline – its pH significantly exceeds 7 and even 8, the type of water being C<sub>I</sub><sup>Na</sup>. The dominant cations are Na<sup>+</sup> or Mg<sup>2+</sup> but not Ca<sup>2+</sup>, the prevailing anions being HCO<sub>3</sub><sup>-</sup> or Cl<sup>-</sup>. But even in the latter case (Cl-anion prevails) groundwater should contain fairly high concentrations of hydrocarbonates (C<sub>I</sub><sup>Na</sup>, C<sub>II</sub><sup>Na</sup> type of water).

## DISCUSSION

If we want to perceive the differences and the common features of the formation of B, F, Sr anomalies in fresh water aquifers, we should know the possibilities and the species of their migration,



Table 7. Highest concentrations of B, F, Sr and groundwater chemical composition in certain aquifers of Lithuania

7 lentelė. B, F, Sr maksimalios koncentracijos ir požeminio vandens cheminė sudėtis kai kuriuose Lietuvos vandeninguosiuose sluoksniuose

Indices	Wellfields, aquifers						
	Gudkaimis (Vilkaviškio)	Kazikėnai (Jurbarko)	Dumpiai (Klaipėdos)	Adakavas (Tauragės)	Šventoji	Palanga II	Kėdainiai
Aquifer	Upper Cretaceous, K <sub>2</sub>	Lower Creta-ceous, K <sub>1</sub>	Upper Jurassic, J <sub>3</sub>	Upper Jurassic, J <sub>3</sub>	Upper Permian, Upper Devonian, P <sub>2</sub> + D <sub>3</sub> žg	Upper Permian, Upper Devonian, P <sub>2</sub> + D <sub>3</sub> žg	Upper-Middle Devonian, D <sub>3</sub> šv + D <sub>2</sub> up
Soil/rock	Marl	Sand	Sand	Sand	Lime-stone	Lime-stone	Sandstone
B, mg/l	0.80	1.61	2.58	2.20	1.16	1.13	1.13
F, mg/l	1.33	0.60	1.11	2.35	2.62	2.58	1.01
Sr, mg/l	–	–	–	–	6.73	3.30	1.36
pH	8.0	8.0	8.3	7.9	7.8	7.9	7.6
Cl <sup>-</sup> , mg/l	512	289	352	12	42	38	276
SO <sub>4</sub> <sup>2-</sup> , mg/l	18	75	112	87	107	78	203
HCO <sub>3</sub> <sup>-</sup> , mg/l	440	565	477	475	256	306	318
Na <sup>+</sup> , mg/l	382	387	415	192	48	98	203
Ca <sup>2+</sup> , mg/l	68	31	32	25	58	40	110
Mg <sup>2+</sup> , mg/l	27	12	14	9	39	27	35
Type of water**	C <sub>1</sub> <sup>Na</sup>	C <sub>1</sub> <sup>Na</sup>	C <sub>1</sub> <sup>Na</sup>	C <sub>1</sub> <sup>Na</sup>	C <sub>II</sub> <sup>Mg</sup>	C <sub>1</sub> <sup>Na</sup>	C <sub>II</sub> <sup>Na</sup>

\* After O. Aliokin (Алекин, 1970).

Table 8. Migration species of boron (B)

8 lentelė. Boro (B) migracinės formos

Characteristics	Wellfields, aquifers					
	Dumpiai	Adakavas	Kėdainiai	Gargždai II	Palanga II	Klaipėda II
Aquifer	Upper Jurassic, J <sub>3</sub>	Upper Jurassic, J <sub>3</sub>	Upper-Middle Devonian, D <sub>3</sub> šv + D <sub>2</sub> up	Upper Jurassic, J <sub>3</sub>	Upper Permian, Upper Devonian, P <sub>2</sub> + D <sub>3</sub> žg	Upper Permian, Upper Devonian, P <sub>2</sub> + D <sub>3</sub> žg
B, mg/l	2.58	2.20	1.20	1.04	0.96	0.84
Migration species of B: H <sub>3</sub> BO <sub>3</sub> , %	91.1	94.9	96.7	95.3	97.3	96.2
H <sub>2</sub> BO <sub>3</sub> <sup>-</sup> , %	8.9	5.1	3.3	4.7	2.7	3.8
TM <sup>a</sup> , mg/l	1183	613	719	348	435	838
pH	8,3	8.1	7.6	8.02	7.74	7.86
Ca <sup>2+</sup> , mg/l	32	24	96.6	20.6	56.4	71.6
Na <sup>+</sup> , mg/l	415	210	123	106	59.2	204
Cl <sup>-</sup> , mg/l	352	12.7	142	13.2	37.5	176
HCO <sub>3</sub> <sup>-</sup> , mg/l	477	504	350	359	369	316
Type of water <sup>b</sup>	C <sub>1</sub> <sup>Na</sup>	C <sub>1</sub> <sup>Na</sup>	C <sub>II</sub> <sup>Na</sup>	C <sub>1</sub> <sup>Na</sup>	C <sub>1</sub> <sup>Ca</sup>	C <sub>1</sub> <sup>Na</sup>
[Na <sup>+</sup> ]/[Ca <sup>2+</sup> ] <sup>c</sup>	11.3	7.65	1.11	4.48	2.27	2.48
[Na <sup>+</sup> +Cl <sup>-</sup> ] / [HCO <sub>3</sub> <sup>-</sup> ] <sup>c</sup>	3.58	1.15	1.63	0.85	0.60	2.67

a – total mineralisation; b – after O. Aliokin (Алекин, 1970); c – concentrations in meq/l.

the correlations between the concentrations of those trace elements in groundwater and the physical / chemical characteristics of this water.

**Migrating species of B, F, Sr.** The computer code WATEQ4F allows calculating the percentage of migration species of various trace elements in groundwater (Ball, Nordstrom, 1992). Although it is well known from the theoretical point of view that the main species of B, F and Sr in groundwater are ions of those trace elements, we decided to simulate and to demonstrate the actual percentage of these species in real groundwater samples taken from the described above anomalies (Tables 8–10).

The highest concentrations of boron in Table 8 decrease from the Dumpiai wellfield and up to the Klaipėda II wellfield. WATEQ-simulation results show that the percentage of H<sub>2</sub>BO<sub>3</sub><sup>-</sup> (anion of B acid H<sub>3</sub>BO<sub>3</sub> in groundwater) similarly varies, depending on groundwater alkalinity (pH and concentration of bicarbonates), concentration of sodium (Na), type of water (Na–HCO<sub>3</sub>, Na–Cl, HCO<sub>3</sub>), the [Na<sup>+</sup>] / [Ca<sup>2+</sup>] ratio and the coefficient of groundwater metamorphisation [Na<sup>+</sup> + Cl<sup>-</sup>] / [HCO<sub>3</sub><sup>-</sup>] (Mokrik, 2003). Of course, there is a certain deviation of actual data from the theoretical line of chemical speciation of B concentrations and forms in groundwater depending on other but supposedly minor factors. We have also tried to find a

Table 9. Migration species of fluoride (F)

9 lentelė. Fluorido (F) migracinės formos

Characteristics	Wellfields, aquifers					
	Salantai	Užventis	Kretinga	Šventoji	Kelmė	Vilkaviškis
Aquifer	Upper Devonian, D <sub>3</sub> žg	Upper Permian, P <sub>2</sub>	Upper Permian, P <sub>2</sub>	Upper Devonian, D <sub>3</sub> žg	Upper Permian, P <sub>2</sub>	Upper Cretaceous, K <sub>2</sub>
F, mg/l	5.35	2.75	2.70	2.60	2.21	1.15
Migration species of F: F <sup>-</sup> , %	98.1	95.4	96.2	96.3	95.4	98.9
MgF <sup>+</sup> , %	1.4	4.0	3.3	3.1	3.9	0.6
CaF <sup>+</sup> , %	0.2	0.5	0.4	0.5	0.6	0.2
NaF <sup>0</sup> aq, %	0.3	0.1	0.1	0.1	0.1	0.3
TM <sup>a</sup> , mg/l	362	494	380	416	443	425
pH	8.2	7.59	7.87	7.74	7.35	8.48
Ca <sup>2+</sup> , mg/l	15	52.9	36.8	58	70.9	14.6
Mg <sup>2+</sup> , mg/l	10.8	33.8	25	24	31.6	4.5
Na <sup>+</sup> , mg/l	118	69.3	66.6	58.3	48.1	168
HCO <sub>3</sub> <sup>-</sup> , mg/l	328	396	332	250	468	429
SO <sub>4</sub> <sup>2-</sup> , mg/l	35.9	109	48.9	89.6	39.6	0
Cl <sup>-</sup> , mg/l	3,3	12.4	18.6	42.5	5	17.4
Type of water <sup>b</sup>	C <sub>I</sub> <sup>Na</sup>	C <sub>I</sub> <sup>Na</sup>	C <sub>I</sub> <sup>Na</sup>	C <sub>II</sub> <sup>Ca</sup>	C <sub>I</sub> <sup>Ca</sup>	C <sub>I</sub> <sup>Na</sup>
[Ca <sup>2+</sup> ] / [Na <sup>+</sup> ] <sup>c</sup>	0.146	0.88	0.63	1.14	1.69	0.10
[Na <sup>+</sup> +Cl <sup>-</sup> ] / [HCO <sub>3</sub> <sup>-</sup> ] <sup>c</sup>	0.97	0.52	0.63	0.91	0.29	1.11

a – total mineralisation; b – after O. Aliokin (Алекин, 1970); c – concentrations in meq/l.

Table 10. Migration species of strontium (Sr)

10 lentelė. Stroncio (Sr) migracinės formos

Characteristics	Wellfields, aquifers					
	Salantai	Kazlų Rūda	Klaipėda II	Skuodas	Dumpliai	Palanga II
Aquifer	Upper Devonian, D <sub>3</sub> žg	Upper Cretaceous, K <sub>2</sub>	Upper Permian, Upper Devonian, P <sub>2</sub> + D <sub>3</sub> žg	Upper Devonian, D <sub>3</sub> žg	Upper Jurassic, J <sub>3</sub>	Upper Permian, Upper Devonian, P <sub>2</sub> + D <sub>3</sub> žg
Sr, mg/l	5.01	4.04	3.56	2,51	2,14	1,89
Migration species of Sr: Sr <sup>2+</sup> , %	93.55	96.68	85.23	91.64	89.90	92.46
SrHCO <sub>3</sub> <sup>+</sup> , %	3.19	2.24	2.68	2.26	3.90	3.58
SrSO <sub>4</sub> , %	2.57	1.00	11.89	5.91	5.17	3.68
SrCO <sub>3</sub> , %	0.68	0.09	0.20	0.20	1.03	0.28
TM <sup>a</sup> , mg/l	351	1226	1112	362	1183	435
pH	7.83	7.49	7.73	7.81	8.3	7.74
Ca <sup>2+</sup> , mg/l	53.1	162	73.8	61.4	32	56.4
Mg <sup>2+</sup> , mg/l	31.5	62.5	49.1	32.7	14	26.5
Na <sup>+</sup> , mg/l	25.0	209	192	20.0	415	59.2
HCO <sub>3</sub> <sup>-</sup> , mg/l	272	295	333	244	477	369
SO <sub>4</sub> <sup>2-</sup> , mg/l	81.9	27.7	284	100	112	52.5
Cl <sup>-</sup> , mg/l	7.0	601	159	9.1	352	37.5
Type of water <sup>b</sup>	C <sub>I</sub> <sup>Ca</sup>	C <sub>I</sub> <sup>Na</sup>	C <sub>I</sub> <sup>Na</sup>	C <sub>III</sub> <sup>Ca</sup>	C <sub>II</sub> <sup>Na</sup>	C <sub>I</sub> <sup>Na</sup>
[Ca <sup>2+</sup> ]/[Na <sup>+</sup> ] <sup>c</sup>	2.44	0.89	0.44	3.52	0.09	1.09

a – total mineralisation; b – after O. Aliokin (Алекин, 1970); c – concentrations in meq/l.

correlation of boron concentrations with the concentrations of other ions present in tested groundwater, but only a few attempts were successful (Fig. 4). For example, from this figure it follows that alkaline water (pH >> 7) contains more boron, but the B concentration is conversely and strictly regulated by the concentration of Ca. An insignificant dependence between the B content and the [Na<sup>+</sup>] / [Ca<sup>2+</sup>] or [Na<sup>+</sup>] / [K<sup>+</sup>] ratio has been

found: it seems that such correlation is more typical of salt water (Крайнов и др., 2004). The highest concentrations of fluoride, as shown above, are intrinsic for the wellfields of West Lithuania, developing P<sub>2</sub>, D<sub>3</sub> or K<sub>2</sub> carbonate aquifers (Table 9).

Data from Table 9 confirm that fluoride does migrate in groundwater mostly as a free F<sup>-</sup> ion: only a few per cent of MgF<sup>+</sup> are present in groundwater which circulates in dolomites,



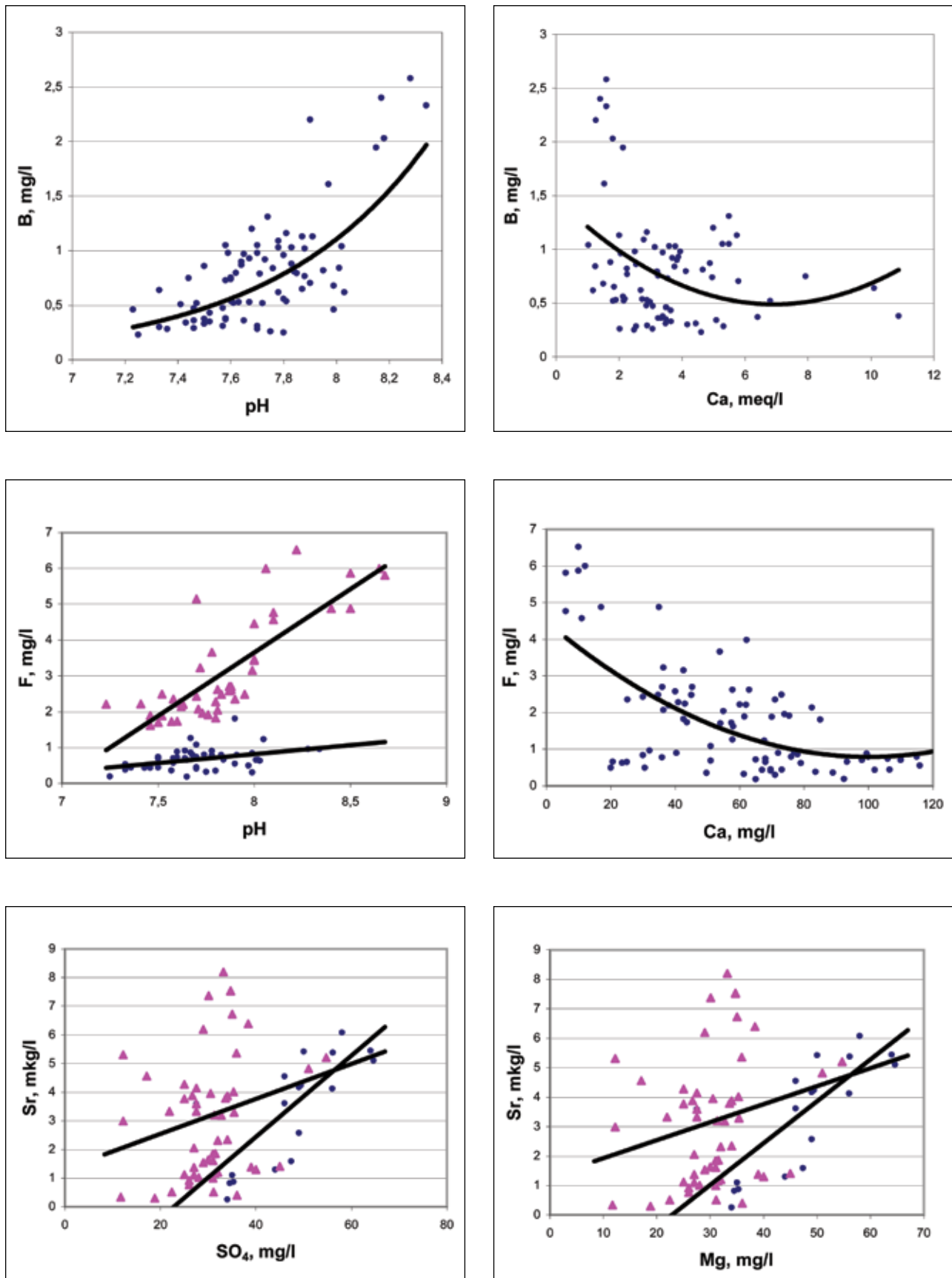


Fig. 4. Correlation between boron (B), fluoride (F), strontium (Sr) content and groundwater physical-chemical parameters

4 pav. Boro (B), fluorida (F), stroncio (Sr) koncentracijų koreliacija su kai kuriais požeminio vandens fizikiniais cheminiais rodikliais

$\text{CaMg}(\text{CO}_3)_2$ . Even from this Table we can see that there exists a certain correlation between the F content and pH and, perhaps, the  $[\text{Ca}^{2+}] / [\text{Na}^+]$  ratio. It means that the highest concentrations of F, similarly as in the B case, should be most typical of alkaline groundwater containing low concentrations of Ca. Data from Fig. 4 confirm this presumption. Besides, Fig. 4 shows two separate lines of the F–pH correlation. Certain explanation of this phenomenon contains the next picture of this figure: F concentration in groundwater fairly and conversely depends on Ca content. By the way, a close analysis of F data shows that the upper line of the F–pH correlation contains data from carbonaceous aquifers ( $\text{P}_2$ ,  $\text{D}_3$ žg) and the lower one from non-carbonate ones. Besides, the F–Ca diagram confirms S. Krainov's statement that the highest F concentrations in groundwater do not exceed 4–5 mg/l if Ca content in this water exceeds 25 mg/l (Крайнов и др., 2004). Nevertheless, no direct evidence of F concentration dependence on Na concentration in fresh groundwater has been found.

From the first sight, Table 10 seems to show that the concentrations of Sr and its migration species do not depend upon the physical or chemical characteristics of groundwater sampled from the most typical wellfields of West Lithuania, exploiting carbonaceous aquifers. However, a close examination of the facts shows that the highest concentrations of Sr are intrinsic for Ca,  $\text{Mg}-\text{HCO}_3$  water, and those concentrations seem to increase together with the  $[\text{Ca}^{2+}] / [\text{Na}^+]$  ratio. Similarly, a high share of  $\text{SrSO}_4$  species in groundwater seems to increase together with sulphate concentrations.

However, our attempts to find a correlation between Sr and Ca content in groundwater or Sr–Ca / Na ratio were not successful. Nevertheless, in Fig. 4 we can see an interesting double Sr– $\text{SO}_4$  and Sr–Mg correlation. It seems that, like in the case of F–pH correlation, one, the upper, line of Sr– $\text{SO}_4$  dependence is somehow more typical of the carbonate aquifers, but it is not so in the Sr–Mg case. Therefore, we can only assume that Sr content in groundwater depends on more factors than we can demonstrate or even imagine.

## CONCLUSIONS

Recent studies and new data on the content of certain trace elements in the groundwater of Lithuania show that the natural anomalies of B, F, Sr and, perhaps, Li in fresh groundwater are related to fresh / salt water transit zones. But of no less importance are two other terms of the formation of these anomalies: i) availability of the above chemical elements in water-bearing sediments, and ii) geochemical conditions inside the aquifer. It is known that a significant amount of these and other trace elements are accumulated in fine-grained clayey sands, in carbonaceous and sulphate beds sedimented in basins and lagoons of high water salinity. When in those beds circulates alkaline (pH ca. 8) groundwater of  $\text{Na}-\text{HCO}_3$  or  $\text{Na}-\text{HCO}_3$ , Cl type (it means that the Ca content in such water is low), the concentration of B and F in this water often exceeds and the concentration of Sr and, perhaps, Li approach the MAC. Meanwhile, we have not enough data on Li content in such water, but first special studies show that the possibilities of Li and B migration in groundwater are rather similar. Presumably,

this can be a certain indication where Li anomalies can be detected first of all.

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## BORO, FLUORIDO, STRONCIO IR LIČIO ANOMALIJOS LIETUVOS GĖLO POŽEMINIO VANDENS SLUOKSNIUOSE

### S a n t r a u k a

Gėlo požeminio vandens sluoksniuose pasitaiko kai kurių mikroelementų didesnių koncentracijų plotai. Pavyzdžiui, seniai yra žinoma, kad Vakarų Lietuvoje, permio–devono sluoksnių vandenyje, vietomis yra daug fluorido. Pastaraisiais metais čia vis dažniau aptinkamos gana didelės ir boro, stroncio koncentracijos. Turimų duomenų analizė rodo, kad B, F, Sr, Li gamtinės kilmės anomalijos formuojasi pereinamose zonos iš gėlo vandens į mineralizuotą, kur požeminis vanduo cirkuliuoja smulkiadispersinėse molingose ar karbonatinėse, gipsingose uolienose, susiklosčiusiose didelio druskingumo vandens baseinų pakraščiuose. Kai tokiose uolienose cirkuliuoja gėlas šarminės reakcijos (pH apie 8) natrio hidrokarbonatinis ar natrio hidrokarbonatinis chloridinis vanduo, boro ir fluorido koncentracijos jame neretai viršija leistinas ribas, o stroncio ir, matyt, ličio – priartėja prie jų. Kol kas per mažai žinome apie ličio koncentracijas tokiame vandenyje, tačiau literatūroje yra duomenų, kad Li ir B migracijos požemyje galimybės yra panašios, todėl aišku, kur Li anomalijų reikėtų ieškoti pirmiausia.

Альгирдас Климас, Альгирдас Малишаускас

## АНОМАЛИИ БОРА, ФТОРА, СТРОНЦИЯ И ЛИТИЯ В ПРЕСНЫХ ПОДЗЕМНЫХ ВОДАХ ЛИТВЫ

### Р е з ю м е

В водоносных горизонтах пресных подземных вод встречаются аномалии некоторых микроэлементов. Например, давно известно, что в Западной Литве, в пермско-девонском водоносном комплексе, в пресных подземных водах местами существенно повышены концентрации фтора. В последние годы здесь все чаще встречаются и высокие концентрации бора, стронция. Анализ имеющихся данных показывает, что аномалии B, F, Sr, Li естественного происхождения формируются в зонах, переходных от пресных вод к минерализованным, где подземные воды циркулируют в мелкодисперсных глинисто-песчаных или карбонатных, гипсовых породах, отложившихся в периферийных частях бассейнов повышенной солености. В тех случаях, когда в таких породах циркулирует пресная щелочная (pH около 8), натриево-гидрокарбонатная или натриево-гидрокарбонатно-хлоридная вода, концентрации бора и фтора в ней нередко превышают ПДК, а концентрации стронция и, возможно, лития приближаются к ПДК. Пока что данных о концентрациях лития в такой воде очень мало, однако из литературных источников ясно, что возможности миграции Li и B в водоносных горизонтах весьма сходны. Поэтому ясно, что аномалии лития следует искать в первую очередь там, где обнаружены аномалии бора.