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MARGE UPPIN

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Geological sources and hydrochemistry of fluoride and boron in Silurian-Ordovician aquifer system

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Department of Geology, Institute of Ecology and Earth Sciences, Faculty of Science and Technology, University of Tartu, Estonia.

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LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following published papers, which are referred to in the text by their Roman numerals. The papers are reprinted by kind permission of the publishers.

I Karro, E., **Uppin, M**. (2013). The occurrence and hydrochemistry of fluoride and boron in carbonate aquifer system, central and western Estonia. Environmental Monitoring and Assessment, 185(5), 3735–3748.

II **Uppin, M**., Karro, E. (2012). Geological sources of boron and fluoride anomalies in Silurian-Ordovician aquifer system, Estonia. Environmental Earth Sciences, 65(4), 1147–1156.

III **Uppin, M**., Karro, E. (2013). Determination of boron and fluoride sources in groundwater: batch dissolution of carbonate rocks in water. Geochemical Journal, 47, 525–535.

Author's contribution

Paper I: The author contributed to planning original research, interpretation of data, and writing of the manuscript.

Paper II: The author was primarily responsible for collection of carbonate rock samples, interpretation of analytical data, and writing of the manuscript.

Paper III: The author's contribution involves planning and running of experiments, data analyses and interpretation, and writing of the manuscript.

1. INTRODUCTION

Groundwater is one of the most important natural resources in Estonia as it provides two thirds of the drinking and domestic water supply. Previous studies have shown that the natural concentrations on fluorides (F^-) and boron (B) in groundwater reach up to 7.2 and 2.1 mg/l, respectively, in western Estonia (Indermitte et al., 2006; Indermitte et al., 2009; Karro et al., 2006; Karro et al., 2009). Elevated fluoride and boron concentrations are associated with Silurian-Ordovician (S-O) aquifer system that provides 30% of Estonian public water supply (Narusk and Nittim, 2003). S-O aquifer system is composed of diverse limestone and dolomite lithologies with several altered volcanic ash (K-bentonite) interlayers. It is an important and often the only source of drinking water in central and western Estonia.

The occurrence of fluoride and boron in groundwater has drawn worldwide attention due to their important physiological role in the health of man. Fluoride in drinking water has both positive and negative effects on human health. Small concentration of fluoride is essential for normal mineralization of bones and the formation of dental enamel, reducing incidence of dental caries. On the other hand, concentrations of fluoride above 1.5 mg/l in drinking water may cause dental fluorosis and intake of F^- concentrations above 3 mg/l may lead to skeletal fluorosis (Grobler et al., 1986; ADA, 2001; Billings et al., 2004; WHO, 2008). Drinking water, usually obtained from groundwater, is the primary source of fluoride intake. According to the EU directive (98/83/EC, 1998) and Estonian requirements for drinking water quality (Joogivee, 2001) the limit value for fluoride is 1.5 mg/l.

Similar to fluoride, high levels of boron are considered to bear risk for human health. The limit value for boron in drinking water is 1.0 mg/l in Estonia (98/83/EC, 1998; Joogivee, 2001). The World Health Organization (WHO) suggested the limit value for boron in water to set at the level of 0.5 mg/l (WHO, 2008). However, the health effects of B have been studied less compared to fluoride. The experiments with animals have shown that excessive content of boron leads to reproductive system malfunctions (e.g. reduced fertility and sterility, low weight of foetus). Incidences of metabolistic disorders and acute neurological effects have been observed as well (Heindel et al., 1992; Price et al., 1996; WHO, 2008). Few available human data show that exposure to boron leads to short-term irritant effects of the upper respiratory tract (Garabrant et al., 1985; Wegman et al., 1994). Study by Chang et al. (2006) reported a relationship between industrial boron exposure and reproductive health.

Fluorine (F) is a ubiquitous element in continental crust, with an average concentration of 625 ppm (Edmunds and Smedley, 2005). It is the most electronegative and reactive element which occurs in water primarily as a negatively charged fluoride ion. Fluoride is mainly released into the groundwater through weathering and leaching of the fluorine-containing minerals in rocks. The most common fluorine-bearing mineral in the geological environment is fluorite (CaF_2), however, its solubility in fresh water is low. Fluorine is also abundant in various other rock forming minerals, for example, apatite, micas (biotite), amphiboles, and certain clay minerals (Hem, 1985; Saxena and Ahmed, 2003; Sujatha, 2003; Edmunds and Smedley, 2005; Rafique et al., 2008; Naseem et al., 2010; Reddy et al., 2010). Because of similar ionic radii, fluoride can easily replace hydroxyl ion (OH^-) in many rock forming minerals. High fluorine contents are also associated with volcanic activity, thus, elevated concentrations of F^- are often found in geothermal waters (Kundu et al., 2001; Desbarats, 2009). Besides, volcanic ash is rich in fluorine, and ash interbedded with other sediments could contribute to high fluoride concentrations in groundwater in such areas (Hem, 1985). Apart from natural sources, the most common anthropogenic source of fluorides in groundwater is the use of phosphate fertilizers which contain fluorine (Saxena and Ahmed, 2003; Sujatha, 2003; Edmunds and Smedley, 2005).

It has been observed that elevated boron concentrations in groundwater are often associated with high F^- contents (Queste et al., 2001; Earle and Krogh, 2006; Karro et al., 2006; Desbarats, 2009; Karro et al., 2009). Similarly to fluoride, boron is released into the groundwater mainly through water-rock interaction, seawater intrusion into aquifers and volcanic activity (Hem, 1985; Gemici and Tarcan, 2002; Pennisi et al., 2006). Boron is an inorganic water-soluble element that is widely distributed in nature with average concentration of 10 ppm in the earth's crust (Yazbeck et al., 2005). Boron occurs in aqueous solutions as undissociated boric acid – $B(OH)_3$ and borate anion – $B(OH)_4^-$. The distribution of these species is related to the pH value of the aqueous environment. At the pH around 7, most of the boron is present as a boric acid, however, borate ion fraction gradually increases with the increase of the pH value (Vengosh et al., 1994; Mather and Porteous, 2001; Gemici and Tarcan, 2002; Gonfiantini and Pennisi, 2006). The leaching of rocks and soils is responsible for the most of the boron dissolved in natural waters. Boron undergoes a number of interactions with the aquifer forming rocks, among which the process of adsorption and desorption of boron to clay mineral surfaces plays a crucial role (Vengosh et al., 1994; Gonfiantini and Pennisi, 2006; Pennisi et al., 2006). To a lesser extent, boron is also released into the environment from anthropogenic sources such as boron-containing detergents, fertilizers, pesticides and glass manufacture (Vengosh et al., 1994; Yazbeck et al., 2005; Pennisi et al., 2006).

The health risks in Estonia arising from drinking water are mainly caused by high levels of fluoride and boron in drinking water (Indermitte et al., 2006; Karro et al., 2006; Indermitte et al., 2009). A strong relationship between the fluoride content in drinking water and the prevalence of dental fluorosis among 12-year-old schoolchildren in Estonia has been found by Indermitte et al. (2007). Despite the health concerns of elevated F^- and B concentrations in drinking water, the geochemistry of those elements in groundwater has not been studied thoroughly in Estonia. Therefore, there is a need for examining the distribution and hydrochemical behaviour of fluorides and boron in groundwater and probable natural sources of F^- and B in groundwater.

The current thesis focuses on the occurrence and hydrochemistry of fluorides and boron in Silurian-Ordovician aquifer system (Karro and Uppin, 2013 – PAPER I). The groundwater chemistry is largely controlled among the other factors by the lithological composition of water-bearing rocks. It has been pointed out by many authors that leaching of F and B rich aquifer forming rocks is the main reason for elevated levels of both elements in groundwater (Gemici and Tarcan, 2002; Saxena and Ahmed, 2003; Sujatha, 2003; Edmunds and Smedley, 2005; Gonfiantini and Pennisi, 2006; Pennisi et al., 2006; Rafique et al., 2008; Naseem et al., 2010; Reddy et al., 2010). Thus, mineralogical and chemical composition and dissolution of the aquifer forming carbonate rocks were studied in order to determine if high F^- and B levels in groundwater could be attributed to certain rock types (Uppin and Karro, 2012 – PAPER II; Uppin and Karro, 2013 – PAPER III).

The objectives of this dissertation are to:

- characterize the spatial distribution of fluoride and boron as potentially toxic elements and to delineate their anomalies in Silurian-Ordovician aquifer system;
- explain the geochemical behaviour of boron and fluoride in groundwater;
- describe the geochemical and mineralogical composition of Silurian and Ordovician carbonate rocks as the natural fluorine and boron sources in Estonia, focusing on the occurrence and variability of fluorine and boron contents in different rock types;
- assess the dissolution of boron and fluoride, focusing on the interaction of water and different carbonate rocks.

2. STUDY AREA

Estonia is situated in the north-western part of the East-European Platform. Its sedimentary beds, lying on the southern slope of the Baltic Shield, are declined southwards at about 3–4 metres per kilometre. The Estonian Paleoproterozoic basement is overlaid by Neoproterozoic (Ediacaran) and Palaeozoic (Cambrian, Ordovician, Silurian and Devonian) sedimentary rocks (Figure 1), covered by Quaternary deposits. Both Ordovician and Silurian sequences in Estonia consist mainly of shallow water carbonates – limestone, dolomite, and marlstone with clayey interlayers. The basal part of Ordovician sequence is represented by terrigenous sediments – silty and clayey sandstones and graptolite argillites (Table 1). Generally, the proportion of clay content in Silurian and Ordovician rocks generally increases to southwards or south-westerly (Nestor and Einasto, 1997).

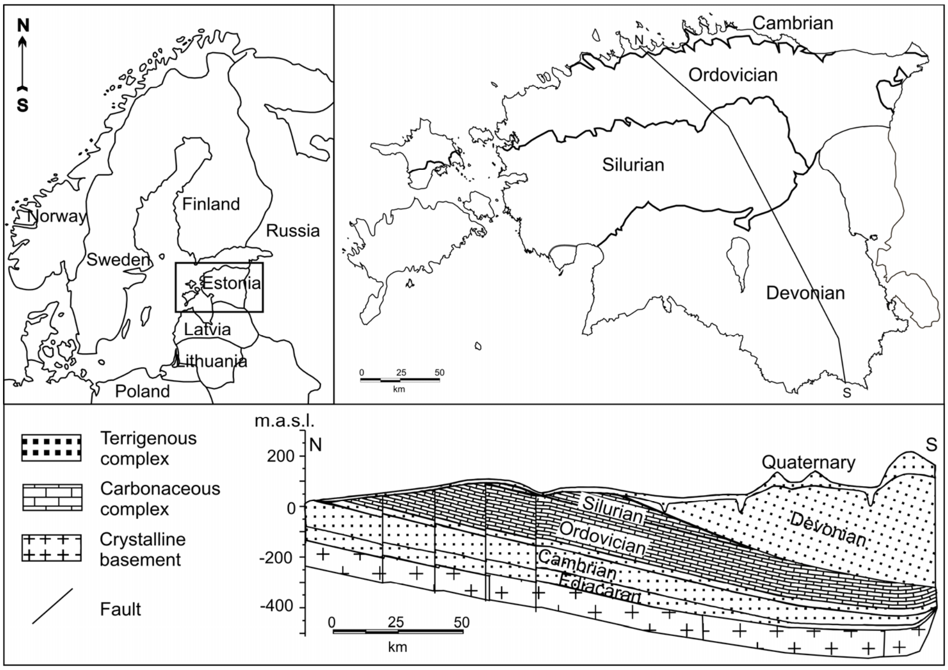

Figure 1. Location, geological map and a north-south geological cross-section of the area. The line indicates the position of the cross section (PAPER III – Uppin and Karro, 2013).

The Silurian and Ordovician stratigraphic record in Estonia and neighbouring areas contains numerous potassium rich altered volcanic ash beds called K-bentonites. The thickness of bentonites ranges from some mm up to 10 cm, rarely up to 20–30 cm and more. The composition of bentonite clay matrix in the Baltic Basin is typically mixed layer illite-smectite with some amount of kaolinite. The interlayers of K-bentonite have been recorded in Jaagarahu, Jaani, Adavere and Raikküla Regional Stages of Silurian System. Ordovician K-bentonite beds in Estonia are present only in the Upper Ordovician Kukruse, Haljala, Keila and Pirgu Regional Stages (Bergstrom et al., 1995; Kiipli et al., 2001; Kiipli et al., 2007; Hints et al., 2008; Somelar et al., 2010).

Table 1. Stratigraphy and lithological characteristics of Estonian Ordovician and Silurian systems (after Raukas and Teedumäe, 1997).

System	Series	Regional Stage	Index	Characteristic rocks
SILURIAN	Pridoli	Ohesaare	S_4oh	Domerite, limestone
		Kaugatuma	S_4kg	Marlstone, limestone
	Ludlow	Kuressaare	S_3kr	Marlstone, clayey limestone
		Paadla	S_3pd	Limestone, dolomite
	Wenlock	Rootsiküla	S_2rt	Clayey dolomite, limestone
		Jaagarahu	S_2jg	Limestone, dolomite
		Jaani	S_2jn	Marlstone, domerite
	Llandovery	Adavere	S_1ad	Marlstone, domerite
		Raikküla	S_1rk	Limestone, dolomite
		Juuru	S_1jr	Clayey limestone, marlstone
ORDOVICIAN	Upper Ordovician	Porkuni	O_3pr	Limestone, dolomite
		Pirgu	O_3pg	Clayey limestone, marlstone
		Vormsi	O_3vr	Clayey limestone, marlstone
		Nabala	O_3nb	Clayey limestone
		Rakvere	O_3rk	Limestone, marlstone
		Oandu	O_3on	Marlstone, limestone
		Keila	O_3kl	Marlstone, clayey limestone
		Haljala	O_3hl	Clayey limestone, marlstone
		Kukruse	O_3kk	Limestone, clayey limestone
	Middle Ordovician	Uhaku	O_2uh	Clayey limestone
		Lasnamägi	O_2ls	Clayey limestone
		Aseri	O_2as	Limestone
		Kunda	O_2kn	Limestone, sandy limestone
		Volkhov	O_2vl	Glauconitic limestone
	Lower Ordovician	Billingen	O_1bl	Glauconitic limestone
		Hunneberg	O_1hb	Glauconitic sandstone
		Varangu	O_1vr	Clay
		Pakerort	O_1pk	Siltstone, sandstone

Ordovician and Silurian carbonate rocks (Figure 1, Table 1) form the Silurian-Ordovician aquifer system which is an important source of drinking water in central and western Estonia. The upper part of the S-O aquifer system with a thickness of 30 m is extremely cavernous, with numerous cracks and fissures. Water in the fissure systems and karst cavities of the carbonate bedrock flows relatively fast. Silurian and Ordovician carbonate rocks have fragmentary 1–2 m thick water-conducting zones with parallel lamination and an abundance of fissures, where groundwater flows in a lateral direction. These zones are separated from each other by 5–10 m thick layers in which groundwater flows predominantly in vertical fissures. The caverns and fissures decrease in deeper part of the S-O aquifer system and the aquifer system transforms into aquitard (Perens and Vallner, 1997). The aquifer system has a characteristic HCO_3-Ca-Mg and HCO_3-Mg-Ca water type with TDS mainly below 600 mg/l in its upper 30–50 m thick portion. In coastal areas and greater depths, the content of Cl^- and Na^+ in groundwater increases and HCO_3-Cl-Na-Mg-Ca type water with TDS between 300–1500 mg/l is widespread (Perens et al., 2001).

3. MATERIAL AND METHODS

3.1. Groundwater analyses

Sixty drinking water supply wells trapping the Silurian-Ordovician aquifer system in Estonia were sampled for major ions as well as fluoride and boron. The depths of the wells range between 60 and 191 m and all sampled wells provide drinking water at the present time. Samples were collected into 1.0 liter clean polyethylene bottles, placed into cool-box and transported to the laboratory at the end of the sampling day. In situ, pH, redox potential, electrical conductivity and temperature were measured using multimeter (pH/mV/EC/T meter). In order to guarantee the precision of field measurements a flow-through cell (Eijkelkamp) was used in which the electrodes were placed, and water samples were taken after stabilizing field parameters.

The concentration of Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, F^{-} and B were determined in the Tartu laboratory of Estonian Environmental Research Centre. The determination of dissolved Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Cl^{-}, SO_4^{2-} and F^{-} was performed by ion chromatography, B by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and HCO_3^{-} potentiometrically. The quality management system of Estonian Environmental Research Centre Ltd has competence according to the standard EN ISO/IEC 17025 and has been accredited by Estonian Accreditation Centre. The reliability of the analyses is guaranteed by continuous internal checking (duplicate analyses, control charts, reference material) and participation in interlaboratory comparison tests and in proficiency testing exercises. The test methods based on international or national standards are validated and estimated for uncertainty of measurements.

3.2. Carbonate rock analyses

Ninety one samples were collected from drillcores and outcrops during 2008 and 2009 in order to study the chemical composition of the aquifer forming Silurian and Ordovician rocks. The chemical composition of carbonate rocks was analyzed at ACME Analytical Laboratories Ltd., Vancouver, Canada in 2008–2010, where SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO, Cr_2O_3, Ba, Sr, Cu, Ni, Co, B, and F contents were measured. Rock samples were crushed and pulverized to a 200-mesh-size and dried at 105 °C prior to analysis. The chemical composition of the rocks was determined using standard Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) techniques, the content of fluorine was analyzed by specific ion electrode.

The relative content of terrigenuous (Ter), dolomite (Dol) and calcite (Cal) fractions in rocks was calculated in order to determine how F and B are related to different rock types. The content of terrigenous component, dolomite and calcite in carbonate rocks was calculated according to the following formulas taking into consideration that terrigenuous material contains on average 2.5% MgO (Kaljo et al., 1997):

$$Ter = (Al_2O_3+SiO_2+Fe_2O_3+K_2O+TiO_2)*1.025$$
$$Dol = 4.57*(MgO-0.025*Ter)$$
$$Cal = 1.786*(CaO-0.304*Dol)$$

The results obtained were recalculated normalizing the sum of Ter+Cal+Dol to 100%.

To identify the main minerals (quartz, calcite, dolomite, apatite, K-feldspar, albite, illite, kaolinite, chlorite, pyrite, biotite) of Silurian and Ordovician carbonate rocks, 20 unoriented powdered whole rock preparations were analysed by means of X-ray powder diffractometry (XRD) at the Department of Geology, Tartu University. Ground and homogenized unoriented powder samples were measured on a Bruker D8 diffractometer using Ni-filtered Cu*K*a radiation over the range 2–70 °2θ, with a scan step of 0.02 °2θ and a count time of 2 s per step. Quantitative mineral composition was determined by full-profile Rietveld analysis using SIROQUANT™ software system (Taylor, 1991; Ward et al., 2001). The full profile XRD pattern Rietveld method considers the integrated intensities of the particular diffractogram peaks and compares natural and artificial mixtures along the whole length of the diffractogram (Ward et al., 2001).

The purpose of the XRD study was to compare calculated mineralogical composition with the results of XRD determinations. The whole-rock mineralogical composition by XRD fairly agrees with calculated values. Thus, calculation methodology provided by Kaljo et al. (1997) could be used in this study.

3.3. Leaching tests

Altogether 20 different carbonate rock (limestone, dolomite, clayey limestone, clayey dolomite, marlstone) samples were selected from 91 previously analyzed rock samples to carry out simple batch dissolution experiments.

Leaching tests of carbonate rocks were carried out in tightly capped conical polyethylene flasks (500 ml), where 30 g powdered rock samples were reacted with 300 ml distilled water. Using a shaker table (GFL 3005), batch dissolution tests were performed at room temperature keeping a constant shaking rate of 150 rpm. The leachates were filtered using 45 μm resin and kept in refrigerator until analyzing. After 48 hours, all 20 leachate samples were analyzed for F^- and B, from which 13 samples were analyzed also for main cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and anions (Cl^-, SO_4^{2-}). B concentrations in leachates were determined colorimetrically (Nicolet Evolution 300) using Azomethine-H method (Watson, 1998). The contents of F^-, Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^- and SO_4^{2-} were analyzed by ion-chromatograph (Dionex ICS-1000) at the Department of Geology, University of Tartu. The accuracy and precision of analyses were tested through running duplicate analyses on selected samples. In addition, the contents of HCO_3^- in solution were determined potentiometrically in the Tartu laboratory of Estonian Environmental Research Centre.

Long-term leaching experiments continued with the 7 samples from the initial leaching test for 49 days. Leachate samples were taken at an increasing time intervals of 7, 14 and 49 days. The batches were designed to maintain a constant water-rock ratio of 10/1. Sufficient amounts of rock powder and distilled water were used to enable repeated samplings of small solution aliquot (6 ml) without significantly changing the water-rock ratio. pH values were obtained using a pH meter (Mettler Toledo SG8-ASK) in all experiments at designated intervals of time.

Throughout the research, data processing, interpretation and hydrochemical assessment of the results was performed by MapInfo Professional, Grapher and AquaChem. The saturation indices (SI) of fluorite and calcite in groundwater samples were calculated using the computer program PHREEQC (Parkhurst and Appelo, 1999). The input data of the geochemical model included the concentrations of main anions and cations in leachates, the values of pH and temperature.

4. RESULTS AND DISCUSSION

4.1. The distribution and hydrochemical behaviour of fluoride and boron

Spatial distribution of fluoride and boron in carbonate Silurian-Ordovician aquifer system and the hydrochemical behaviour of those elements are discussed in Paper I - Karro and Uppin, 2013.

Water samples from 60 groundwater abstraction wells were collected and analyzed from Silurian-Ordovician aquifer system. The results of chemical analyses are plotted on the distribution maps of fluoride and boron (Figure 2) which show large variation both in fluoride and boron concentrations in S-O aquifer system. Fluoride concentrations in collected groundwater vary from 0.1 to 6.1 mg/l with a mean of 1.95 mg/l. Considering the requirements of EU directive (98/83/EC, 1998) and the Estonian requirements for drinking water quality (Joogivee, 2001), the limit value for fluoride (1.5 mg/l) is exceeded in 28 groundwater samples, which are about 47% of all studied samples. Boron contents in groundwater samples range from 0.05 mg/l to 2.1 mg/l with a mean of 0.66 mg/l. Boron contents are higher than the limit value of 1.0 mg/l (98/83/EC, 1998; Joogivee, 2001) in 17 groundwater samples, being about 28% of all water samples. Groundwater with excessive values of both fluoride and boron occurs mostly in West-Estonia (Figure 2). A strong positive correlation between F^- and B contents in groundwater ($r = 0.85$) refers to the similarity in spatial distribution, possible natural sources and geochemical behaviour of these elements in groundwater.

In order to interpret the behaviour of F^- and B in groundwater, the major ion chemistry of water samples was studied using the Piper diagram. Groundwater in Silurian and Ordovician carbonate rocks is predominantly HCO_3-Ca-Mg chemical type with high calcium content and low amounts of fluoride and boron (Figure 3). Accordingly, Ca^{2+} contents are negatively correlated with fluoride ($r = -0.8$) and boron ($r = -0.79$) concentrations in groundwater that has been reported by other authors as well (Gemici and Tarcan, 2002; Saxena and Ahmed, 2003; Sujatha, 2003; Chae et al., 2007). High fluoride and boron concentrations are rather associated with Cl-HCO_3-Na and HCO_3-Cl-Na type of waters (Figure 3) that are widespread in western Estonia. The groundwater pH in the study area range from 6.76 to 8.48 and is positively correlated with F^- ($r = 0.81$) and B ($r = 0.80$) concentrations (Figure 4) that has been also pointed out in different earlier hydrochemical studies (Queste et al., 2001; Gemici and Tarcan, 2002; Chae et al., 2007; Rafique et al., 2008; Desbarats, 2009; Kim et al., 2011). Higher pH values are rather common to groundwater in West-Estonia. Elevated F^- and B concentrations at high pH values imply that alkaline environment is responsible for the release of F^- and B into the groundwater. As the clay content of the carbonate rocks in Silurian and Ordovician sequences is somewhat higher in West-Estonia (Nestor and Einasto, 1997) and due to the prolonged water-rock interaction, Ca^{2+} is replaced by Na^+ through ion-exchange processes, and the pH value of groundwater slightly increases. This leads to the formation of alkaline Cl-HCO_3-Na and HCO_3-Cl-Na type of waters which favours the leaching of fluorides and boron into the groundwater.

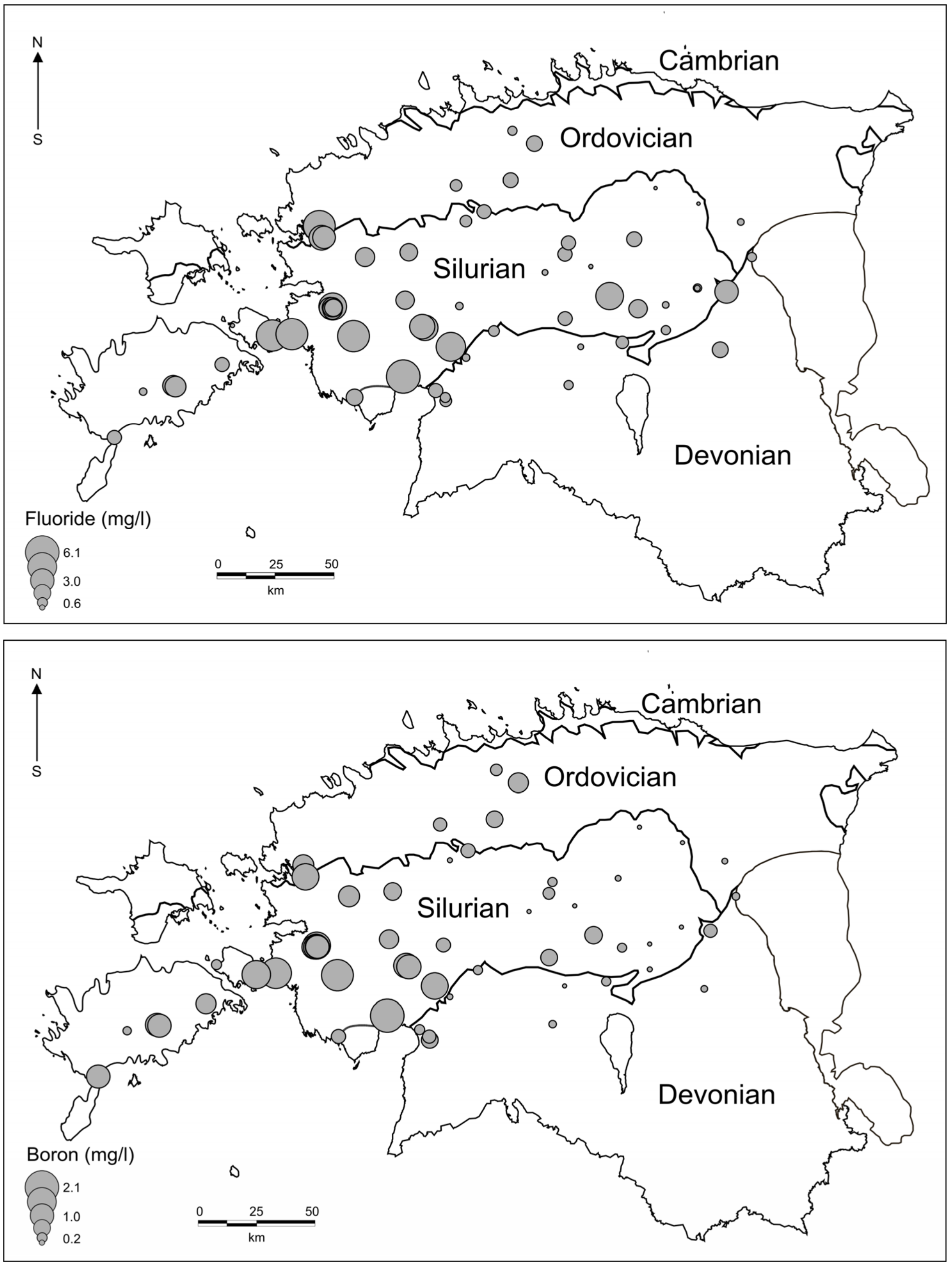

Figure 2. Spatial distribution of fluoride and boron in Silurian-Ordovician aquifer system (PAPER I – Karro and Uppin, 2013).

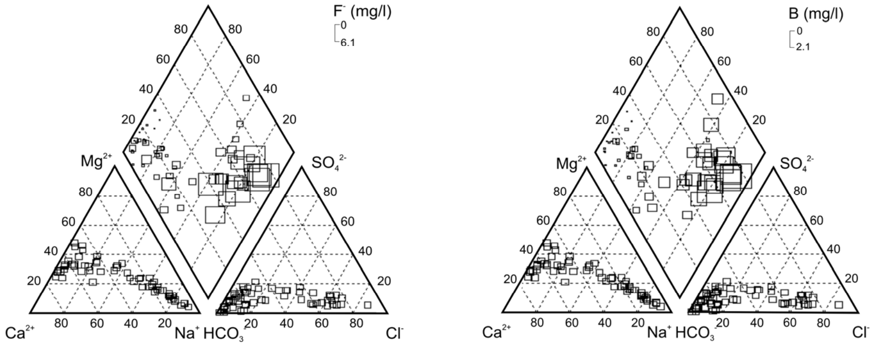

Figure 3. Piper diagrams reflecting the chemical type of groundwater and proportional concentrations of fluoride and boron (PAPER I – Karro and Uppin, 2013).

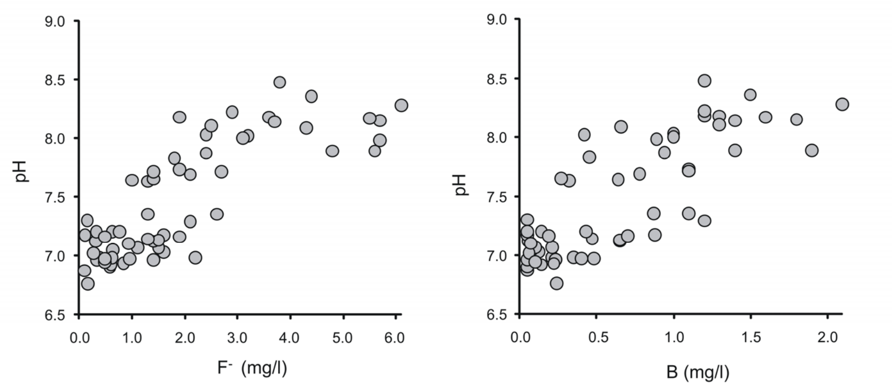

Figure 4. Bivariate plots of F^-, B and pH values in Silurian-Ordovician aquifer system (after PAPER I – Karro and Uppin, 2013).

Further, the amount of dissolved chemical substances in groundwater increase towards the depth in hydrogeological profile as the slower water exchange and a longer residence time in aquifer (Appelo and Postma, 1999; Hiscock, 2005). Thus, it can be assumed that fluoride and boron concentrations in groundwater increase in deeper portions of S-O aquifer system. However, relationships between fluoride (r = 0.25) and boron (r = 0.17) concentration and depth of the well are not evident. On the whole, F^- and B concentrations above 2 mg/l and 1 mg/l, respectively, were determined from wells deeper than 50 metres. Higher fluoride (>4 mg/l) and boron (>1.5 mg/l) values were determined in wells deeper than 100 metres. Deviations from the general tendency in abstracted groundwater can be explained with the differences in the constructions of wells, their open intervals and also in the type and structure of the opened rocks.

Fluoride ions released into the groundwater are considered to be controlled among other natural geochemical processes by the degree of saturation of fluorite (CaF_2) and calcite ($CaCO_3$), and the concentration of calcium, bicarbonate and sodium ions in groundwater (Saxena and Ahmed, 2003; Rafique et al., 2008; Mamatha and Rao, 2010). Therefore, the saturation indices (SI) of fluorite and calcite have been calculated using PHREEQC (Parkhurst and Appelo, 1999). A positive saturation index indicates that the solution is supersaturated with respect to observed mineral and the mineral should precipitate out from the solution. A negative value indicates that the solution is undersaturated with respect to observed mineral, thus, the mineral should dissolve. The calculated SI values for fluorite and calcite are plotted in Figure 5. All groundwater samples, except for one with fluoride concentration of 5.7 mg/l, are undersaturated or near equilibrium with respect to fluorite. Samples approaching equilibrium with respect to fluorite have typically F^- values higher than 2 mg/l. Majority of the samples are found to be equilibrium with respect to calcite (Figure 5). Solubility control on the higher concentration of fluoride can be explained by the fact that fluoride content in groundwater can be increased as a result of precipitation of $CaCO_3$ at alkaline pH values, which removes Ca^{2+} from solution allowing more fluorine containing minerals to dissolve.

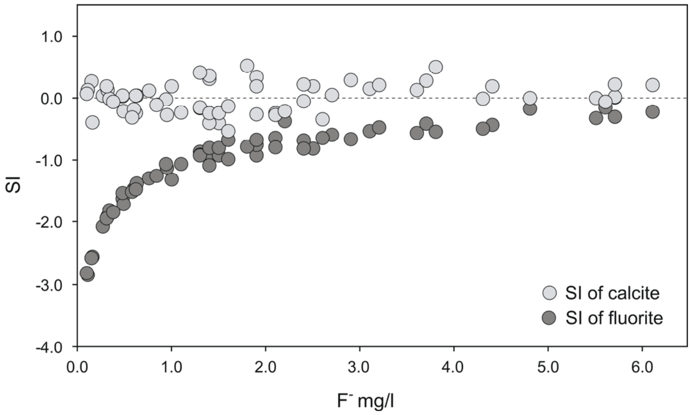

Figure 5. Saturation indices of calcite and fluorite versus F^- concentrations in groundwater.

Total dissolved solids (TDS) and Na/(Na+Ca) ratio as well as TDS and Cl/(Cl+HCO_3) ratio of the groundwater may be used to estimate the impact of geological processes on the composition of groundwater (Gibbs, 1970). Thus, groundwater chemistry data from Silurian-Ordovician aquifer system in Estonia are plotted in the Gibbs' diagram (Figure 6). The distribution of sample points on diagrams suggests that rock weathering is the main process controlling the groundwater chemistry in the study area, as the majority of the samples plot within the "rock weathering dominance" area.

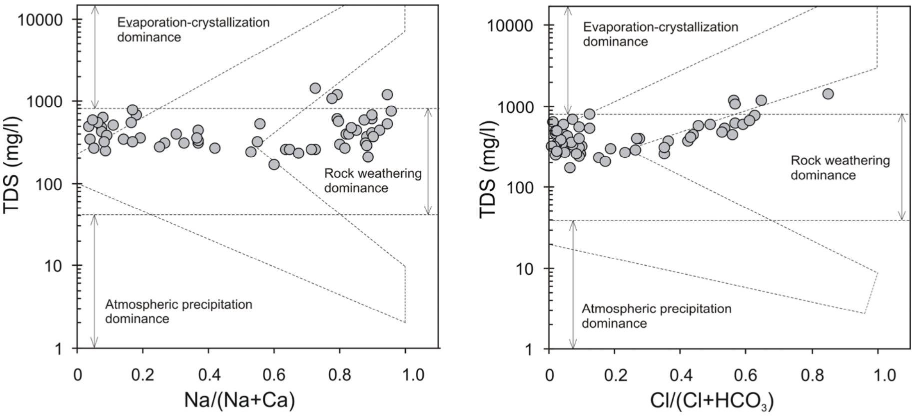

Figure 6. Plots of TDS versus Na/(Na+Ca) and TDS versus Cl/(Cl+HCO_3) illustrating the mechanisms controlling the chemistry of groundwater samples (PAPER I – Karro and Uppin, 2013).

4.2. Carbonate rocks as the natural sources of fluoride and boron

Geochemical and mineralogical composition of Silurian and Ordovician carbonate rocks, focusing on the occurrence and variability of fluorine and boron contents in different rock types, were discussed in Paper II – Uppin and Karro, 2012.

Presence of fluorine and boron bearing minerals in the host rock and their interaction with water are considered to be the main causes for fluoride and boron enrichment in groundwater. Therefore, chemical composition of 91 rock (79 carbonate rock and 12 K-bentonite) samples and mineralogical composition of 20 carbonate rocks all over the Estonia were determined. The F and B contents in the rocks clearly depend on the composition of the aquifer forming rock. Total fluorine and boron content of limestones and dolomites are 70–1001 mg/kg and 3–54 mg/kg, respectively, being slightly higher in dolomites. The fluorine and boron contents in marlstones and domerites reach up to 1030 mg/kg and 160 mg/kg, respectively, thus being higher compared to limestones and dolomites. Calcite-dolomite-clay ternary diagrams are used to illustrate how F and B contents vary in different rock types. Generally, the increase in the clay compound is followed by the increase in the F and B contents in the carbonate rocks (Figure 7).

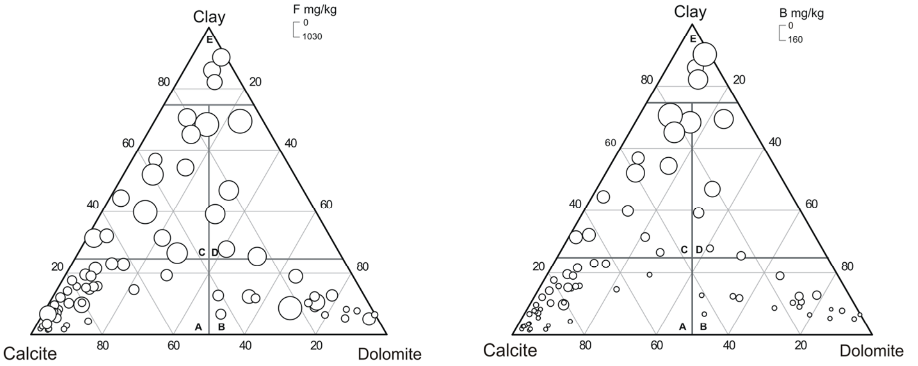

Figure 7. Ternary diagram showing F and B contents in various rock types. Classification of rocks is based on the lithological diagram of carbonate rocks provided by Vingissaar et al. (1965): A – limestone, B – dolomite, C – marlstone, D – domerite, E – clay (PAPER II – Uppin and Karro, 2012).

Several studies have suggested that F-containing minerals like fluorite, micas (biotite), apatite, amphiboles, and clay minerals could be possible sources of F^- in groundwater (Hem, 1985; Kundu et al., 2001; Saxena and Ahmed, 2003; Sujatha, 2003; Rafique et al., 2008; Desbarats, 2009; Naseem et al., 2010; Reddy et al., 2010). Boron is usually associated with clay minerals, but may also occur as an accessory constituent of tourmaline, biotite, and amphiboles (Hem, 1985; Gemici and Tarcan, 2002; Gonfiantini and Pennisi, 2006; Pennisi et al., 2006). Based on the XRD analyses, the main constituents of the 20 selected carbonate rock samples are determined to be calcite and dolomite (up to 99%, depending on the rock type) with the addition of quartz (0.7–31.1%), K-feldspar (0.5–6.9%), and illitic clay minerals (0.8–32.5%). Among the studied carbonate rocks, the proportion of illitic clay minerals is highest in clay rich carbonate rocks (e.g. marlstones). Additionally, small amounts of apatite (up to 1.2%), albite (up to 1.9%), chlorite (up to 8.3%), and pyrite (up to 1.2%) can be found in some rock samples. Biotite was not detected in the studied carbonate rocks, however, concentrations of up to 4.2% of the whole rock can be found in K-bentonite samples (Hints et al., 2008).

Although, fluorite (CaF_2) is the most common fluorine-bearing mineral, being abundant in granitic rocks (Hem, 1985; Kundu et al., 2001; Saxena and Ahmed, 2003; Sujatha, 2003; Reddy et al., 2010), it is a minor accessory mineral in carbonate rocks and its solubility in fresh water is low. Biotite may be rich in fluorine and is common mineral in granitic areas as well. In present research, small amount of biotite was found only in terrigenuos material, especially in K-bentonite samples. Thus, dissolution of fluorite and biotite is probably not the noteworthy source of fluorides in carbonaceous groundwater of Estonia.

Beside the fluorite and biotite, apatite and fluorapatite are also considered to be possible sources of fluorides in groundwaters in granitic areas (Hem, 1985; Rafique et al., 2008; Desbarats, 2009; Reddy et al., 2010). Estonian carbonate rocks containing apatite tend to be rich in fluorine. Rock samples rich in apatite deviate from the normal limestone and dolomite samples on the rock composition diagrams (Figures 8a-b). The geochemical behaviour of F is more complicated compared to B due to the presence of Ca-phosphate minerals (apatite), which occur both in terrigenuous as well as in authigenic fraction. Therefore, elevated F (450–1000 mg/kg) content may be also found in apatite rich limestones and dolomites which are poor in clay minerals. As the solubility of apatite is rather low, apatite rich carbonate rocks are probably not considerable sources of fluorides.

Remarkable amount of fluorine and boron in rocks are considered to be related to clay minerals. Ion-exchange and adsorption are the most typical processes through which boron and fluorine could be bounded to clay minerals (Hem, 1985; Saxena and Ahmed, 2003; Sujatha, 2003; Edmunds and Smedley, 2005; Gonfiantini and Pennisi, 2006; Pennisi et al., 2006; Rafique et al., 2008; Naseem et al., 2010). The average clay content in the rocks of Silurian and Ordovician sequences tends to increase from north to south and south-west in the Baltic Basin (Nestor and Einasto, 2007). Due to the increase of clay content in aquifer forming rocks and prolonged residence time of groundwater, Ca is replaced by Na through ion-exchange processes and pH value of groundwater slightly increases (up to 8.5) in West-Estonia. As the result, the alkaline Na-rich groundwater of HCO_3-Cl-Na-Mg-Ca chemical type favours the leaching of boron and fluorine into the groundwater. Long-term leaching of those clayey rocks might provide the elevated fluoride and boron content in groundwater of western Estonia.

K-bentonites, a clay-rich sediments formed by the weathering of volcanic ash deposits, are rich in total fluorine (363–4578 mg/kg) and boron (57–1124 mg/kg). The interlayers of K-bentonite have been recorded in Jaagarahu, Jaani, Adavere and Raikküla Stages of Silurian System. Ordovician K-bentonite beds in Estonia are present in the Upper Ordovician Series: Kukruse, Haljala, Keila and Pirgu Stages (Bergstrom et al., 1995; Kiipli et al., 2001; Hints et al., 2008; Kiipli et al., 2008; Somelar et al., 2010). Presence of those clay rich K-bentonite layers may also lead to the formation of F and B rich groundwater.

According to Uppin and Karro (2012 – PAPER II), fluorine and boron are most likely leached out from clayey material, like marlstones, domerites and K-bentonites. The CaO/Al_2O_3 and K_2O/Al_2O_3 ratios reflect the relationship between carbonaceous and terrigenuous component, and between terrigenuous compounds (K-feldspar and clay) in rock samples, respectively (Figure 8a–b). Higher values of CaO/Al_2O_3 ratios refer to carbonate rock samples, lower ones to terrigenous material, including clay. It can be seen that the values of CaO/Al_2O_3 ratios rapidly rise in limestone and dolomite samples where the contents of F and B are low, generally below 400 mg/kg and 20 mg/kg, respectively. Lower CaO/Al_2O_3 ratios (up to 25) refer to terrigenuos material with elevated F

(350–1000 mg/kg) and B (20–160 mg/kg) concentrations. Using the K_2O/Al_2O_3 ratio as the indicator of terrigenuos material, the lower ratios are characteristic for a finer grain size, higher ratios for coarser grain size. Figure 8b shows that the limestones and dolomites have K_2O/Al_2O_3 ratios varying from 0.4 to 0.8 with low F (up to 350 mg/kg) and B (up 20 mg/kg) contents. K_2O/Al_2O_3 ratios up to 0.5 are common to clayey rocks with higher F and B concentrations. Altogether, elevated B and F contents are clearly concentrated in the terrigenuous fraction of the rock (Figure 8a) and, furthermore, are bounded to clay mineral phases (Figure 8b), represented mainly by illitic clay minerals (illite, illite-smectite). Thus, clay rich sediments, providing ion exchange and adsorption sites for F^- and B, contribute to elevated concentrations of those elements in groundwater.

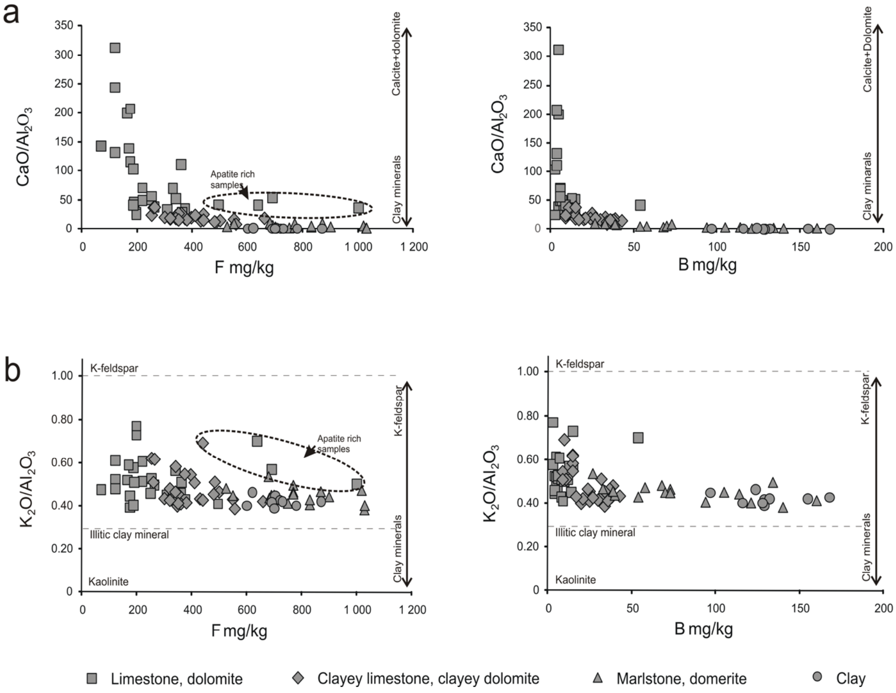

Figure 8. The F and B content plotted against the content of the major element oxides and their ratios in aquifer forming rocks (after PAPER II – Uppin and Karro, 2012).

4.2. Fluoride and boron concentrations in wells with different construction and lithology

The effect of the well construction and lithology on fluoride and boron concentrations in groundwater were discussed in Paper I – Karro and Uppin, 2013 and PAPER II – Uppin and Karro, 2012.

Groundwater rich in sodium and chloride with slightly alkaline character that favours the leaching of F^- and B into groundwater spreads mostly in western Estonia (Perens et al., 2001). Besides, the amount of dissolved chemical substances in groundwater tends to increase with depth because of slower water exchange and longer residence time in the aquifer (Appelo and Postma, 1999; Hiscock, 2005). Thus, elevated fluoride and boron levels are expected in deeper wells in western Estonia. Like it has been pointed out previously, positive correlation between fluoride and boron concentrations in groundwater samples and depth of the wells is not evident due to the differences in the construction of the wells and the type of the opened rocks.

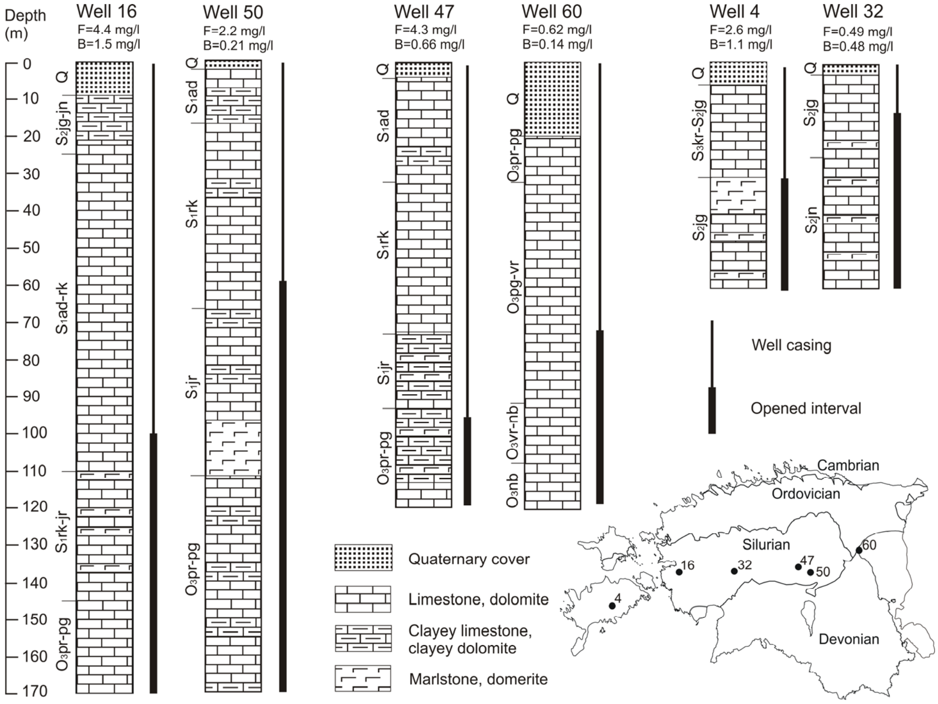

Figure 9. The variation of F^- and B concentrations in wells with different construction and lithology (after PAPER I – Karro and Uppin, 2013).

The groundwater chemistry is largely controlled by lithological and mineralogical composition of water-bearing rocks. Presence of fluorine- and boron-bearing minerals in the host rock and their interactions with water are the main causes for fluoride and boron enrichment in groundwater (Gemici and Tarcan, 2002; Saxena and Ahmed, 2003; Sujatha, 2003; Edmunds and Smedley, 2005; Gonfiantini and Pennisi, 2006; Pennisi et al., 2006; Rafique et al., 2008; Naseem et al., 2010; Reddy et al., 2010). Fluorine and boron in Silurian and Ordovician carbonate rocks are clearly bounded to clay mineral phase. Consequently, the local geology must be considered when developing new water supply wells. The clay content in Silurian and Ordovician carbonate rocks is highly variable. Therefore, it is possible, that the wells drilled into the same stratigraphic unit and having the same depth exhibit different F^- and B concentrations (Figure 9). Fluoride and boron contents in boreholes, where the dominating rock types are clayey limestone and marlstone, are significantly higher (well 47) compared to those drilled into limestone or dolomite (well 60). Furthermore, F^- and B contents depend on the length of the open intervals of boreholes. Wells with high fluoride and boron concentrations have generally shorter open intervals than those with low F^- and B contents (compare wells 16 and 50, 47 and 60, 4 and 32). The long open interval of the drilled well enables the mixing of waters with different chemical composition which results in groundwater dilution and lower F^- and B concentrations. Generally, elevated fluoride and boron contents tend to be related to deeper wells with short screens. Although, shallow wells drilled into marlstone or clayey limestone and dolomite could also show high F^- and B contents (well 4). Thus, F^- and B concentrations in wells predominantly depend on the type of the opened rocks of the well.

Groundwater is an important drinking water source. Both fluorine and boron are considered to be toxic at large quantities to human body, acquired largely from drinking water and food (WHO, 2008). In order to avoid or eliminate the water quality problems, water supply wells with high F^- and B concentrations should be monitored and, if needed, water treatment should be provided. The opening of clayey rocks by well screens should be avoided to ensure a safe drinking water supply with appropriate F^- and B concentrations.

4.3. Batch dissolution of carbonate rocks

The results of dissolution experiments of fluorine and boron from carbonate rocks were presented in Paper III – Uppin and Karro, 2013.

The dissolution rate of chemical elements, including F and B, into groundwater depends on numerous factors like chemical and mineralogical composition of aquifer forming rocks, chemical type of groundwater, pH value and the temperature of the environment, time elapsed for water-rock interaction, etc. All these factors should be considered when interpreting the formation of groundwater chemistry. In order to estimate and compare the share of the different rock types as the natural sources of F^- and B, the side-effect of different environmental factors (e.g. differences in groundwater chemistry) should be minimized. Simple laboratory batch dissolution tests enable to create the uniform conditions for leaching experiments. Therefore, 2 limestone, 5 dolomite, 7 clayey limestone, 3 clayey dolomite and 3 marlstone samples were used in batch dissolution tests. First, all crushed rock samples were leached in distilled water for two days, then the long-term test continued with seven rock samples and leachate samples were taken on the 7, 14 and 49 day of the test.

After two days of leaching, the fluoride concentration ranged from 0.10 to 0.85 mg/l, and boron content varied from 0.04 mg/l to 1.40 mg/l in leachates. The highest amounts of F^- and B were leached out from the clay rich marlstone samples. According to several studies (Saxena and Ahmed, 2003; Sujatha, 2003; Gonfiantini and Pennisi, 2006; Pennisi et al., 2006; Rafique et al., 2008; Naseem et al., 2010), remarkable amount of fluorine and boron in rocks are considered to be related to clay minerals. Ion-exchange and adsorption are the most typical processes through which F and B could be bounded to clay minerals. Thorough study by Du et al. (2011) describes the adsorption mechanisms of fluoride on kaolinite, montmorillonite, chlorite and illite. In present study, fluoride (r = 0.82) and boron (r = 0.97) concentrations in leachates show a good correlation with the amount of illite and illite/smectite in the carbonate rock samples (Figure 10). Thus, F and B in groundwater are mainly leached out from clayey material, like clayey limestones, clayey dolomites, marlstones and domerites. As mentioned previously, the average clay content of Silurian and Ordovician rocks in Estonia tends to increase from north to south and south-west (Nestor and Einasto, 2007). Consequently, the long-term leaching of those clayey carbonate rocks could provide the elevated F^- and B content in groundwater observed in western part of the country.

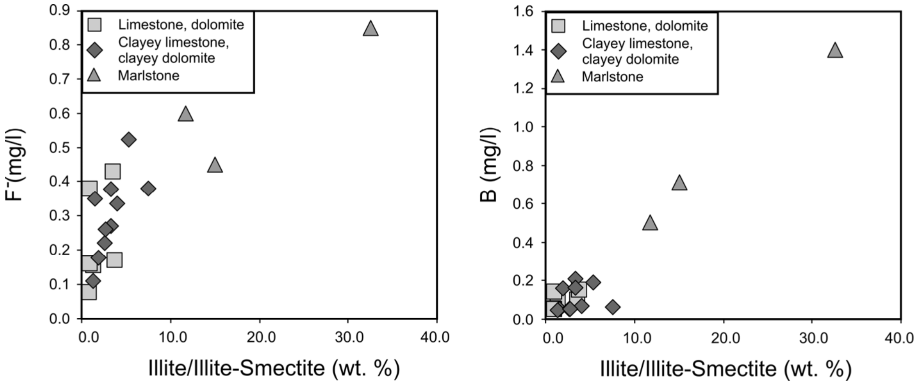

Figure 10. F^- and B concentrations in leachates plotted against the content of illite and illitic mixed-layer mineral illite-smectite in carbonate rocks (after PAPER III – Uppin and Karro, 2013).

After 49 days of the leaching test, F^- and B concentrations in solutions continually exhibit the increasing trend (Figure 11), however, remarkable amounts of F^- and B were leached out during the first week of the test. The same trend has been observed during the batch dissolution experiments of granite samples in water (Chae et al., 2006, Abdelgawad et al., 2009), where the leached F^- contents increased rapidly at the beginning of the test with only a only slight increase in its concentration thereafter. Batch dissolution experiments by Chae et al. (2006) showed that F^- concentrations approached a maximum value of about 10 mg/l during the first week of leaching and then decreased to the level of 8 mg/l. Calculated saturation indices showed that the solution approached a saturated or supersaturated state with respect to fluorite after less than 200 h, while calcite saturation was not reached within this time. Therefore, Chae et al. (2006) suggested that fluorite precipitation occurred in the latter part of the experiments, which controlled the F^- concentration in the solution. However, the results of the batch dissolution tests of the current study (Figure 11) as well as the study by Abdelgawad et al. (2009) demonstrate a continuous increasing trend in dissolved F^- and B concentrations. This indicates that the saturation state of the solution with respect to fluorite was not achieved during the dissolution tests. Furthermore, saturation indices of calcite and fluorite from selected samples were calculated after 2 days and 49 days of shaking. All the samples were near equilibrium state with respect to calcite and undersaturated with respect to fluorite. Saturation indices for fluorite slightly increase with reaction time without reaching equilibrium state after 49 days of the leaching. The increase of F^- and B concentrations with reaction time implies the importance of the residence time of the groundwater in aquifer forming rocks.

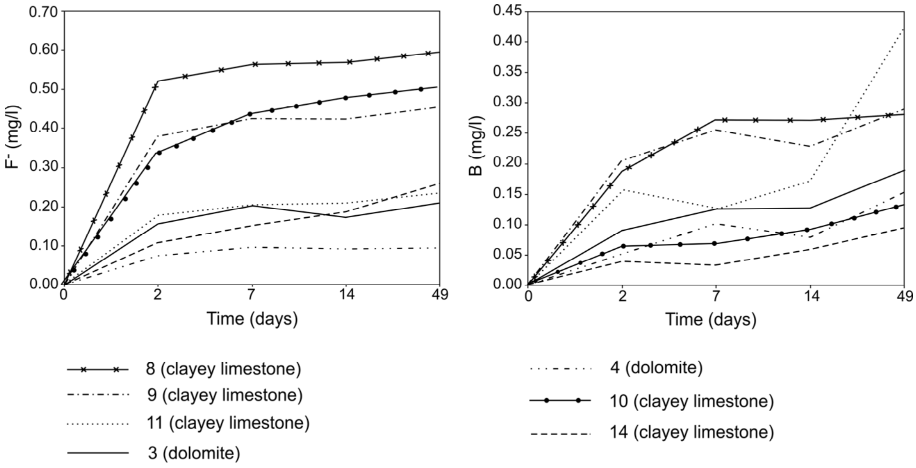

Figure 11. Variations of F^- and B concentrations in leachates during water-rock interaction test (PAPER III – Uppin and Karro, 2013).

The batch dissolution tests of the current study showed that pH values of the leachates increased rapidly up to 8.9 during the first days of the experiments due to the consumption of hydrogen ions during the dissolution of carbonate minerals and then decreased gradually to <8.0 by the end of the test. Analogous behavior of pH values was observed by Chae et al. (2006), where the solution pH reached 9.5 at the beginning of the experiment and decreased slightly over the next 500 h, and then stabilized at ~8.0. Several hydrochemical studies suggest that the pH value of groundwater is positively correlated with F^- and B (Queste et al., 2001; Gemici and Tarcan, 2002; Chae et al., 2007; Rafique et al., 2008; Desbarats, 2009; Karro and Uppin, 2013). This implies that an alkaline environment preferably favors the release of F^- and B into the water. Thus, the high pH value at the beginning of the batch dissolution test could be one of the factors that contribute the leaching most of the F^- and B during the first two days.

5. CONCLUSIONS

Anomalously high fluoride and boron concentrations are common in groundwater in western Estonia, where drinking water resource is Silurian-Ordovician aquifer system that mainly consists of diverse limestones and dolomites with clayey interlayers. Both fluorine and boron are toxic in large quantities to human body, acquired largely from drinking water and food. Therefore, there is a need for examining the distribution, hydrochemical behaviour and natural sources of fluoride and boron in groundwater.

1. Fluoride concentrations show a wide variation in the study area (from 0.1 to 6.1 mg/l with a mean of 1.95 mg/l). Boron contents in groundwater samples range from 0.05 mg/l to 2.1 mg/l with a mean of 0.66 mg/l. Strong positive correlation between F^- and B contents in groundwater points to the similarity in their hydrochemical behavior and the same geological sources.
2. Groundwater in Silurian and Ordovician carbonate rocks is predominantly HCO_3-Ca-Mg chemical type with high calcium content and low amounts of fluoride and boron. High fluoride and boron concentrations are associated mainly with slightly alkaline waters rich in Na^+ and Cl^- ions (Cl-HCO_3-Na and HCO_3-Cl-Na type) that are prevalent in western part of the study area and in deeper portions of the aquifer system.
3. The amount of dissolved chemical substances in groundwater generally increase towards the depth in hydrogeological profile due to the slower water exchange and a longer residence time in aquifer. However, relationships between fluoride and boron concentration and depth of the well are not evident. Deviations from the general tendency in abstracted groundwater can be explained with the differences in the constructions of wells, their open intervals and also in the type and structure of the opened rocks. Generally, elevated fluoride and boron concentrations are related to deeper wells with short screens opening clay rich carbonate rocks.
4. F^- ions released into the groundwater are controlled by the degree of saturation of fluorite and calcite. Groundwater of the study area is undersaturated with respect to fluorite and near to equilibrium phase with respect to calcite. Thus, higher contents of fluoride in groundwater can be explained as a result of $CaCO_3$ precipitation, which removes Ca^{2+} from solution allowing more fluorite to dissolve.
5. The results of this study show that fluorine and boron in carbonate rocks are clearly bounded to clay mineral phase. B and F contents in Estonian limestones and dolomites roughly vary between 5–20 mg/kg and 100–500 mg/kg, and reach up to 150 mg/kg and 1000 mg/kg in marlstones, respectively. Consequently, clay rich sediments such as marlstones, domerites and K-bentonites are the most probable sources of high fluoride and boron levels in groundwater.
6. Ca-phosphate minerals (apatite) are generally rich in fluorine, although, the solubility of apatite is rather slow. Fluorite, the most common fluorine bearing mineral, and biotite are not widespread minerals in carbonate rocks.

Thus, leaching of fluorite, biotite and Ca-phosphate minerals cannot be remarkable sources of fluorides and boron in S-O aquifer system.

7. Batch dissolution tests show that F^- and B concentrations in the leachates are correlated with terrigenous material and further with the illite/illite-smectite fraction in rock samples, which indicates that the most likely sources of F^- and B in water are ion-exchange and adsorption processes associated with clay minerals (illite, illite-smectite and chlorite). The saturation state of the solution with respect to fluorite was not achieved during the long-term dissolution tests. The increase of F^- and B contents with reaction time denotes the importance of the residence time in respect to the formation of the groundwater chemistry.
8. Because of the toxicity of fluoride and boron and in order to avoid or eliminate the water quality problems, water supply wells with high F^- and B concentrations should be monitored and, if needed, water treatment should be provided. The results of this study show that the local geology must be considered when developing new wells. The opening of clayey rocks by well screens should be avoided to ensure a safe drinking water supply with appropriate F^- and B concentrations.

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SUMMARY IN ESTONIAN

Fluoriidide ja boori hüdrokeemia ja geoloogilised allikad Siluri-Ordoviitsiumi veekompleksis

Käesolev doktoritöö uurib fluoriidide ja boori levikut ja hüdrogeokeemilist käitumist ning võimalikke looduslikke allikaid põhjavees.

Põhjavesi kui peamine joogivee allikas on Eestis üks olulisemaid loodusvarasid. Vees leiduvad keemilised elemendid ja ühendid osalevad ainevahetuses ja avaldavad mõju organismide arengule, kasvule ning paljunemisele. Seepärast on väga oluline tarbitava vee ohutus ja keemiline koostis. Eesti põhjavees võib inimorganismi kõige enam kahjustavateks elementideks pidada fluori ja boori, mille sisaldused põhjavees on paljudes puurkaevudes üle joogiveele kehtestatud piirkontsentratsioonide (Indermitte et al., 2007; Indermitte et al., 2006; Karro et al., 2006; Indermitte et al., 2009) ning sellest tuleneb ka vajadus põhjavee keemilisteks uuringuteks. Fluor on inimorganismis vajalik eelkõige hammaste ja luude arenguks. Elemendi optimaalne toimeala on suhteliselt kitsas. Defitsiidi korral tarbitavas joogivees (alla 0,5 mg/l) on soodustatud hambakaariese teke ja areng, mistõttu väike kogus fluori on organismile vajalik kaariese profülaktikaks. Liigse sisalduse korral joogivees avaldub fluori toksiline toime hambafluoroosi ($F^- > 1{,}5$ mg/l) ja skeletifluoroosina ($F^- > 4$ mg/l) (Grobler et al., 1986; ADA, 2001; Billings et al., 2004; WHO, 2008). Pikaajalised loomkatsed on näidanud, et liigne boorisisaldus joogivees põhjustab reproduktsioonisüsteemi häireid ja loote kehakaalu mahajäämust, aga ka ainevahetushäireid ja soolepõletikke (Heindel et al., 1992; Price et al., 1996; WHO, 2008).

Kõrgenenud F^- ja B sisaldused esinevad Eestis eelkõige Siluri-Ordoviitsiumi veekompleksis, mis on oluliseks veevarustuse allikaks Pärnu-Põlva joonest põhja pool ja Lääne-Eesti saartel (Karro et al., 2006; Karro et al., 2009; Karro and Uppin, 2013). Siluri-Ordoviitsiumi veekompleksi vesi moodustab ligikaudu 30% Eestis tarbitavast põhjaveest. Siluri-Ordoviitsiumi veekompleks hõlmab Siluri ja Ordoviitsiumi ladestute erineva savikusega lubjakivisid ja dolomiite ning savikaid vulkaanilise tuha kihte – K-bentoniite (Nestor and Einasto, 1997). Veekompleksi ülemine 30 meetri paksune osa on tugevasti karstunud ja lõheline. Karbonaatkivimite lõhelisus ja karstumus kahaneb kiiresti koos sügavuse suurenemisega, mistõttu väheneb oluliselt ka veekompleksi veeandvus ning see muutub Siluri-Ordoviitsiumi veepidemeks (Perens ja Vallner, 1997).

Euroopa Liidu joogivee direktiivi (98/83/EC, 1998) ja sellega kooskõlastatud Eesti joogivee kvaliteedinõuete (Joogivee, 2001) kohaselt on kehtestanud fluoriidi piirsisalduseks 1,5 mg/l ning boori puhul 1,0 mg/l. Analüüsitud 60 põhjavee proovist ületasid F^- sisaldused normi 28 puurkaevus ning B väärtused 17 puurkaevus, moodustades vastavalt 46,7% ja 28,3% proovidest. Kõrgenenud F^- ja B väärtused on seotud peamiselt sügavamate puurkaevudega Lääne-Eestis (Karro and Uppin, 2013).

Põhjavee keemiline koostis sõltub eelkõige veega kontaktis oleva kivimi koostisest. Siluri–Ordoviitsiumi veekompleksis on kõige enam levinud Ca^{2+} ja

Mg^{2+} rikkad HCO_3-Ca-Mg- ja HCO_3-Mg-Ca-tüüpi veed, kus F^- ja B sisaldus on üldiselt madal. Kõrgenenud F^- ja B sisaldused on iseloomulikud peamiselt Na^+ ja Cl^- rikkale Cl-HCO_3-Na-tüüpi veele, mis on valdavaks veetüübiks Lääne-Eestis ning veekompleksi sügavamas osas. Fluoriidi ja boori sisaldusi põhjavees mõjutab ka põhjavee pH, mis Siluri-Ordoviitsiumi veekompleksis jääb vahemikku 6.76–8.48, kusjuures kõrgemad väärtused esinevad valdavalt Lääne-Eestis. Eesti karbonaatsete kivimite savikus suureneb lääne suunas ning kivimite pikaajalise leostumise tulemusena asendub Ca^{2+} Na^+-ga, mis toob kaasa Na-rikka aluselise põhjavee kujunemise Lääne-Eestis. Sügavuse suunas veevahetus aeglustub ning vesi on pikema aja vältel kontaktis ümbritseva kivimiga, mille tulemusena põhjavees lahustunud keemiliste komponentide (sh. F^- ja B) hulk kasvab. Seega võib järeldada, et F^- ja B kõrged sisaldused on seotud pigem sügavamate puurkaevudega. Tegelikkuses esineb sellisest seaduspärasusest kõrvalekaldeid, mille põhjuseks on puurkaevude erinev konstruktsioon ning avatud intervalli jäävate kivimite koostis (Karro and Uppin, 2013).

Fluoriidide ja boori looduslikud allikad on üsna sarnased. Peamised fluori sisaldavad mineraalid on fluoriit, apatiit, vilgud (biotiit), amfiboolid ning boori võib sisalduda turmaliinis, biotiidis ja amfiboolides. Lisaks eelnevatele seostatakse mõlemaid elemente savikate setetega, kus F ja B võivad asendada savimineraalide struktuuris olevat OH-iooni. Fluori ja boori leidub hulgaliselt ka vulkaanilises materjalis ning hüdrotermaalsetes setetes (Hem, 1985). Valdav osa fluori ja boori on sedimentatsiooni käigus setetesse kuhjunud ning alluvad hilisematele geokeemilistele protsessidele, sattudes põhjavette peamiselt veekompleksi moodustavate kivimite leostumisel.

Siluri ja Ordoviitsiumi ladestute lubjakivid ja dolomiidid sisaldavad fluori ligikaudu 100–500 mg/kg ja boori 5–20 mg/kg, kusjuures nende elementide kontsentratsioonid tõusevad kivimis vastavalt savisisalduse kasvule, ulatudes merglites vastavalt 500–1000 mg/kg ja 30–150 mg/kg. K-bentoniidi kihtides esineb fluori 400–4500 mg/kg ning boori 50–1000 mg/kg. Kivimiproovide mineraloogiline analüüs näitab, et kaltsiit ja dolomiit moodustavad kuni 99% kivimi koostisest, lisaks esineb kivimiproovides kvartsi, K-päevakivi ja illiitseid savimineraale. Vähemal määral leidub apatiiti, albiiti, kloriiti ja püriiti (Uppin and Karro, 2012; Uppin and Karro, 2013). K-bentoniidi proovid võivad sisaldada kuni 4.2% biotiiti (Hints et al., 2008), kuid uuritud karbonaatsetes kivimipalades biotiiti ei sisaldu või leidub seda väga vähestes kogustes. Fluoriiti ja apatiiti peetakse olulisteks F^- allikateks põhjavees ning biotiidi leostumisel satub põhjavette nii fluori kui ka boori (Hem, 1995). Võttes arvesse uuritud kivimite mineraloogilist koostist, siis fluoriit, apatiit ja biotiit ei saa olla peamisteks F^- ja B allikateks Siluri-Ordoviitsiumi veekompleksis, kuna nende mineraalide sisaldus veekompleksi moodustavates kivimites on väike. Seega võib eeldada, et F^- ja B leostub põhjavette peamiselt savikatest karbonaatsetest kivimitest – merglitest ja domeriitidest, aga ka K-bentoniidi kihtidest (Uppin and Karro, 2012). Selgitamaks fluori ja boori geoloogilisi allikaid põhjavees viidi läbi laboratoorsed leostuskatsed, kus purustatud kivimiproove leostati destilleeritud vees. Katsete tulemused näitavad selgelt, et mõlemat elementi leostub vette tunduvalt rohkem savikamast materjalist (Uppin and Karro, 2013).

Detailsed uuringud fluori ja boori sisalduste, hüdrokeemiliste seoste ja võimalike looduslike allikate kohta põhjavees on vajalikud, kuna tegemist on suurtes kogustes organismidele toksiliste elementidega. Uut tarbekaevu projekteerides tuleb selle sügavust ja asukohta hoolikalt valida, et vältida liigseid kulutusi hilisemale veepuhastusele.

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