Kadri Haamer

Hydrochemistry and sources of fluoride in Silurian-Ordovician aquifer system

MSc thesis

supervisor: PhD E. Karro

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ANNOTATION


The purpose of the current MSc thesis is to give an overview of the fluoride content in the Silurian-Ordovician aquifer system. The study aims to find the connections between environmental factors, the concentration of fluoride and other chemical elements in groundwater, as well as to explain the importance of the chemical type of groundwater as the controller of the fluoride content.

In order to study the fluoride content of the aquifer material twenty-five limestone, dolomite and K-bentonite samples were analysed. The high fluoride concentrations are well preserved in K-bentonite beds and therefore contribute to the formation of F-rich groundwater in the Silurian-Ordovician aquifer system.

Key words: Estonia, fluoride, groundwater, K-bentonite.
INTRODUCTION

Fluorides in the environment are of public and scientific interest because of their effects on health. Small doses of fluoride have beneficial effects on the teeth by hardening the enamel and reducing the incidence of caries, but excessive intake of fluoride results in dental and skeletal fluorosis. Unlike many other elements, a large portion of fluoride (F) is ingested from drinking water.

According to the WHO Guidelines for Drinking Water Quality (WHO, 2004) and EU Directive 98/83/EC (1998), as well as the Estonian Requirements for Drinking Water Quality (Joogivee, 2001) the limit value for fluoride is 1.5 mg/L.

Only few studies on the occurrence and distribution of fluoride in drinking water have been carried out in Estonia (Kuik, 1964; Saava et al., 1973; Karro & Rosentau, 2005). Unfortunately, these former studies have focused on particular region or city. On the other hand, health problems arising from different fluoride intake have been recorded (Kiik, 1973; Saava, 1998; Russak et al., 2002). There was thus a need for a study examining the spatial distribution and identifying probable natural sources of fluoride in drinking water. The results of the current study should help to work out the strategies for safe drinking water supply in case of excessive fluoride content.

The purpose of the present MSc thesis is to give an overview of the fluoride content in the Silurian-Ordovician aquifer system and to determine the areas, where the concentration of this element in groundwater is higher than the limit value set by the ministry of social affairs’ s regulation. The study aims to find the connections between environmental factors, the concentration of fluoride and other chemical elements in groundwater, as well as to explain the importance of the chemical type of groundwater as the controller of the fluoride content. The dependence of abstracted groundwater chemistry on the construction of drilled wells has been studied and the possible geological sources of the high fluoride content in groundwater are also discussed.
MATERIALS AND METHODS

Current study is based on the groundwater monitoring data collected during years 1964 to 2005 and on the existing information obtained from Geological Survey of Estonia, local environmental departments and Institute of Geology, University of Tartu. The gathered groundwater chemistry data include pH, anions (HCO$_3^-$, SO$_4^{2-}$, Cl$^-$), cations (Na$^+$, Ca$^{2+}$, K$^+$, Mg$^{2+}$), F$^-$ and B. The location, cadastre number and the depth of the wells, year of water sampling and the names of sampled aquifer systems were included into joint groundwater database, which contains all together 430 analyses (Appendix 1).

For data processing, interpretation of the results and compilation of cross-sections, MapInfo Professional 6.5, CorelDRAW 9 and AquaChem 3.7 were used.

Twenty-five limestone, dolomite and K-bentonite samples were analysed in order to study the fluoride content of the aquifer material. Rock samples for leaching experiments were ground using agate mortar.

The samples were studied using a sequential leaching method: previously boiled 18-megohm water (Millipore, Rios, Milli-Q) and 0.5 M Tiron (3,5 Pyrocacholdisulfonic acid disodium salt) solution. At first, 500 mg of rock samples were leached in 20 mL of water for 16 hr at 24 °C using an orbital swinging shaker (GFL 3011). The leachings were performed under argon atmosphere. Secondly, the 0.5 M Tiron that is regarded to dissolve F associated with oxidic Fe and Al sites of the K-bentonites, was applied for the K-bentonite samples. 15 mL of the Tiron leachate was used for 1 hr at 80 °C (Biermans & Baert, 1977).

For total fluorine contents, 500 mg of ground samples were mixed and sintered with 3500 mg of Na$_2$O$_2$ in covered Pt-dishes (Seelye & Rafter, 1950) for 45 minutes at 460 °C. After cooling, the sintrates were let to react with 50 mL of double distilled water and dissolved stepwise using four times 3.5 mL of
6 M HCl, and made up to 100 mL in 18-megohm water. Polypropylene test flasks were used in order to avoid complexation of fluorine with boron from borosilicate glass.

The F contents were measured using a fluoride selective electrode under magnetic stirring (Orion Research, Model 920+). Total ionic strength adjustment buffer (TISAB) solution was used to decomplex the F and buffer the system. The determinations of fluoride were made under even temperature and illumination (Nicholson, 1983).
GENERAL GEOCHEMISTRY OF FLUORINE

Fluorine (F) is the most electronegative and reactive of elements, and reacts with practically all of the organic and inorganic substances. It never occurs in the elemental state in nature because its high reactivity. The average fluorine concentrations in the Earth’s crust is estimated at 0.05 – 0.1 % or 500 – 1000 mg/kg and ranks 13th among the elements (Turekian & Wedepohl, 1961; Adriano, 1986; Wedepohl, 1995). It is enriched during differentiation in the late stages of crystallizing magmas as well as in the residual solutions and vapour. Consequently, it is concentrated in highly siliceous granitic and alkaline rocks, and in hydrothermal mineral deposits (Hopkins, 1977).

Fluorine may occur in limestones associated with tremolite-, actinolite-pyroxene- or with mica-chlorite-skarn formations, where F⁻ concentrations may reach the level of 0.4 – 1.2 %. Part of fluorine may be present in clay material admixed with weathered limestones. It can also be combined with phosphate minerals (Lahermo & Backman, 2000).

The most important fluorous minerals are fluorite (CaF₂), fluor-apatite Ca₅(PO₄)₃F and apatite Ca₅(PO₄)₃(F,OH,Cl). They are characteristic accessory minerals in many types of rocks. Since fluorite may contain nearly half of fluorine by weight, it contributes substantially to F⁻ concentrations in rock and water even though the mineral is present in small quantities (Correns, 1956). Pure fluor-apatite (Ca₅(PO₄)₃F) could contain up to 3.8 % fluorine.

Fluorine may occur also in the composition of clay minerals, micas and pyroxenes. Soils dominated by clay minerals have high sorption capacity and frequently serve as natural geochemical barriers preventing pollutants from reaching groundwater. Fluorides are adsorbed on clay minerals, where ionic exchange takes place – F⁻ ions partly replace OH⁻ groups (Hübner, 1969; Flühler et al., 1982). More than 90 % of natural F⁻ in soils is bound to clay particles (Lahermo & Backman, 2000).
The role of micas and amphiboles in the occurrence and mobility of fluorides in soils is enhanced by their relative readiness to disintegrate in weathering processes. Fluorides in micas are likely to be released soon after the onset of weathering. According to Korting (1972) in clay fractions 80 – 90 % of fluorides are contained in muscovite, illite and related minerals of the mica group.

Apart from natural sources, a considerable amount of fluoride may be contributed due to anthropogenic activities. Remarkable amounts of fluorides are transferred into agricultural soils by phosphate fertilizers. Phosphorites may contain up to 4 % of fluorine depending on its origin and contents of fluorapatite (Fleischer et al., 1974). The use of fluorocarbons, insecticides and week killers may also contribute to local F⁻ concentrations in soils. In addition to agriculture part of the fluorides are derived from industrial emissions and waste waters. The steel, aluminium, glass, brick and ceramic industries use fluoride in their production process that occurs with the encounter of F-containing aerosols, dust and wastewater into the surrounding environment (Arnesen et al., 1995; Haidouti, 1995).

In groundwater fluorine occurs as fluoride ions (F⁻) and forms soluble complexes with many kinds of inorganic and organic ligands. Fluorides are released into aqueous solution during weathering process of rocks and minerals and through anthropogenic pollution. Solubility of F from F-bearing minerals is relatively low under normal conditions, but the slow kinetics often enhances leaching and F enrichment in groundwater (Hem, 1989). Part of fluorides may occur in groundwater as a result of mineral fluorite (CaF₂) dissolution. The solubility product for fluorite (K_{fluor}) can be determined according to the following dissociation formula (Helgeson, 1969):

\[
\text{CaF}_2 \leftrightarrow \text{Ca}^{2+} + 2\text{F}^-
\]

\[
K_{\text{fluor}} = [a_{\text{Ca}^{2+}}] * [a_{\text{F}^-}]^2 = 10^{-9.04}, \quad \text{at } 25^\circ \text{C}
\]
where \([a_{Ca}^{2+}]\) and \([a_{F^-}]\) are the activities of the concerned ions. Both Smyshlyaev and Edeleva (1962) and Handa (1975) have reported for \(K_{fluor}\) the values of \(10^{-10.75}\). Due to the relatively low solubility of fluoride, the occurrence of aqueous \(F^-\) is predominantly controlled by the availability of free \(Ca^{2+}\)-ions in water (Jacks, 1973).

The dissolution constant of calcium carbonate (CaCO\(_3\)) is much larger than that of fluorite:

\[
CaCO_3(s) + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \\
K_{cal} = a_{Ca}^{2+} \cdot a_{HCO_3^-}/a_{H^+} = 0.97*10^2
\]

Since the solubility product for fluorite is constant, the activity of fluoride is directly proportional to \(HCO_3^-\), if the pH is constant. When computing the thermodynamic equilibrium in the groundwater system in contact with both calcite and fluorite, a combined equation is derived (Handa, 1975):

\[
CaCO_3(s) + H^+ + 2F^- \leftrightarrow CaF_2(s) + HCO_3^- \\
K_{cal-fluor} = a_{HCO_3^-}/a_{H^+} \cdot [a_{F^-}]^2 = 1.06*10^{-11}
\]

The above values are taken from Helgeson (1969). The corresponding value by Smyshlyaev and Edeleva (1962) is \(K_{cal-fluor}=3.6*10^{-12}\). From the last equation can be concluded that the aqueous \(F^-\) concentrations are proportional to \(HCO_3^-\) concentrations and pH values. Consequently, highly fluorous waters are usually \(HCO_3^-\)-dominating waters what favour the dissociation of fluoride from soils. Therefore, water with high concentrations of fluorides can form in the areas where alkaline carbonate-containing waters are in contact with fluorine-bearing rocks.

Fluoride concentrations are relatively independent of the other water-soluble components, but noteworthy correlation exists between \(F^-\) and pH values. The \(F^-\) solubility in soils is lowest in the pH range of 5.0-6.5 (Adriano, 1986). At higher pH values ionic exchange occur between \(F^-\) and \(OH^-\) ions (illites, chlorites, micas and amphiboles) (Englund & Myhrstad, 1980) that leads to
fluoride increase in groundwater. In acid environment (pH < 6) both F⁻ and Al³⁺ steep into water and formation of [AlF]²⁺ and [AlF₂]⁺ complexes mainly takes place in solution (Hem, 1989; Wenzel & Blum, 1992; Haidouti, 1995; Neal, 1995). Hitchon (1995) has observed that the formation of [MgF]⁺ complexes on the account of F-ions, intensifies while the saltiness of groundwater, Ca²⁺ content and temperature increases.

During the volcanic eruptions a lot of volcanic gas and ash fall into atmosphere and to ground from there. Plumes of ash and dust, which may cover hundreds of kilometres, may carry a variety of adsorbed chemicals. After the ash settles to the ground, these toxins may be dissolved and thus leach into the environment. The dominant chemicals that may adsorb to tephra and thus act as leachates are: chlorine, sulphur compounds, sodium, calcium, potassium, magnesium and fluorine (Weinstein & Cook, 2005). Other elements are present in smaller quantities. Various studies of volcanic emission have shown that volcanic gases and ash are rich in fluorine (Barclay et al., 1996; Cronin et al., 2003), thus clay-rich volcanic ash beds provide adsorption and ion exchange sites for F-ions. Fluorine occurs mainly in the form of HF, H₂F₂ or F₂ as well as SiF₄ and H₂SiF₆ (Fleischer et al., 1974).
HEALTH EFFECTS OF FLUORIDE

Fluorides in the drinking water are in the focus of public and scientific interest because of their effects on health. Unlike many other elements, a large portion of fluoride is ingested from drinking water. The optimal value for fluoride in drinking water is considered to be around 0.8-1.5 mg/L (WHO, 2004), whereas both deficiency and excess of F⁻ might be harmful from the dental point of view. A higher concentration of F⁻ causes dental fluorosis, and a concentration less than 0.8 mg/L results in dental caries. Fluoride makes the tooth structure stronger, so teeth are more resistant to acid attacks. Acid is formed when the bacteria in plaque break down sugars and carbohydrates from the diet. Repeated acid attacks break down the tooth, which causes cavities. Fluoride also acts to repair, or remineralize, areas in which acid attacks have already begun. The remineralization effect of fluoride is important because it reverses the early decay process as well as creating a tooth surface that is more resistant to decay (ADA, 1999). Therefore in the areas with fluorine-rich drinking water the damage of caries to teeth is significantly smaller compared with the areas with fluoride-deficient drinking water. Table 1 illustrates the different tooth decays according to the content of fluoride in drinking water.

Table 1. Relation between tooth decays and fluoride content in the drinking water (Kuik, 1964).

<table>
<thead>
<tr>
<th>F⁻ content in drinking water (mg/L)</th>
<th>Tooth damages</th>
</tr>
</thead>
<tbody>
<tr>
<td>up to 0.5</td>
<td>Wide spread of dental caries.</td>
</tr>
<tr>
<td>0.6-0.8</td>
<td>Dental caries appears often, but not so widely.</td>
</tr>
<tr>
<td>0.9-1.2</td>
<td>Dental caries spreads narrowly. No fluorosis.</td>
</tr>
<tr>
<td>1.3-1.5</td>
<td>Dental caries spreads narrowly. Rarely mild fluorosis.</td>
</tr>
<tr>
<td>1.6-2.0</td>
<td>Dental caries spreads narrowly. Mild fluorosis.</td>
</tr>
<tr>
<td>above 2.0</td>
<td>Spread of dental fluorosis.</td>
</tr>
</tbody>
</table>

Dental fluorosis is the damage of tooth enamel, which is caused by the long-time consumption of water with high fluoride content during the period of development of the tooth. After tooth enamel is completely formed, dental
fluorosis cannot develop even if excessive fluoride is ingested (WHO, 1984). Hence, older children and adults are not at risk for dental fluorosis. Teeth impacted by fluorosis have visible discoloration, ranging from white spots to brown and black stains. Teeth with fluorosis also have an increased porosity of the enamel. In the milder forms, the porosity is mostly limited to the sub-surface enamel, whereas in the more advanced forms, the porosity impacts the surface enamel as well, resulting in extensive pitting, chipping, fracturing, and decay of the teeth (Russak, 1996; Altosaar et al., 1998). Dental fluorosis has been classified in a number of ways. Dean (1934) developed one of the most universally accepted classifications, where Dean’s index measures the degree of mottled enamel (fluorosis) in teeth. According to the damage of tooth very mild, mild, moderate and severe fluorosis can be defined (Table 2). Long-term ingestion of large amounts of fluoride can lead to potentially severe skeletal problems, such as osteosclerosis - an abnormal hardening or increased density of bone tissue. Links between high fluoride and other health problems, including birth defects (Hamilton, 1992) and cancer (Marshall, 1990) are less clearly defined.

Table 2. Degree of difficulty of dental fluorosis (Dean, 1934).

<table>
<thead>
<tr>
<th>Dean's index</th>
<th>Tooth damages</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Very mild fluorosis: small opaque, paper white areas scattered irregularly over the tooth but not involving as much as 25% of the tooth surface.</td>
</tr>
<tr>
<td>II</td>
<td>Mild fluorosis: the white opaque areas in the enamel of the teeth are more extensive but do not involve as much as 50% of the tooth.</td>
</tr>
<tr>
<td>III</td>
<td>Moderate fluorosis: all enamel surfaces of the teeth are affected, and the surfaces subject to attrition show wear. Brown stain is frequently a disfiguring feature.</td>
</tr>
<tr>
<td>IV</td>
<td>Severe fluorosis: all enamel surfaces are affected and hypoplasia is so marked that the general form of the tooth may be affected. The major diagnostic sign of this classification is discrete or confluent pitting. Brown stains are widespread and teeth often present a corroded-like appearance.</td>
</tr>
</tbody>
</table>

Many high-fluoride groundwater provinces have been recognized in various parts of the world. High fluoride contents, up to 40 mg/L have been reported in China, India, Africa, Japan and Mexico (Agrawal & Vaish, 1998; Lahermo et al., 1991; Yong & Hua, 1991; Alarcón-Herrera et al., 2001). Fluoride removal
practices vary widely and many high-fluoride water sources are used without treatment. As a result, large populations throughout the world suffer the effects of chronic endemic fluorosis.

The concentration of fluoride in Estonian drinking water varies widely, from 0.01 mg/L to 7.2 mg/L (Karro et al., 2006). As a result of that the extent of health problems, like dental caries and dental fluorosis must be studied in detail. The results of same earlier studies performed in Estonia are shown in Table 3. There exists a clear relation between fluoride content and the degree of occurrence of dental fluorosis and caries.

Table 3. Incidence of dental caries and fluorosis depending on the fluoride content in drinking water (Kiik, 1973; Saava, 1998).

<table>
<thead>
<tr>
<th>Fluoride content in drinking water (mg/L)</th>
<th>Prevalence of caries (%)</th>
<th>Prevalence of fluorosis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1-0.5</td>
<td>82.6</td>
<td></td>
</tr>
<tr>
<td>0.6-1.0</td>
<td>70.7</td>
<td>6.3</td>
</tr>
<tr>
<td>1.1-1.5</td>
<td>59.1</td>
<td>11.2</td>
</tr>
<tr>
<td>1.6-2.0</td>
<td>48.6</td>
<td>38</td>
</tr>
<tr>
<td>2.1-2.4</td>
<td>50.9</td>
<td>41.9</td>
</tr>
<tr>
<td>2.5-2.8</td>
<td>50.9</td>
<td>54.5</td>
</tr>
<tr>
<td>2.9-5.0</td>
<td>88.9</td>
<td></td>
</tr>
</tbody>
</table>
GEOLOGICAL SETTING

The Ordovician rocks are exposed in a narrow (40-50 km) belt extending from the west to east for about 300 km in Estonia. The practically undisturbed strata are almost flat-lying with a small dip to the south. The sequence consists of highly fossiliferous shallow water open shelf carbonates – clayey limestones and marlstones, with the exception of its basal part which is represented by terrigenous sediments: sandstones, clays and graptolite argillites (Table 4). The total thickness of the Ordovician varies from 70 to 180 m, being maximal in the central and eastern Estonia (Rõõmusoks, 1983).

Two main facies belts of the Ordovician Basin are distributed in Estonia: the marginal and the central belt. Shallow water carbonate sediments with a lot of discontinuity surfaces dominated in the marginal confacies belt, while the relatively deeper water central belt comprised predominantly clayey sediments such as clayey limestones and marlstones (Nestor & Einasto, 1997). The Ordovician System of Estonia includes all three global Series: Lower-, Middle- and Upper-Ordovician and eighteen regional Stages are used as regional stratigraphic standard for Baltoscandian area (Table 4).

During the Silurian, relatively shallow water sedimentary conditions prevailed in Estonia. According to the facies model worked out by Nestor and Einasto (1997), five facies belts can be distinguished in the Silurian Basin: tidal flat/lagoon, shoal, open shelf, transition and basin depression. The first three facies belts formed a carbonate shelf or carbonate platform and the latter two - a deeper basin with fine-clastic deposits. During the Silurian shallow marine facies belts generally shifted in basinward direction as a result of basin infilling, but local conditions changed in course of sea level changes (Nestor & Einasto, 1997). The composition of sediments (mainly clay content) reflects the sea level changes of the Silurian Basin. The Silurian transgression maximum coincides with Juuru, Adavere and Jaani Stage. The regression episodes in Raikküla, Rootsiküla and Paadla Stages correspond to minimum amount of clay in carbonates (Viiding, 1995).
The Silurian sequence in Estonia spreads on Hiiumaa, Saaremaa and Muhu islands and in the central part of Estonia. Thicknesses of the Silurian

Table 4. Stratigraphy and lithological characteristics of Estonian Ordovician and Silurian systems (Raukas & Teedumäe, 1997).

<table>
<thead>
<tr>
<th>System</th>
<th>Series</th>
<th>Stage</th>
<th>Characteristic rocks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SILURIAN</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Přidoli</td>
<td></td>
<td>Ohesaare: Clayey limestone, marlstone, dolomite, domerite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Kaugatumaa: Detritic limestone, marlstone, clayey limestone</td>
</tr>
<tr>
<td></td>
<td>Ludlow</td>
<td></td>
<td>Kuressaare: Clayey limestone, marlstone, domerite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Paadla: Detritic limestone, micritic limestone, dolomite, clayey limestone, marlstone, domerite</td>
</tr>
<tr>
<td></td>
<td>Wenlock</td>
<td></td>
<td>Rootsiküla: Limestone, dolomite, domerite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Jaagarahu: Detritic limestone, micritic limestone, clayey limestone, marlstone, dolomite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Jaani: Clayey limestone, marlstone, calcareous clay, domerite, clayey dolomite</td>
</tr>
<tr>
<td></td>
<td>Llandovery</td>
<td></td>
<td>Adavere: Marlstone, domerite, clay, detritic limestone, clayey limestone, dolomite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Raikküla: Detritic limestone, aphanitic limestone, micritic limestone, dolomite, marlstone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Juuru: Micritic limestone, detritic limestone, clayey limestone, marlstone, domerite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Upper</td>
<td>Porkuni: Detritic limestone, sandy limestone, dolomite, marlstone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ordovician</td>
<td>Pirgu: Clayey limestone, marlstone, aphanitic limestone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Vormsi: Clayey limestone, marlstone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Nabala: Aphanitic and clayey limestone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rakvere: Aphanitic and microcrystalline limestone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oandu: Clayey limestone, marlstone, detritic and micritic limestone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Keila: Detritic limestone, clayey or microcrystalline limestone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Haljala: Clayey limestone, marlstone, detritic limestone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Kukruse: Limestone, clayey limestone, kukersite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Middle</td>
<td>Uhaku: Clayey limestone, marlstone with interlayers of kukersite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ordovician</td>
<td>Lasnamägi: Detritic limestone, dolomitized limestone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aseri: Oolitic limestone, detritic limestone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Kunda: Detritic limestone, sandy limestone, dolomitized limestone, oolitic limestone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Volkhov: Glaucolistic limestone, microcrystalline limestone, Dolomitized limestone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lower</td>
<td>Billing: Glaucolistic limestone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ordovician</td>
<td>Hunneberg: Glaucolithic sandstone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Varangu: Clayey siltstone, argillite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pakerort: Argillite, siltstone, sandstone, obolus sandstone</td>
</tr>
</tbody>
</table>
sediments are measured up to 436 m in Saaremaa (Viiding, 1995). The Silurian sequence consists mostly of carbonate rocks – limestones, dolomites and marlstones and is divided into ten regional Stages, representing all four global Series (Table 4).

The Silurian and Ordovician stratigraphic record in Estonia contains numerous volcanic ash layers whose composition is dominated by the mineral assemblage of illite – smectite – K-feldspar - kaolinite. The contents of these minerals may vary between individual bentonite layers. Clay-rich interbeds of volcanic origin in Palaeozoic sedimentary sections are commonly called K-bentonites. K-bentonite is a product of chemical weathering of volcanic ash, where an apposition from terrigenous material is found. The seawater has turned into the strongest factor in the process of chemical weathering (Jürgenson, 1958). The main mineralogical characteristics of K-bentonites are: presence of illite-smectite and kaolinite; low content or absence of quartz; low content or absence of carbonate minerals; a high content of authigenic K-feldspar (low-sanidine); presence of visually detectable biotite flakes, commonly absence of chlorite; presence of zircon and apatite. The thicknesses of K-bentonites vary from some mm up to 10 cm, rarely up to 20-30 cm (Kiipli et al., 1997).

The interlayers of K-bentonite have been recorded in Jaani, Adavere and Juuru Stages of Silurian System (Jürgenson, 1964; Kiipli et al., 2001; Kiipli & Kallaste, 1996; Kiipli, 1998). Only the Adavere Stage itself contains 27 volcanic beds, the most prominent of which is the “O” K-bentonite bed with thickness up to 25 cm. Ordovician K-bentonite beds in Estonia are present only in the Upper Ordovician Series: Kukruse, Haljala, Keila and Pirgu Stages (Bergström et al., 1995; Kiipli et al., 2004). Most outstanding of them is the Kinnekulle bentonite bed with thickness up to 70 cm in Saaremaa Island.
THE SILURIAN-ORDOVICIAN AQUIFER SYSTEM

The Silurian-Ordovician (S-O) aquifer system consists of diverse limestones and dolomites with clayey interlayers and it is an important and often the only source of drinking water in central and western Estonia and on the islands of the West-Estonian Archipelago.

The upper part of the S-O aquifer system with a thickness of 30 m is extremely cavernous, with numerous cracks and fissures. Karst cavities form some half-a-metre-deep canals trending in the direction of bedrock fissures. Caverns are especially abundant in dolomites and dolomitized limestones. Close to the ground surface, bigger karst cavities, a couple of metres deep and some twenty or thirty meters long, occur in some places. Water in the fissure systems and karst cavities of the carbonate bedrock flows relatively fast. Groundwater recharges from the Quaternary deposits in the outcrop area and therefore can easily become polluted in the areas with a thin Quaternary cover. Silurian and Ordovician carbonate rocks have fragmentary water conducting zones with parallel lamination and an abundance of fissures. In these 1-2 m thick zones groundwater flows in a lateral direction. Zones with high lateral conductivity are separated from each other by 5-10 m thick layers - aquitards in which groundwater flows mainly in vertical fissures (Perens & Vallner, 1997; Heinsalu, 1995). Fractures and karst are most common near the ground surface, downwards the fracturing of carbonate rocks decreases. In the topmost 20 m of carbonate aquifer the lateral conductivity is 10-50 m/d, 5-8 m/d at a depth of 20-50 m and only 1-2 m/d at a depth of 50-100 m (Perens & Vallner, 1997; Heinsalu, 1995). The hydraulic conductivity of rocks decreases with depth and S-O aquifer system transforms into S-O aquitard.

The aquifer system has a characteristic $\text{HCO}_3$-Ca-Mg and $\text{HCO}_3$-Mg-Ca water type with TDS mainly below 0.6 g/L in its upper 30-50 m thick portion. In coastal areas and greater depths the content of $\text{Cl}^-$ and $\text{Na}^+$ in groundwater increases and $\text{HCO}_3$-Cl-Na-Mg-Ca type water with TDS between 0.3-1.5 g/L is widespread (Perens et al., 2001).
FLUORIDE CONTENTS IN SILURIAN-ORDOVICIAN AQUIFER SYSTEM

All aquifer systems found in the sedimentary cover are used in drinking and domestic water supply in Estonia. Estonian hydrostratigraphical cross-section begins with Quaternary aquifer system, followed by Upper-Devonian, Middle-Devonian, Middle-Lower-Devonian, Silurian-Ordovician, Ordovician-Cambrian and Cambrian-Vendian aquifer system, that are isolated from each other by impervious beds. Aquifer systems differ from each other in distribution, bedding conditions, hydraulic parameters and chemical composition.

Four hundred thirty (430) groundwater samples were collected from Silurian-Ordovician aquifer system, whence 48.2 % does not comply with Estonian as well as EU and WHO requirements in respect of F⁻ (1.5 mg/L). On the other hand, 19.4 % of the drinking water samples contained fluoride less than 0.5 mg/L. Consumption of drinking water with such low fluoride content is insufficient to prevent caries.

Figure 1 shows the spatial distribution of the investigated drinking water wells, where fluoride levels range from 0.01 to 7.2 mg/L. An analysis of the regional distribution of fluoride concentrations shows a great variation. Northern Estonia as well as eastern Estonia are characterised predominantly with low fluoride content in drinking water, with exception only in Kernu district (3.6 mg/L). Fluoride concentrations in Järva and Jõgeva County reach up to 2.24 mg/L and 5.0 mg/L, respectively. Fluoride contents exceed the limit value set for drinking water also in Viljandi (F=0.32-2.46 mg/L) and Rapla (0.1-2.75 mg/L) County. It is possible to delimit an area with anomalously high F⁻ content, which primarily involves Pärnu and Lääne Counties (Fig. 1). Almost half of the Pärnu districts have F-rich groundwaters, what is a serious problem for local administrations and water-companies. High concentrations of F⁻ are determined in wells of Tõstamaa, Audru, Koogna, Halinga, Are, Kaisma, Tori and Paikuse districts. Highest F⁻ values (up to 7.2 mg/L) have been measured in Audru, Tõstamaa and Pärnu-Jaagupi. Majority of the wells in western Estonia have F⁻ concentrations over the limit value; the highest values are detected in Hanila, Taebla and Lihula districts, where fluoride concentrations
Fig. 1. Groundwater sampling sites are marked on the background of schematic geological map. Fluoride concentrations over 1.5 mg/L are marked with red spots.
reach up to 5.7 mg/L. Therefore, high F⁻ concentrations of natural origin are common in western Estonia, where drinking and domestic water originates from aquifers associated with Ordovician and Silurian carbonate rocks.

**Vertical distribution of fluoride in groundwater**

High fluoride concentrations can be achieved in groundwaters that have long residence times in the host aquifers. Shallow groundwaters usually have low concentrations of fluoride because they represent recently infiltrated rainwater. Deeper (older) groundwaters with long residence time contain therefore most likely high concentrations of fluoride. This is in accordance with analytical results, which show that the highest concentrations of fluoride (up to 7.2 mg/L) are analysed in wells having a depth of 150-200 m (Fig. 2). The lowest F values are detected in shallow wells (<30 m) since water flows relatively fast and is strongly affected by infiltration of rainwater. Such

![Graph](image)

Fig. 2. Bivariate plot of F⁻ versus well depth in Silurian-Ordovician aquifer system.

This tendency is explained by geological characteristics of Silurian-Ordovician aquifer system. The upper part of the aquifer system with a thickness of 30 m is extremely karstified and fissured. Karst phenomena and the frequency of fissures decrease downwards, as the total transmissivity of carbonate rocks.
Generally, the amount of dissolved chemical substances in groundwater increase with depth, because of the deceleration of water exchange and a longer contact time with host rocks. In reality, there also exist deviations from the general tendencies that 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.

Vingisaar et al. (1981) have been studied the chemical composition of Estonian Silurian and Ordovician carbonate rocks. Correlation of fluoride content with lithology, particularly with siliciclastic clay and dolomite content is shown in the lithological diagram (Fig. 3). Fluoride content is remarkable higher in dolomites compared to limestones. If clay content of the rock increases, it is followed by the increase on F⁻ content, therefore the maximum amount of fluoride can be found in clayey dolomites. The average F⁻ contents in pure limestone, dolomite and clayey dolomite are 650, 2000 and 2500 g/t, respectively (Fig. 3). Comparing the geological cross-sections and water chemistry of boreholes the same trend can be followed in western Estonia.

Fig. 3. The lithological diagram of carbonate rocks. Isolines reflect the fluoride content (g/t) in the rocks (Vingissaar et al., 1965; 1981).
The boreholes (Figs. 4, 5 and 6) with the same depth but different lithological composition enable to make assumptions on the variation of groundwater fluoride content. For example, fluoride content in Audru borehole (well no. 6189) is 6.1 mg/L, where dominating rock types are dolomite and clayey limestone. Well with the same depth in Märjamaa (well no. 8718) exhibits fluoride content almost three times lower than in Audru, because the dominating rock types there are mainly limestone and clayey limestone. Similar principle exists in 170 m (well no.6671 and 9737) and in 105 m (well no. 6671 and 9737) deep boreholes. Low fluoride concentrations can be found in boreholes that open limestones and high contents correlate with the presence of marl and dolomite interlayers in limestones. Even shallow wells (well no. 7923, 6154 and 6586) drilled into rocks of Adavere and Jaagarahu Stage could show high F contents. As a rule, there occurs predominantly intensive water exchange in shallow wells and therefore low concentration of chemical components. However, in places thick Quaternary cover prevents from infiltration of rainwater and consequent dilution of groundwater, which

Fig. 4. Location of the boreholes (Figs. 5 and 6).
Fig. 5. Geological cross-sections of boreholes (cadastre number 8544, 8749, 8718 and 6189) and groundwater chemistry.
Fig. 6. Geological cross-sections of boreholes (cadastre number 6671, 9737, 6154, 6586) and groundwater chemistry.
could lead to F-rich groundwaters in small depths (well no. 7923 and 6586). Therefore, the intensity of water exchange acts as an important factor regulating the content of F in groundwater.

The F contents of the water are in good correlation with the length of the open intervals of boreholes (Figs. 5 and 6). Wells with low fluoride concentration have twice longer open intervals than the wells with the same depth but high fluoride contents. The long open interval of the bored well enables the mixing and dilution of waters with different salinity and fluoride content. Therefore, the higher F⁻ contents are related to deep wells with short screens.

Since, in the open interval of bored wells several rock types are often presented, no apparent correlation between F content and host rocks exists. The correlation between groundwater and host rock chemistry might be stronger, if the open intervals of wells are shorter and only one rock type is exposed.

**Hydrochemistry of fluoride**

The chemical composition of groundwater is affected by concurrence of several factors. Downwards the fissures of carbonate rocks and the water exchange rate decrease. Groundwater that has long residence time in host rocks reflects the chemical composition of rocks, geochemistry of aquifer and hydrodynamics.

According to Lahermo et al. (1991) groundwaters with high F⁻ contents are generally HCO₃-Na-type waters, particularly poor in Ca²⁺. Several authors have shown that in waters with high F concentrations, the amount of F is proportional to the HCO₃⁻ concentration and the pH (Handa, 1975; Saxena & Ahmed, 2001). Same trend can be observed in Silurian-Ordovician aquifer system, where elevated F concentrations are mostly associated with pH values over 7.6 (Fig. 7). The pH values from 7.6 to 8.6 and high HCO₃⁻ contents (350-450 mg/L) are favourable for fluoride dissolution.
Groundwater in Silurian-Ordovician aquifer system is mainly HCO$_3$-Ca-Mg-type (Perens & Vallner, 1997) and owing to the high Ca$^{2+}$ contents, quite low amounts of F$^{-}$ may be mobilised. The highest F$^{-}$ concentrations exist in wells that produce the water with low Ca$^{2+}$ content (Fig. 8).
The dissolution and deposition of fluoride in groundwater is controlled by chemical type of water, which varies considerably in the study area. Therefore, major ion chemistry of sampled groundwater is examined as a whole using the Piper diagram (Fig. 9). In order to construct the Piper diagram main cations (Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\)) and anions (Cl\(^-\), SO\(_4^{2-}\), HCO\(_3^-\)) are counted. In Piper diagram the concentrations of main ions are expressed as % meq/L and it shows direct relation between proportional fluoride content and the chemical type of groundwater. High fluoride concentrations are associated with HCO\(_3^-\)-Cl-Na or HCO\(_3^-\)-Cl-SO\(_4^-\)-Na type waters. The lowest fluoride values can be found in the HCO\(_3^-\)-SO\(_4^-\)-Ca-Mg type waters, where F concentrations are below 0.5 mg/L. Groundwater with HCO\(_3^-\)-Na chemical type has always very high
fluoride content. As the concentration of calcium in groundwater increases the concentration of fluorine decreases.

Relation between fluoride content and groundwater chemical type is expressed on hydrogeochemical maps of Silurian and Ordovician aquifers, where proportional fluoride concentrations are marked (Figs. 10 and 11). Cations and anions that have equivalent concentrations higher than 20 % are plotted on the hydrogeochemical map. The groundwater chemistry varies remarkably in different parts of the study area. In the Silurian aquifer HCO$_3^-$Ca-Mg type groundwater is mainly spread in Rapla County, where the concentration of F$^-$ in groundwater is low. In the Lihula district high F$^-$ values (1.6-4.4 mg/L) are associated with Cl-HCO$_3$-Na-Mg or Cl-HCO$_3$-Na type groundwaters, where favourable hydrochemical conditions for dissolved F$^-$ in groundwater exist. Practically three hydrochemical types can be distinguished in Pärnu County (F$^-$=0.01-7.2 mg/L): Cl-HCO$_3$-Na-Mg-, Cl-HCO$_3$-Na type groundwater, HCO$_3$-Mg-Ca type and HCO$_3$-Cl-Na-Mg-Ca-, HCO$_3$-Cl-Na type water. As the hydrochemical types gradually change to the bicarbonate calcium magnesium (HCO$_3$-Ca-Mg) or bicarbonate sodium magnesium calcium (HCO$_3$-Na-Mg-Ca) waters, the concentration of F$^-$ falls. Therefore Viljandi, Jõgeva and Lääne-Viru County are mainly represented by F$^-$ poor groundwater. Vertical zonation is also characteristic to the Silurian aquifer that is expressed by the downward increase of Cl$^-$ and Na$^+$ content and mineralization of water. Therefore, some derivations may occur between groundwater chemical type and F$^-$ content.

In the Ordovician aquifer changes in fluoride concentration are also followed by changes in general water chemistry. In chloride bicarbonate sodium magnesium (Cl-HCO$_3$-Na-Mg), chloride bicarbonate sodium (Cl-HCO$_3$-Na), bicarbonate chloride sodium magnesium calcium (HCO$_3$-Cl-Na-Mg-Ca) and bicarbonate chloride sodium (HCO$_3$-Cl-Na) waters the concentration of F$^-$ in groundwater is high. As the hydrochemical types change to the HCO$_3$-Mg-Ca, HCO$_3$-Na-Mg-Ca and HCO$_3$-Ca-Mg waters, the concentration of F$^-$ falls. Accordingly, high values of fluoride can be attributed to Lääne County, where Cl-HCO$_3$-Na-Mg and Cl-HCO$_3$-Na type waters dominate. Low levels of fluoride
Fig. 10. The concentrations of fluoride on the hydrogeochemical map of Ordovician aquifer system. Groundwater chemical types after Perens et al., 2001.
Fig. 11. The concentrations of fluoride on the hydrogeochemical map of Silurian aquifer system. Chemical types of groundwater after Perens et al., 2001.
in the groundwater are determined in Ida-Viru and Lääne-Viru County, elsewhere in the country F⁻ concentrations remain below the permitted limit value (1.5 mg/L).

Deviations from the above mentioned general tendencies can be explained by the differences in the depth and construction of wells and also in the type and structure of the opened rocks. Therefore, the occurrence of wells with different groundwater chemical type close to each other is possible.

Fluoride concentrations are relatively independent of the other water-soluble components, but have noteworthy correlation with boron (B). Highest F values coincide with anomalously high B concentrations and are analysed from Silurian-Ordovician aquifer system (Fig. 12).

![Fig. 12. The concentrations of B plotted against fluoride concentration.](image)

Since ocean water contains abundantly boron (4.4 mg/L) beside fluorides, the correlation between these two elements in groundwater is anticipated. Boron concentrations range from 0.016 to 2.1 mg/L, with a spatial distribution roughly similar to that of fluoride. The upper officially permissible B concentration in drinking water in Estonia is 1.0 mg/L (Joogivee, 2001). This value is often exceeded in western Estonia where boron-rich groundwaters may cause different health hazards - mild gastrointestinal irritation (Saava, 1998).
POSSIBLE SOURCE OF FLUORIDE-RICH GROUNDWATER

Various studies of volcanic emissions have shown that volcanic gases and tephra are rich in F (Barclay et al., 1996; Horn & Schmincke, 2000; Weinstein & Cook, 2005). In 1980 Óskarsson demonstrated that the tephra from the 1970 eruption of Hekla (Iceland) contained up to 2000 mg F/kg. In leaching studies on the Hekla ash (2 g tephra in 100 mL water), after 15 min of shaking, 1000 µg F was released per g of tephra. From fresh samples of Guatamalan volcanoes an average of 14–29 µg F/g was leached into water during the first step of a three-step successive leaching study (Smith et al., 1982). A study of tephra from the Ruapehu volcano in New Zealand showed that the F concentration was as high as 67.9 mg/kg after the 24 hr of leaching with water (Cronin et al., 2003). Ion probe analyses of matrix glasses and melt inclusions of different minerals in tephra of the tenth century A.D. eruption of the Baitoushan volcano (China/North Korea) revealed F contents of 2430–3990 mg/kg and 2630-6200 mg/kg, respectively (Horn & Schmincke, 2000).

It might be supposed, that the volcanic material in carbonate rocks is one of the most probable source of high F⁻ in groundwater. The interlayers of K-bentonite have been recorded in Adavere and Jaani Stages of Silurian system in the study area. The layers of volcanic ashes have been also found in Kukruse, Haljala, Keila and Pirgu Stages from the cross-sections of Ordovician system.

Fluoride concentration in 25 rock samples was studied in ten drillcores of Estonia – Paatsalu, Ikla, Varbla, Pärnu, Laitse, Valga, Laeva, Pürksi, Ingliste and Oru (Figs. 13, 14 and 15). The results of the chemical analyses and leaching experiments are presented in the Table 5. The content of F leached into water from carbonate rocks (limestone, dolomite) varies between 4-10 mg/kg and is remarkably higher in clayey dolomite (26.8 mg/kg). The total F content of studied carbonate rocks is mostly 100-400 mg/kg, being highest in clayey dolomite (1100 mg/kg). The concentration of F in seawater (salinity 35‰) is 1.3-1.4 mg/L (Skinner & Turekian, 1973). Calcium carbonate
precipitation dominates the removal of dissolved fluoride from seawater and remarkable amounts of fluorides will be incorporated into clay minerals (Carpenter, 1969). Therefore, the dissolution of fluorides from carbonate rocks is one probable source of fluoride-rich groundwater.

K-bentonites are rich in total F – 1400-4500 mg/kg and several times higher amounts of F (25-52 mg/kg) were leached into water compared to carbonate rocks (Table 5). During the second extraction (0.5 M Tiron) 33-191 mg/kg of F associated with oxidic Fe and Al sites was solubilised from K-bentonites.
Fig. 14. The lithology of studied Silurian core sections and locations of sampled carbonates and K-bentonites. Paatsalu core section after Nestor, 1997; Ikla core section after Nestor & Nestor, 2002; Varbla core section after Nestor, 1994.
Fig. 15. The lithology of studied Ordovician core sections and locations of sampled K-bentonites. The lithology of studied core sections by Leho Ainsaar (unpublished data).
Table 5. The results of the chemical analyses. The total F content of the rocks ($F_{\text{Tot}}$) and F concentrations leached into water ($F_{\text{Water}}$) and Tiron solution ($F_{\text{Tiron}}$). Numbering of samples as shown in Figs. 14 and 15.

<table>
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<tr>
<th>SAMPLE NO.</th>
<th>CORE</th>
<th>DEPTH (m)</th>
<th>STAGE</th>
<th>ROCK</th>
<th>$F_{\text{Tot}}$ (mg/kg)</th>
<th>$F_{\text{Water}}$ (mg/kg)</th>
<th>$F_{\text{Tiron}}$ (mg/kg)</th>
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Thus, the total F contents and the results of the leaching experiments of the current study coincide well with previously published results. The high F concentrations are well preserved in altered volcanic ash beds and contribute to the formation of F-rich groundwater in the Silurian-Ordovician aquifer system.
CONCLUSIONS

Fluorides have widely been in the focus of public and scientific interest because of their important physiological role in the health of a man. Their beneficial effect in decreasing the incidence of dental caries is well known while the toxic effects of fluorides, when occurring in abundances in drinking water, cause increased worries. The fluoride concentrations in the wells analyzed, were found to deviate from the safe content range (0.8-1.2 mg/L) recommended by WHO as well as limit values set by EU and Estonian drinking water standards.

Silurian-Ordovician aquifer system is problematic because it does not meet the requirements for fluoride concentration and therefore is unqualified as a drinking water. The excess of fluoride in groundwater is of special concern in western Estonia because S-O aquifer system is often the only drinking water source in this region. It is possible to delimit an area with anomalously high F⁻ content (up to 7.2 mg/L) which primarily involves Pärnu and Lääne Counties. Health problems arising from excess fluoride intake (dental fluorosis) must be studied in this region.

The content of fluoride in Silurian-Ordovician aquifer system is related with the depth of the wells. High fluoride concentrations are associated with deep groundwaters that have long residence time in the host rock. Some deviations may also exist that 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. The long open interval of the bored well enables the mixing and dilution of waters with different salinity and fluoride content. Therefore, the higher F⁻ contents are related to deep wells with short screens.

The fluoride dissolution and deposition in groundwater is controlled by chemical type of water, which varies considerably in the study area. High fluoride concentrations are associated with HCO₃-CI-Na or HCO₃-CI-SO₄-Na type waters. Groundwater characterized by HCO₃-Na type has always very
high fluorine content. As the concentration of calcium in groundwater increases the concentration of fluorine decreases.

Probable geological source of fluoride is the leaching of clayey carbonate rocks and clay-rich K-bentonite beds. The interlayers of K-bentonite have been recorded in Adavere and Jaani Stages of Silurian system in the study area. The layers of volcanic ashes have been also found in Kukruse, Haljala, Keila and Pirgu Stages from the cross-sections of Ordovician system.

Because of the toxicity of fluoride it would be necessary to undertake a systematic and detailed study of the relationship between water chemistry and the host lithology.

Groundwater abstracted from wells is directly, without fluoride removal, distributed between consumers. Because of that the location and the depth of new water supply wells must be selected very carefully to avoid need for later construction of expensive raw water treatment facilities and increase in the price of water. The wells that are operating at the moment should be carefully mapped and monitored, if needed, water treatment should be provided or the wells closed.
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Joogivee kvaliteedi-ja kontrollinoosed ning analüüsimeetodid. 2001. SOMm RTL 100, 1369.


Joogiveele fluoriidi osas kehtestatud nõuetele mittevastavaks ning seega probleemseimaks veekompleksiks on Siluri-Ordoviitsiumi veekompleks. Nimetatud veekompleksi piires on võimalik välja eraldada anomaalselt kõrge F⁻ sisaldusega ala, mis hõlmab eelkõige Pärnu- ja Läänemaad.

S-O veekompleksi piires võivad fluoriidi sisaldused kõikuda väga laiades piirides. Üldiselt võib väita, et veekompleksi rajatud sügavad puurkaevud annavad F⁻-rikkamat põhjavett kui madalamad. Madalamad puurkaevud jäävad aktiivsema veevahetuse võõsse, kus mikroelementide sisaldus põhjavees on reeglina madalam kui aeglase veevahetusega sügavamates kivimikihtides.

Samuti eksisteerib seos puurkaevu avatud intervalli pikkuse ning fluoriidi sisalduse vahel. Puurkaevu pikk avatud intervall võimaldab erineva mineralisatsiooniga ning erineva fluoriidi sisaldusega vete segunemist ning lahjendumist, mistõttu samasuguse sügavusega puurkaevude puhul, on kõrgemad F⁻-sisaldused seotud madalamad intervallid, mille töötavad intervallid on lühemad.

Põhjavee keemilises koostises eksisteerib rida seaduspärasusi, mis väljenduvad hüdrogeokeemilises võõndilisuses. Veetüüpide pindalaline muutlikkus, mis on tingitud mitmetest geoloogilistest teguritest (vetjuhtivate kivimite mineralogilis-geokeemiline koostis, lasumissügavus, hüdrodünaamiline taustsüsteem, paleogeograafilised tingimused) määrab ka vees esineva mirkoelementide koosluse. Fluoriidi esinemine põhjavees on seotud mitmete makrokomponentide (Ca²⁺, Na⁺, Cl⁻, HCO₃⁻) sisalduse ja keskkonna pH-ga. Seega võib põhjavee keemiline tüüp kontrollida F⁻-lahustumist ja väljasettimist vees.

Arvestades F⁻ toksilisust, tuleks süvendatult ja komplekselt uurida S-O põhjaveekompleksi kui Lääne-Eesti peamise joogiveeallika vee ning veekompleksi moodustavate kivimite keemilist koostist. Vältimaks suuri kulutusi fluoridi ärastamiseks toorveest, tuleks enne uue puurkaevu rajamist uurida piirkonna hüdrogeoloogilisi ning geoloogilisi tingimusi.