Chemical peculiarities of the Silurian–Ordovician and Cambrian–Vendian aquifer systems in Estonia: an overview of hydrochemical studies

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Abstract. The chemical composition of groundwater was studied and plausible reasons for its peculiarities were evaluated on the basis of long-term groundwater monitoring data. Fluoride and boron anomaly was distinguished in the Silurian–Ordovician aquifer system in western Estonia. The chemical type of groundwater controls the dissolution of fluorides and boron in water. Their concentrations are highest in deep groundwater having long residence time in the host rocks. The dissolution of carbonate rocks and clayey K-bentonite beds are the sources of F in groundwater. Barium anomaly in the Cambrian–Vendian aquifer system occurs in northeastern Estonia, where the intrusion of saline groundwater from the weathered crystalline basement contributes to the formation of Ba-rich groundwater. The overexploitation of fresh groundwater has resulted in the increase in groundwater salinity, however, detectable intrusion of seawater into the Cambrian–Vendian aquifer system is ruled out by the stable isotope signature.

INTRODUCTION

Groundwater is one of the most important natural resources in Estonia as it provides two thirds of the drinking and domestic water supply. It is the drinking water source for most of Estonia's towns and settlements, except Tallinn and Narva where groundwater resources are limited and therefore surface water is mainly used. Approximately 75% of the inhabitants use the public water supply; the rest obtain their water from shallow drilled or dug wells. During the last 15 years the water consumption has reduced by more than a half and is currently 50 million m^3 per year (Narusk & Jürimägi 2008). The reason for this is primarily decrease in industrial production, and increase in the price of water, resulting in a more sustainable usage of drinking water by the population and the reduction of leakage from the water supply systems. Owing to decreasing water consumption, more attention can be paid to water quality problems.

The chemical composition of groundwater abstracted for drinking purposes is generally closely related to local geology. The groundwater chemistry is controlled, among other factors, by the lithological composition of water-bearing rocks and geochemical processes that occur in the saturated zone. Besides, the water quality is influenced by the intrusion of present-day seawater into coastal areas and pumping-induced upward migration of deeper saline groundwater in deep-seated aquifer systems. These processes lead to an increase in the content of certain dissolved chemical species, as well as to the overall change in chemical water composition. Thus, the geochemical peculiarities of water-bearing rocks and pumping-induced groundwater deterioration may locally restrict the use of groundwater as a source of drinking water supply. The purpose of this paper is to summarize and present the main outcomes of the hydrochemical studies performed by the authors in 2001–09.

GEOLOGICAL SETTING AND HYDROGEOLOGY

Estonia is situated in the northwestern part of the East European Platform. Its sedimentary beds, lying on the southern slope of the Baltic Shield, are declined southwards at about 2–4 m per kilometre. The Estonian crystalline Palaeoproterozoic basement is overlain by Neoproterozoic (Vendian) and Palaeozoic (Cambrian, Ordovician, Silurian, and Devonian) sedimentary rocks (Fig. 1) covered by Quaternary deposits (Raukas & Teedumäe 1997).

Hydrogeologically Estonian sedimentary rocks form a typical artesian basin, where five aquifer systems (Middle Devonian, Middle–Lower Devonian, Silurian–Ordovician, Ordovician–Cambrian, and Cambrian–
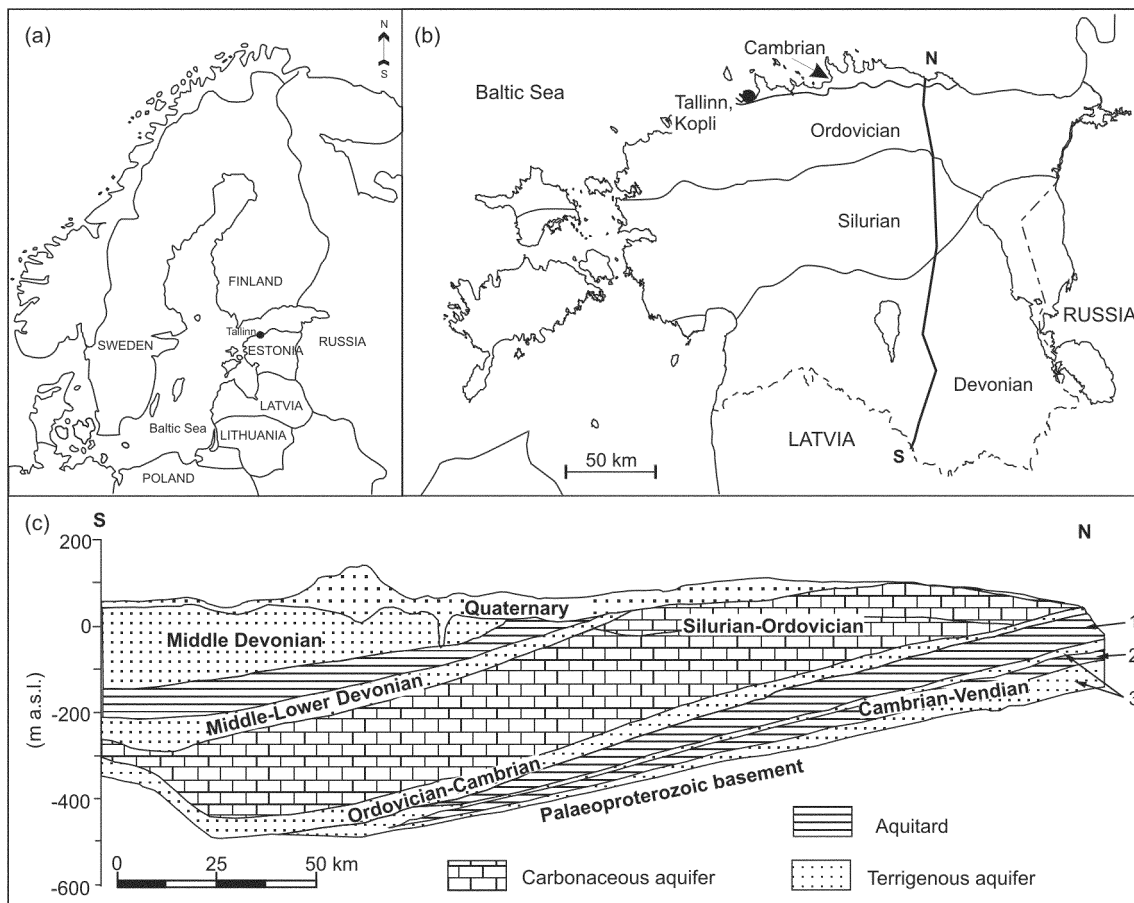
Fig. 1. (a) Schematic map showing the location of Estonia. (b) Geological map of Estonia with the position of the line of the cross section. (c) North–south cross section of major hydrogeological units of Estonia. 1, Voronka aquifer; 2, Kotlin aquitard; 3, Gdov aquifer.

Vendian) are isolated from each other by impervious beds (Fig. 1). The aquifer systems differ from each other in distribution, bedding conditions, hydraulic parameters, and chemical composition. Quaternary deposits consisting predominantly of glacial till and glaciolacustrine and glaciofluvial sand form the uppermost aquifer system, which is used as a drinking water source mostly in private households.

The Silurian–Ordovician aquifer system (S–O) 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. It consists of diverse limestone and dolomite with clayey interlayers. The upper portion of the water-bearing rocks with the thickness of 30 m is largely fractured and cavernous. Silurian and Ordovician carbonate rocks contain 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 (Perens & Vallner 1997). The aquifer system has a characteristic HCO_3–Ca–Mg and HCO_3–Mg–Ca water type with total dissolved solids (TDS) mainly below 0.6 g/L in its upper 30–50 m thick portion. In coastal areas and at greater depths the content of Cl^- and Na^+ in groundwater increases and the HCO_3–Cl–Na–Mg–Ca type water with TDS between 0.3 and 1.5 g/L is widespread (Perens et al. 2001).

The deepest economically important Cambrian–Vendian aquifer system (Є–V) is distributed throughout Estonia, except the Lokno–Mõniste uplift area in southern Estonia. The water-yielding portion of the aquifer system consists of sand- and siltstones with interlayers of clay. There is an obvious difference between the cross sections of the Cambrian–Vendian aquifer system in western Estonia and those in the east. In the eastern part of the country, up to 53 m thick clays of the Kotlin Formation (V_2kt) divide the aquifer system into two aquifers (Voronka and Gdov). The aquifer system is

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mostly confined by 60–90 m thick clays of the Lontova Formation, which has a strong isolation capacity due to its low transversal conductivity of 10^{-7} to 10^{-5} m/d (Vallner 1997). In places the aquitard is penetrated by ancient buried valleys. The Cambrian–Vendian aquifer system is underlain by the Palaeoproterozoic crystalline basement; its cracks and fissures contain a small amount of water but it is not exploited. The lower portion of the basement serves as an impermeable base layer for all the overlying aquifer systems (Vallner 1997). In southern and central Estonia the aquifer system contains relict saline groundwater of marine origin with TDS values up to 22 g/L. Cl^- and Na^+ predominate over all other ions in this zone (Karise 1997). In northern Estonia the aquifer has a characteristic $Cl–HCO_3–Na–Ca$ and $HCO_3–Cl–Ca–Na$ composition with TDS mainly below 1.0 g/L (Perens et al. 2001). The Cambrian–Vendian aquifer system is besides the surface water the major source of public water supply in northern Estonia.

THE SILURIAN–ORDOVICIAN AQUIFER SYSTEM

Fluorides and boron in groundwater

Fluorine and boron have for a long time been in the focus of public and scientific interest because of their important physiological role in the health of man. Fluorine is a common element of the earth's crust, which is present in the form of fluorides in a number of minerals (fluorite, apatite) and rocks. During calcium carbonate precipitation dissolved fluoride is removed from seawater and will be incorporated into carbonate rocks (Carpenter 1969). Fluoride is associated with volcanic or fumarolic gases, and in some areas these may be important sources of fluoride for natural water (Cronin et al. 2003; Weinstein & Cook 2005). Fresh volcanic ash may be rather rich in F, and ash that is interbedded with other sediments could later contribute to F concentrations in groundwater (Hem 1985). Fluoride is known to have both beneficial and adverse effects on humans, depending on the total intake. 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 (Grobler et al. 1986; ADA 2001; Billings et al. 2004). According to the EU Directive 98/83/EC (EC 1998), as well as the Estonian requirements for drinking water quality (Joogivee 2001), the limit value for fluoride is 1.5 mg/L.

The natural sources of boron in groundwater are water–rock (carbonate rocks, evaporates, bentonites) interaction, sea water encroachment, mixing with fossil brines and hydrothermal fluids (Hem 1985; Vengosh

et al. 1994; Molina et al. 2003). The process of sorption and desorption of boron to mineral surfaces is an important control on its concentration in groundwater (Goldberg et al. 1993). High boron levels have been shown to cause irritation of the upper respiratory tract in humans (Wegman et al. 1994) and the disturbance of the reproductive system (Fail et al. 1998). The highest officially permissible boron concentration in drinking water in Estonia is 1.0 mg/L (Joogivee 2001). This value is often exceeded in western Estonia where boron-rich groundwater may cause mild gastrointestinal irritation (Saava 1998).

Sixty drinking water supply wells trapping the Silurian–Ordovician aquifer system in Estonia were sampled for major ions as well as F^- and B during the hydrochemical mapping performed in 2005–06. An analysis of the regional distribution of fluoride concentration shows great variation among different parts of the country (Fig. 2).

Over 46% of analyses do not meet the drinking water requirement. In eastern Estonia as well as in northern Estonia the fluoride content of groundwater is low. Thus, the population in the northern and central parts of the country consumes the water with optimal fluoride concentration. However, in some cases fluoride contents exceed the limit value set for drinking water in central and eastern Estonia. Excess fluoride in groundwater is most typically found in wells of southwestern and western Estonia, where analysed fluoride contents reach up to 6.1 mg/L. This is the region where Silurian and Ordovician limestones and dolomites occur and the Silurian–Ordovician aquifer system is the only drinking water source. The same pattern in regional fluoride distribution has been revealed by a tap water study (Karro et al. 2006; Indermitte et al. 2007), where 735 samples were collected from water distribution systems over the entire Estonian territory.
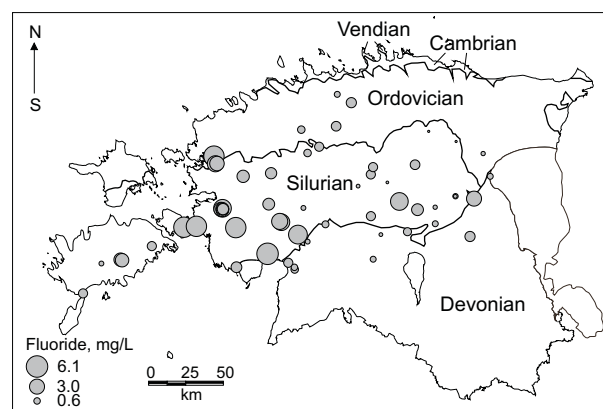

Fig. 2. Spatial distribution of fluoride in the Silurian–Ordovician aquifer system.

Fluoride concentrations are relatively independent of the other water-soluble components, but have noteworthy correlation with boron contents (Fig. 3). The highest F values coincide with anomalously high B concentrations (up to 2.1 mg/L), which have also been measured in the wells of western Estonia. Since the ocean water contains abundantly boron (4.4 mg/L) beside fluorides, the correlation between these two elements in groundwater is anticipated. Good relationship ($R^2 = 0.72$) of F and B contents in groundwater points to a similar origin (marine, volcanic) and hydrochemical behaviour of those elements.

The natural concentrations of fluoride and boron in groundwater depend on the geological, chemical, and physical characteristics of the aquifer, the action of the other chemical compounds, and the depth of water abstraction wells. Major ion chemistry of groundwater in the Silurian–Ordovician aquifer system is examined as a whole using the Piper diagrams (Fig. 4). Marked differences in relations between main cations and anions within the aquifer system can be followed in the diagram. Both the concentrations of fluorides and boron are closely correlated to variations in groundwater chemical type. Several authors (Handa 1975; Lahermo et al. 1991; Saxena & Ahmed 2001) have shown that groundwaters with high F^- contents are generally of Na–HCO_3 type, poor in Ca^{2+}. The groundwater in the Silurian–Ordovician aquifer system is mainly of HCO_3–Ca–Mg type and owing to the high Ca^{2+} contents, quite low amounts of F^- may be mobilized. The highest F^- and B concentrations prevail in wells with low Ca^{2+} content (Fig. 4). Generally, the contents of Na^+ and Cl^- increase with depth and the groundwater changes towards the HCO_3–Cl–Na
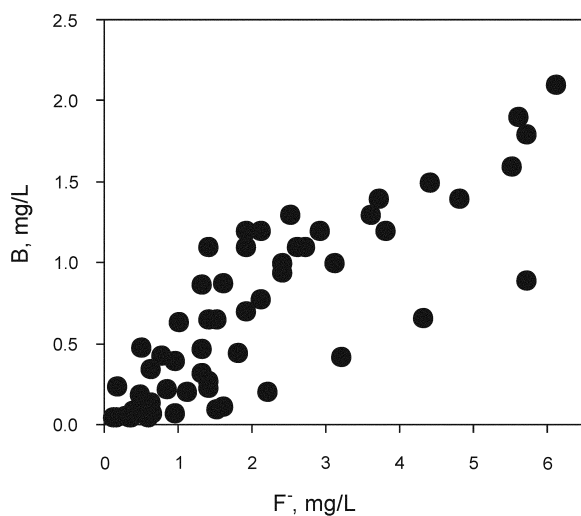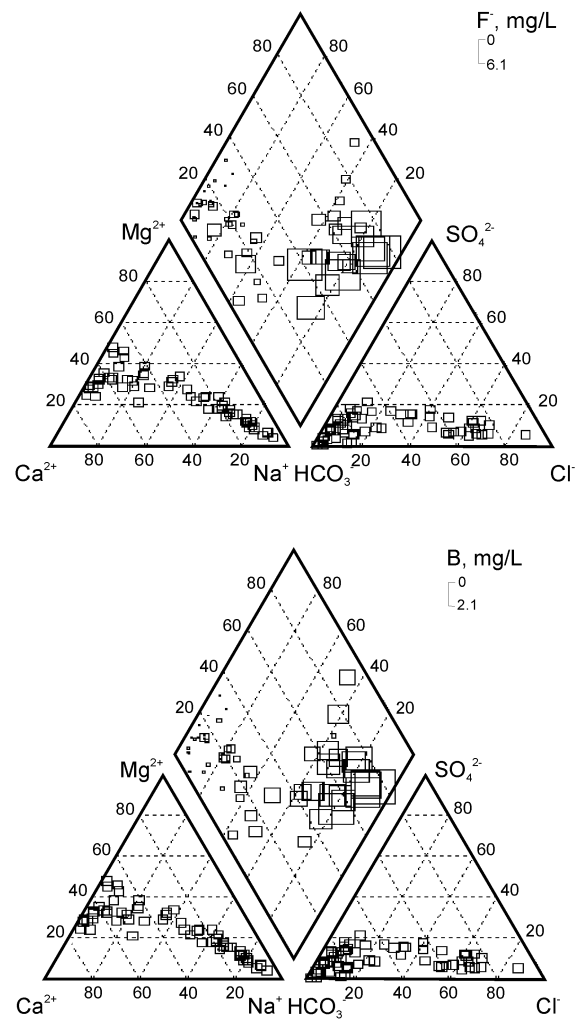

Fig. 4. Piper diagrams reflecting the chemical type of groundwater and proportional content of F^- and B.

chemical type. Accordingly, geochemically favourable conditions for high dissolved F^- and B in water prevail in deeper portions of the Silurian–Ordovician aquifer system due to the slow water exchange and long-term water–rock interaction.

Geological sources of fluorides in groundwater

The Ordovician sequence in Estonia consists of shallow-water open shelf carbonates – clayey limestones and marlstones, with the exception of its basal part which is represented by terrigenous sediments: silty and clayey sandstones and graptolite argillites. The Silurian sequence consists mainly of carbonate rocks – limestones, dolomites, and marlstones. Besides, the Ordovician and Silurian carbonate rocks contain 2–40 cm thick K-bentonite beds, whose composition is similar to Scandinavian bentonite

Fig. 3. Bivariate plot of fluoride content versus boron content in the Silurian–Ordovician aquifer system.

layers (Bergström et al. 1995; Huff et al. 1998; Kiipli et al. 2001). Estonian K-bentonites are composed of altered volcanic material mixed up with terrigenous material (Kiipli et al. 1997). Volcanic gases and tephra are rich in fluorine (Barclay et al. 1996; Cronin et al. 2003; Weinstein & Cook 2005), thus clay-rich K-bentonite beds provide adsorption and ion exchange sites for F^- ions.

In order to study the natural fluoride sources, limestone, dolomite, and K-bentonite samples were analysed using a sequential leaching method with previously boiled 18-megohm water and 0.5 M aqueous Tiron (Haamer & Karro 2006). The Tiron is regarded to dissolve F associated with oxidic Fe and Al sites of the bentonites (Biermans & Baert 1977). Also the total fluorine contents in rock samples were determined. The content of F leached into water varies between 4–10 mg/kg (limestone, dolomite) and 25–51 mg/kg (K-bentonite). During the second extraction (0.5 M Tiron) 55–126 mg/kg of F was solubilized from K-bentonites. The total F content of studied carbonate rocks is mostly 100–400 mg/kg, being highest in clayey dolomite (1100 mg/kg). K-bentonites are rich in total F – 2800–4500 mg/kg. Thus, the dissolution of fluorides from host rocks contributes to the formation of fluoride-rich groundwater in the Silurian–Ordovician aquifer system. So far, the natural sources of B in the aquifer system have not been studied. However, the results of the groundwater mapping show that high B concentrations prevail in regions where groundwater is rich in F.

THE CAMBRIAN–VENDIAN AQUIFER SYSTEM

Major ion chemistry

The chemical evolution of groundwater in aquifers along flow paths depends on the age distribution with depth and distance, geological conditions, and the lithological composition of water-bearing rocks and sediments. However, considering the extremely low velocity of groundwater flow in the Cambrian–Vendian aquifer system and taking into account both the palaeohydrological situation during the Late Pleistocene (Vaikmäe et al. 2001), as well as the contemporary situation in northern Estonia where the groundwater geochemistry is influenced by intensive abstraction, the overall picture of the aquifer system is rather complicated and not yet well understood.

All processes described in the previous section have led to a complicated picture of Cambrian–Vendian groundwater chemistry, which can be described by the areal distribution of the TDS value in groundwater. The TDS ranges from 0.2 g/L to 22 g/L in Estonia, while the length of the groundwater flow line is up to 250 km. Therefore, the best way to follow the changes in natural baseline characteristics is to use the Piper diagram (Fig. 5).

Four major groundwater types can be distinguished in the diagram based on their chemical composition (Marandi 2007).

(1) The Cl–Na type, which can be interpreted as a saline baseline or relict groundwater of the Cambrian–Vendian aquifer system. Relict groundwater of the Cl–Na type is widely distributed in the Cambrian–Vendian aquifer system in southern and central Estonia but also in the Voronka aquifer in north-eastern Estonia. It may be very old and was probably formed long before the last ice age. The TDS concentrations in waters of this type are higher than 2 g/L, which means that they are mineral waters. The $\delta^{18}O$ values of this groundwater type are higher than −14‰.

(2) The Ca–Na–HCO_3–Cl or Ca–Na–Cl–HCO_3 type water, which is the 'fresh baseline' water of glacial origin, recharged during the last glaciation (Vaikmäe et al. 2008). The chemical composition of this type of water was formed through the water–rock interaction during the last more than 10 ka. This water type has the largest spatial distribution, spreading from the northern coast to central Estonia, and also shows mixing with other water types (except with type 1) on the Piper diagram. The $\delta^{18}O$ values range between −19 and −22‰, indicating the formation of the water under cold climatic conditions. Strongly depleted stable isotope composition is the most characteristic feature for this groundwater type.

(3) The Cl–HCO_3–Na groundwater type, interpreted as a mixture of glacial melt water with some remains of relict saline groundwater. This groundwater type is mainly distributed in northeastern Estonia, where the Kotlin clays divide the Cambrian–Vendian aquifer system into two aquifers and the overlying clays reach their maximum thickness in Estonia. A freshening effect by glacial melt water is also reflected in the ^{18}O content, which here is below −19‰ (Fig. 6).

(4) The Ca–HCO_3 groundwater type found in northern Estonia, in areas around ancient buried valleys, where the intrusion of fresh groundwater from overlying aquifers and/or rainwater takes place. The intensity of such fresh water intrusions varies spatially and temporally, depending on the extent of groundwater exploitation near the valleys. In areas where groundwater drawdown is significant, fresh water intruded the aquifer through the buried valleys and caused changes in the groundwater chemistry and isotopic composition (Fig. 6). The $\delta^{18}O$ values are usually higher than −14‰ due to freshwater intrusions and the TDS contents are low (200–500 mg/L).
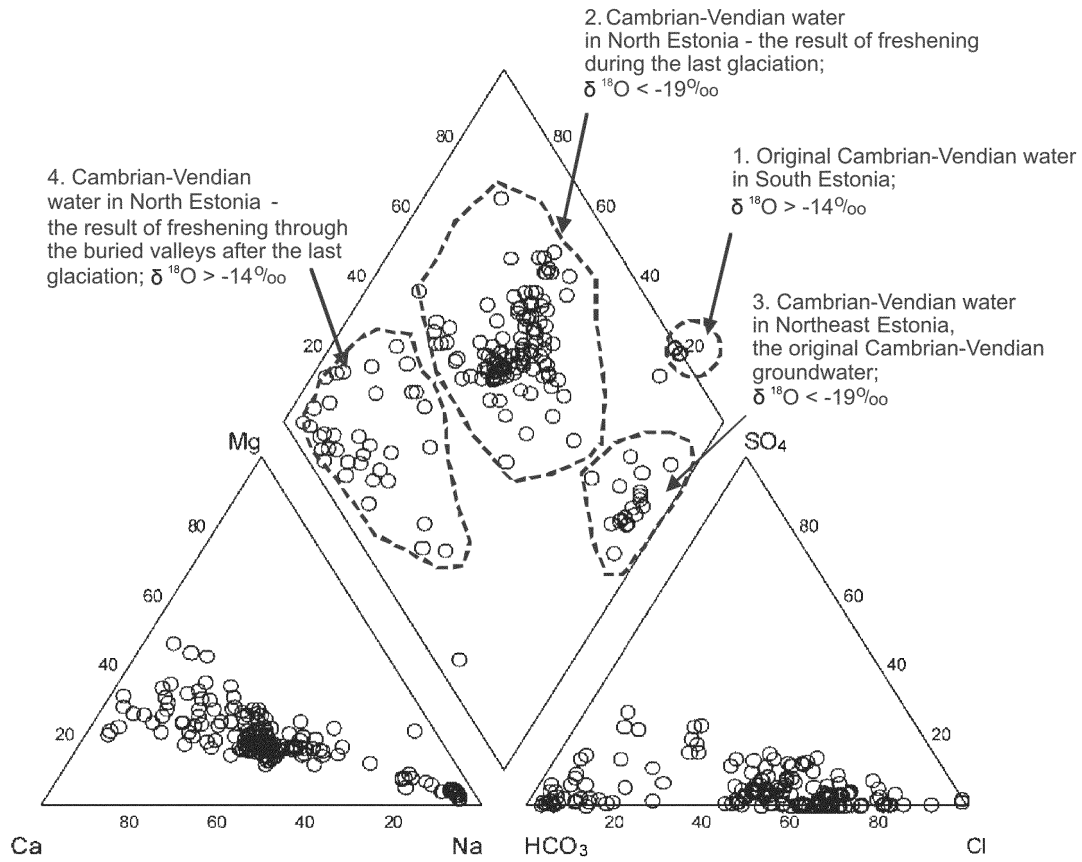
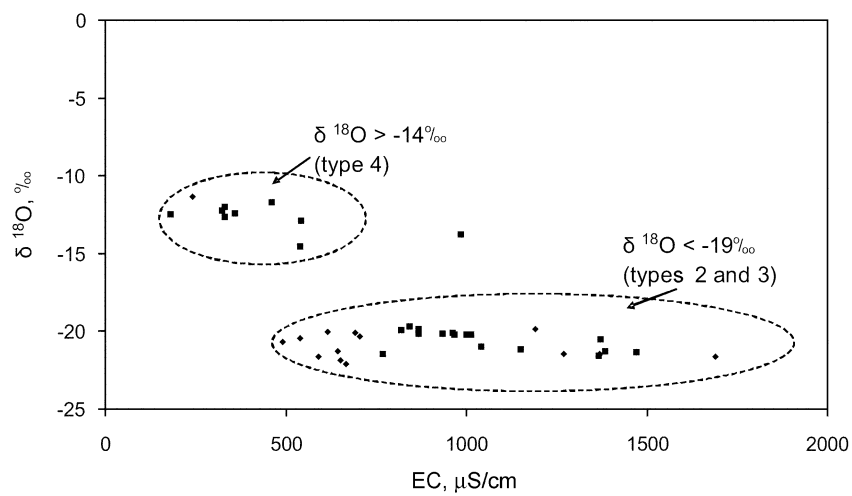**Fig. 5.** Piper plot reflecting major chemical types of groundwater in the Cambrian–Vendian aquifer system.

Fig. 6. $\delta^{18}O$ versus electrical conductivity (EC) values in the Cambrian–Vendian aquifer system.

The use of isotopes and major ion composition in hydrochemical interpretations

The most serious consequence of intensive groundwater use in northern Estonia is the formation of regional depressions in potentiometric levels (Perens & Vallner 1997). In order to investigate the impact of intensive groundwater abstraction on water quality, a study was performed in the Kopli area in northern Estonia, where overexploitation of the Cambrian–Vendian aquifer system has resulted in 3-fold increase (from 500 to 1500 mg/L) in the TDS content and concentration of major ions in groundwater (Karro et al. 2004).

Three possible sources of salinity in the Cambrian–Vendian aquifer system on the Kopli Peninsula were analysed: (1) intrusion of present-day seawater, (2) pumping-induced upconing of salt water from below the fresh water, and (3) a combination of the two. Major ion chemistry in groundwater was examined using the Piper diagram (Fig. 7). Water types (I–III) on the diagram represent an attempt to systematize the chemistry of groundwater, and the progression from group I to III represents the evolution of waters with an increasing degree of water–rock interaction and mixing with brackish water from the crystalline basement.

The abstracted groundwater is depleted in sodium relative to seawater, and the abundance of calcium and potassium in groundwater relative to seawater (Fig. 7) points rather to the upconing of saline deep-seated ground-
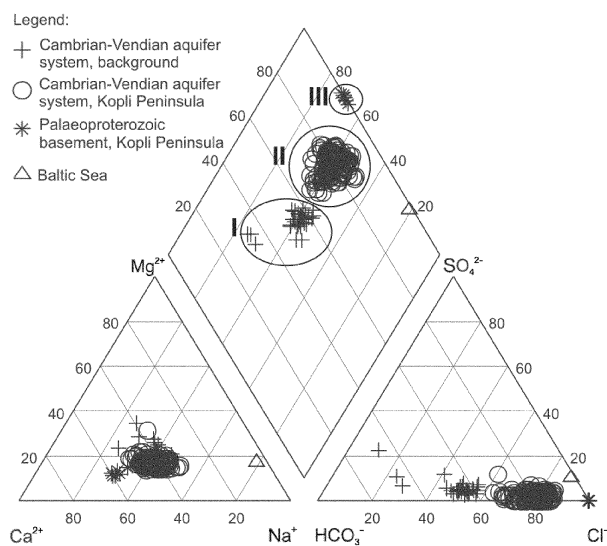
water than to lateral seawater intrusion. The changes in water chemistry can be explained by the mineralogical and chemical characteristics of the reservoir rocks and water exchange with the underlying water-bearing weathering core of the fractured crystalline basement, which hosts brackish Ca–Cl type water.

The theory of upconing of saline deep-seated groundwater was also supported by the results of isotope investigations carried out in the Kopli area. The oxygen isotope composition of groundwater in most aquifer systems of Estonia ranges from -11.0 to -14‰ (Vaikmäe et al. 2001). However, the groundwater in the Cambrian–Vendian aquifer system has a heavily depleted oxygen isotope composition (Fig. 8). The values of $\delta^{18}O$ vary mainly from -18.1 to -22.0‰ in northern Estonia (Vaikmäe et al. 2001; Mokrik & Mažeika 2002). At the same time, the long-term mean annual $\delta^{18}O$ values in contemporary precipitation in Estonia are -10.4‰ (Punning et al. 1987). Groundwater samples from six wells on the Kopli Peninsula were analysed for their isotopic composition in 2001. Low $\delta^{18}O$ values (from -19.8 to -21.6‰) in the Cambrian–Vendian aquifer system are indicative of recharge in cold conditions, whilst low ^{14}C concentrations (from 2.5 to 5.4 pmC) are indicative of a long residence time of groundwater.

Fig. 7. Piper diagram showing the ionic composition of Cambrian–Vendian groundwater from wells in northern Estonia (Group I), on the Kopli Peninsula (Group II), and in the Palaeoproterozoic basement (Group III). For reference, data of the Baltic Sea are presented.
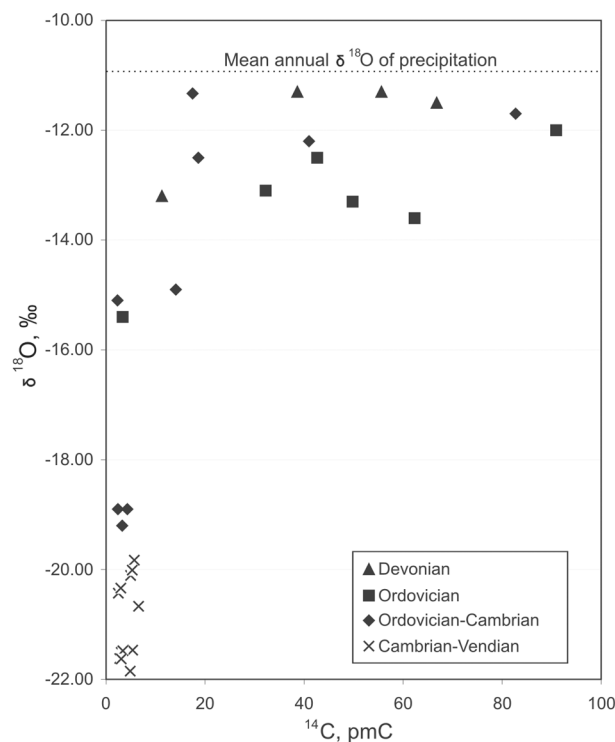
Fig. 8. Distribution of $\delta^{18}O$ values of groundwater in different aquifers of Estonia according to their ^{14}C concentrations.

Barium anomaly in the Cambrian–Vendian aquifer system

The Estonian drinking water standard (Joogivee 2001), which is compatible with the Drinking Water Directive of the European Union (98/83/EEC) does not limit barium concentration. However, it cannot be supposed that the EU standard does not consider barium toxic. The Environmental Protection Agency of the United States (US EPA) has set the maximum concentration limit (MCL) for barium in the drinking water at 2.0 mg/L. The World Health Organisation has published a guideline value of 0.7 mg/L for barium (WHO 2004). According to the EPA, the exposure to barium at levels above the MCL for relatively short periods of time may cause gastrointestinal disturbances and muscular weakness in people. A lifetime exposure at levels above the MCL may lead to high blood pressure diseases. If barium levels were found to be consistently above the MCL, the water suppliers would have to use water treatment methods for barium removal (EPA 1995).

Several studies have indicated a low content of micro-compounds in the Cambrian–Vendian aquifer system. However, an anomalously high content of barium was discovered during investigations in the northeastern area. Groundwater was sampled systematically from west to south in northern Estonia in order to follow any lateral geochemical changes in its composition during the comprehensive study in 2001 and 2002. At every sampling point groundwater samples from both the Gdov and Voronka aquifers were analysed in order to follow any vertical changes (Karro & Marandi 2003; Marandi et al. 2004).

The results showed that general lateral changes in the chemical composition as well as in the type of groundwater are much greater than those in the vertical

direction at certain sampling points. The prevalence of Ca and HCO₃ ions in groundwater decreases eastwards where Na and Cl ions become dominant. The contents of Na^+ and Cl^- in the Cambrian–Vendian aquifer system vary from 26 to 405 mg/L and from 46 to 700 mg/L, respectively, being highest in the eastern part of the country. The concentrations of Ca^{2+} (6–188 mg/L) and HCO_3^- (103–264 mg/L) are somewhat higher in the western part of the studied area. The highest SO_4^{2-} values are also detected in the western margin of the area.

The content of barium in groundwater varies from 0.07 to 6.37 mg/L. Territorially, an evident pattern in the distribution of barium can be observed. The marginal parts of the studied area are characterized by low barium content, while high barium values (0.41–6.37 mg/L, median 2.41 mg/L) concentrate in the Kunda–Rakvere–Kohtla-Järve region, which can be outlined as a Ba-anomaly in the aquifer system (Fig. 9).

Generally, the deep-seated Gdov aquifer is enriched in barium compared to the overlying Voronka aquifer. All high Ba^{2+} values (>2 mg/L) in the Gdov aquifer are associated with the anomaly. Furthermore, some ground-water abstraction wells opening the Cambrian–Vendian aquifer system in its full thickness (both the Voronka and Gdov aquifers) exhibit elevated barium concentrations. The highest barium value (3.77 mg/L) in such a well type has been detected in a deep well reaching 3 m into the crystalline basement.

The results of the geochemical mapping of Finland (Koljonen 1992) showed that the highest barium values (>650 ppm) in bedrock are associated with granulites, granitoids, gneisses, mica schists, and granites. According to Klein et al. (1983), the concentration of barium in the gneisses of the Estonian crystalline basement (700 ppm) exceeds the average concentration in the crust (500 ppm).
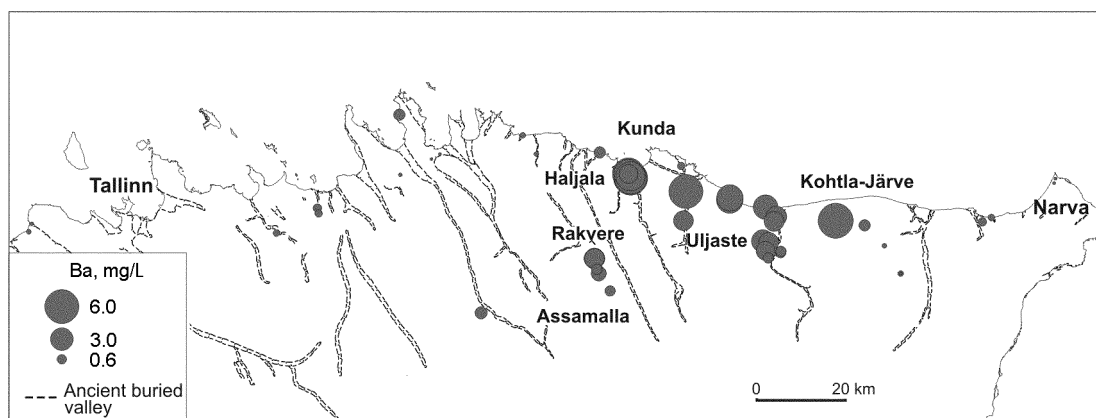

Fig. 9. The content of Ba^{2+} in the Cambrian–Vendian aquifer system in northern Estonia.

The crystalline basement comprises groundwater in its upper weathered and fissured portion and is in places hydraulically connected with the overlying Cambrian–Vendian aquifer system. Therefore the potential source of barium is most probably ion exchange with the water-bearing underlying weathering core, but also the major ion chemistry of groundwater plays an important role in generating a high concentration of barium in ground-water. The hydrochemical modelling, performed by the PHREEQC software, showed that sulphate and bicarbonate ions are the main compounds that precipitate barium ion out of the solute, although bicarbonate ion has practically no influence when barium ion concentrations are low (<10 mg/L). Therefore in case of a low (<3 mg/L) concentration of sulphate ion, the barium ion content in the Cambrian–Vendian aquifer system can be higher than the limit value (2 mg/L) set for drinking water by the EPA. The content of chloride ion, on the contrary, contributes to an increased solubility of barium ion (Marandi et al. 2004).

CONCLUSIONS

Drinking water supply in Estonia is based mainly on groundwater and in many areas, especially in the Silurian–Ordovician aquifer system, the natural concentrations of boron and fluorides exceed considerably the limit values set for drinking water quality. The results of the hydro-geochemical studies enabled us to delimit the F and B anomaly (up to 7.2 and 2.1 mg/L, respectively) in western Estonia. The chemical type of groundwater is an important factor controlling the dissolution of F and B in water. The highest concentrations of those elements are detected in deep wells where the groundwater has a long residence time in the host rock. Fluoride exhibits a good relationship with the B content, which points to a similar geochemical behaviour of those elements. The dissolution of carbonate rocks and clayey K-bentonite beds, providing adsorption and ion exchange sites, are the probable sources of fluoride and boron in ground-water.

Barium anomaly with the maximum Ba^{2+} content of 6.37 mg/L has been detected in the Cambrian–Vendian aquifer system that is widely used as a drinking water source in North Estonian towns. Marginal parts of the studied area are characterized by a low barium content, while high values concentrate within the Kunda–Rakvere–Kohtla-Järve region. Clear vertical Ba distribution can be followed – the deep-seated Gdov aquifer is enriched with barium compared to the overlying Voronka aquifer. All high values in the Gdov aquifer are associated with the anomaly. The geochemical modelling results show that sulphate and bicarbonate ions are the main compounds

that precipitate barium ion out of the solution and that the chloride ion contributes to increased solubility of barium ion. The results also showed that in case of a low (<3 mg/L) concentration of sulphate ion, the barium ion content in the Cambrian–Vendian aquifer system can be higher than 2 mg/L. The crystalline basement and its weathering core, which are hydraulically connected with the overlying Vendian and Cambrian terrigenous rocks, are the probable sources of barium and fluorides in groundwater. The intrusion of deep-seated and saline groundwater by intensive exploitation of wells is possible.

The overexploitation of freshwater resources of the Cambrian–Vendian aquifer system on the Kopli Peninsula has resulted in the development of depression of the potentiometric levels and in the increase in the TDS content and concentration of major ions in groundwater. The changes in water chemistry can be explained by the mineralogical and chemical characteristics of the reservoir rocks and water exchange with the underlying water-bearing weathered and fractured crystalline basement. According to the results of isotope analysis, detectable intrusion of modern seawater into the aquifer system is ruled out.

So far, the natural sources of B and Ba in ground-water have not been completely studied. Because of the potential toxicity of barium, fluorides, and boron, it would be necessary to continue a systematic and detailed study of the relationship between water chemistry and the host lithology. The results of hydrochemical research should be transformed to instructions of how to avoid or eliminate the quality problems in the risk areas. In order to prevent salt-water intrusion, the freshwater resources should be exploited by maintaining a balance between groundwater pumping and recharge. The location and depth of new water supply wells must be selected very carefully to fulfil the water quality requirements.

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Siluri-Ordoviitsiumi ja Kambriumi-Vendi veekompleksi põhjavee keemilised iseärasused: ülevaade hüdrokeemilistest uuringutest

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Põhjavee keemilise koostise uuringute tulemused võimaldavad piiritleda kõrge fluoriidi- ja boorisisaldusega ala Siluri-Ordoviitsiumi veekompleksis Lääne-Eestis ning baariumi anomaalia Kambriumi-Vendi veekompleksis Kirde-Eestis. Boori ja fluoriidide esinemist põhjavees kontrollib vee keemiline tüüp. Elementide kõrged sisaldused esinevad sügaval lasuvas aeglase veevahetuse vööndis, kus domineerib Ca-vaene HCO_3-Cl-Na-tüüpi põhjavesi. Fluori geoloogilisteks allikateks on savikad karbonaatkivimid ja K-bentoniitide kihid. Intensiivne pikaajaline põhjavee pumpamine on põhjustanud Kambriumi-Vendi veekompleksi kaevudes vee soolsuse suurenemise ja baariumi anomaalia kujunemise Kirde-Eesti põhjavees. Kõrge baariumisisaldus esineb valdavalt Gdovi veekihis, mis on hüdrauliliselt seotud lamavate lõheliste murenenud aluskorra kivimitega. Põhjavee isotoopkoostise uuringute tulemused välistavad tänapäeva merevee sissetungi võimaluse ja põhjavee soolsuse suurenemise põhjuseks on sügaval lasuva kõrge soolsusega põhjavee intrusioon magedasse põhjaveekihti.