

The occurrence and geological sources of naturally high iron in the Middle Devonian aquifer system, Estonia

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Abstract. Groundwater pumped from the terrigenous Middle Devonian (D₂) aquifer system is naturally rich in iron (Fe), making it a challenge to fulfil the requirements for drinking water quality. The total iron (Fe_{tot}) concentrations are above the limit value set for drinking water (0.2 mg/L) in 81% of the analysed water samples. The highest Fe_{tot} values reach up to 26 mg/L in some locations of southern Estonia. Due to the reducing conditions in the aquifer system, most of the Fe_{tot} concentrations are caused by a high Fe²⁺ content. Infiltrated aerobic water becomes anaerobic and Fe³⁺ reducing along a deep flow path, leading to the downgradient increase in dissolved Fe concentrations. In order to study the natural sources of Fe in the Middle Devonian aquifer system, rock samples from the Narva, Aruküla, Burtneki and Gauja stages were used for chemical analyses and leaching experiments. The whole-rock chemical analyses showed large variation in the Fe₂O₃ content (1.20–9.91%), whereas the values were higher in aquifer-forming siltstones than in sandstones. The amount of the leached Fe in groundwater is partly controlled by the granulometric composition of terrigenous rocks. The highest leached Fe_{tot} (up to 1.7 mg/L) concentrations were detected in the rocks where the share of the sand fraction is over 70%. As a rule, water is abstracted from sandstones having large pores and good groundwater yield, therefore water quality problems could only be solved by installing Fe removal facilities in southern Estonia.

Key words: iron, drinking water, sandstone, siltstone, sedimentary rocks, Middle Devonian aquifer system, Estonia.

INTRODUCTION

Groundwater used in Estonia for drinking purposes is abstracted from different sedimentary rocks, which form a typical artesian basin with five aquifer systems. Water chemistry does not meet the drinking water quality standards in several parts of the country due to the lithological and geochemical peculiarities of the aquifer-forming rocks. The Silurian–Ordovician aquifer system consisting of limestone and dolomite is rich in fluorine and boron (Karro & Uppin 2013). The deep-seated terrigenous Cambrian–Vendian aquifer system exhibits high natural radionuclide (Forte et al. 2010) and barium (Mokrik et al. 2009) concentrations.

Groundwater abstracted from sand- and siltstones of the Middle Devonian (D₂) aquifer system is widely used for water supply in South Estonia (Fig. 1). Naturally high iron concentrations are the major problem in this region, complicating the fulfilment of the EU requirements concerning the drinking water quality. According to the EU

drinking water directive 98/83/EC (European Communities 1998) and Estonian regulation (Ministry of Social Affairs 2001), the iron content in drinking water should not exceed 0.2 mg/L. The deficit or excess of chemical compounds in drinking water may affect physiological processes in the human body and cause several diseases. It has been found that the long-term nutritious iron surplus causes a positive serum iron balance, which leads to an increased oxidative stress (Rehema et al. 1998). Besides, if present in water in excessive amounts, Fe compounds stain laundry and plumbing fixtures, being an objectionable impurity in water supplies. For all those reasons, Fe determinations are commonly included in chemical analyses of water. In order to meet the quality standards set for drinking water, excessive iron should be removed at water treatment plants. The most common processes for iron removal in Estonia include the aeration or adding oxidizing chemicals into water to convert the dissolved ferrous iron to an insoluble ferric iron, which is subsequently filtered out from the water (Hiiob & Karro 2012).

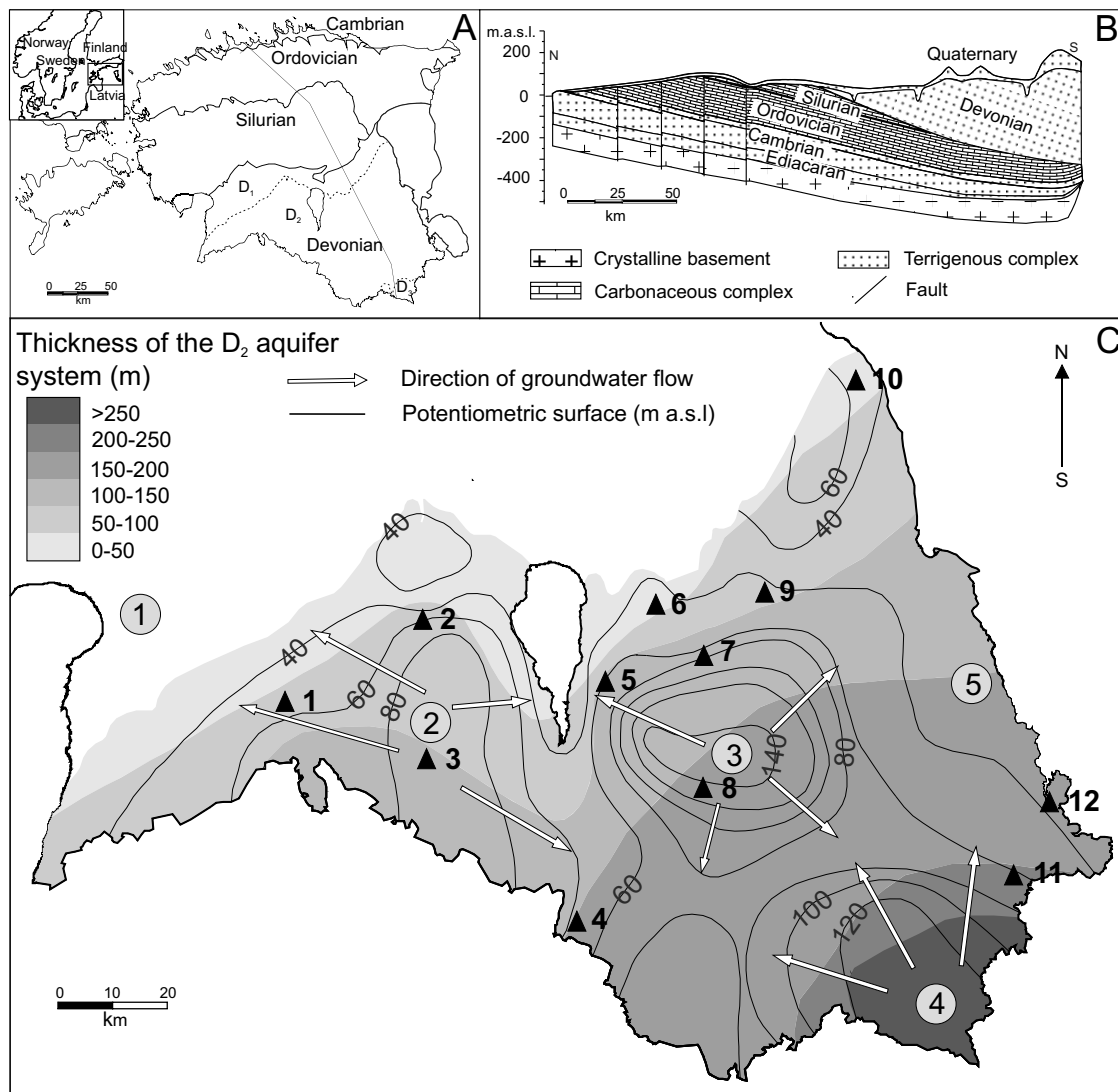


Fig. 1. A, schematic geological map; B, geological cross section of Estonia (N–S); C, the distribution, thickness and potentiometric surface of the Middle Devonian (D_2) aquifer system in South Estonia (after Raukas & Teedumäe 1997; Marandi 2010) and sampling sites (\blacktriangle). Rock samples were collected from the following boreholes and outcrops: 1, Tõlla 1; 2, Viljandi; 3, Karksi; 4, Valga; 5, Valguta 263; 6, Karijärve 304; 7, Elva 262; 8, Otepää 2; 9, Mõra; 10, Pala 75; 11, Piusa; 12, Värskä 1. Relief forms in the study area: 1, Pärnu Lowland; 2, Sakala Heights; 3, Otepää Heights; 4, Haanja Heights; 5, Peipsi Lowland.

The lithological and mineralogical composition of water-bearing rocks and geochemical processes occurring in the saturated zone control the groundwater chemistry (Appelo & Postma 2005). These processes lead to an increase in the content of dissolved chemical species, as well as to the overall change in the chemical water composition. Accordingly, the geochemical characteristics of water-bearing rocks can locally restrict the use of groundwater as a source of drinking water supply.

The content of iron in the Earth’s crust is approximately 5%, but its concentrations in water are

generally small. Iron in elemental form is rare in nature; it tends to form oxides, hydroxides, sulphides and carbonates (Ponka et al. 2007). The availability of iron for aqueous solutions is affected by the presence and solubility of iron-bearing minerals (e.g. pyrite, magnetite, siderite, olivine, amphiboles, glauconite, pyroxenes, biotite) in rocks and sediments. Besides, the probable geological sources of iron are the reduction of hematite (Fe_2O_3) and goethite ($FeO(OH)$) as well as the amorphous $Fe(OH)_3$ filling the pores between the sediment grains (Hem 1985; Appelo & Postma 2005).

The Devonian sedimentary sequence in southern Estonia is mainly composed of sandstones, but includes also carbonate and mixed carbonate–terrigenous complexes and interlayers. The presence of iron as Fe-oxides (hematite and goethite) and Fe-sulphides (pyrite and sphalerite) in Estonian Devonian sand- and siltstones is the result of the detrital input which took place during the primary sedimentation or is related to the later diagenetic processes as cementation and dolomitization (Shogenova & Kleesment 2006). During diagenesis the total iron (Fe_{tot}) content of sediments could increase, decrease or iron could change its valence (Elmore et al. 1993; Mücke 1994; Shogenova 1999; Funkt et al. 2004; Zwing et al. 2005). These processes are mainly controlled by redox potentials of diagenetic fluids. Iron oxides dissolve in suboxic and anoxic (sulphate-reducing) environments, but precipitate in oxidizing conditions (Passier et al. 2001). The reddish-grey colour of the Devonian rocks is due to the Fe(III) mineral coatings around the quartz grains and dispersed distribution of Fe-oxides in dolomite cement (Shogenova & Kleesment 2006).

The form or state in which Fe is found in groundwater mainly depends on the aquifer's oxygen balance. This is related to multiple environmental factors including the geological structure and characteristic of the aquifer, type of soil and bedrock, species of Fe bacteria and the pattern of groundwater flow. Other important factors affecting the Fe content of groundwater are the oxidation/reduction conditions and pH. Generally, the content of dissolved chemical substances increases towards the depth, where the groundwater exchange is slower and the residence time and contact with rock matrix is longer. In anaerobic groundwater, where iron is in the form of Fe^{2+} , concentrations will usually be 0.5–10 mg/L, but concentrations up to 50 mg/L can be found as well (Hem 1985). As groundwater migrates from recharge zones to areas of discharge, different stages in the redox sequences may be recognized, the most important being the removal of oxygen (Edmunds et al. 1984). Iron oxides are soluble and Fe is mobilized as Fe(II) under moderately reducing and acidic conditions. Under oxidizing conditions Fe(III) prevails. This forms insoluble Fe oxyhydroxides at circum-neutral pH (Drever 1997).

The aim of the current research is to assess the concentrations and distribution of Fe in the Middle Devonian aquifer system and to examine the hydrochemical behaviour of this element in groundwater. Secondly, this paper summarizes and presents the outcomes of the geochemical and lithological study of the aquifer-forming Devonian terrigenous rocks as the natural iron source in groundwater. As the studied rock samples originate from different geological units of the Devonian System and in places the number of samples was taken along the vertical geological cross section, the spatial distribution of iron in

Devonian rocks is not discussed in this research. In order to perform the throughout and representative geochemical mapping of Fe, a denser sampling set should be designed. The results of the current study should be taken into account when selecting the location of new water supply wells and developing strategies for safe drinking water supply in southern Estonia.

GEOLOGICAL AND HYDROGEOLOGICAL SETTING OF THE STUDY AREA

Estonia is located in the northwestern part of the East European Platform on the southern slope of the Baltic Shield. The crystalline Palaeoproterozoic basement is covered by the sedimentary rocks belonging to the Ediacaran (Upper Vendian), Cambrian, Ordovician, Silurian and Devonian systems (Fig. 1) and Quaternary deposits.

The groundwater system in Estonia can be divided into three principal units – Quaternary deposits, bedrock and the crystalline basement. Groundwater in sandy and clayey Quaternary deposits is used as the drinking water mainly by private households. The terrigenous and carbonate Palaeozoic and Proterozoic rocks form porous and fissured confined aquifer systems (Upper Devonian, Middle Devonian, Middle–Lower Devonian, Silurian–Ordovician, Ordovician–Cambrian and Cambrian–Vendian), which are isolated from each other with aquitards. The crystalline basement of Estonia contains the saline groundwater in its uppermost portion and is not used for drinking water production.

The households and the enterprises of southern Estonia obtain their drinking water from the Middle Devonian aquifer system (Table 1), which is the most important and easily accessible aquifer in this region. The aquifer-forming terrigenous rocks of the Aruküla, Burtnieki and Gauja stages cover the whole of southern Estonia and are represented by sand- and siltstones. The interlayers of dolomitized and clayey sandstones are locally present in the geological cross section. The maximum thickness of the Middle Devonian aquifer system reaches 250 m and the potentiometric surface of the groundwater lies at 40–140 m a.s.l. (Fig. 1). The lateral hydraulic conductivity of the rocks ranges mainly between 1 and 3 m/d. Groundwater is fresh with the total dissolved solids (TDS) value of 0.2–0.6 g/L and the HCO_3 –Ca–Mg chemical type of water is dominating in the aquifer system (Perens & Vallner 1997).

The Narva Stage with a highly variable lithology (Table 1) is considered as an aquitard between the Middle Devonian and Middle–Lower Devonian aquifer systems, but in several locations it consists of sandstones and yields groundwater. The total thickness of the stage increases from 30 in the north to 109 m in the south and it overlies

Table 1. Stratigraphical (Mark-Kurik & Põldvere 2012) and hydrostratigraphical (Perens & Vallner 1997) background of the rock samples. D_{3sn}–D_{2am}, Snetnaja Gora–Amata aquitard; D₂, Middle Devonian aquifer system; D_{2nr}, Narva aquitard; D₂₋₁, Middle–Lower Devonian aquifer system; No. *, borehole or outcrop number in accordance with Fig. 1C; Sample ID, sample number in the database SARV; nd, no data

System	Aquifer system, aquitard	Regional stage	Formation	Member	Borehole, outcrop (No.*)	Sample No.	Lithology	Depth (m)	Sample ID
Devonian (D)	D _{3sn} –D _{2am}	Amata	Amata						
	D ₂	Gauja	Gauja	Lode Sietini	Piusa outcrop (11)	30	Sandstone	nd	GIT 72909
					Värskä 1 (12)	29	Sandstone	23.0	GIT 76706
		Burtnieki	Burtnieki	Abava Koorküla Härma	Värskä 1 (12)	28	Sandstone	33.3	GIT 76707
					Värskä 1 (12)	27	Sandstone	68.0	GIT 76711
					Värskä 1 (12)	24	Sandstone	96.0	GIT 76717
					Karksi outcrop (3)	25	Sandstone	nd	GIT 109362
					Karksi outcrop (3)	26	Sandstone	nd	GIT 109365
		Aruküla	Aruküla	Tarvastu Kureküla Viljandi	Valguta 263 (5)	20	Sandstone	13.4	GIT 72878
					Värskä 1 (12)	21	Siltstone	109.7	GIT 109360
					Värskä 1 (12)	22	Sandstone	120.5	GIT 76719
					Mõra outcrop (9)	23	Sandstone	nd	GIT 109361
					Pala 75 (10)	17	Sandstone	29.7	GIT 68698
					Valguta 263 (5)	19	Sandstone	52.7	GIT 72880
					Valga 324 (4)	18	Sandstone	136.8	GIT 68665
					Karijärve 304 (6)	13	Sandstone	31.0	GIT 72840
	Karijärve 304 (6)				14	Sandstone	34.4	GIT 72841	
	Viljandi* (2)				10	Clayey siltstone	35.8	GIT 68774	
	Pala 75 (10)	9	Sandstone	41.0	GIT 68703				
	Valguta 263 (5)	16	Sandstone	72.9	GIT 72882				
	Elva 262 (7)	11	Clayey siltstone	77.7	GIT 72821				
	Elva 262 (7)	12	Sandstone	82.8	GIT 72823				
	Otepää 2 (8)	15	Sandstone	180.2	GIT 73070				
	D _{2nr}	Narva	Kernavé	Tõlla 1 (1)	1	Siltstone	8.4	GIT 68767	
				Tõlla 1 (1)	2	Sandy siltstone	22.9	GIT 68771	
				Karijärve 304 (6)	5	Sandstone	71.2	GIT 72847	
				Valguta 263 (5)	8	Siltstone	82.7	GIT 72883	
Elva 262 (7)				4	Sandstone	104.0	GIT 72827		
Valga 324 (4)				3	Sandstone	176.8	GIT 68673		
Otepää 2 (8)				6	Sandstone	185.9	GIT 72832		
Otepää 2 (8)				7	Siltstone	188.6	GIT 72833		
	Leivu								
	Vadja								
D ₂₋₁	Pärnu	Pärnu	Tamme Tori						

the sandstone of the Pärnu Stage. The sequence of the stage corresponds to the Vadja, Leivu and Kernavé formations (Mark-Kurik & Põldvere 2012; mostly termed ‘members’ in older publications). The basal part (Vadja Formation) is characterized by a complex of dolomitic marl, silty clay and dolomite which often includes pyrite- or sphalerite-filled vugs. The middle, Leivu Formation is prevailed by dolomitic marl and the upper, Kernavé Formation consists of dolomite-cemented silty sandstone with interlayers of siltstone, dolomitic marl and clay (Kleesment & Mark-Kurik 1997).

The Aruküla Stage is equivalent to the Aruküla Formation that consists of reddish-brown cross-bedded sandstone with the thickness of 66–97 m and forms the lowermost part of the Middle Devonian aquifer system (Table 1). The formation is subdivided into the Viljandi, Kureküla and Tarvastu members (Mark-Kurik & Põldvere 2012; mostly termed ‘beds’ in older publications). Each member begins with relatively coarse and poorly sorted sandstones but ends with a clayey–silty complex. The lower, Viljandi Member is dominated by very fine sandstones. The Kureküla Member is characterized by

irregularly cemented interbeds of variegated siltstones, pockets of white sandstone, lenses of conglomeratic sandstone and interlayers with large clay pebbles. The section of the Tarvastu Member contains typically conglomeratic interbeds and surfaces and crusts of Fe hydroxide (Kleesment 1994).

The Burtneki Stage with the thickness of 60–90 m corresponds to the Burtneki Formation consisting of light fine-grained weakly cemented cross-bedded sandstones with interlayers of siltstone and clay (Kleesment 1995; Kleesment & Mark-Kurik 1997). The formation is divided into the Härma, Koorküla and Abava members (Mark-Kurik & Pöldvere 2012; mostly termed ‘beds’ in older papers). Each unit begins with relatively coarse-grained light (yellowish, pinkish, greyish and brownish) sandstones and ends with clayey silt layers (Kleesment 1995). Strongly cemented platy lens-shaped interlayers of iron-oxide-rich sandstone are found in the Burtneki Formation. The cement, forming 27–40% of the rock in the middle part of the lens, is composed of hematite and goethite (Shogenova et al. 2009).

The 78–80 m thick Gauja Stage forms the uppermost part of the Middle Devonian aquifer system (Table 1) and is spread in the southeastern part of Estonia. The stage corresponds to the Gauja Formation which is divided into the Sietini and Lode members (Mark-Kurik & Pöldvere 2012). The cross-bedded sandstones of the Gauja Formation are fine-grained. The Sietini Member consists mostly of sandstones, with siltstone in the topmost part. The lower part of the Lode Member is represented by light sandstones; its upper part is dominated by siltstones and clays (Kleesment & Mark-Kurik 1997).

The Middle Devonian aquifer system is covered by the Snetnaja Gora–Amata aquitard in southeastern Estonia. The lowest part of the aquitard (Amata Formation) consists of sandy and silty sediments alternating with clay layers (Kleesment & Mark-Kurik 1997).

MATERIALS AND METHODS

The Estonian Environment Agency (EEA) is responsible for collecting and storing the groundwater monitoring data in Estonia. The database of the EEA (KESE 2020) comprising about 4000 water analyses performed during the last 60 years from the Middle Devonian aquifer system was used in this study. Depending on the purpose of the analysis, the spectrum of chemical parameters studied over the years is very variable. For example, the content of Fe_{tot} has been determined in 2567 cases, both ferric and ferrous iron have been analysed in 550 groundwater samples. However, the dataset of analysed parameters is sufficiently representative in order to study the areal distribution of iron (Fig. 2) and to characterize its hydro-

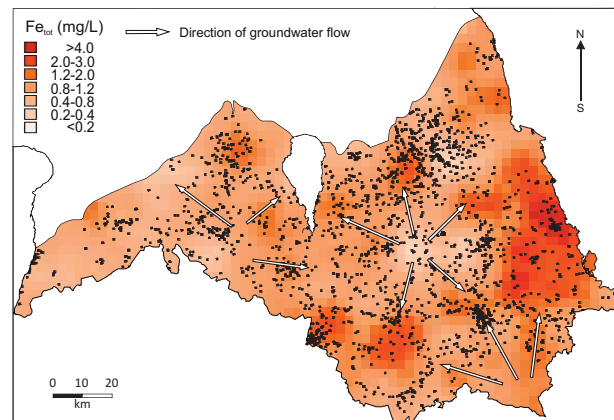


Fig. 2. Spatial distribution of Fe_{tot} in the Middle Devonian aquifer system. The arrows indicate the approximate direction of groundwater flow in the aquifer system. The black dots mark the locations of sampled groundwater abstraction wells.

chemical behaviour in the aquifer system as a whole. Unfortunately, the determination of oxygen content, which is an important parameter when explaining the behaviour of Fe in water, is not included in the routine groundwater monitoring programme.

More than 800 000 units are stored in the national geological collection of Estonia, including among others rock and sediment samples and drill cores. The database SARV, which is used for managing geocollections-related data (e.g. the results of the different analyses), holds records about more than 340 000 collection specimens and rock samples (SARV 2020). The geological collections are open for researchers and the rock samples incorporated into the current study are listed in Table 1 by referring to their ID (specimen number with the institutional abbreviation) in the database SARV. In total, 23 sandstone and 7 siltstone samples from the Narva, Aruküla, Burtneki and Gauja stages (Table 1) were used for chemical analyses and leaching experiments. Analysed rock samples originate from different geological units of the Devonian System and from different localities (Fig. 1). During the further interpretations the results of the leaching experiments and whole-rock analyses were matched with the granulometric data obtained from the database SARV.

Rock samples were analysed for FeO, Fe_2O_3 and other major and minor chemical constituents (SiO_2 , Al_2O_3 , MgO, CaO, Na_2O , K_2O , TiO_2 , P_2O_5 , MnO, Cr_2O_3 , Ba, Sr, Ni, Sc, Zr, Nb, Y). Samples were crushed and pulverized to the 200 mesh and dried at 60 °C prior to analysis. The chemical composition of the rocks was determined using standard ICP–ES techniques; the content of FeO was analysed by titration at Bureau Veritas Laboratories (ACME Labs), Vancouver, Canada.

The methodology by Xu et al. (2006) has been modified and used for leaching experiments. Leaching tests of 18 terrigenous rocks samples were carried out in tightly capped conical polyethylene flasks (500 mL), where 30 g powdered rock samples (mesh size <1 mm) were treated with 300 mL distilled water. Batch dissolution tests were performed at room temperature (20 °C) using a shaker table (GFL 3005) at a constant shaking rate of 150 rpm for 48 h. The leachates (10 mL) were filtered (45 µm resin) and refrigerated until analysis. Leachate samples were analysed for Fe_{tot} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- and SO_4^{2-} using an ion-chromatograph (Dionex ICS-1000) at the Department of Geology, University of Tartu. The accuracy and precision of analyses were tested by running duplicate analyses on selected samples. In addition, the HCO_3^- concentrations of the solutions were determined potentiometrically at the laboratory of the Estonian Environmental Research Centre. Long-term leaching experiments were continued for 14 days, when the second series of leachate samples was taken and analysed by the same methodology. 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 aliquots (10 mL) without significantly changing the water–rock ratio. For data processing, the interpretation and hydrogeochemical assessment of the results, MapInfo Professional and AquaChem were used.

RESULTS AND DISCUSSION

The distribution and hydrochemistry of iron in the Middle Devonian aquifer system

Earlier groundwater mapping reports by the Geological Survey of Estonia (Savitskaja et al. 1996a, 1996b) and the distribution regularities of major components in Estonian groundwater summarized as the hydrochemical atlas of Estonia (Perens et al. 2001) have shown that the high iron content in the groundwater is a widespread problem and in order to fulfil the drinking water quality requirements, in most water intakes iron removal should be carried out. The study by Hiiob & Karro (2012) has shown that the drinking water quality problems in the northeastern corner of Estonia are caused by high iron and manganese contents in abstracted groundwater. However, the same quality problems are common in the entire southern Estonia (Perens et al. 2001), where terrigenous rocks of Devonian age are present in the uppermost part of the geological cross section and water for drinking purposes is abstracted from the Middle and Middle–Lower Devonian aquifer systems. In southern Estonia, water infiltrates through the thick and often clayey Quaternary cover and becomes depleted in oxygen. The high NH_4^+ , Fe^{2+}

and H_2S contents in groundwater are common in deeper portions of the geological profile (Perens et al. 2001), where the anoxic environmental conditions prevail. However, the elevated content of the aforementioned compounds in water distribution systems may also be caused by depreciated wells and pipelines as well as by the activity of anaerobic bacteria. Due to decreased groundwater utilization in Estonia (Karro 2019), water exchange in pipelines is slow in places and stagnant water tends to damage the water supply systems.

According to the 2567 groundwater analyses from 1978 water supply wells in the study area (Fig. 2), the Fe_{tot} content is above 0.2 mg/L in 2071 cases. Fe_{tot} concentrations up to 26 mg/L have been recorded in wells of the Middle Devonian aquifer system. The arithmetic mean of those 2567 Fe_{tot} determinations is 1.38 mg/L and the median value is 0.60 mg/L, pointing to the severe Fe-problem in the groundwater.

The spatial distribution of Fe_{tot} concentrations is delineated in Fig. 2. In spite of the fact that the naturally high iron contents are found in the whole aquifer system, the analysis of the regional distribution of Fe_{tot} concentration shows some variations between different parts of the study area. Preliminary comparison of water chemistry data, the topography of land surface and the potentiometric heads of the groundwater show that high iron areas in southern Estonia coincide with topographically low regions. For example, the highest detected iron values occur in the eastern part of the study area, which forms a part of the Peipsi Lowland (5 in Fig. 1C) and acts as a discharge area for groundwater (Fig. 2). The lowest average Fe concentrations are present in recharge areas, which in the studied region are represented by the Otepää and Haanja heights. Infiltrated aerobic groundwater becomes along a deep flow path anaerobic and Fe^{3+} reducing. Such a redox environment corresponds to the downgradient increase in dissolved Fe concentrations. Preliminary analyses of Fe distribution in groundwater shows that iron contents tend to be lower in the areas of deep ancient buried valleys filled by Quaternary sediments. The reason for this phenomenon is that the mixing of Fe-rich groundwater from the Middle Devonian and Fe-poor water from the Quaternary aquifer system takes place through those valleys.

The chemical type of groundwater controls the occurrence and hydrochemical behaviour of several minor and trace elements in groundwater (Drever 1997; Appelo & Postma 2005). For example, fluoride- and boron-rich waters in Estonian aquifers are slightly alkaline (pH = 7–8), $\text{Cl-HCO}_3\text{-Na}$ and $\text{HCO}_3\text{-Cl-Na}$ chemical type (Karro & Uppin 2013). Groundwater in the Middle Devonian aquifer system is also fresh with the TDS value of 0.2–0.6 g/L, but the dominating water type is $\text{HCO}_3\text{-Ca-Mg}$. Some variations in basic groundwater chemistry could be followed on the Piper diagram (Fig. 3), however, the highest Fe_{tot} concentrations coincide with the samples

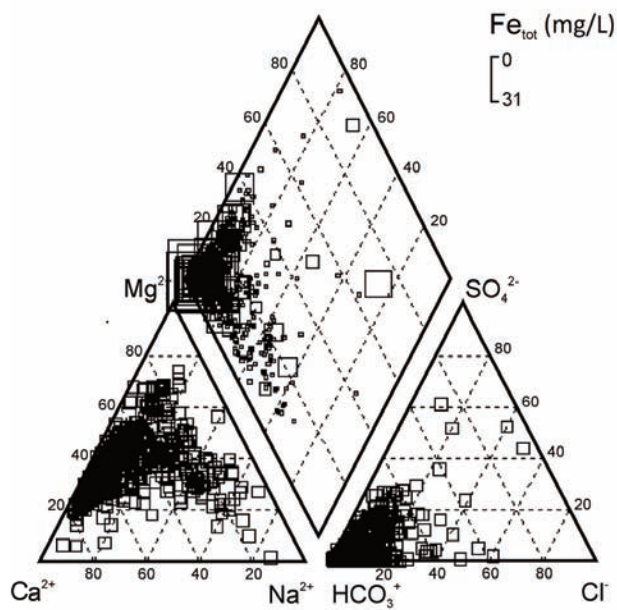


Fig. 3. Piper diagram showing the content of Fe_{tot} as a function of the water type in the Middle Devonian aquifer system. The size of a rectangle refers to Fe_{tot} concentration.

representing the dominating $\text{HCO}_3\text{-Ca-Mg}$ chemical type of water. The terrigenous rocks of Devonian age in southern Estonia are covered by a thick layer of Quaternary sediments. During the infiltration through this thick and mostly clayey layer of sediments, the environmental conditions change from oxidative to reductive. According to water chemistry analyses, the share of Fe^{2+} in the Fe_{tot} content is much higher compared to Fe^{3+} in groundwater (Fig. 4), referring to the prevalence of anoxic environmental conditions in the Middle

Devonian aquifer system. The highest Fe^{2+} values in groundwater (10–26 mg/L) are present in wells, where HCO_3^- concentration varies between 300 and 600 mg/L (Fig. 5). The content of TDS in groundwater increases beside the other major ions also with the increase in the HCO_3^- concentration along the flow path. Thus, the high Fe^{2+} as well as Fe_{tot} values in groundwater occur in discharge areas where groundwater salinity is high.

The concentrations of Fe^{2+} are inversely proportional to the contents of the oxygen-containing ions (SO_4^{2-} and NO_3^-) in groundwater (Fig. 5). The last ones, especially NO_3^- , are characteristic of the aerobic environment and high NO_3^- values dominate in shallow drilled wells located in recharge areas. The pH values of the Middle Devonian aquifer vary mostly between 7 and 8 (Fig. 5). The highest Fe concentrations occur within this pH range and both Fe^{2+} and Fe^{3+} contents exhibit a decreasing trend towards the more alkaline and acidic environment.

Generally, the concentration of dissolved chemical constituents in groundwater is higher in greater depths, characterized by slow water movement and consequent prolonged water–rock interaction. However, when comparing the groundwater chemistry data with the technical information of the wells, one can see no direct relation between the well depth and the iron values in abstracted water (Fig. 4). Consequently, high iron contents could be found within the entire 250 m thick Middle Devonian aquifer system. Sandstones and siltstones alternating with each other in the geological cross section are the main aquifer-forming rocks in the study area (Table 1). Thus, in order to identify their contribution as the natural iron sources in groundwater, the whole-rock chemical analyses as well as the laboratory leaching tests were performed.

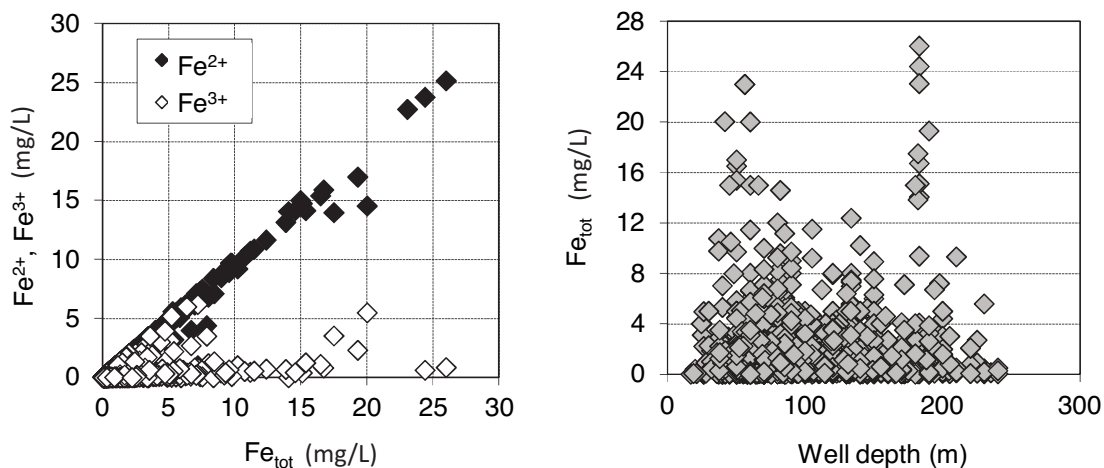


Fig. 4. The proportion of Fe^{2+} and Fe^{3+} in Fe_{tot} concentration and bivariate plot of the Fe_{tot} content versus well depth in groundwater.

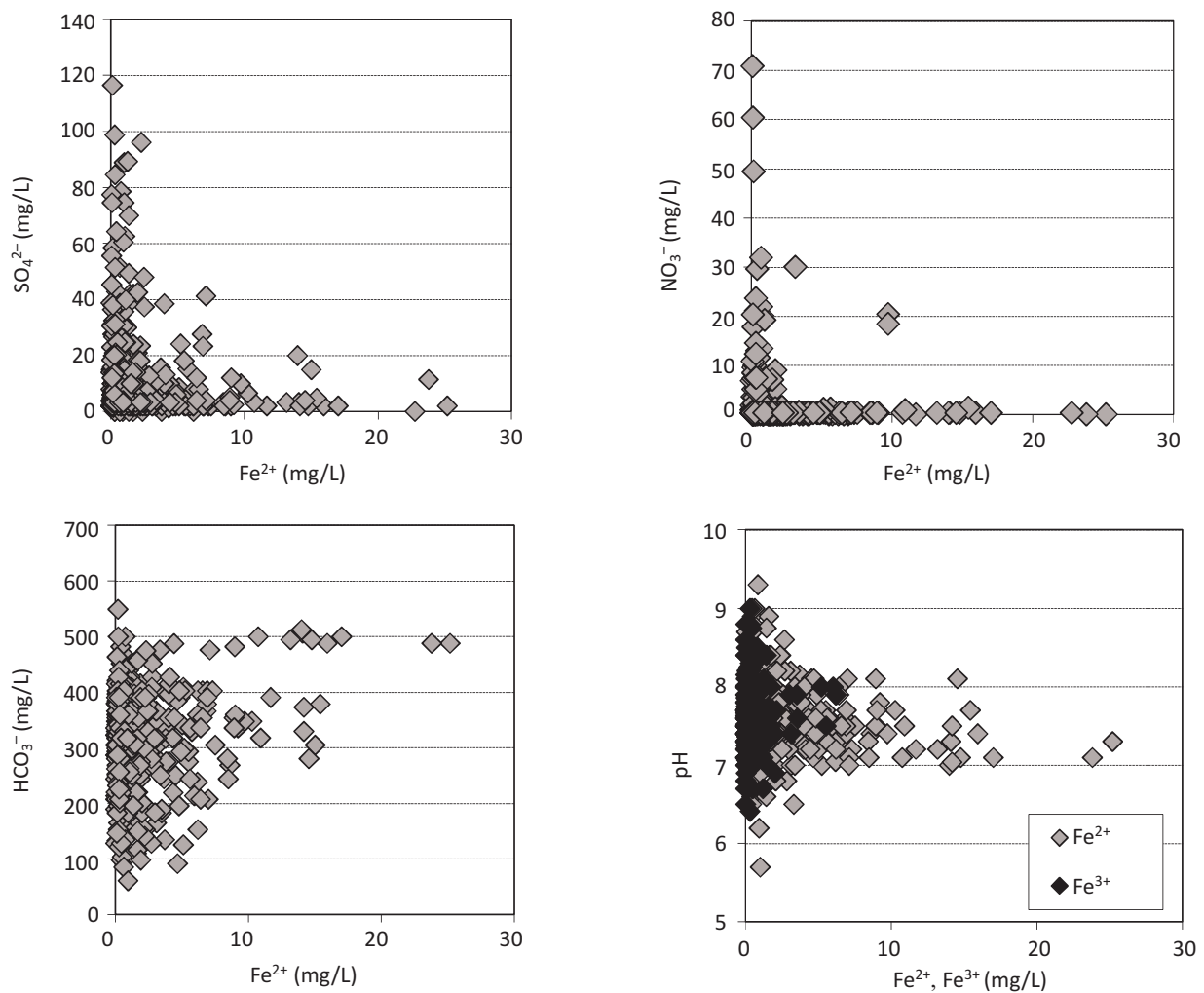


Fig. 5. Fe^{2+} and Fe^{3+} concentrations in groundwater plotted against the SO_4^{2-} , NO_3^- and HCO_3^- contents and pH value.

Iron is considered to be an aesthetic indicator and indicating parameter (Ministry of Social Affairs 2001). It means that such parameters are mainly used for the monitoring purposes and the results are used as the source of information for the water quality marks and implementing additional treatment in the case when the value of the analysed parameter is over the norm. Although the high iron concentration in drinking water is not considered as a health risk, iron ‘overload’ in drinking water may cause vomiting, bleeding and circulatory disorders (Bun-ei et al. 2006) or oxidative stress (Rehema et al. 1998). Therefore, the control of drinking water quality is critical in preventing aesthetic as well as some negative health effects to consumers.

Geological sources of iron in the Middle Devonian aquifer system

The iron content of Devonian rocks is related to the detrital input during primary sedimentation or diagenetic products formed during cementation, dolomitization and

authigenic mineral growth. Iron minerals underwent chemical alteration during diagenesis and are partly corroded and dissolved. Fe (III) minerals became dominant due to oxidation, low water table and arid climate, which prevailed during diagenesis. The red coloration of Devonian rocks is due to hematite coatings of quartz grains and dispersed distribution of Fe-oxides occurring in the form of films, matrix or pore filling (Shogenova & Kleesment 2006).

The leaching of the host rocks is considered to be a major natural source of Fe in groundwater (Hem 1985), therefore, the chemical composition of aquifer-forming rocks was examined. The studied terrigenous rocks are represented by sandstones and siltstones with cement consisting of clay, dolomite and iron-bearing minerals. The content of SiO_2 is well associated with the lithology of the studied rocks, being higher in sandstones than in siltstones (Fig. 6, Table 2) and pointing to the dominance of quartz and feldspars as the main rock-forming minerals in sandstones. The content of SiO_2 decreases with the

Table 2. The results of the chemical analyses of the rock samples. Units – %, Sc – ppm. The numbering of the rock samples is in accordance with Table 1

Sample No.	Lithology	SiO ₂	Al ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	Fe ₂ O ₃	FeO	Sc	LOI
1	Siltstone	69.8	10.9	2.1	1.3	0.1	6.5	0.6	4.94	1.11	10	3.3
2	Sandy siltstone	71.4	7.1	3.0	3.8	0.1	5.2	0.6	1.76	0.82	5	6.7
3	Sandstone	78.7	8.8	0.9	0.2	0.1	6.0	0.4	3.25	0.93	6	1.4
4	Sandstone	72.7	6.1	3.1	4.1	0.1	4.5	0.3	1.77	0.78	5	7.0
5	Sandstone	75.7	6.1	2.4	3.1	0.1	4.8	0.4	1.43	0.68	3	5.8
6	Sandstone	80.4	7.7	0.9	0.8	0.1	5.5	0.4	2.13	0.85	5	1.8
7	Siltstone	76.0	9.8	1.1	0.8	0.1	6.7	0.5	3.00	0.80	7	1.5
8	Siltstone	77.2	7.1	1.7	2.1	0.1	5.2	0.4	2.17	0.71	5	3.8
9	Sandstone	88.7	3.7	0.7	0.8	0.1	2.6	0.2	1.81	1.05	3	1.4
10	Clayey siltstone	53.8	17.8	3.5	0.3	0.1	8.1	0.9	9.91	1.40	18	5.1
11	Clayey siltstone	54.0	13.4	4.9	3.6	0.1	6.2	0.7	7.07	0.98	13	9.6
12	Sandstone	80.4	6.4	1.4	1.8	0.1	4.9	0.4	1.32	0.62	4	2.9
13	Sandstone	59.3	5.8	5.3	6.9	0.1	3.5	0.4	5.60	2.47	8	12.8
14	Sandstone	65.7	8.8	3.6	4.2	0.1	5.5	0.5	2.70	0.88	8	8.5
15	Sandstone	87.9	4.9	0.3	0.5	0.1	3.6	0.3	1.66	0.71	3	0.4
16	Sandstone	88.7	4.4	0.3	0.2	0.1	3.1	0.4	1.98	0.81	3	0.7
17	Sandstone	77.5	7.8	1.5	1.2	0.1	4.8	0.4	3.38	1.31	7	2.9
18	Sandstone	83.9	6.8	0.7	0.5	0.1	4.7	0.4	1.62	0.96	4	1.0
19	Sandstone	89.5	4.0	0.3	0.3	0.1	2.7	0.3	1.78	0.94	3	0.8
20	Sandstone	88.3	4.5	0.4	0.6	0.1	2.5	0.3	2.07	1.10	4	0.8
21	Siltstone	67.4	11.6	2.4	1.2	0.1	4.1	0.7	6.34	0.70	10	5.9
22	Sandstone	92.3	2.9	0.2	0.1	0.1	1.6	0.2	1.62	0.84	2	0.8
23	Sandstone	88.4	4.4	0.5	0.3	0.1	2.9	0.2	1.84	0.85	3	1.3
24	Sandstone	94.9	1.9	0.1	0.1	0.1	1.1	0.1	1.35	1.01	1	0.3
25	Sandstone	85.3	6.3	0.6	0.1	0.1	3.1	0.3	2.50	0.97	5	1.5
26	Sandstone	88.9	4.5	0.3	0.1	0.1	2.6	0.2	1.94	1.01	3	1.3
27	Sandstone	93.9	2.7	0.1	0.1	0.1	1.5	0.1	1.20	0.79	1	0.2
28	Sandstone	92.8	2.9	0.1	0.1	0.1	1.6	0.2	1.37	0.86	2	0.8
29	Sandstone	92.8	2.7	0.1	0.1	0.1	1.5	0.2	1.42	0.89	2	1.0
30	Sandstone	97.4	0.5	0.0	0.0	0.0	0.2	0.1	1.08	0.85	1	0.7

increase in the silt and clay fraction and thus in the share of clay minerals in the rocks. According to whole-rock chemical analyses, the Fe₂O₃ content varies largely (1.20–9.91%) in the studied rock samples (Table 2), being higher in siltstones than in sandstones. The FeO content of Devonian rocks is rather low, in the range of 0.62–2.47%. The Fe₂O₃ contents of aquifer-forming rocks increase with the increasing silt and clay content of the rocks (Fig. 6); in contrast, FeO concentrations do not exhibit a similar

relationship. The higher values of Fe₂O₃ in siltstones point to the fact that clay minerals play an important role as the source of iron in the rocks.

The bivariate plots (Fig. 7) show that the Fe₂O₃ contents in the rocks correlate positively with the Sc and TiO₂ concentrations. Scandium and TiO₂ are typical constituents of clay minerals (Kabata-Pendias 2001). Thus, iron in the studied rock samples is partly bound as Fe-oxyhydrates on the illite- and illite-smectite-type minerals.

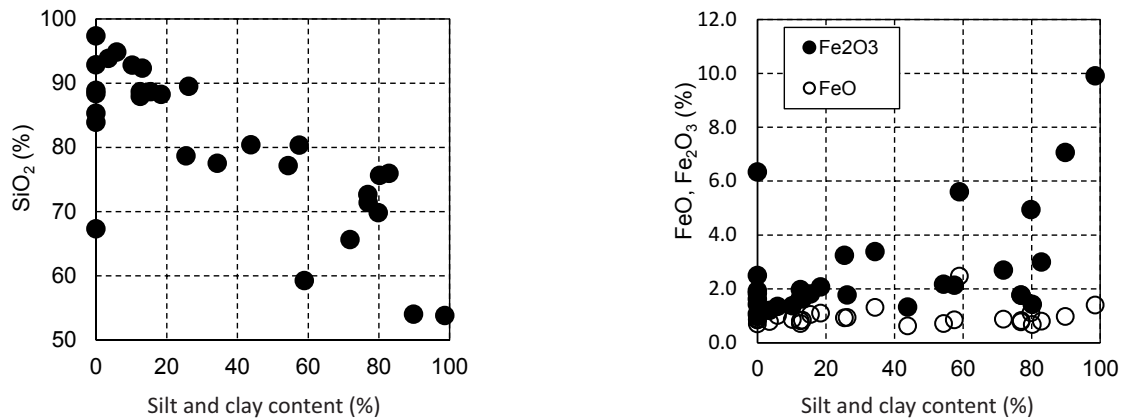


Fig. 6. Bivariate plots showing the SiO_2 , FeO and Fe_2O_3 contents versus the silt and clay content of terrigenous rocks.

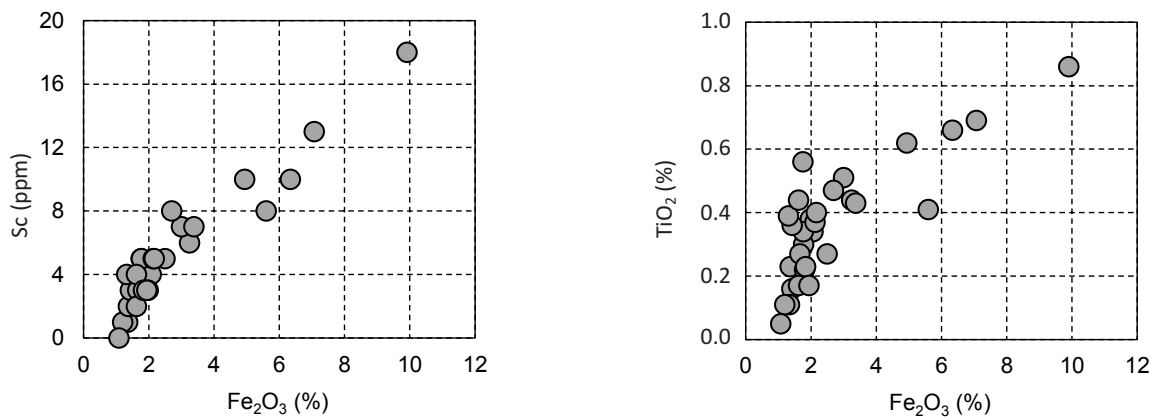


Fig. 7. Bivariate plots showing the Sc and TiO_2 contents versus the Fe_2O_3 contents of rocks.

Besides clay minerals, some iron is associated with carbonate cement in Devonian rocks (Shogenova & Kleesment 2006). Loss on ignition (LOI) as a method for estimating the organic and carbonate content of sediments is widely used when performing whole-rock analysis (Heiri et al. 2001). The LOI values determined within the current study (Table 2) vary from 0.2% to 12.8% and there is no clear difference between sandstones and siltstones when comparing their LOI contents. However, the lowest LOI values were recorded in sandstones, which allows us to assume that in some cases the iron content of sandstones is somewhat lower due to the low presence of carbonate cement.

The granulometric composition of terrigenous rocks varies considerably within the studied geological units, thus the trends described above are clearly observable both in the Aruküla and Narva stages (Fig. 8). The Burtņieki Stage, which is mainly composed of grains belonging to sand fraction, exhibits low Fe_2O_3 and FeO contents.

The dissolution degree of chemical elements, including Fe, into groundwater depends on several factors such as the chemical and mineralogical composition of rocks, groundwater chemistry, the time available for water–rock interaction, etc. (Brown et al. 2000; Appelo & Postma 2005). In order to estimate and compare the contribution of the different rock types as the sources of Fe in water, the impact of other environmental factors (e.g. differences in groundwater chemistry) should be minimized. Simple laboratory batch dissolution tests enable creating the uniform conditions for leaching experiments. In this study, 18 crushed rock samples were leached in distilled water for 2 and 14 days. The results of the tests, focusing on Fe_{tot} concentrations in leachates, are summarized in Table 3.

After two days of leaching, Fe_{tot} concentrations varied between 10 and 1500 $\mu\text{g/L}$ in the leachates. The highest amounts of Fe_{tot} were leached out of the sandstones of the Aruküla, Gauja and Burtņieki stages with the sand content over 70% (Fig. 9). A basic assumption is that the concentrations of Fe in the leachates depend on the

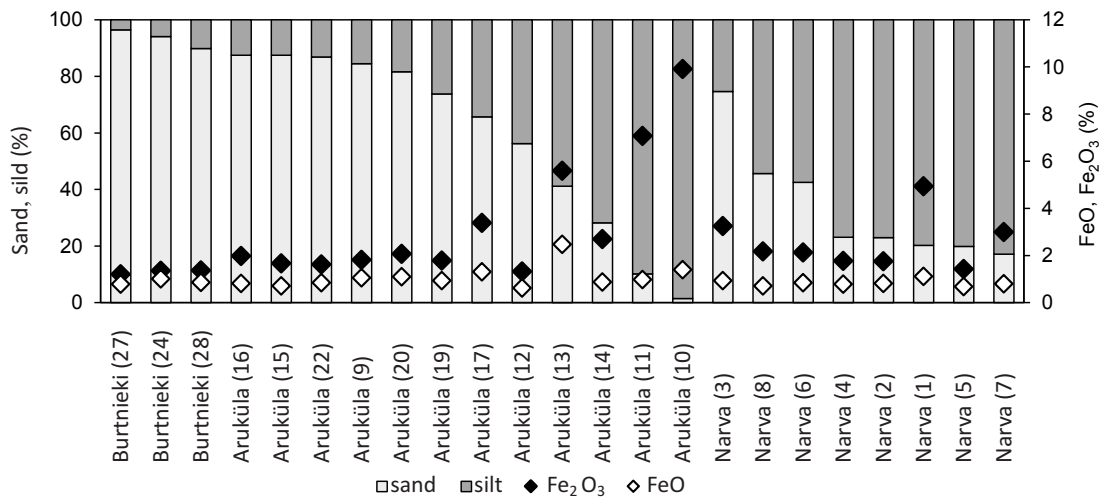


Fig. 8. The share of sand and silt fractions and the content of Fe_2O_3 and FeO in the studied Devonian rock samples. The numbering of the rock samples is in accordance with Table 1.

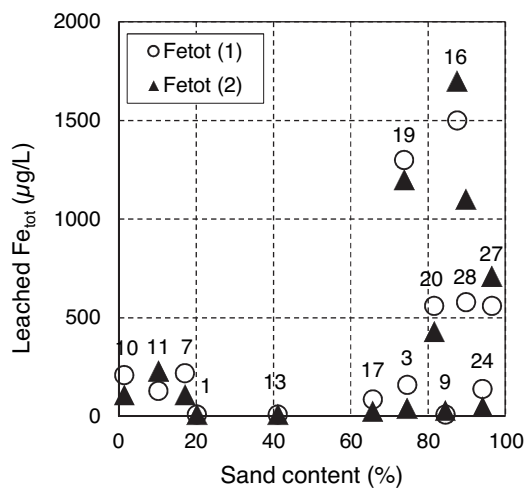


Fig. 9. The leached Fe_{tot} concentrations versus sand content of rocks. Fe_{tot} (1), concentrations after 2 days of leaching; Fe_{tot} (2), concentrations after 14 days of leaching. The numbering of the rock samples is in accordance with Table 1.

abundance of this element in rocks. However, those sandstones exhibit a lower Fe_2O_3 content compared to more clayey sediments. After 14 days of leaching, Fe_{tot} concentrations in the solutions exhibited an increasing trend in sandstones (Fig. 9, Table 3), but in many cases, mostly in rocks where silt and clay fractions dominate, a decrease or no change in leached Fe_{tot} concentrations was observed. Besides, substantial amounts of Fe were leached out during the first two days of the test. Thus, it could be concluded that the circulation of water in large

pores of sandstones is more intensive, leading to higher leached Fe contents. The preliminary XRD and SEM analyses showed that in clayey material the leached Fe is adsorbed to the colloidal clay and is fixed in Fe-oxyhydrates (goethite-type minerals).

Insofar as water abstraction wells are mainly drilled into sandstones with high porosity and good groundwater yield in the Middle Devonian aquifer system, the water quality problems concerning the naturally high Fe in Estonia could be solved only by installing the treatment facilities. In order to fulfil the requirements of drinking water quality (0.2 mg/L), Fe removal is mainly achieved by aeration or adding oxidizing chemical compounds into water to convert the dissolved ferrous iron to an insoluble form of ferric iron, followed by filtering (Hiiob & Karro 2012).

CONCLUSIONS

The terrigenous Middle Devonian aquifer system is the drinking water supply of the southeastern Estonian population. The major water quality concern is associated with a high iron content in abstracted water, which in places reaches up to 26 mg/L. The concentration of Fe_{tot} is above the limit value for drinking water (0.2 mg/L) in 81% of the studied 2567 water samples. High Fe_{tot} concentrations in wells are in most cases caused by elevated Fe^{2+} contents, pointing to the reducing conditions in groundwater. The lowest Fe concentrations are present in recharge areas and highest in discharge areas, referring to the increase in dissolved Fe concentrations along the groundwater flow path.

Table 3. The granulometric composition, contents of Fe₂O₃ and FeO in aquifer-forming rocks and the leached Fe_{tot} concentrations in solutions after 2 and 14 days of leaching experiments. The numbering of the rock samples is in accordance with Table 1. na, not analysed; nd, no data

Sample No.	Lithology	Rock samples				Leachates (µg/L)	
		Granulometry (%)		Whole-rock chemistry (%)		2 days	14 days
		Sand	Silt	Fe ₂ O ₃	FeO	Fe _{tot}	Fe _{tot}
1	Siltstone	20.2	79.8	4.94	1.11	10	10
2	Sandy siltstone	23.0	77.0	1.76	0.82	na	na
3	Sandstone	74.6	25.4	3.25	0.93	160	41
4	Sandstone	23.1	76.9	1.77	0.78	na	na
5	Sandstone	19.8	80.2	1.43	0.68	na	na
6	Sandstone	42.5	57.5	2.13	0.85	na	na
7	Siltstone	17.1	82.9	3.00	0.80	220	110
8	Siltstone	45.7	54.3	2.17	0.71	na	na
9	Sandstone	84.5	15.5	1.81	1.05	10	32
10	Clayey siltstone	1.4	98.6	9.91	1.40	210	110
11	Clayey siltstone	10.2	89.8	7.07	0.98	130	230
12	Sandstone	56.2	43.8	1.32	0.62	na	na
13	Sandstone	41.1	58.9	5.60	2.47	10	10
14	Sandstone	28.2	71.8	2.70	0.88	na	na
15	Sandstone	87.5	12.5	1.66	0.71	na	na
16	Sandstone	87.5	12.5	1.98	0.81	1500	1700
17	Sandstone	65.7	34.3	3.38	1.31	86	26
18	Sandstone	nd	nd	1.62	0.96	na	na
19	Sandstone	73.8	26.2	1.78	0.94	1300	1200
20	Sandstone	81.6	18.4	2.07	1.10	560	430
21	Siltstone	nd	nd	6.34	0.70	10	10
22	Sandstone	86.9	13.1	1.62	0.84	na	na
23	Sandstone	nd	nd	1.84	0.85	na	na
24	Sandstone	94.1	5.9	1.35	1.01	140	50
25	Sandstone	nd	nd	2.50	0.97	650	650
26	Sandstone	nd	nd	1.94	1.01	na	na
27	Sandstone	96.5	3.5	1.20	0.79	560	710
28	Sandstone	89.8	10.2	1.37	0.86	580	1100
29	Sandstone	nd	nd	1.42	0.89	320	140
30	Sandstone	nd	nd	1.08	0.85	1100	1300

The natural groundwater chemistry is controlled by the lithological composition and geochemistry of water-bearing rocks. The iron content of Devonian sandstones and siltstones is related to the Fe minerals, which occur in the form of films, matrix or pore filling and are responsible for red coloration of rocks. The Fe₂O₃ content varied largely (1.20–9.90%) in the studied rock samples, being higher in siltstones than in sandstones. However, the highest leached Fe_{tot} concentrations (1000–1700 µg/L) were detected in sandy terrigenous rocks, where large pores enhance the circulation of groundwater and leaching

of iron. Thus, the leached Fe in groundwater is at least partly controlled by the granulometric composition of terrigenous rocks. Generally, water supply wells are drilled into porous sandstones to ensure good groundwater yield, but according to the outcomes of the current study, it is highly probable to encounter water quality problems in those wells.

In order to prevent the water quality problems, it is necessary to continue the study of the relationship between groundwater chemistry and aquifer-forming rocks. The results of the current study show that in future, if it is

necessary to construct new water supply plants based on the groundwater from the Middle Devonian aquifer system, the need for the installation of an iron removal system is quite probable. Problems with water quality are more serious in groundwater discharge areas, where iron concentrations in water tend to be higher than in recharge areas.

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Raua esinemine ja selle looduslikult suurte sisalduste geoloogilised allikad Kesk-Devoni veekompleksis

Enn Karro, Kaire Veeperv, Mariina Hiiob ja Marge Uppin

Kesk-Devoni (D₂) veekompleks, mille moodustavad Gauja, Burtneki ja Aruküla lademete liivakivid ning aleuoliidid, levib kogu Lõuna-Eestis ja on seetõttu piirkonna üheks olulisemaks joogivee allikaks. Veekompleksi peamiseks kvaliteediprobleemiks on looduslikult suur rauasisaldus, mis ulatub kohati 26 mg/L. Analüüsitud 2567 veeproovi üldraua (Fe_{üld}) sisaldusest 81% ületavad joogiveele kehtestatud piirväärtuse (0,2 mg/L). Põhjavee kõrged üldrauväärtused on tingitud suurest Fe²⁺-sisaldusest, mis viitab veekompleksis domineerivatele redutseerivatele tingimustele. Filtratsiooniteekonnal toitealalt väljavooluala suunas toimub põhjavee rikastumine raua osas. Raua geoloogiliste allikate selgitamiseks analüüsiti veekompleksi moodustavate kivimite keemilist koostist ja kõrvutati seda kivimite lõimise andmete ning laboratoorsete leostuskatsete tulemustega. Selgus, et väiksema rauasisaldusega, kuid suure pooriruumiga liivakividest leostub enam rauda (kuni 1700 µg/L) kui Fe₂O₃-rikastest aleuoliitidest. Leovete rauasisaldus ajas ei tõusnud oluliselt, mis viitab sellele, et osa vesilahusesse leostunud rauda seotakse peenpurdse materjali poolt tagasi või see setib rauaühendite moodustumise kaudu vesilahusesse välja. Jämedateraline liivakivi, mis on suure filtratsioonimooduli tõttu hea veejuht ja sobiv keskkond veevõtuks, mõjutab vee rauasisaldust enam kui rauarikkam ning savikam veepide. Seega on rauaga seonduvad joogivee kvaliteediprobleemid Lõuna-Eestis lahendatavad vaid puhastusseadmete paigaldamise teel.