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Iron in the Middle Devonian aquifer system and its removal at Võru County water treatment plants, Estonia

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Abstract. Groundwater abstracted from the Middle Devonian aquifer system is the main source of drinking water in South Estonia. High iron and manganese concentrations in groundwater are the greatest problems in this region. The total iron concentrations up to 16 mg L^{-1} are mainly caused by a high Fe^{2+} content in water, pointing to the dominance of reducing conditions in the aquifer system. A pilot study was carried out to estimate the effectiveness of 20 groundwater purification plants with eight different water treatment systems (aeration combined with Manganese Greensand, Birm, Nevtraco, Hydrolit-Mn, Magno-Dol and quartz sand filters) in Võru County. The results demonstrate that in most cases the systems with pre-aeration effectively purify groundwater from iron, but only 13 out of 20 water treatment plants achieved a reduction of iron concentration to the level fixed in drinking water requirements (0.2 mg L^{-1}). Manganese content decreased below the maximum allowed concentration in only 25% of systems and in cases where the filter media was Birm or quartz sand and pre-oxidation was applied. The study showed that the high level of iron purification does not guarantee effective removal of manganese.

Key words: iron, manganese, water treatment, groundwater, Middle Devonian aquifer system.

INTRODUCTION

Most of the Estonian population (87% in 2010) uses drinking water from public water supply systems; the rest is consuming water from shallow private wells. In some areas, due to the geological conditions, groundwater chemistry does not meet the quality standards set for drinking water. Primarily natural radionuclide, fluorine, boron and iron concentrations are high (Saava 1998; Karro et al. 2009; Karro & Uppin 2010; Forte et al. 2010).

The quality of drinking water is a powerful environmental determinant of health, thus it should have good chemical properties. The deficiency or redundancy of some substance in drinking water may disturb physiological processes and cause illnesses. For example, exposure to long-term alimentary iron overload results in a positive serum iron (Fe) balance, which, in turn, causes an increased oxidative stress (Rehema et al. 1998). In Estonia iron concentration is above the limit value in 39.4% of water supply facilities (Birk 2010), which means that approximately 20% of inhabitants consume Fe-rich drinking water. According to the EU directive 98/83/EC (EC 1998) and Estonian requirements for drinking water quality (MSA 2001), the limit value set for iron in tap water is 0.2 mg L^{-1} and for manganese 0.05 mg L^{-1}.

Iron is the second most abundant metal in the earth's crust, accounting for about 5% of it. Elemental iron is rarely found in nature, as it readily combines with oxygen- and sulphur-containing compounds to form oxides, hydroxides, carbonates and sulphides. Iron is most commonly found in nature in the form of its oxides (Ponka et al. 2007). The main natural sources of Fe in groundwater are the dissolution of iron-bearing minerals like magnetite, pyrite, siderite, amphiboles, pyroxenes, olivine, biotite, glauconite and smectite, and the reduction of Fe-oxyhydroxides as hematite (Fe_2O_3) and goethite ($FeO(OH)$) and amorphous $Fe(OH)_3$ present in sediments (Hem 1985; Appelo & Postma 2005).

The hydrochemical behaviour of iron can be considered as a function of solution pH, redox potential (Eh) and activity of other ions. In natural waters iron is mostly in the ferrous (Fe^{2+}) oxidation state and in the form of $Fe(HCO_3)_2$. The monohydroxide complex $FeOH^+$ can be predominant above the pH value of 9.5 (Baes & Mesmer 1976). If pH increases above 11, Fe could be present in water as $Fe(OH_3)^-$ or $HFeO_2^-$ in appreciable concentrations, but such a high pH is rarely attained in natural systems. Ferric iron can occur in acid solutions as Fe^{3+}, $FeOH^{2+}$ or $Fe(OH)_2^+$. It is geochemically possible that the solution contains as much as 50 mg L^{-1} of ferrous iron when pH is 6–8 and bicarbonate content does not exceed 61 mg L^{-1}. In many areas the iron content of 1.0–10 mg L^{-1} in groundwater is rather common (Hem 1985).

Although manganese (Mn) is one of the most abundant metallic elements, its content in the Earth's crust is only about one fiftieth of that of iron. Manganese is not an essential constituent of any of the common silicate rock minerals, but it can substitute for iron, magnesium or calcium in silicate structures. It is a constituent of amphibole, pyroxene and olivine. Small amounts of Mn are present in dolomite and limestone, substituting for calcium (Hem 1985).

The chemistry of Mn somewhat resembles iron in that both metals participate in redox processes. Manganese can exist in different oxidation states, but the most frequent forms in the environment are soluble Mn (II) and insoluble Mn (IV). Reduced soluble Mn^{2+} is present at lower pH and Eh, but oxidizes to form precipitates in the presence of oxygen and at higher pH (Hem 1985). The significant relationship of both Mn and Fe with Eh suggests that interaction between the two elements in groundwater is mediated by Eh (Homoncik et al. 2010).

High iron and manganese concentrations in groundwater are one of the greatest problems in South Estonia. In order to produce high-quality drinking water, excessive iron and manganese must be removed. The general treatment process for iron and manganese removal is basically achieved by aeration or adding oxidizing chemical compounds into water to convert the dissolved ferrous iron and manganous manganese to an insoluble form of ferric iron and manganic manganese, followed by filtering. The most efficient water treatment results are achieved when the purification method is chosen according to the local general groundwater chemistry as well as Fe and Mn concentration in water.

Most of the drinking water in Estonia is abstracted from the upper layers of sedimentary rocks, where good conditions exist for the infiltration of the rain- and surface water. The Middle Devonian aquifer system is the main source of drinking water in South Estonia. The aims of the current research are to assess the concentrations of Fe in the Middle Devonian aquifer system and examine the efficiency of its removal in water purification plants in Võru County, southern Estonia.

GEOLOGICAL AND HYDROLOGICAL SETTING

The hydrostratigraphic cross section of the study area (Fig. 1) starts with the Quaternary aquifer system, which is followed by the Upper Devonian, Middle Devonian, Middle–Lower Devonian, Ordovician–Cambrian and Cambrian–Vendian aquifer systems. The aquifer systems differ from each other in the distribution, bedding conditions, hydraulic parameters and chemical composition. Quaternary deposits, consisting predominantly of glacial till and glaciolacustrine sandy loam, form the uppermost aquifer system, which serves as a source of drinking water for most of the private households. In southern Estonia groundwater for drinking purposes is mainly abstracted from the Middle Devonian aquifer system (Table 1).

The Upper Devonian aquifer system (D_3) consists of karstified and fissured dolomites and dolomitized limestones of the Dubniki and Plavinas stages. The total thickness of this aquifer system is 17–25 m and it covers approximately 500 km^2 in southeastern Estonia. The aquifer system is overlain by the Quaternary cover with a thickness of 40–80 m. Groundwater is mostly confined and its potentiometric surface lies at a depth

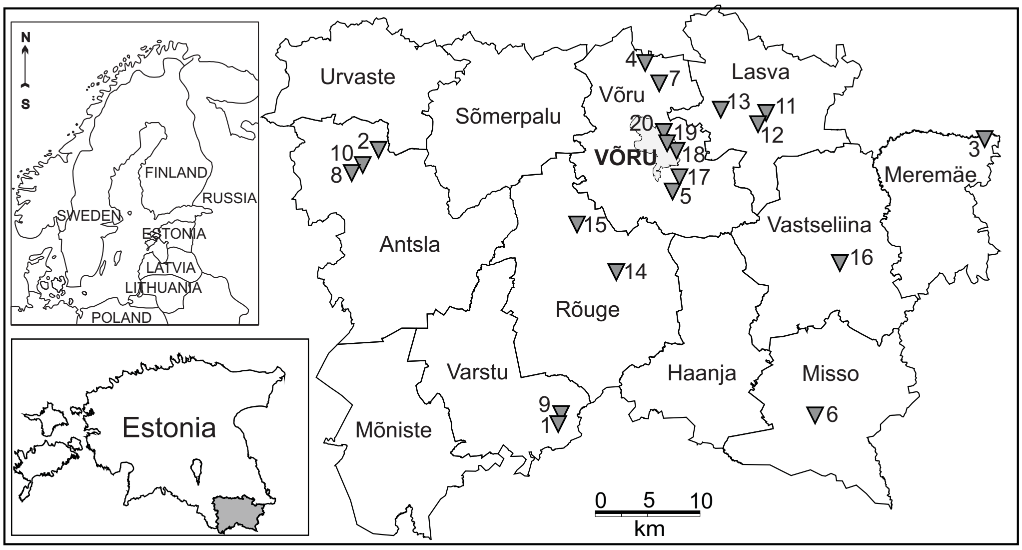

Fig. 1. The study area and the locations of the water purification systems in Võru County. The numbering of the purification systems is in accordance with Table 2.

Table 1. Quaternary and Devonian stratigraphy and hydrostratigraphy in southern Estonia (Perens & Vallner 1997; Karise et al. 2004)

System	Formation, stage	Aquifer system	Aquitard
Quaternary (Q)		Quaternary (Q)	Glaciolacustrine varved clay (lgQIII), loamy glacigenic deposits (gQIII)
Devonian (D)	Daugava	Upper Devonian (D_3)	
	Dubniki		
	Plavinas		Snetnaya Gora–Amata (D_{3sn}–D_{2am})
	Amata		
	Gauja	Middle Devonian (D_2)	
	Burtnieki		
	Aruküla		
	Narva		Narva (D_{2nr})
	Pärnu	Middle–Lower Devonian ($D_{2\text{-}1}$)	
	Rezekne		
	Tilže		

of 3–8 m from the ground surface. Hydraulic conductivity of karstified carbonate rocks varies between 1 and 50 m day^{-1} (Perens & Vallner 1997). Due to its limited occurrence, the Upper Devonian aquifer system is used for the public water supply in a few places only.

The Middle Devonian aquifer system (D_2) is distributed over the whole of southern Estonia and is the most important source of public water supply. It consists of terrigenous material – sand- and siltstones with interlayers of clayey and dolomitized sandstones of the Gauja, Burtnieki and Aruküla stages. The thickness of the aquifer system is up to 250 m and the absolute height of the potentiometric surface ranges from 50 to 130 m. The lateral conductivity of the aquifer system is rather equable: predominantly 1–3 m day^{-1}. Groundwater in the D_2 aquifer system is mainly fresh, of HCO_3–Ca–Mg chemical type with total dissolved solids (TDS) of 0.2–0.6 g L^{-1} (Perens & Vallner 1997; Perens et al. 2001).

The Middle–Lower Devonian ($D_{2\text{-}1}$) aquifer system is isolated from the overlying D_2 aquifer system by the Narva aquitard, but the water-bearing rocks consist also of fine-grained weakly cemented sand- and siltstones. The conductivity of sandstones is 2–6 m day^{-1} and groundwater abstracted for drinking purposes is of HCO_3–Ca–Mg and HCO_3–Mg–Ca chemical type (Perens et al. 2001).

MATERIALS AND METHODS

A pilot study was performed in Võru County, south-eastern Estonia, where the effectiveness of 20 groundwater purification systems was investigated (Fig. 1). All studied water supply plants use groundwater from the Middle Devonian aquifer system. Water samples for chemical analyses were collected before and after the purification process. Samples from groundwater abstraction wells were taken only after stabilizing and measuring field parameters (temperature, pH, O_2 content). The concentrations of total iron (Fe_{tot}), Fe^{2+}, Mn, NH_4^+, NO_3^- and the values of electrical conductivity were determined in the Laboratory of Tartu Waterworks Ltd by spectrometric detection (SPEKOL 11, Hach DR/2000). The measurement uncertainty ranges from 5.8% to 10%.

In order to describe the occurrence of iron in the Middle Devonian aquifer system, the hydrochemical database of the Estonian Environmental Information Centre was used. It contains approximately 500 groundwater chemistry analyses, including iron determinations.

WATER TREATMENT PLANTS

Eight different water treatment methods were used in the studied water treatment plants (Table 2).

Type 1. The main body of the purification system is the Manganese Greensand filter. Manganese Greensand is natural or industrial material composed of aluminosilicate, which is treated with $MnCl_2$ and regenerated with $KMnO_4$ (Keller 2005). Iron is precipitated directly by greensand in a redox reaction.

$KMnO_4$ can also be fed continuously or periodically ahead of the bed. In this type of regeneration iron is precipitated prior to the bed as well as by the bed. The oxidation process that causes iron to precipitate before

Table 2. Water treatment plants in Võru County

Plant number	Name	Location	Type number	Type
1	Krabi 1	Varstu Parish	1	Manganese Greensand
2	Kraavi	Antsla Parish		
3	Võmmorski	Meremäe Parish		
4	Parksepa	Võru Parish		
5	Puiga	Võru Parish		
6	Misso	Misso Parish		
7	Väimela	Võru Parish	2	Birm
8	Lusti	Antsla town	3	Nevtraco, Hydrolit-Mn, Magno-Dol
9	Krabi 2	Varstu Parish	4	Open aeration and Birm
10	Antsla	Antsla town		
11	Lasva	Lasva Parish	5	Open aeration, prefilter and Birm
12	Pässa	Lasva Parish		
13	Kääpa	Lasva Parish		
14	Rõuge	Rõuge Parish	6	Closed aeration and Birm
15	Nursi	Rõuge Parish		
16	Vastseliina	Vastseliina Parish	7	Closed aeration and Manganese Greensand
17	Kose	Võru Parish		
18	Valio Võru	Võru Parish	8	Closed aeration and quartz sand
19	Võrusoo	Võru town		
20	Kirsi-Veski	Võru town		

the contact of Manganese Greensand can be seen in the following reaction:

$$KMnO_4 + 3Fe(HCO_3)_2 + 7H_2O \rightarrow MnO_2 + 3Fe(OH)_3 + KHCO_3 + 5CO_2 + 5H_2O.$$

For iron removal, the pH of water must be at least 6.2, because acid water damages the MnO_2 layer on the filter material (Keller 2005). For the removal of manganese, the pH of water must be above 7.5 (Dvorak et al. 2007). When the oxidizing capacity of the Manganese Greensand bed is exhausted, the bed has to be regenerated with $KMnO_4$ solution, thus restoring the oxidizing capacity of the bed.

Type 2. The main body of the purification system is the Birm iron filter. Birm is a material made of aluminium silicate, or silicon that has been doped with aluminium particles and then coated with manganese dioxide. Birm relies on its ability to act as a catalyst between iron and oxygen (Keller 2005):

$$MnO_2 + 2Fe(HCO_3)_2 + H_2O \rightarrow MnO + 2Fe(OH)_3 + 4CO_2 + H_2O.$$

Because the amount of MnO_2 is limited in the filter material, there is not enough oxygen for the whole process. So oxygen concentration must be 15% of the Fe_{tot} amount. If oxygen concentration is lower than 15%, pre-aeration of water is necessary. For the maintenance of the working capacity of Birm, the filter should be periodically backwashed. For iron removal, the pH of water must be at least 6.8 (Munter et al. 2000). For the removal of manganese, the pH of water must be above 8 (Green 1997).

Type 3. The main body of the purification system is the Nevtraco, Hydrolit-Mn and Magno-Dol iron pressure-filter. For the removal and filtration of iron, Nevtraco material is used, which consists of $CaCO_3$ (calcite) and works with the pH in between 5.8 and 7.0. For the removal of manganese, special material Hydrolit-Mn is used. It is granulated, slightly acid material, where the catalyst is Mn. For the neutralization of water acidity, Magno-Dol (acicular dolomite material) is used, which reduces the aggressiveness (CO_2) of water and increases the pH value. The reaction lasts as long as the saturation of calcite is achieved – calcium, manganese and bicarbonate concentration will increase in the solution.

Type 4. The main body of the purification system is open aeration and the Birm iron filter. In addition to the Birm iron filter, pre-oxidative mechanical filtration is used at the water treatment plant – the air is pumped through water, which promotes the oxidation of iron and manganese.

Type 5. The purification system consists of open aeration, a pre-filter and Birm iron filter. According to technological solution, water is pumped to pressureless contact containers where it will be aerated, to ensure that all dissolved gases will separate, pass through the cartridge filter and finally through the Birm iron filter.

Type 6. The purification system consists of closed aeration and the Birm iron filter. Incoming water is pumped through a special aerator which is under pressure and then through the catalytic iron filter. Effective work of the aerator is guaranteed by the compressor through which additional oxidative air is added to the system.

Type 7. The purification system consists of closed aeration and the Manganese Greensand iron filter. Water is pumped through granulated filter material which acts as catalyst. Ferrous iron oxidizes to ferric iron and precipitates with the other non-soluble particles between the granules. The filter material backwash is done in between the filtration intermissions. Every 1 to 6 months of operation, the filter material needs, for the maintenance of the catalytic features, regeneration with chemicals. The quality of the backwash depends on the pressure of incoming water, which generally should be from 2.5 to 6.0 bars. If the pressure is low during the backwash, the active catalytic surface layer of the granules could be contaminated as a result of non-sufficient backwash, and the filter material as a whole could permanently lose its ability to oxidize iron. When the pressure is too high during the backwash, it is possible that the filter material will be washed out.

Type 8. The purification system consists of closed aeration and a quartz sand iron filter. The purification is designed as simple aeration – water is saturated with oxygen and ferrous iron is oxidized to ferric iron. To do that, compressed air is added via compressor. Ferric iron sticks to the quartz sand filling in pressure-filters (Kornel 2003). From time to time the precipitated particles are washed out of the surface of the quartz sand granules. During the backwash, the filter material swills and its purifying ability restores. The removal of iron depends on the amount of ferric iron on the surface of sand granules, velocity of the water flow in the filter, which determines the duration of the contact, amount of the oxygen added into water and the overall concentration of iron in water.

RESULTS AND DISCUSSION

Through years the problems related to the water quality in Võru County have been associated with high iron, hydrogen sulphide (H_2S) and manganese concentrations in groundwater. During infiltration through a clayey and mostly thick layer of Quaternary sediments, water is depleted of oxygen and the environmental conditions change form oxidative to reductive in deeper parts of the geological profile. The indicators of the anoxic environment are high concentrations of Fe^{2+}, H_2S and NH_4^+ in groundwater.

On the other hand, high concentrations of those compounds in drinking water may also be related to the technical condition of the water supply system – depreciated wells and water pipes. Water consumption has decreased in Võru County over the years, so water remains in the pipeline and damages the water supply system. The slower water exchange leads to higher Fe^{2+} concentrations and presence of H_2S as a result of the SO_4^{2-} reduction by anaerobic bacteria.

According to the 500 groundwater analyses, recorded in the database of the Estonian Environment Information Centre, the concentration of Fe_{tot} exceeds the limit value set to drinking water (0.2 mg L^{-1}) in 70% of the wells abstracting water from the Middle Devonian aquifer system. Total iron concentrations as high as 16 mg L^{-1} have been determined in places. The results of chemical analyses show that high Fe_{tot} concentrations are mainly caused by high Fe^{2+} contents in water (Fig. 2), which in turn points to the domination of reducing conditions in the D_2 aquifer system. Comparison of drilled well construction data and groundwater chemistry shows that there is no direct connection between the depth of the well and the iron concentration in abstracted groundwater (Fig. 3). Thus, high iron contents could be found through the whole of the (250 m thick) aquifer system.

Water treatment facilities convert the dissolved forms of iron and manganese into insoluble forms so that they could be filtered out. In addition, iron removal filters help to increase the pH of water (Kornel 2002) and therefore achieve better acid-alkaline balance and reduce the CO_2 concentration in water. During the treatment process, the content of Mn and H_2S is also reduced. According to the drinking water standards (EC 1998;

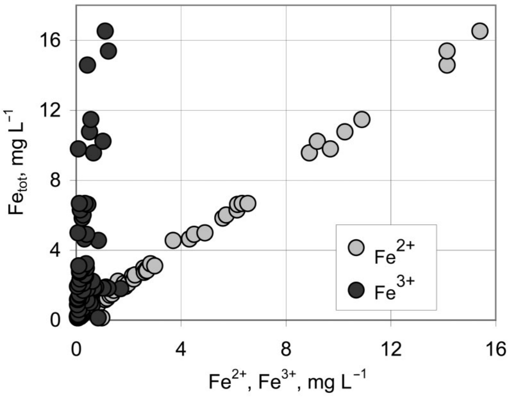

Fig. 2. The proportion of Fe^{2+} and Fe^{3+} in Fe_{tot} concentration.

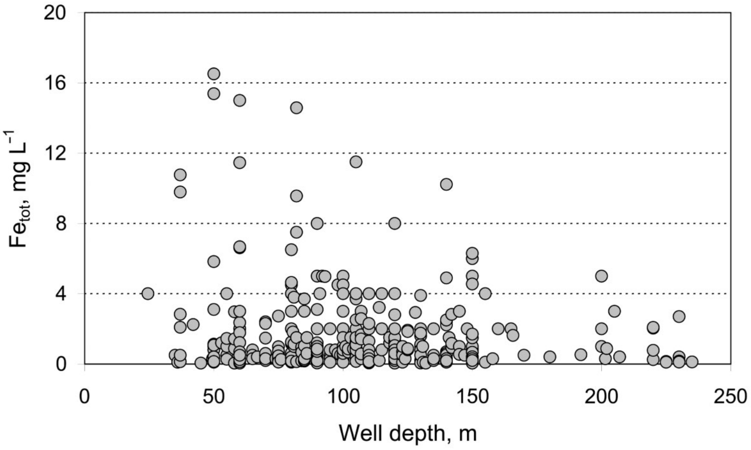

Fig. 3. Bivariate plot of Fe$_{tot}$ content versus well depth in the Middle Devonian aquifer system.

MSA 2001), the Fe$_{tot}$ concentration in drinking water should be below 0.2 mg L^{-1}.

Iron was oxidized in all water treatment plants with different technologies, and the concentration of iron in water was lowered during the purification everywhere. Generally, the highest iron concentrations (>2 mg L^{-1}) in groundwater entering the purification system were successfully reduced to the required level of 0.2 mg L^{-1}. However, of 20 studied water purification systems, only 13 achieved the reduction of iron concentration to the level corresponding to the drinking water requirements (Fig. 4, Table 3).

During the treatment process ferrous iron is oxidized by oxygen to ferric iron, a heavily soluble compound which will settle out of water. If the active surface material of the filter is MnO_2, the presumption of the successful progress of the chemical reaction is that the amount of dissolved oxygen in groundwater is at least 15% of iron concentration (Munter et al. 2000). Often the oxygen concentration in groundwater is close to zero, which makes pre-aeration very important. The results of the analysis show that in most cases the systems with pre-aeration purify groundwater from iron effectively (Fig. 4).

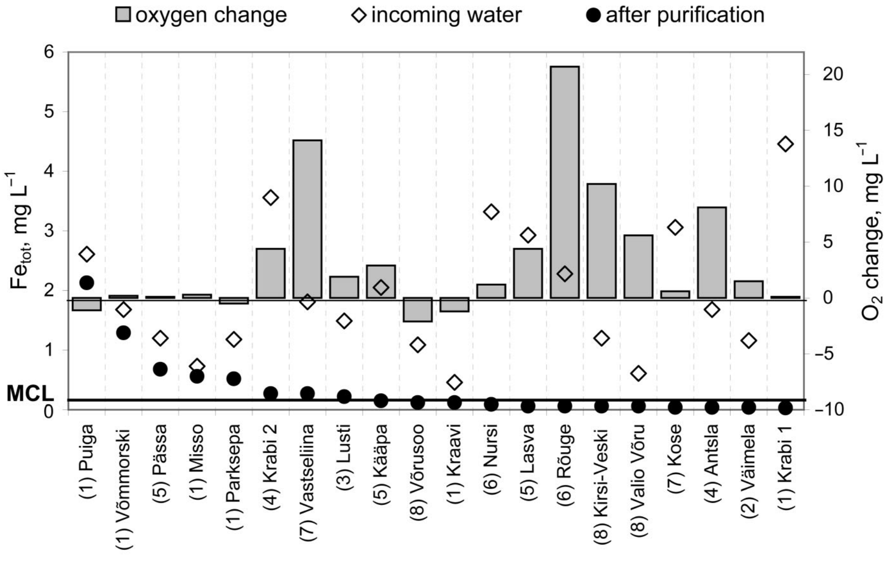

Fig. 4. Total iron (Fe$_{tot}$) concentration in incoming and purified water and the change in oxygen concentration during the purification process. MCL – maximum concentration limit of Fe$_{tot}$ in drinking water (0.2 mg L^{-1}). The numbers before the purification system names denote the types of the water treatment facilities as indicated in Table 2.

Table 3. Water chemistry before and after the treatment process. MCL – maximum concentration limit in drinking water

Plant	Water chemistry before and after the treatment							
	Before	After	Before	After	Before	After	Before	After
	O_2, mg L^{-1}	O_2, mg L^{-1}	pH	pH	Fe_{tot}, mg L^{-1}	Fe_{tot}, mg L^{-1}	Mn, µg L^{-1}	Mn, µg L^{-1}
Krabi 1	1.2	1.2	7.35	7.42	4.46	0.03	206	1355
Kraavi	3.6	2.4	7.36	7.37	0.46	0.12	209	322
Võmmorski	2.2	2.4	7.23	7.22	1.68	1.29	129	197
Parksepa	2.2	1.7	7.42	7.20	1.18	0.52	200	360
Puiga	1.9	0.8	7.27	7.42	2.61	2.13	140	485
Misso	2.3	2.6	7.77	7.76	0.73	0.56	71	100
Väimela	1.1	2.6	7.26	7.30	1.16	0.04	319	329
Lusti	2.6	4.5	7.25	7.18	1.49	0.22	262	469
Krabi 2	3.2	7.6	7.41	7.59	3.56	0.27	148	46
Antsla	1.5	9.6	7.30	7.33	1.68	0.04	268	30
Lasva	1.8	6.2	7.35	7.43	2.93	0.06	530	37
Pässa	0.8	0.9	7.35	7.37	1.20	0.68	247	585
Kääpa	2.4	5.3	7.64	7.28	2.05	0.15	376	123
Rõuge	0.6	21.3	7.51	7.49	2.28	0.06	78	88
Nursi	0.9	2.1	7.91	7.31	3.32	0.09	120	283
Vastseliina	1.2	15.3	7.59	7.66	1.81	0.27	136	110
Kose	1.5	2.1	7.41	7.35	3.06	0.04	182	155
Valio Võru	3.0	8.6	7.51	7.59	0.61	0.06	57	32
Võrusoo	3.4	1.3	7.35	7.28	1.09	0.12	86	92
Kirsi-Veski	1.8	12.0	7.30	7.42	1.20	0.06	97	37
MCL				6.50–9.50		0.20		50

The assumption that during the operation of the purification system the content of oxygen in water will arise does not apply to every studied system. For example, in the Puiga, Parksepa and Kraavi purification systems, which belong to the first type (Manganese Greensand filter), the oxygen level has decreased in cleaned water compared to raw groundwater (Fig. 4). In Puiga, this trend is explained by the breakdown of the purification system. Despite the decreased oxygen content, the iron concentration in water was successfully reduced to the acceptable level in Kraavi. This could be explained by the low iron content in groundwater (0.46 mg L^{-1}). The water entering the treatment system in Parksepa contains almost three times more iron (1.18 mg L^{-1}) than in Kraavi and the Manganese Greensand filter is not able to reduce the iron content to the level of 0.2 mg L^{-1}.

The Manganese Greensand filter is used in eight purification systems (Krabi 1, Kraavi, Võmmorski, Parksepa, Puiga, Misso, Vastseliina, Kose). Yet, after the treatment, the quality of drinking water meets the requirements set to iron only in three locations – Krabi 1, Kraavi and Kose (Fig. 4).

The manganese content decreased below the maximum concentration limit only in 25% of systems when the filter material was Birm or quartz sand and the pre-oxidation was applied (Fig. 5). Manganese concentration increased in 12 of 20 systems studied during the treatment process. The removal of Mn is effective at those water treatment plants (Krabi 2, Antsla, Valio Võru, Kirsi-Veski, Lasva) where the increase in oxygen concentration is notable (Fig. 5, Table 3), but not in all cases. In spite of the noticeable increase in O_2 content (from 1.2 to 15.3 mg L^{-1}), Mn concentration decreased only from 136 to 110 µg L^{-1}, remaining still above the limit value at the Vastseliina treatment plant.

Purification systems with the Manganese Greensand filter (type 1) are not able to reduce the manganese content in water to the required level of 50 µg L^{-1} (Fig. 5). Slight decrease in Mn content occurred at the Kose and Vastseliina plants where pre-oxidation is used, but in most cases Mn concentration increased during filtration.

Bivalent manganese is geochemically more stable than ferrous iron, because $Fe(OH)_3$ formed precipitates first from the solution. Iron is effectively removed at the Krabi 1, Kraavi and Kose plants (Fig. 4). The Fe_{tot} concentration in incoming water at the Krabi 1 plant is high, 4.46 mg L^{-1}. Thus, all available oxygen is used for Fe^{2+} oxidation and the Manganese Greensand filter is able to capture only iron compounds. Iron is removed also at the Puiga, Parksepa, Võmmorski and Misso plants, but in limited amounts (Fig. 4). Therefore, in these cases, the filter needs either instant regeneration for restoration of its working ability or it needs to be replaced.

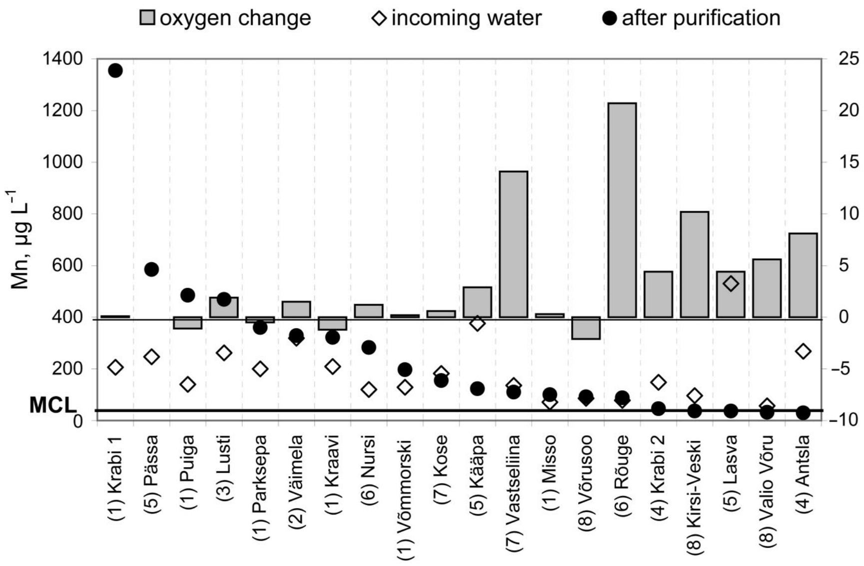

Fig. 5. Manganese concentration (µg L^{-1}) in incoming and purified water and the change in oxygen concentration during the purification process. MCL – maximum concentration limit of Mn in drinking water (50 µg L^{-1}). The numbers before the purification system names denote the types of the water treatment facilities as indicated in Table 2.

Marked increase in oxygen content at the Rõuge plant is explained by closed aeration, which is one part of the treatment process. Although the added oxygen has no effect on Mn concentration (Fig. 5), the Fe_{tot} content in water is successfully reduced from 2.28 to 0.06 mg L^{-1} (Fig. 4). Thus, in this case, the Birm filter can remove only Fe from the water. The same filter type, combined with open aeration (Krabi 2, Antsla and Lasva plants), reduces both Fe and Mn concentrations to the values that meet the drinking water requirements. However, the Pässa plant that uses the same treatment method is not able to reduce Fe and Mn content to the required level. The reason for the ineffective work of the Pässa plant is probably the lowest and most stable O_2 content among the studied treatment plants (Table 3). Thus, considering the naturally high Fe and Mn contents in groundwater of Võru County, the water treatment plants using Birm filters should also apply pre-aeration in order to increase the effectiveness of the purification process. In addition, the maintenance of the facilities and the through-wash of the filters ensure their long-term efficient work.

In this study the effectiveness of the purification system was estimated by introducing the term of purification level (PL). The purification level is the ratio between the Fe concentration (mg L^{-1}) in water before and after treatment (PL_{Fe}) or Mn concentration (µg L^{-1}) before and after treatment (PL_{Mn}):

$$PL_{Fe} = \frac{Fe_{tot}^{before}}{Fe_{tot}^{after}}, \quad PL_{Mn} = \frac{Mn^{before}}{Mn^{after}}.$$

The comparison of PL_{Fe} and PL_{Mn} shows that the high level of iron purification does not guarantee simultaneously an effective removal of manganese (Fig. 6).

Most of the studied purification plants are single-step systems where iron is oxidated and removed. Manganese, however, is geochemically more stable in water than Fe^{2+} and thus only partially or not at all removed during the oxidation process. Manganese accumulates in the purifying system and even the correctly performed through-wash does not remove it from the filter. If the pressure during the through-wash is not selected properly, it may happen that manganese will be washed out, but the working ability of the filter will be damaged.

The pH value is the factor influencing the effectiveness of the purification system. For Fe removal, pH must be at least 6.2 (Keller 2005) when Manganese Greensand is

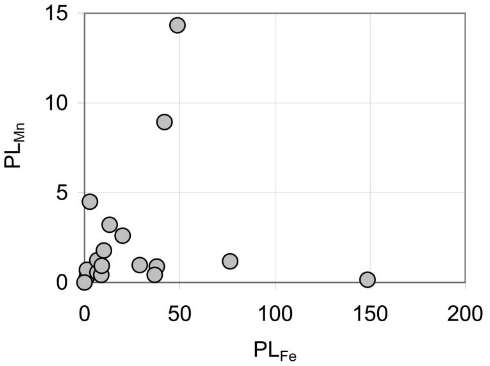

Fig. 6. Correlation of the Fe_{tot} and Mn purification levels.

used and 6.8 in the case of Birm (Green 1997; Munter et al. 2000). The oxidation of Mn takes place at pH values above 7.5 if Manganese Greensand (Dvorak et al. 2007) is used, and it should be between 8.0 and 8.5 in case of Birm (Green 1997).

The pH of studied groundwater samples varies between 7.25 and 7.91, which is suitable for Fe removal, but still too low for overall Mn oxidation. In order to increase the pH of water and therefore enhance Mn removal, it is possible to add alkaline (usually NaOH) solution via a special dosing system (Sutt 2003). Still, it must be taken into account that by doing this, at the pH value of 8.2, Ca^{2+} and Mg^{2+} precipitation intensifies (Geen 1997; Appelo & Postma 2005), which may cause the clogging of pipes.

CONCLUSIONS

Water supply of Võru County is based on the Middle Devonian (D_2) aquifer system. The main water quality problems are associated with high iron and manganese contents in water. The concentration of Fe_{tot} exceeds the limit value of 0.2 mg L^{-1} set to the drinking water in 70% of the wells abstracting water from the aquifer system. In places the total iron concentrations up to 16 mg L^{-1} have been detected. The results of the analyses show that high Fe_{tot} concentrations are mainly caused by high Fe^{2+} contents in water, referring to the domination of reducing conditions in the D_2 aquifer system. In order to produce high-quality drinking water, excessive iron and manganese must be removed at water treatment plants.

A pilot study was performed to estimate the effectiveness of groundwater purification systems in Võru County. Water treatment facilities convert the dissolved forms of iron and manganese into insoluble forms so that those could be filtered out. Eight different water treatment systems were used in 20 studied water treatment plants. Filter materials such as Manganese Greensand, Birm, Nevtraco, Hydrolit-Mn, Magno-Dol and quartz sand were combined with aeration. Water was abstracted from the D_2 aquifer system at all water supply plants.

The results of the study show that in most cases the systems with pre-aeration purify groundwater from iron effectively. Still, of 20 water purification systems studied only 13 achieved a reduction of iron concentration to the level corresponding to the drinking water requirements.

Manganese content decreased below the maximum concentration limit in only 25% of the systems and when the filter material was Birm or quartz sand and pre-oxidation was applied. Manganese concentration increased in 12 systems during the treatment process. Manganese is geochemically more stable in water than Fe^{2+}. Iron is oxidated and removed from water, but manganese is only partially or not at all removed by oxidation. While the oxygen-poor conditions prevail in the D_2 aquifer system, pre-aeration is needed for iron and manganese removal, in order to increase the effectiveness of the purification process. Furthermore, to achieve the best results in water cleaning, the treatment facilities should be maintained regularly and according to the requirements of their deliverer and producer.

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Raud Kesk-Devoni põhjaveekompleksis ja selle ärastus Võrumaa veepuhastussüsteemide näitel

Mariina Hiiob ja Enn Karro

Võrumaa veevarustus baseerub valdavalt Kesk-Devoni põhjaveekompleksi veel ja kogu maakonna ulatuses on põhiliseks veevarustuse probleemiks põhjavee suur raua- ning mangaanisisaldus. Vee looduslik rauasisaldus on suur, olenemata selle lasumissügavusest. Kesk-Devoni veekompleksis valitsevate redutseerivate tingimuste tõttu moodustab üldraua bilansist põhilise osa kahevalentne raud. Joogiveeks kasutatava põhjavee rauasisaldus ületab enamikul juhtudel joogiveele kehtestatud piirkontsentratsiooni (0,2 mg/l): kõrgeimad analüüsitud väärtused ulatuvad 10–16 mg/l. Suured raua kontsentratsioonid esinevad kogu Võrumaa ulatuses. Joogiveena tarbitava põhjavee kvaliteedi vastavusse viimiseks kehtestatud nõuetega puhastatakse vett erinevate veepuhastusmeetoditega, kasutatakse nii vee eelnevat aereerimist kui ka erinevaid filtermaterjale (Roheline Mangaaniliiv, Birm, Nevtraco, Hydrolit-Mn, Magno-Dol, kvartsliiv). Käesoleva uuringu tulemused näitasid, et raua ärastus toimus kõige efektiivsemalt eelaereerimisega puhastusseadmetes. Kesk-Devoni veekompleksis valdavate redutseerivate tingimuste tõttu oleks vaja Võrumaal puhastatavat põhjavett eelnevalt kindlasti aereerida. See intensiivistaks raua oksüdatsiooniprotsessi ja veest väljasettimist. Veepuhastites kasutatavatest mangaani sisaldavatest filtermaterjalidest osutus efektiivseimaks Birm. Kuivõrd mangaani ärastus toimub vaid 25% juhtudest, on vaja uurida tehnoloogilisi võimalusi mangaani efektiivsemaks ärastuseks põhjaveest. Veepuhastussüsteemi tõrgeteta toimimiseks on väga oluline seadme hooldus, mis peab olema regulaarne ja vastama seadme valmistaja ning tarnija nõuetele.