Other constituents in the drinking water impacting its quality and their removal needs

Overview of the HMO technology and the pilot set up at Viimsi DWTP

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WHAT ARE INDICATOR PARAMETERS AND WHY SHOULD WATER SUPPLIERS REDUCE THEIR CONCENTRATION IN DRINKING WATER?

- A failure to meet an indicator parameter value does not necessarily mean that there is a human health risk from the supply!
- A failure is a signal that there may be a problem with the supply that needs investigation and consideration of whether there is a human health risk.
- Many of the indicator parameters describe the aesthetic quality of water supplies – the characteristics of drinking water that are noticed by consumers because of its appearance, taste or smell
- According to Estonian Regulatory Act [RT I, 26.09.2019, 2] the parametric indicators are as follows:

Al, NH_4^+, Conductivity, Residual Chlorine, Cl^- , Mn, Na, COD, TOC, Fe, SO_4^{2-}, pH, Turbidity, Taste, Smell, Colour, *Clostridium perfringens*, Coliform bacteria, Total Colony count

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TOTAL CONCENTRATION OF Fe, Mn, NH_4^+ , AND OTHER PARAMETERS IN STUDIED GROUNDWATER (OCTOBER 2018 – FEBRUARY 2020)

Table 1. Average values of water quality parameters and corresponding threshold limits according to [RT I, 26.09.2019, 2]

Parameter	Results of analyses (average ± st. dev)	Threshold limit
Fe, mg/L	**0.195 ± 0.055**	**0.200**
Mn, mg/L	**0.118 ± 0.050**	**0.050**
NH_4^+, mg/L	**0.644 ± 0.144**	**0.500**
pH	8.12 ± 0.27	**6.5 – 9.5**
Conductivity, µS/cm	883 ± 67	**<2500**

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IRON IN DRINKING WATER

- Iron is the second most abundant metal in the earth's crust, of which it accounts for about 5%
- In drinking-water supplies, iron(II) salts are unstable and are precipitated as insoluble iron(III) hydroxide, which settles out as a rust-coloured silt.
- Anaerobic groundwaters may contain iron(II) at concentrations of up to several milligrams per litre without discoloration or turbidity in the water when directly pumped from a well, although turbidity and colour may develop in piped systems at iron levels above 0.05–0.1 mg/litre
- Staining of laundry and plumbing may occur at concentrations above 0.3 mg/litre

Figure 1. Iron staining
https://www.americanwatercollege.org/

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MANGANESE IN DRINKING WATER

- Curious facts:
  - Manganese is an essential element for many living organisms, including humans
  - However, the syndrome known as "manganism" is caused by exposure to very high levels of manganese dusts or fumes and is characterized by a "Parkinson-like syndrome"
- Manganese occurs naturally in many surface water and groundwater sources and in soils that may erode into these waters.
- The greatest exposure to manganese is usually from food. Adults consume between 0.7 and 10.9 mg/day in the diet
- The maximum desirable level of manganese is 0.05 mg/L to avoid staining
- At concentrations exceeding 0.1 mg/l, the manganese ion imparts an undesirable taste to beverages

Figure 2. Iron and manganese staining

https://www.americanwatercollege.org/

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AMMONIUM ION IN DRINKING WATER

- Despite NH_4^+ is not considered as a toxic substance, this ion is a major constituent of many contaminated aquifers
- There is no conclusive evidence for NH_4^+ - consuming reactions (nitrification or anammox) in the anoxic core of aquifer
- The presence of the ammonium cation in raw water may result in drinking-water containing nitrite (NO_2^-)

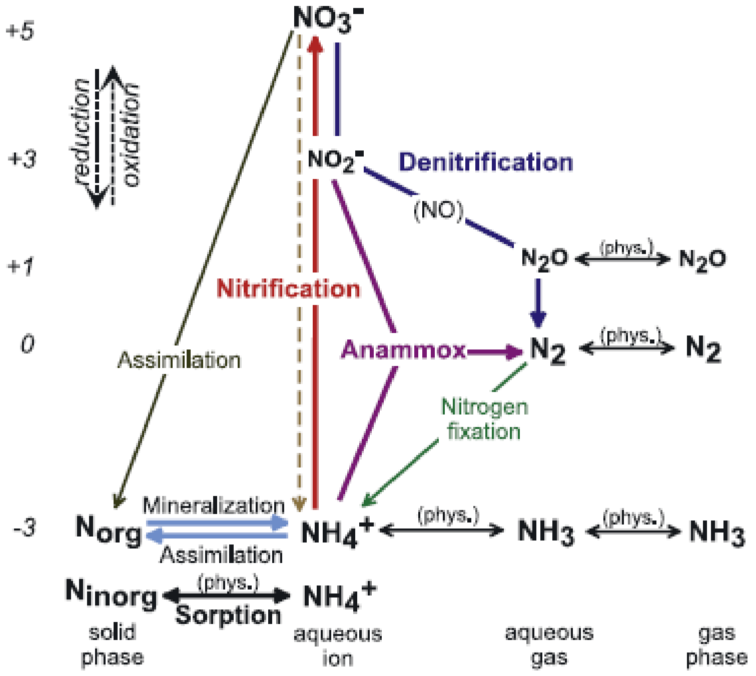

Figure 3. Biogeochemical and physical-chemical processes affecting the speciation of nitrogen in aquatic systems

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CONVENTIONAL TECHNOLOGIES FOR THE REMOVAL OF Mn, Fe, NH_4^+ FROM WATER

Possible Options

Ion exchange

- Zeolites, ion-exchange resins etc
- Has limited application for the removal of iron and manganese
- Suits perfectly for NH_4^+ removal
- Removes positively charged **radionuclides as Ra^{2+}**

Catalytic Oxidation

MnO_2 -based technologies

- Solid MnO_2 –based filter media
- Preformed hydrous manganese oxide (HMO) technology
- Adsorbs positively charged Ra^{2+}, but ineffective for NH_4^+

Aeration

- Very effective for Fe removal
- Less effective for Mn removal
- Initially, it is not intended for NH_4^+ removal

Oxidation using chemicals

- Chlorine, chlorine dioxide, $KMnO_4$, ozone

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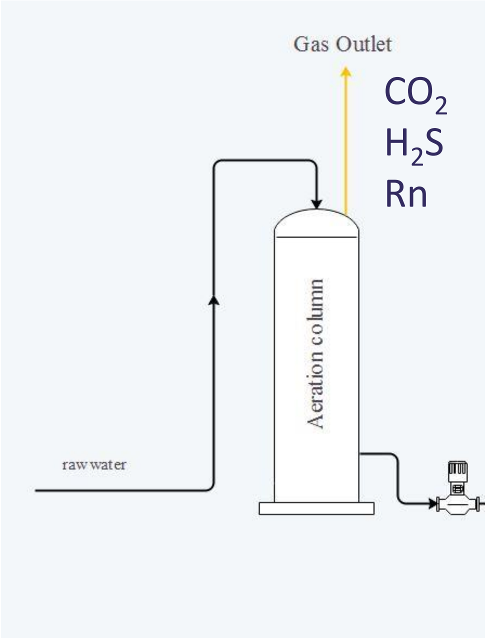
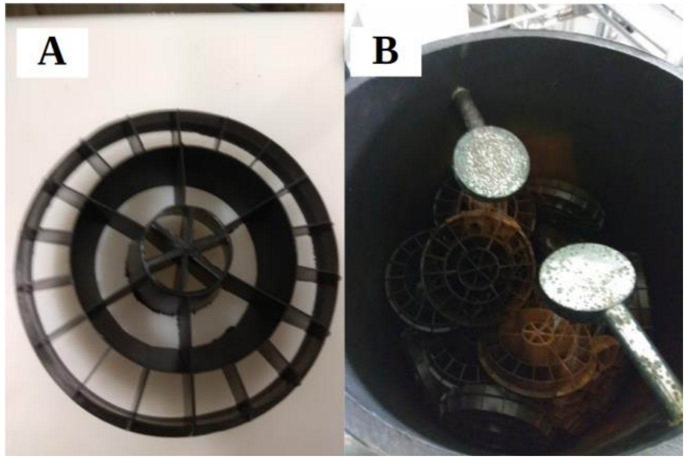
The process of water aeration





- Aeration is often the first major process at the drinking water treatment plant
- Aeration is the process of bringing water and air into close contact in order to
  - ✓ Remove dissolved gases
  - ✓ Saturate water with oxygen

$$4Fe(HCO_3)_2 + 2H_2O + O_2 = 4Fe(OH)_3 \downarrow + 8CO_2$$
$$2Mn(HCO_3)_2 + 2H_2O + O_2 = 2Mn(OH)_4 \downarrow + 4CO_2$$

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MnO_2–BASED TREATMENT

MnO_2 –based filter media

- Pure granular form of MnO_2 (Filox ®, Pyrolox® etc)
- MnO_2 coated on a mineral like silica (Birm®, GreensandPlus™ etc)

Figure 5. Granular MnO_2 and GreensandPlus™

Application of MnO_2 –slurry

- Manganese dioxide is often called hydrous manganese oxide **(HMO)**
- HMO slurry can be prepared using $MnSO_4{\cdot}H_2O$ and $KMnO_4$ according to the reaction:
- $3MnSO_4{\cdot}H_2O + 2KMnO_4 \rightarrow 5MnO_2\downarrow + K_2SO_4 + 2H_2SO_4 + H_2O$
- NaOH solution is used to maintain pH 8 - 9.5

Figure 6. Preparation of HMO-slurry in laboratory

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MECHANISM OF HMO PROCESS

The mechanism of redox precipitation of Fe and Mn

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

Why does HMO adsorb Ra^{2+} ?

- At acidic conditions H^+ reacts with MnO_2 surface to give an anionic exchanger site

$$MnO_2 + H^+ \rightarrow MnO_2H^+$$

- At alkaline conditions hydroxide ion OH^- produces the surface for removing cationic species

$$MnO_2 + OH^- \rightarrow MnO_2OH^-$$

- The rise of water pH supports the increase of cationic capacity of HMO particle

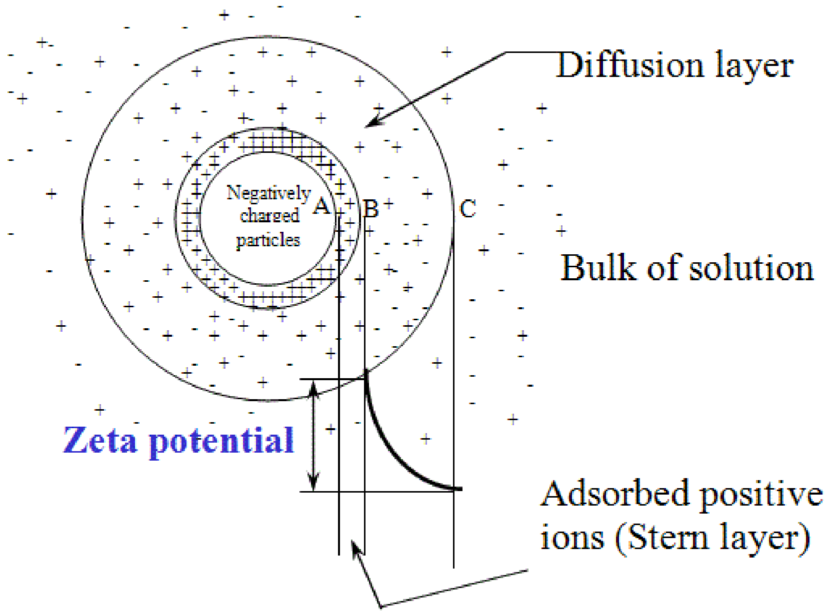

Figure 7. The concentration of positively charged ions across negatively charged particle

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HMO-based pilot plant structure and principle of operation

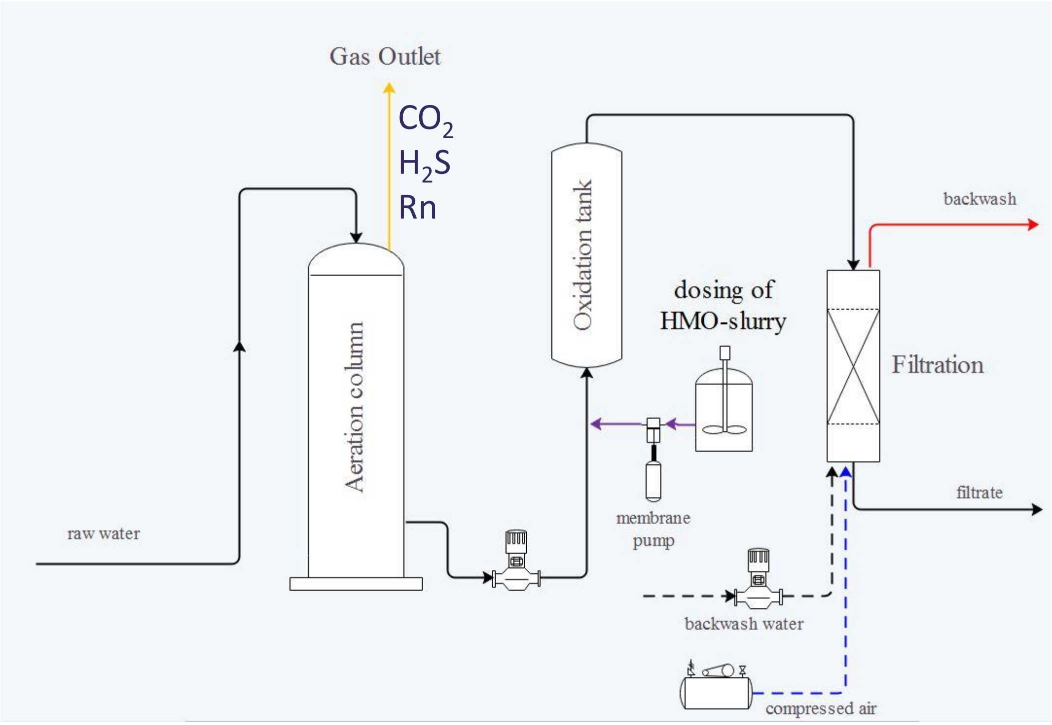

Figure 6. Process flow diagram

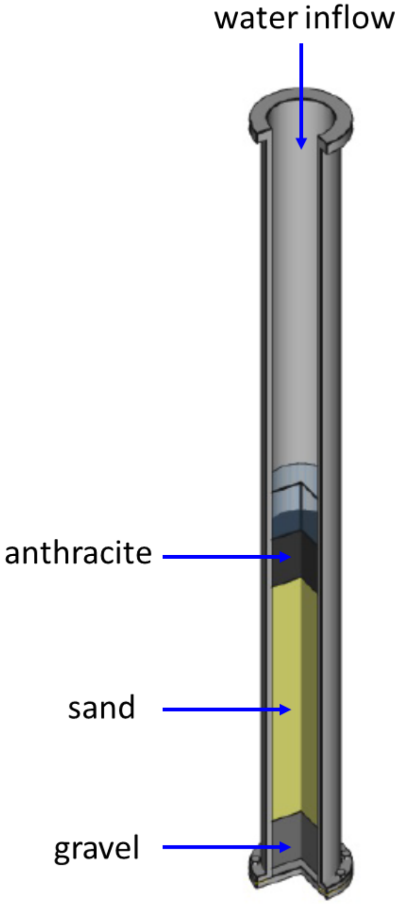

Figure 7. Composition of filter

HMO-based pilot plant structure and principle of operation

Table 2. Operation of pilot plant

Parameter*	Value
Electricity consumption (kWh/m^3)	1.9
Water flow (L/h)	300
Air consumption (kg/m^3)	0.0113
MnO_2 (g/m^3)	0.9 – 1.8
Filtration rate (m^3/m^2/day)	7.0
The rate of HMO-slurry injection (L/h)	**0.1 – 0.2**

*- electricity, air, and MnO_2 consumptions are given per m^3 of treated water

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Removal of Fe and Mn. (September 2019 – February 2020)

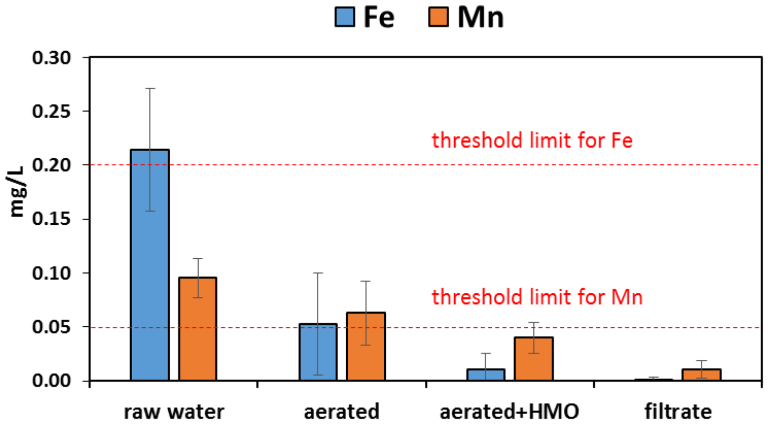

Figure 7. Average concentration of Fe and Mn after each step of treatment

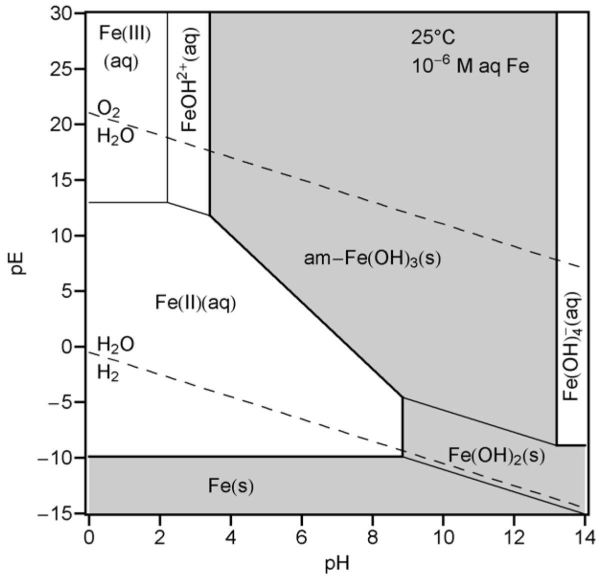

Figure 8. Pourbaix diagram of Fe

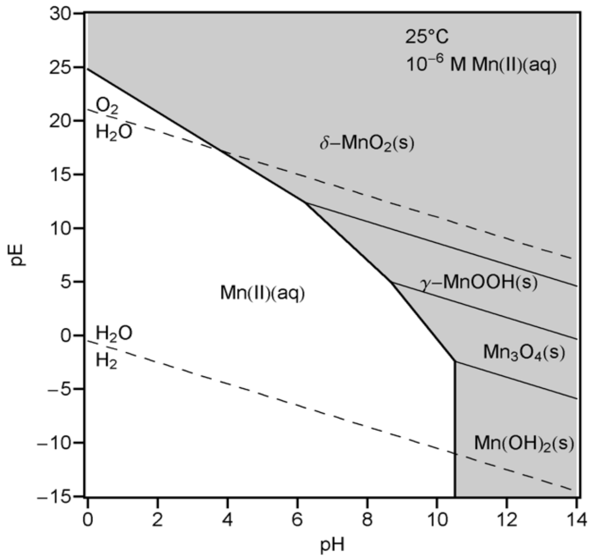

Figure 9. Pourbaix diagram of Mn

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What about NH_4^+ ?

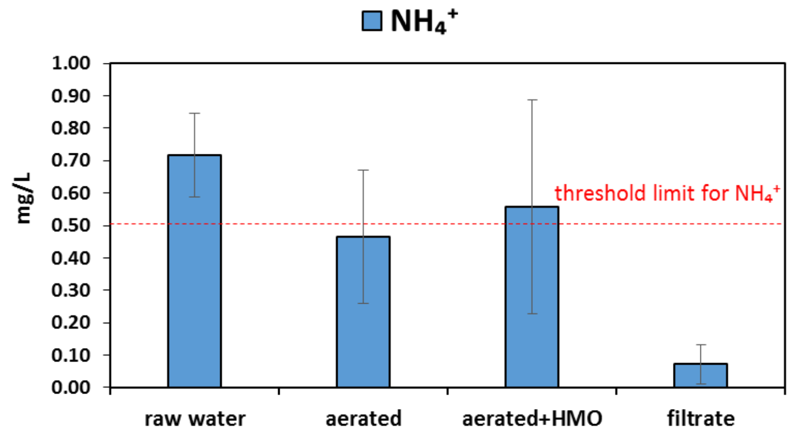

Figure 7. Average concentration within treatment stages in pilot plant

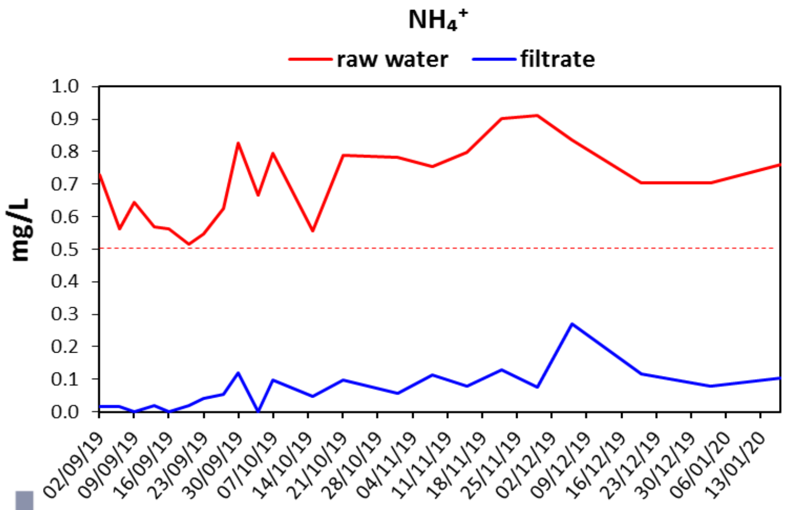

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Figure 7. Concentration of ammonium in raw water and after treatment

The oxidation of NH_4^+ to nitrate could be described by the net reaction:

$$NH_4^+ + 3.3O_2 + 6.7HCO_3^- \rightarrow 0.129C_5H_7O_2N + 3.37 NO_3^- + 1.04\ H_2O + 6.46H_2CO_3$$

The nitrification process consists usually of two stages:

- ammonium-oxidizing bacteria, i.e. *Nitrosomonas, Nitrosospira, Nitrosococcus, Nitrosolobus* and *Nitrosovibrio*, oxidize ammonium ion to nitrite as follows:

$$NH_4^+ + O_2 \rightarrow 2H^+ + H_2O + \mathbf{NO_2^-}$$

- the nitrite-oxidizing bacteria, i.e. *Nitrobacter, Nitrospira, Nitrospina, and Nitrococcus*, oxidize next the nitrite to nitrate:

$$NO_2^- + 0,5O_2 \rightarrow NO_3^-$$

What if NO_2^- has been formed during bio-oxidation of NH_4^+ ?

Table 1. Threshold limits stated in [RT I, 26.09.2019, 2]

Parameter	Threshold limit
NH_4^+, mg/L	0.5
NO_2^-, mg/L	0.5
NO_3^-, mg/L	50.0

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ANALÜÜSIAKT EE19002895 - Vesi

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Proovivõtuaeg: 20.09.2019 09:30
Laborisse tulek: 23.09.2019 14:20
Analüüsi lõpp: 24.09.2019 12:01
Proovivõtukoha valdaja:
Proovivõtukoht:
Proovi märgistus: Filtraat

Näitaja	Katsemeetod	Tulemus	Ühik
Nitrit (NO_2^-)	EVS-EN ISO 13395	< 0,016	mg/l

Kinnitas: keskkonna- ja analüütilise keemia osakonna juhataja Katri Vooro 26.09.2019

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