TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

REMOVAL OF IRON, MANGANESE, AMMONIUM, AND RADIONUCLIDES FROM DRINKING WATER USING HMO-TECHNOLOGY – A PILOT STUDY

RAUA, MANGAANI, AMMOONIUMI JA RADIONUKLIIDIDE EEMALDAMINE JOOGIVEEST KASUTADES HMO TEHNOLOOGIAT – PILOOTUURING

MASTER THESIS

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Tallinn 2021

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THESIS TASK

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Thesis topic:

(in English) Removal of iron, manganese, ammonium, and radionuclides from drinking water using HMO-technology – a pilot study

(in Estonian) Raua, mangaani, ammooniumi ja radionukliidide eemaldamine joogivest kasutades HMO tehnoloogiat – pilootuuring

Thesis main objectives:

1. Conduct a research on the presence of radionuclides and other constituents (Fe, Mn, NH_4^+) in the groundwater of the Cm-V aquifer system
2. Provide information about conventional water treatment technologies
3. Assess the performance of HMO-technology on the pilot scale

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Life Alchemia seminar participation „Purification of drinking water from natural radionuclides and management options for NORM" in Viimsi	March, 2020
2.	Cm-V groundwater radiological review, analysis of conventional treament methods	January, 2021
3.	Fe, Mn, NH_4^+, ^{226}Ra, ^{228}Ra removal efficiency assessment	February, 2021
4.	Identification of the most appropriate treatment mode	March, 2021

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CONTENTS

PREFACE

This thesis was prepared on the basis of data collected from pilot scale research in Viimsi. The HMO-technology implemented there, based on collaboration between Spain and Estonia, is a part of European Life Project (LIFE16 ENV/ES/000437).

I wish to express my appreciation to all the organizations and their people that made this project possible. These include University of Tartu, Viimsi Vesi AS, and others. I would like to thank both of my supervisors, PhD Juri Bolobajev and PhD Siiri Salupere, for their pragmatic approach as well as continuous support during the period of work on my Master Thesis.

Tallinn,
May 2021
Jaana Ehiloo

List of abbreviations and symbols

ADS – adsorption
BAT – Best Available Technology
Bq – the becquerel, SI unit of radioactivity
Ci – the curie, non-SI unit of radioactivity
Cm-V – Cambrian-Vendian
DNA – deoxyribonucleic acid
EGT – *Eesti Geoloogiateenistus*; Geological Survey of Estonia
EPA – US Environmental Protection Agency
EU – European Union
Euratom – European Atomic Energy Community
FMH – MnO_2 based catalytic filter material
Gy – the gray, SI unit of absorbed dose
HMO – hydrous manganese oxide
ICRP – International Commission on Radiological Protection
ID – indicative dose
IX – ion-exchange
LOD – the limits of detection
MBBR – Moving Bed Biofilm Reactor
NORM – Naturally Occurring Radioactive Materials
PAN – 1-(2-pyridylazo)-2-naphthol method
RO – reverse osmosis
SI – International System of Units
Sv – the sievert, SI unit of biological doses (equivalent dose, effective dose)
WFB – water filter backwash
WHO – World Health Organization
WTP – water treatment plant

INTRODUCTION

Safe and sufficient, high quality drinking water is essential for our everyday activities. Nonetheless, only a minor part of water sources provide water pure enough to be consumed directly. In order to meet the demands of all sectors of the population, standards and regulations, which are based on recent scientific research, impose obligations to monitor drinking water thoroughly.

Nowadays, special attention is paid to the presence of natural radioactivity in the groundwater. According to the Geological Survey of Estonia, more than 40% of Estonian towns and cities receive their water from the Cambrian-Vendian aquifer system, which is endowed with naturally occurring radionuclides. To assess the possible health effects caused by radionuclides in drinking water, indicative dose is estimated based on the concentrations of radionuclides in a drinking water source. The International Commission on Radiological Protection suggests using 0.1 $\text{mSv}\cdot\text{year}^{-1}$ as a parametric value for the indicative dose. Below this value, drinking water can be considered safe from the radiological viewpoint. Exceeding the parametric value should serve as a trigger for further investigation.

The problem of radioactivity in drinking water exists in the USA, the Middle East, and several European countries. However, radioisotopes ^{226}Ra and ^{228}Ra are believed to be the most problematic in the groundwater of Northern and North-Eastern regions of Estonia. Besides the presence of radionuclides, groundwater may contain other inorganic constituents, such as iron (Fe), manganese (Mn), and ammonium cation (NH_4^+), in concentrations that do not always satisfy the drinking water quality requirements.

In Estonia, the concentration of substances and microorganisms in drinking water should not exceed the threshold limits provided in the Regulation №61 of the Minister of Social Affairs (RT I, 26.09.2019, 2) on "Quality and monitoring standards and methods of analysis for drinking water". To comply with drinking water quality standards, it is important to implement appropriate treatment techniques.

The types of treatment technologies that are reasonable to overview include reverse osmosis, ion-exchange, adsorption, chemical precipitation, and lime-softening. These technologies, however, would have a number of drawbacks such as high operational costs or a generation of naturally occuring radioactive materials.

The primary focus of this thesis was to examine the preformed hydrous manganise oxide technology for water treatment as an alternative to current removal methods. The object of research was the pilot plant located at the Viimsi water treatment facility (Viimsi, Estonia). Several tests and analyses have been carried out throughout the operational period from October 2018 to February 2020, which formed the basis of this thesis.

1. LITERATURE REVIEW

1.1 The presence of Fe, Mn, and NH_4^+ in drinking water

Possessing unique solvent properties water has an ability to dissolve a variety of substances of either organic, or inorganic origin. Most of water constituents are essential to maintaining life on Earth, but at some circumstances the presence of certain elements in water could be undesirable, especially if water is used for drinking purposes.

Since manganese and iron are one of the most abundant elements in the Earth's crust, their concentrations in the groundwater are above normal [65]. The metal ions could be considered as natural emissions, whereas ammonium's presence in the catchment area has more complex anthropogenic background [63].

1.1.1 Iron

Iron is a transition metal that easily reacts with air oxygen forming insoluble oxyhydroxides known as a rust. Generally, iron exists in the environment in the form of its oxides. However, hydroxides, carbonates, and sulphides are also present [44].

In the absence of oxygen in water, aqueous Fe(II) could be present at concentrations up to several $mg \cdot L^{-1}$ without any discoloration or turbidity of water. Getting in contact with oxygen, e.g., in plumbing systems of drinking water supplies, Fe(II) oxidizes to its insoluble state Fe(III) forming a rust-coloured silt [64].

Despite concentrations of iron below 0.3 $mg \cdot L^{-1}$ do not affect the taste of drinking water, turbidity and colour could develop at levels as low as 0.05-0.1 $mg \cdot L^{-1}$. In addition, iron could stimulate the progress of undesirable bacterial growth, which negatively influences the water quality [64].

In Estonia, the maximum permissible limit for iron is 0.2 $mg \cdot L^{-1}$ [12]. High iron concentrations are common to groundwater bodies over the country because of continuous infiltration and movement through a layered sedimentary rock. For instance, high iron levels were detected in the well of Vasavere (35.59 $mg \cdot L^{-1}$) as well as in the wells of the Middle Devonian aquifer system in South Estonia (6.26 $mg \cdot L^{-1}$). Furthermore, groundwater bodies of northern islands, e.g., Naissaar, Aegna, and Prangli, are also rich in iron [47].

According to the US National Research Council, the Recommended Dietary Allowances of iron for adult women is 18 mg·day^{-1} and for adult men 8 mg·day^{-1}. Reported daily consumptions of iron in food vary from 10 to 14 mg [41].

For example, drinking water containing 0.3 mg·L^{-1} of iron would add about 0.6 mg to the daily intake. Dosage of 200-250 mg·kg^{-1} of body weight is considered lethal, though under certain circumstances death has occurred following much lower ingestion of doses [64]. Iron chronic overdosing can damage primarily the digestive system and other organs. The intoxication poses a risk to people with a genetic disorder (hemochromatosis) and to those receiving continuous blood transfusions [35].

1.1.2 Manganese

In most cases, manganese coexists with iron. As with iron, manganese does not present naturally in its elemental form existing mainly as a part of several minerals of the Earth’s crust. The most environmentally significant manganese complexes are those that contain Mn^{2+}, Mn^{4+} and Mn^{7+}. Mn, along with Fe, plays an important role in several processes undergoing in living organisms including human body, e.g., in cellular metabolism, such as superoxide dismutase formation, or processing of cholesterol [65].

It is known that aqueous manganese could be oxidized to insoluble MnO_4^- by means of using domestic bleach. This in turn may cause the formation of brown or grey stains on laundry. At concentrations above 0.1 mg·L^{-1}, Mn imparts an unpleasant taste to beverages. Furthermore, at concentrations as low as 0.02 mg·L^{-1}, manganese precipitates from water and settles in plumbing systems forming an undesirable black slurry. The World Health Organization (WHO) and the European Economic Community have set the standard of manganese at 0.05 mg·L^{-1} for both industrial and drinking water, which is also an indicator for Estonia [62].

It is clear that manganese intake from food is considerably higher than that from drinking water. Reported daily intake of manganese for adults varies between 0.7 to 10.9 mg. The variance is attributable to gender, eating habits, age difference, and environmental conditions. The latter depends mostly on proximity to a manganese source [65].

At the average concentration of 10 $\mu g \cdot L^{-1}$ in drinking water reported in the National Inorganic and Radionuclide Survey (USA; data collected between 1984 and 1986), the ingestion of manganese would be 20 $\mu g \cdot day^{-1}$ for an adult accepting a daily water intake of 2 litres. Therefore, drinking mineral water systematically will enhance the manganese amount [65].

Inadequate manganese intake may lead to negative health effects. Manganese deficiency in human organism is quite a rare condition, whereas long-lasting exposure to high manganese concentrations causes a syndrome known as "manganism". This syndrome is characterized by mood changes, feeling of weakness, reduced response state, and other compulsive behaviors. Generally, the symptoms were observed in those cases, where high concentrations (above 5 $\mu g \cdot m^{-3}$) of manganese were inhaled from air rich in manganese containing dust, e.g., during the mining of manganese ores [65].

1.1.3 Ammonia

The term "ammonia" refers to the compound containing nitrogen and hydrogen (NH_3) as well as the ammonium cation (NH_4^+). The latter is prevalent in aqueous phase at circumneutral pH values. NH_4^+ is less reactive than NH_3 and plays a major role in biological nitrogen fixation, nitrification, and mineralization [63].

In groundwaters, natural levels of ammonia are below 0.2 $mg \cdot L^{-1}$. Nonetheless, ammonia may appear in drinking water because of disinfection with chloramines. High concentrations of ammonia in water bodies may indicate the potential risk of the faecal pollution, e.g., through runoffs from agricultural activity, etc [63].

High content of ammonia in raw water could lead to manganese-removal filters' malfunction as a result of increased oxygen consumption during the nitrification processes, spawning musty odour and earthy taste. Nitrite occurs as the product of catalytic reaction, which includes ammonium cation, or during the spontaneous colonization of filter material by ammonia-oxidizing microorganisms [2].

Despite ammonium is a general by-product of nitrogen metabolism in mammalian organisms, its inorganic salts, e.g., ammonium chloride (NH_4Cl), may have negative impact on several biochemical processes affecting by displacement of acid-base equilibrium, or lowering the tissue tolerance to insulin [63].

In Estonia, the threshold limit for ammonia in drinking water is 0.5 $mg \cdot L^{-1}$ [12]. Although NH_4^+ is not considered as a toxic substance, it is known to negatively influence the quality and usability of groundwater. The situation is complicated by the fact that at anoxic conditions of groundwater aquifers there is no mechanism available for oxidation or removal of NH_4^+ from water. For example, there is no compelling evidence for nitrification nor anammox (the process during which NH_4^+ oxidizes anaerobically with reduction of NO_2^- to form N_2) in the anoxic stratum of aquifer [2].

1.2 Ionizing radiation and radioactivity

Radiation occurs between two surfaces without direct contact in the form of electromagnetic waves or as a particle beam. Its electromagnetic spectrum obeys the same laws as light, e.g., it may be transmitted through space and vacuum environment, etc. Depending on the amount of energy there are two categories of radiation: a) ionizing and b) non-ionizing [17].

Ionizing radiation possesses enough energy to remove electrons from atoms causing ionization. α-, β-, or γ-rays emitted from radioactive materials are regarded as being ionizing [68].

Compared to beta and gamma radiation, alpha radiation has little penetrating power. Alpha particle is a helium nucleus consisting of two protons and two neutrons. In natural environment, α-rays are emitted by the radioactive decay of heavy elements, e.g., thorium, uranium, and radon, where long transformation chains occur. Alpha radiation loses its energy rapidly when transferring through matter making it impossible to travel through an ordinary sheet of paper. Nevertheless, once emitted inside or near a cell, these heavy (ca 7 200 times the mass of an electron) and slow-moving particles may cause irreparable damage to biological material [1].

Beta radiation, depending on the amount of neutrons in a radioactive nucleus, may be either negatively or positively charged. During a β^- transformation, a neutron is changed into a proton and an electron, which is emitted from the nucleus. On the other hand, the opposite β^+ process involves a proton converting into a neutron which leads to positron emission. β-rays are known for their high velocity and the ability to cause injuries, a.k.a. "beta burns", to the superficial body tissues [1].

Alpha- or beta decay usually leaves the nucleus in an excited energy state. However, the nucleus cannot remain in this state and will release the residual energy in the form of γ-rays in order to achieve stability. The process is also called de-excitation. Gamma radiation originates in the nucleus of an element; its high-energy photons are highly penetrating, which makes gamma emission the leading source of external radiation hazard [1]. Other types of ionizing radiation include X-rays (also referred to as Röntgen radiation which has applications in medicine), neutron, and positron radiation [68].

The impromptu decay of atoms is called radioactivity, and the surplus energy emitted is a type of ionizing radiation. Radionuclides, i.e., radioactive nuclides, radioactive isotopes, or radioisotopes, are unstable elements that emit ionizing radiation as a consequence of disintegration [66]. The type of emitted radiation, its energy, and the element’s half-life are used to describe and identify radionuclides. Half-life is the range of time required for the activity of a radionuclide to fall to half its original value. For example, ^{228}Ra has a half-life of 5.75 years, while ^{226}Ra has a half-life of 1 600 years [4].

The term “activity” is used to quantify radioactive substances. It is expressed as the decay rate of a radionuclide. According to the International System of Units (SI), activity is expressed in becquerels (Bq); 1 Bq equals one radioactive decay per second. The old unit – the curie (Ci), named after Pierre and Marie Curie, who discovered polonium and radium, – was based on the activity of 1 gram of ^{226}Ra ($3.7 \cdot 10^{10}$ s^{-1}) [68].

1.2.1 Exposure to ionizing radiation

The negative impact of ionizing radiation on the structure of deoxyribonucleic acid (DNA), one of the two types of molecules that encrypt genetic information, has been examined over the years. Apparently, DNA modifications that cannot be repaired during the replication cause irreparable harm resulting in tumour formation at the macro level. Ionizing radiation may induce DNA breaks, which undoubtedly makes substantial changes in cellular processes especially in case of reproduction mechanism [51].

Radiation-evoked DNA damage proceeds through two complex mechanisms: a) direct and b) indirect. The direct effect occurs, when ionizing radiation comes into direct contact with the DNA molecule and ionizes it. This results in an ejection of an electron from the DNA molecule [51].

The indirect effect is caused by the reactions between DNA and free radicals (including the hydroxyl radicals, HO°), which are formed when ionizing radiation causes ionization and excitation of water molecules [51].

Radiation is widespread throughout the environment. In fact, a greater part of the average radiation dose (ca 80%), which people receive annually, is related to natural sources. Natural radiation originates from air, food, and water. For example, radon is the leading component of natural radiation mostly emerging from rocks and minerals of the Earth's crust [68]. Background levels differ geographically due to geological variations. In that regard, radiation in certain areas may be far above the average value [66]. In addition, humans are exposed to cosmic radiation which is dependent on the altitude.

Nuclear power generation, consumer products, e.g., smoke detectors, televisions, building materials, etc., and medical devices, such as X-ray and radiography machines, are all types of man-made radiation sources. According to Nuclear Regulatory Commission, major isotopes in the field of artificial assets would be ^{131}I, ^{137}Cs, ^{60}Co, ^{192}Ir, and others [60].

Radiation exposure may be either internal or external. Internal impact to ionizing radiation involves radionuclides, which enter organism directly, e.g., inhalation, ingestion, or through injuries. On the other hand, external impact occurs due to cosmic and terrestrial radiation, e.g., gamma radiation emitted from the ground and building materials. In specific situations, e.g., radiation accidents, deposition of air-based radioactive substances, such as liquid or dust, on the skin becomes an additional source of external radiation. External exposure can be preventable, when the subject avoids the exposure by removing the radioactive material or moving outside the radiation field [66].

Furthermore, exposure from different sources of ionizing radiation can be classified into three exposure situations [66]. The first, a planned exposure situation, is defined as:

- daily activities involving the deliberate introduction of radiation sources with concrete targets or planned operations that result in an exposure to a radiation source, e.g., use of radiation in industry, medical purposes, or research [23].

The second one, an existing exposure situation, is:

- a situation that already exists, and a decision on control must be taken, e.g., natural background radiation from the environment or exposure to indoor radon. Existing exposure situations are more problematic to assess than planned exposure situations [23].

The last type, an emergency exposure situation, may be described as:

- an unexpected event that requires immediate prevention, e.g., nuclear power plant accident, malicious act, etc [23].

In order to implement the assessment correctly, it is necessary to understand that only the energy absorbed by the body has deleterious health consequences. This is expressed through amount of energy ($d\varepsilon$) per unit mass (dm) of the tissue and/or organs and is called an absorbed dose (Equation 1.1). SI unit of measure for the absorbed dose is the gray (Gy, or J·kg^{-1}) [68].

$$D = \frac{d\varepsilon}{dm}, \tag{1.1}$$

where D – the absorbed dose, Gy,

$d\varepsilon$ – the mean energy, J,

dm – the mass element, kg.

However, the concept of the "absorbed dose" does not take into account the biological effects of ionizing radiation. Radiation-related health risks to an organ or a tissue are measured by equivalent dose, which considers the type of ionizing radiation caused by the absorbed dose. For example, in the 1950s it has been established that neutrons cause ten times more harm, i.e., neutrons are more mutagenic than photons. All biological doses are measured in sieverts (Sv, or J·kg^{-1}) [49].

In practice, to express the quantities of the biological doses it is more efficient to use smaller units, such as millisieverts (mSv) or microsieverts (μSv), instead of larger ones. Moreover, the rate, at which the dose is received, is of great importance. Commonly, dose rate is expressed in mSv or μSv per time unit, e.g., a year, an hour, etc [66].

When estimating the value of the equivalent dose, a radiation weighting factor (w_R) is highly relevant. Radiation weighting factors depend on the radiation type, while tissue weighting factors depend on the tissue which is specifically affected by this radiation [23].

If different types of radiation affect an organ simultaneously, the summation formula (Equation 1.2) is applied [23]:

$$H_T = \sum_R w_R \cdot D_{T,R}, \tag{1.2}$$

where H_T – the equivalent dose in an organ or tissue T, Sv,

w_R – the weighting factor for radiation R, standard units,

$D_{T,R}$ – the absorbed dose in a specified organ or tissue T for radiation R, Gy.

Values of radiation and tissue weighting factors can be found in the publications of the International Commission on Radiological Protection (ICRP) [23]. Calculations of the equivalent dose provide information on the amount of energy taken by an organ, or any other part of the organism, whereas an effective dose represents a full-body exposure, i.e., an individual's vulnerability to radiation. The term "effective dose" is fundamental in a scope of radioprotection [48].

The effective dose is computed on the basis of the equivalent dose multiplied by a tissue weighting factor. As indicated in the Equation 1.3, if all the organs and tissues in the human body are irritated, the sum of various tissue weighting factors equals 1 ($\Sigma w_T = 1$) [23]:

$$E = \sum_T w_T \cdot H_T = \sum_T w_T \sum_R w_R \cdot D_{T,R}, \tag{1.3}$$

where E – the effective dose, Sv,

w_T – the weighting factor for organ or tissue T, standard units.

In terms of drinking water safety, the concept of an indicative dose (ID) applies. ID corresponds to the committed effective dose, which takes into account a yearly water consumption of 730 L (2 L·day^{-1}) and the activity concentration of radioisotopes in water (Bq·L^{-1}). ID is usually expressed in mSv·year^{-1}. All natural and artificial radionuclides present in drinking water should be taken into consideration, besides tritium, potassium-40, radon, and short-lived radon decay products [7].

The ID from radionuclides in drinking water can be calculated by the Equation 1.4 [57]:

$$ID = \sum A_i \cdot f_i \cdot V, \tag{1.4}$$

where ID – the indicative dose, mSv·year^{-1},

A_i – the activity concentration of radionuclide i in water, mBq·L^{-1},

f_i – the effective dose coefficient for ingestion of radionuclide i, Sv·Bq^{-1},

V – yearly water consumption of 730 L, 2 L·day^{-1}.

1.2.2 The presence of radionuclides

Problems of natural radioactivity exist all over the world, including the United States, the Middle East, and several European countries (Table 1.1). The presence of radioisotopes in water supply is considered to be a part of terrestrial radiation. Natural radionuclides in drinking water are either of primordial origin – originating from radionuclides which have been presented on Earth since it was formed – or cosmogenic – radionuclides produced by cosmic radiation. Primordial radionuclides typically prevail [42].

Table 1.1 Effective doses of drinking water consumption for different European countries [13]

Country	**Effective dose** ***mSv·year^{-1}***	**Radionuclides present**	**Comment**
Spain	4.20	Primordial radionuclides	Maximum dose
Spain	3.30	^{222}Rn	Maximum dose
Sweden	0.51	^{222}Rn, ^{226}Ra, ^{238}U, ^{234}U	Well water
Finland	0.39	^{222}Rn, ^{226}Ra, ^{238}U, ^{234}U	Well water
Ukraine	0.22	^{222}Rn, ^{226}Ra, ^{238}U	Well water
Denmark	0.16	^{222}Rn, ^{226}Ra	Well water (Bornholm island)

Crystalline rocks, such as granites, are enriched with ^{238}U. Sedimentary rocks, e.g., crystalline limestones, can also be rich in uranium, if they are derived from crystalline rocks. ^{238}U is not potentially mutagenic; however, it is toxic enough to cause kidney damage at elevated levels coming from drinking water consumption. Concentrations of uranium in groundwater depend on various factors such as redox (reduction-oxidation) potential of water, pH, and the presence of HCO_3^- [59].

Concentrations of uranium in drinking water vary drastically at intervals between 0.02 to 200 $\mu g \cdot L^{-1}$. Thorium in drinking water is not usually measured due to its low water solubility, although thorium concentration in human bones corresponds to $1 \cdot 10^{-15}$ $Ci \cdot g^{-1}$ (in ash, equals $3.7 \cdot 10^{-5}$ $Bq \cdot g^{-1}$); the uranium's presence in the bones is approximately ten times greater [42].

^{222}Rn is a noble gas presented in most groundwaters in a dissolved state. Due to desorption mechanisms, radon emanates into the atmosphere, where it could be inhaled. Inhalation of the gas poses a risk of lung cancer. The amount of ^{222}Rn, in contrast to ^{238}U, is not related to geochemical conditions of groundwater. ^{222}Rn prevails over ^{220}Rn because of the latter's short half-life (ca 55 s), which prevents ^{220}Rn build-up in an environmental compartment [59].

Furthermore, both ^{222}Rn, which is formed as a next stage of the uranium-238 decay chain, and ^{220}Rn, which is formed as a next stage of the thorium-232 decay chain, concentrations depend primarily on the concentration of the parent nuclide.

In surface water, the levels of radon gas reach $1 \cdot 10^{-12}$ Ci$\cdot$L^{-1} (equals $3.7 \cdot 10^{-2}$ Bq$\cdot$L^{-1}), whereas in groundwater radioactivity concentrations are usually a thousand times higher [42].

Radium isotopes are the daughter products of the decay of uranium and thorium. Both ^{226}Ra and ^{228}Ra are classified as carcinogenic. Radionuclides dissolved in drinking water have been revealed to human health concerns, increasing the cancer risk as a result of accumulation in bones and soft tissues [59]. According to National Research Council, radium isotopes have the greatest potential in producing radiation doses. Its concentration in drinking water may be as high as $1 \cdot 10^{-10}$ Ci$\cdot$L^{-1} (equals 3.7 Bq$\cdot$L^{-1}) [42].

1.2.3 Natural radioactivity in the Cambrian-Vendian aquifer

In Estonia, more specifically in the Cambrian-Vendian (Cm-V) aquifer (Figure 1.1), ^{226}Ra and ^{228}Ra are of great concern. Their occurrence is thoroughly examined by government organizations.

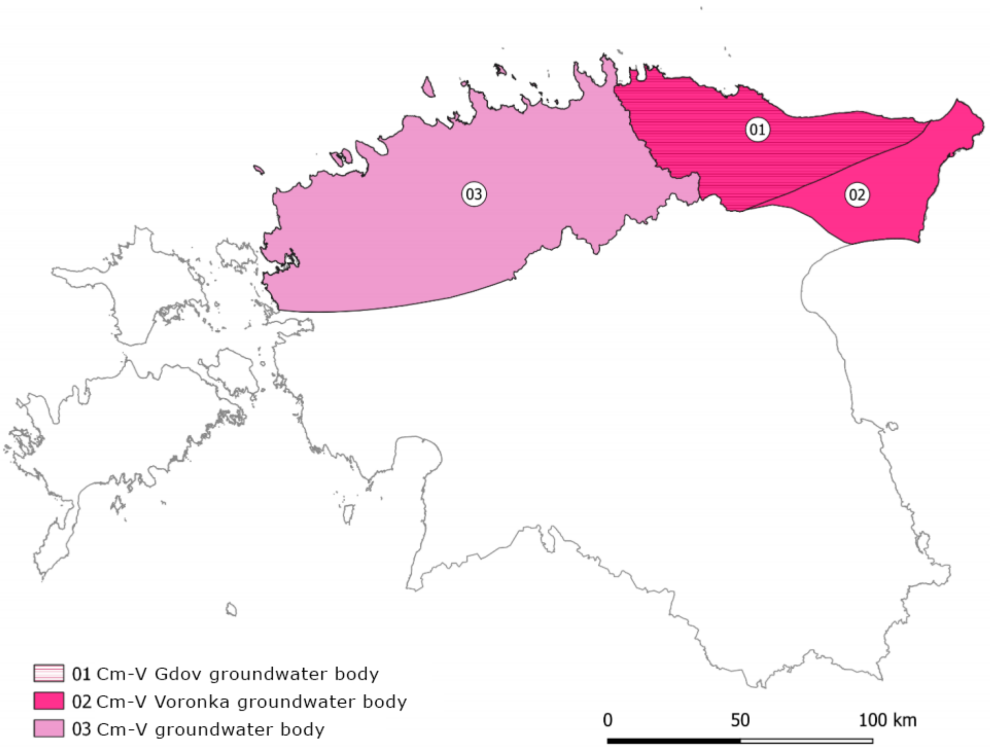

Figure 1.1 Location of the Cm-V aquifer system [34]

The Cm-V aquifer system is situated in the water exchange zone with predominantly reducing conditions. Its deep-seated groundwater is rich in microelements and various constituents [33]. According to the report of the Geological Survey of Estonia (EGT), more than 40% of Estonian towns and cities receive their water from the Cm-V aquifer [47]. There are three important groundwater bodies within the system: Cm-V, Cm-V Gdov, and Cm-V Voronka [25].

Several studies have been carried out to evaluate the quality of Cm-V groundwater bodies and determine their radiological hazards. In the year of 2005, Estonian Radiation Protection Centre reported that ID of 80% of the wells exceed the parametric value of 0.1 mSv·year^{-1} [68].

In the year of 2010, Forte et al. calculated the total ID from ^{226}Ra and ^{228}Ra in Estonian drinking water for different age classes. The research revealed that the doses tend to be higher in the younger age categories because of the high radium metabolic adsorption into bones during the growth process. For example, radiation doses for Cm-V waters may reach 12 mSv·year^{-1} in case of children under one year old and 0.3 mSv·year^{-1} in case of adults. According to the report, 18% of the Estonian population, i.e., 230 000 inhabitants, drink water with higher radioisotopes concentration than the parametric value [16].

1.3 Drinking water quality standards and corresponding aspects of legislation

In Estonia, drinking water quality related matters are regulated by Ministry of Social Affairs. Corresponding legislative aspects are controlled through the Public Health Act (RT I 1995, 57, 978) and the Water Act (RT I, 22.02.2019, 1). Ministry of the Environment, an authority engaged in drinking water safety aspects, is responsible for the protection of drinking water supplies and project investments [38].

The procedure for the water analyses and the indicators that determine the quality of drinking water are described by the Regulation №61 of the Minister of Social Affairs (RT I, 26.09.2019, 2) on “Quality and monitoring standards and methods of analysis for drinking water” [38].

This regulation implements the requirements given by the Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption into Estonian legislation [38]. The abovementioned Regulation №61 also contains the requirements given by the Council Directive 2013/51/Euratom of 22 October 2013 laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption [7].

Estonian groundwater bodies, including the Cm-V aquifer system, are listed in the Regulation №48 (RT I, 02.10.2019, 5) "Water classes of groundwater bodies, values of the quality indicators complying with the water classes of groundwater bodies, and the procedure for defining water classes" [33].

From the viewpoint of exposure situations, intake of radioactive nuclides by drinking water consumption could be classified as: a) a planned exposure situation and b) an existing exposure situation. However, ICRP classifies drinking water consumption as a planned exposure situation only; the same approach is used by EU.

The dose constraint for planned exposure situations (0.1 $\mathrm{mSv \cdot year^{-1}}$) suggested by ICRP is used as the parametric value of ID in EU. Exceeding the parametric value should serve as a trigger for further investigation [22]. This in turn does not mean that the drinking water is unsafe; nonetheless, a risk assessment should be carried out to determine whether preventive actions are necessary to reduce the potential health risks [67]. An example of a preventive action is implementation of a water treatment technology.

1.4 Available technologies for removal of the constituents

1.4.1 Reverse osmosis (membrane processes)

The term "desalination" is used to describe the process during which salt and other mineral components are being separated from water. As indicated in The Biennial Report on Freshwater Resources [18], desalination is confirmed as a potential source for producing drinking water.

Membrane and distillation processes are both applied to achieve desalination. Yet reverse osmosis (RO) possesses the greatest potential for drinking water production [37]. In addition, US Environmental Protection Agency (EPA) identifies RO as the Best Available Technology (BAT) for uranium, radium, and photon emitters removal.

According to EPA, RO technology can remove up to 99% of these radioisotopes as well as other constituents, e.g., arsenic and nitrate [11]. For instance, Clifford et al. examined the efficiency of three different RO modules (thin-film composite, thin-film polyamide hollow-fibre, and composite spiral-wound). In all three studies, radium-226 rejection exceeded 90% [5].

The basis of RO is a phenomenon called osmosis; the movement of solids through a selectively permeable membrane, where the concentration gradient serves as a driving force. When the water proceeds through a semipermeable membrane, it always diffuses from the state of the lower osmotic potential to the one with the higher osmotic potential [50].

In the case of RO, hydraulic pressure functions as a driving force. It is a separation technique, which can be used either to concentrate or purify liquids without a change of the phase state. Flow of water from the dilute solution side to the concentrated solution side may be prevented by an opposing hydrostatic pressure. In the context of membrane processes, this pressure is known as the osmotic pressure [50].

To force the liquid flow to the direction opposite to that caused by osmosis, hydrostatic pressure of RO must be higher than the osmotic pressure gradient. The transport of water via RO system may be described as follows: a) absorption through the membrane surface, b) diffusion across the thickness of the membrane, and c) desorption from the permeate [50].

Recognizing the need of high-pressure, the RO technology requires high energy demands. For example, operating pressures of 100 to 300 kPa are needed to overcome the osmotic pressure for low salinity waters, i.e., for typical drinking waters [50]. Nevertheless, membrane systems may experience the risk of fouling and flux decline, which eventually leads to membrane replacement [46]. Another drawback of membrane processes (as a technology used for radioisotopes removal) is the generation of radioactive wastewater, which must be disposed of with subsequent posttreatment of the membrane media [40].

1.4.2 Ion-exchange

Ion-exchange (IX) is a stoichiometrically balanced process under which undesired ionic contaminants are removed from an aqueous solution by means of their binding to the surface of the solid polymeric IX resin with the simultaneous exchange for other ions with a similar charge. IX resins consist of insoluble microporous beads that contain approximately 50% of water dispersed in the gel-like sections of the polymeric material, from which polystyrene and polyacrylate are widely distributed [43]. Moreover, IX resin undergoes supersaturation with a loosely held solution. The selection of this solution depends on the process and the composition of water. For example, sodium is used for bead covering to remove hardness ions [56].

In water treatment, IX technology is used mainly for water softening focusing on removal of calcium and magnesium ions. Depending on the softener's effectiveness rate, the process may be applied to remove as much as 5-10 $mg \cdot L^{-1}$ of iron and manganese. In addition, IX is applied to remove ammonium cation and toxic metals such as radium, uranium, etc [56]. In order to eliminate both uranium and radium, mixed bed resins with cation and anion exchangers are applied [26].

To set an ion exchange reaction, both the contaminant and the exchanged substance must be either positively (cations) or negatively (anions) charged. However, by examining the reaction's mechanisms it was found that different ions of the constituents interact differently with the exchangers' ions. A weakly bound ion may predominantly be replaced with a stronger binding ion [43]. The effect is known as the principle of selectivity (Figure 1.2), on which IX acts [27].

Cation-exchange resin:

$Ra^{+2} > Ba^{+2} > Ca^{+2} > Mg^{+2} > K^{+1} > NH_3^{+1} > Na^{+1} > Li^{+1} > H^{+1}$

Anion-exchange resin:

$SO_4^{-2} > NO_3^{-2} > CO_3^{-2} > HCO_3^{-1} > Cl^{-1} > OH^{-1}$

Figure 1.2 The principle of selectivity

Monovalent ions, e.g., sodium, have one positive charge and their selectivity is weak, whereas divalent molecules, e.g., calcium, magnesium, etc., have two positive charges. As a result, sodium ion will be displaced. Another factor influencing the selectivity is the molecular weight. The greater it is, the higher is the affinity of IX resin towards the ion [27].

According to the selectivity series, heavy metals bind more strongly than alkaline earth metals and those bind more strongly than alkali metals etc. The exchange continues until resin's beads become preloaded, or fouled, with ions attached to its surface. When this occurs, IX resin must be recharged, or regenerated, using the backwash with regeneration solution, i.e., concentrated salt solutions [43]. Waste solutions produced throughout these procedures are typically rich in the contaminants removed and the regenerant. Nonetheless, resin fouling may become a point of concern with IX. In the case of radionuclides, the resin may require radioactive waste management instead of regeneration [9].

1.4.3 Adsorption

Adsorption (ADS) is the process of deposition of one or more fluid components (the mobile phase) onto the surface of the solid adsorbent (the stationary phase). In drinking water treatment, ADS is used mainly to remove organic substances such as carboxylic acids, lipids, and hydrocarbons [15]. In addition, ADS technology is capable to improve water taste and odour [24].

ADS mechanism may be presented as: a) the molecule transfer through the adsorbent's film, b) diffusion within the macro-, meso-, and micropores of the adsorbent, c) the final adsorption onto the adsorbent's surface.

Selection of the adsorptive material is crucial in terms of the treatment effectiveness. There are a large number of solids that can be utilized including flocculants, synthetic materials, etc [15]. Generally, drinking water treatment columns are equipped either with activated alumina or activated carbon media.

Activated alumina is a granular, porous form of aluminium oxide, Al_2O_3, with a surface area significantly over 200 $m^2 \cdot g^{-1}$. EPA suggests using activated alumina ADS as a small system compliance technology to remove uranium isotopes as well as other constituents, e.g., arsenate, selenate, and fluoride. It is known that activated alumina ADS is capable to remove approximately 99% of uranium isotopes [8].

Despite the abovementioned advantages, ADS with activated alumina is a pH sensitive process. For example, arsenic removal is favourable at pH levels from 5 to 6, whereas higher values (from 7 to 10) may be required to remove uranium isotopes. When multiple contaminants undergo activated alumina ADS, the primary treatment objective should be precisely determined [8].

Activated carbon used in ADS may be presented either in powdered or granular form depending on the adsorbers installed on a particular treatment plant. For instance, one of the most widespread granular media in the water treatment industry is Filtrasorb 400, which has a surface area of ca 1000 $m^2 \cdot g^{-1}$, 75% of which is located within the pores [24].

As with activated alumina, activated carbon ADS depends on the water chemistry to be treated, e.g., pH adjustments and addition of chemicals. It is advisable to apply activated carbon prior to oxidant injection due to the latter's negative impact on the ADS performance. As a matter of fact, when used with coagulation, the ADS removal effectiveness may be reduced [24].

The specific nature of groundwater used for drinking water production and interactions between water treatment technologies affect the overall ADS productivity. It is important to assess physical-chemical properties of the influent before indicating the possible application locations, which may be complex and financially costly, especially in the case of already operating water treatment plants [24]. When the adsorbent becomes exhausted, regeneration of the ADS media or its disposal may be required [8].

1.4.4 Chemical precipitation

In water treatment, precipitation occurs during a chemical reaction under which undesirable dissolved constituents are being converted into an insoluble form [61]. The latter is then called the precipitate, and the remaining liquid is called the supernatant.

Chemical precipitation is applied in order to remove soluble metallic ions, e.g., nickel, cadmium, etc., as well as anionic species, such as fluoride, phosphate, and organic molecules, e.g., phenols, aromatic amines. Major precipitation objective, however, remains water softening and stabilization, removal of heavy metals and phosphate [61]. It is known that iron and manganese may also be removed by chemical precipitation [6].

If compared with RO and IX, chemical precipitation is simpler in operation; it has the advantage of low energy and capital costs [61].

Nonetheless, the disposal of sludge produced during the precipitation constitutes a serious challenge as it should be treated before the landfill. Prediction the amount of sludge is crucial to define appropriate parameters involved in the following sludge treatment, e.g., total suspended solids and chemical oxygen demand [54].

Depending on the chemicals used, there are different types of precipitation. Wang et al. reports the presence of water treatment technologies based on hydroxide precipitation, sulphide precipitation, and carbonate precipitation. In the case of the hydroxide precipitation, ions of dissolved heavy metals precipitate under the influence of an alkaline agent. Usually, lime or caustic soda is used. Lime is generally converted into slurry, after which the generated solution is being fed into a mixing tank. Hydroxide precipitation by lime has many similarities to the lime-softening that will be discussed in the section below. The Equation 1.5 may be assumed as a summarized reaction of the hydroxide precipitation [61]:

$$M^{2+} + 2(OH)^{-} \rightarrow M(OH)_2, \tag{1.5}$$

where M^{2+} – heavy metal ion,

OH^- – alkaline reagent,

$M(OH)_2$ – insoluble metal hydroxide.

In the alkaline pH conditions, metal sulphides have lower solubilities than hydroxides. The operation principle of the sulphide precipitation is analogous to that of the hydroxide. Depending on the economic considerations, sodium sulphide, Na_2S, and sodium bisulphide, $NaHSO_3$, are the most common chemicals used. Due to the toxicity of the excess sulphide formed, this type of precipitation requires both pre- and posttreatment [61].

Cyanide may be precipitated by the addition of ferrous sulphate, $FeSO_4$, or zinc sulphate, $ZnSO_4$. The residuals generated in the end must be disposed with caution because of the cyanide tendency to break its complexes in response to sunlight [61]. The same approach is implemented to precipitate radium, where a radium-containing barium sulphate sludge undergoes treatment with barium chloride (so-called co-precipitation) [39]. However, regardless of the precipitation type, the observed treatment technology is strongly affected by both reaction and solubility equilibria.

1.4.5 Lime-softening

Lime-softening is a water treatment method where quicklime, CaO, is hydrated in order to form calcium hydroxide, $Ca(OH)_2$. The latter, also known as limewater, is then added to the feed to increase pH and precipitate objectionable ions [32].

In most of the cases, lime-softening is implemented to remove carbonate hardness from water. However, EPA recognizes lime-softening as a BAT for uranium and radium. It is assumed that single-stage softening may remove 80% of ^{226}Ra and ^{228}Ra. With enhanced lime-softening, these percentages increase up to 90% for radium [10] and up to 95% for uranium [40] isotopes. In addition, enhanced lime-softening is used to remove iron, manganese, and arsenic [10].

The difference between conventional and enhanced softening is that the latter has multiple treatment stages. The process aims at improving the removal of certain elements, e.g., radionuclides, without radically affecting the overall operation [53].

It is known that under nearly neutral conditions (pH between 6.5 and 7.5) uranium forms anionic uranyl carbonate complexes, such as $UO_2(CO_3)_2^{2-}$ or $UO_2(CO_3)_3^{4-}$, in contrast to radium isotopes, which tend to form the complexes with carbonates only at pH 10.25 or higher; high carbonate concentrations ($>60\ mg\cdot L^{-1}$) are also required for radium to precipitate. Therefore, water softening may be effective in radium removal as Ra belongs to the group of alkaline earth metals and usually behaves in a solution similarly to that of Ca and Mg [40].

Nevertheless, the enhanced lime-softening is an expensive technology, which requires monitoring and special personnel training. After the water is treated by lime, the treatment residuals must be extracted before the water can be used for drinking purposes. As with the chemical precipitation, those residuals undergo filtration or sedimentation. The total waste produced by the end of the process includes sludge, disposable media, and a backwash. It is reported that for every 0.45 kg of lime used, 0.90 kg of sludge are formed, i.e., the quantity of the waste is doubled [32].

1.5 HMO process

Manganese dioxide, or MnO_2, is a blackish material that exists in nature as the mineral pyrolusite. It was observed that manganese oxides have a great potential in removing heavy metal ions from water due to their high affinity. One of the characteristics of MnO_2 is a large surface area as well as a micro- or mesoporous structure [69]. Apart from the water treatment, MnO_2 has many other applications, e.g., the manufacture of dry cell batteries.

The implementation of manganese dioxide has proven its ability to remove Fe and Mn from water [62]. The tool is relatively inexpensive and has been widely used in the water treatment industry. In the case of hydrous manganese oxide (HMO) process, two important objectives are achieved. First, Fe and Mn are oxidized by HMO into insoluble forms (Equations 1.6 and 1.7) [40]. Second, it is believed that MnO_2 has relatively high sorption capacity towards divalent metal ions, including Ra^{2+}, due to the manganese particles being negatively charged [20].

$$4Fe(HCO_3)_2 + 2H_2O + O_2 \leftrightarrow 4Fe(OH)_3 \downarrow + 8CO_2, \tag{1.6}$$

$$2Mn(HCO_3)_2 + 2H_2O + O_2 \leftrightarrow 2Mn(OH)_4 + 4CO_2, \tag{1.7}$$

The sorption of metal ions on hydrous oxides and the exchange of hydrogen ions with cations may be described as follows (Equation 1.8) [55]:

$$M^{n+} + x[= R— OH] = M[R— O]_x^{(n-x)^+} + xH^+, \tag{1.8}$$

where *M* – the metal ion to be sorbed,

x – the number of moles in oxide,

[=R—OH] and *[=R—O]* – the oxide surface sites.

It is known that the effectiveness of radium sorption onto the manganese dioxide filter materials could be low in case of water with high salinity. The sorption of Ra depends mostly on the pH with its most efficient range from 4 to 8 [39]. Different removal mechanisms were proposed for radium and uranium radioisotopes. In the case of Ra, radium cations are being sorbed onto $Fe(OH)_3$ flocs and especially onto hydrated particles of $Mn(OH)_4$ (Figure 1.3). For uranium, however, the process is more complex. It includes adsorption, occlusion, and the formation of a precipitate [40].

The effect of iron and manganese on radium removal was also observed by Patel et. al [45] at the laboratory scale in Houston, Texas, USA. The presence of positively charged iron oligomers caused the reduction in radium sorption, while manganese had the opposite effect. Adsorption of Fe to the negatively charged surface of HMO was detected during in-situ $Fe(OH)_3$ precipitation with MnO_2.

Generally, the HMO-technology is not applied in NH_4^+ removal from water [19]. However, the experiments conducted at the Viimsi water treatment plant (WTP) demonstrated high ability in removal of ammonium ion. As a result, NH_4^+ concentration decreased below threshold limit. Bacterial oxidation of ammonium-nitrogen has been discovered in both aerator and filter media indicating the nitrification process. The results were obtained using ion-chromatography, where remarkable rise of NO_3^- was detected.

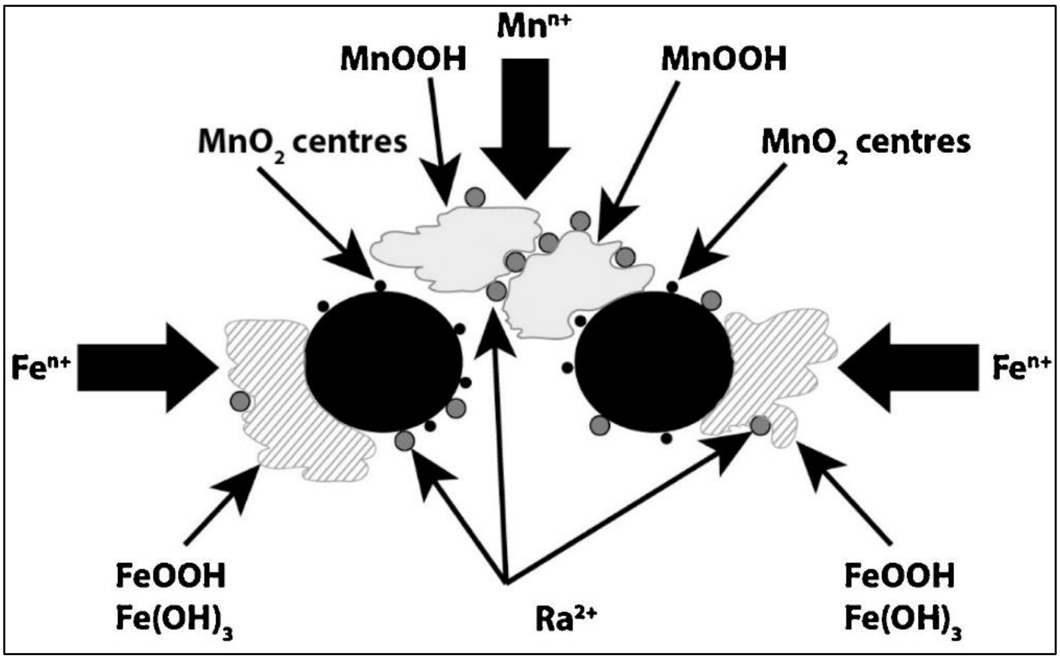

Figure 1.3 Formation of Ra-contaminated Fe and Mn complexes on the centres of MnO_2, Ra sorption on the filter material [19]

Contemporary manganese dioxide-based treatment is listed among the BAT by EPA for removal of manganese, iron, and radionuclides [19]; it includes the use of catalytic filter materials [40], e.g., manganese oxide coated media with a support base or manganese greensand [3]. Catalytic oxidation may also be achieved by injection of preformed HMO slurry into water and subsequent filtration of the resultant suspension. As indicated in the Equation 1.9, HMO slurry may be synthesized on site using affordable chemicals such as potassium permanganate ($KMnO_4$) and manganese sulphate ($MnSO_4$) [40].

$$2KMnO_4 + 3(MnSO_4 \cdot H_2O) \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4 + H_2O, \tag{1.9}$$

Proper dosage of HMO is required for providing optimal service capability. An overabundance of HMO may influence the filtration process; nevertheless, a lack of the reagent may lead to insufficient radionuclides removal. High iron concentrations can affect the overall sorption process resulting in lower ^{226}Ra and ^{228}Ra removal. It is known that adding aeration to the treatment scheme can enhance the contaminants elimination rate [40].

In spite of the effectiveness of manganese dioxide-based applications in water treatment, accumulation of radioisotopes in the filter material constitutes a major challenge. It is acknowledged that MnO_2 technology produces Naturally Occurring Radioactive Materials (NORM)-containing wastes, which are difficult to dispose. As recommended by manufacturers, radium-containing Fe and Mn complexes trapped in the MnO_2-based filter bed should be regularly eliminated during backwash [19].

However, in the case of preformed HMO slurry injection, radium-containing particles accumulate in the upper part of the filter. Thus, both the backwashing procedure and the regeneration of filtration media may be accomplished by the use of water and compressed air; no expensive chemicals are implemented.

In addition, the filter material catalytic centres, i.e., MnO_2 centres, can be restored with $KMnO_4$ that serves also as a disinfecting agent against iron reducing or ammonium-oxidizing bacteria [14].

As a matter of fact, ^{226}Ra and ^{228}Ra accumulated in the filter material decay into ^{222}Rn and ^{228}Th, accordingly. ^{220}Rn is also formed during the ^{228}Ra decay chain. The formation of gaseous radon isotopes in turn may lead to increased indoor air radon contamination in the facility. However, as it was stated in the Item 1.2.2, half-life of radon-220 is too short for the isotope to diffuse over long distances. Under normal circumstances, ^{220}Rn does not pose a risk or a hazard to workers health. Therefore, in normal working conditions exhalation dose of the workers is not underestimated if only the concentration of indoor ^{222}Rn is taken into account. On the other hand, if replacement of a filter material is required, dose received from the radon-220 inhalation may increase drastically because of proximity to the radiation source, e.g., in case worker must reach inside the filtration column during maintenance services, etc.

2. MATERIALS AND METHODS

The following technology, based on collaboration between Spain and Estonia, is a part of European Life Project (LIFE16 ENV/ES/000437). The latter aims to minimize the environmental impact of radioactivity removal in water provision services by optimizing bed filters and reducing the generation of NORM [31].

In order to produce high quality drinking water and enhance its aesthetical attractiveness for inhabitants consumption, a WTP was constructed in 2012 by the Viimsi Parish (municipality in Northern Estonia, located North-East; 15 km from capital of Estonia, Tallinn) [19].

2.1 Pilot plant construction and design

2.1.1 Process description and technological data

The pilot setup (Figure 2.1) was constructed in 2018 [30] in filtration hall of the facility to examine HMO-technology removal effectiveness as an alternative to the current treatment process used at the Viimsi WTP.

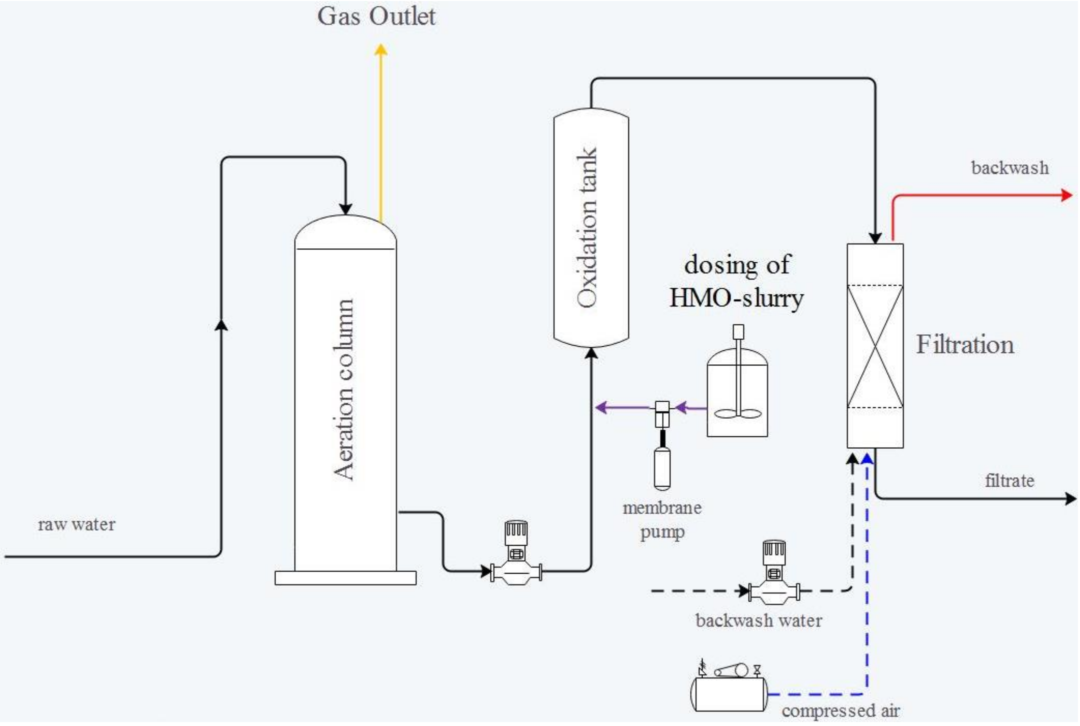

Figure 2.1 Technological scheme of the pilot setup introduced at the Viimsi WTP

At the first stage, the groundwater (raw water from the well) is directed into the aeration column (4400 x 475 mm inner diameter; OÜ Eccua). This process allows to remove undesirable gases from water, e.g., H_2S, CO_2, Rn, and to saturate water with air-oxygen. Oxygen oxidizes ferrous iron to insoluble ferric hydroxide ($Fe(OH)_3$) according to the Equation 1.6. Water passes through the aeration column by gravity. In order to provide better surface contact between gaseous and aqueous phases, aeration column was packed with Moving Bed Biofilm Reactor (MBBR) carriers with a diameter of 18 cm.

Aeration is an effective technique for iron removal, yet it is not sufficient for manganese removal. For an effective oxidation of manganese by means of oxygen, pH>9.5 is required [19]. Thereafter, the stream flows throughout the contact column (2000 x 160 mm inner diameter; OÜ Eccua), where mixing and reaction with HMO suspension takes place. For this purpose, water pump (0.84-0.55 kW; Wilo SE) is installed between the aeration and oxidation columns.

In the final step, the filtration column is implemented in order to capture preformed HMO particles as well as the insoluble Fe(III) and Mn(IV) oxides, and their complexes with radium isotopes. The filtration column (3200 x 242 mm inner diameter; OÜ Eccua) is packed with anthracite (bed depth of 200 mm, bed volume of 0.0092 m^3, dry density 1.40-1.69 $t \cdot m^{-3}$), quartz sand (bed depth of 1000 mm, bed volume of 0.0459 m^3, dry density 1.42 $t \cdot m^{-3}$), and gravel (bed depth of 200 mm, bed volume of 0.0092 m^3, dry density 1.73 $t \cdot m^{-3}$) layers (Figure 2.2).

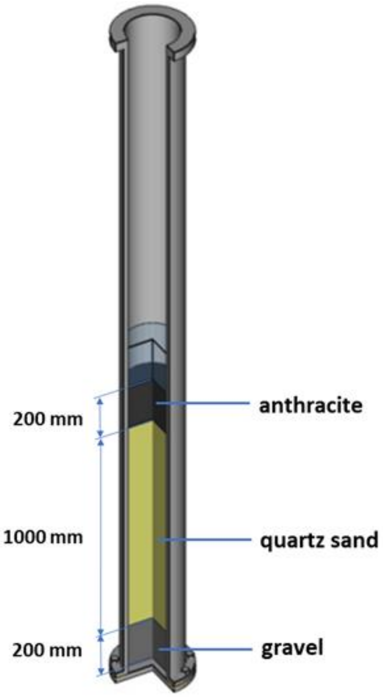

Figure 2.2 The composition of the filtration column

2.1.2 HMO slurry preparation

In the present case, 40 L of HMO-slurry stock solution containing 1.67 gMn·L^{-1} were prepared in advance in 60 L tank (Cipax Eesti OÜ) equipped with agitator (0.2 kW, MOTIVE) as demonstrated in the Figure 2.3. Tap water was used for preparation. According to recommendations described by Patel et al. [45], potassium permanganate was added in 5% stochiometric excess to avoid the presence of undesirable ions (unreacted Mn(II) and Fe). NaOH was added to maintain pH between 8 to 9 as the generation of HMO suspension is followed by drastic pH decrease (Equation 1.9).

Figure 2.3 HMO tank and the backwash vessel near the contact column [30]

For the preparation of HMO-slurry stock solution, reagents were added in stoichiometric ratio according to the Equations 2.1 and 2.2. Subsequent injection of HMO was achieved using the membrane pump (ProMinent® Beta/4).

$$m_{MnSO_4 \cdot H_2O} = \frac{C_{HMO} \cdot V \cdot M_{MnSO_4 \cdot H_2O} \cdot 3}{A_{Mn} \cdot 5}, \tag{2.1}$$

where $m_{MnSO_4 \cdot H_2O}$ – the mass of $MnSO_4 \cdot H_2O$, g,

C_{HMO} – the concentration of HMO in stock solution (1.67), $gMn \cdot L^{-1}$,

V – slurry volume (40), L,

$M_{MnSO_4 \cdot H_2O}$ – molar mass of $MnSO_4 \cdot H_2O$ (169), $g \cdot mol^{-1}$,

A_{Mn} – atomic mass of Mn (55), $g \cdot mol^{-1}$,

3 and 5 are stoichiometric coefficients obtained from the Equation 1.9.

$$m_{KMnO_4} = \frac{C_{HMO} \cdot V \cdot M_{KMnO_4} \cdot 2}{A_{Mn} \cdot 5} \cdot 1.05, \tag{2.2}$$

where m_{KMnO_4} – the mass of $KMnO_4$, g,

M_{KMnO_4} – molar mass of $KMnO_4$ (158), $g \cdot mol^{-1}$,

1.05 considers 5% stoichiometric excess,

2 and 5 are stoichiometric coefficients obtained from the Equation 1.9.

2.1.3 Modes of treatment

In order to determine the most appropriate treatment mode, three process schemes were proposed (Table 2.1), whereas for certain reasons only Scheme 1 and Scheme 3 were investigated at the pilot plant scale.

Table 2.1 Treatment schemes examined during the project

Number	**Process #1**	**Process #2**	**Process #3**	**Process #4**
1	Aeration	HMO continuous injection	Filtration (anthracite/sand/gravel)	▨
2	Aeration	HMO continuous injection	Filtration (anthracite/sand/gravel)	Filtration (sand/zeolite/gravel)
3	Aeration	HMO periodic injection	Filtration (anthracite/sand/gravel)	▨

The first scheme corresponds to the conventional HMO process with standard operation procedures. In the second scheme, additional zeolite filtration was proposed to reduce ammonium concentration by means of IX. Scheme 3 was based on the results obtained during the laboratory scale experiments [29], where HMO particles accumulated in the filter bed remained active after several treatment cycles and were able to remove Fe, Mn, and radionuclides. As the alternation of HMO dosing cycles with temporary pauses could reduce the overall HMO consumption, it was proposed to test this approach at the Viimsi WTP.

Scheme 1 represents the continuous HMO dosing (24 h), whereas Scheme 3 involves pauses between HMO addition, i.e., 8 h of dosing with subsequent 16 h long pause. Depending on the mode, the membrane pump was set to either continuous or periodic dosing (Figure 2.4).

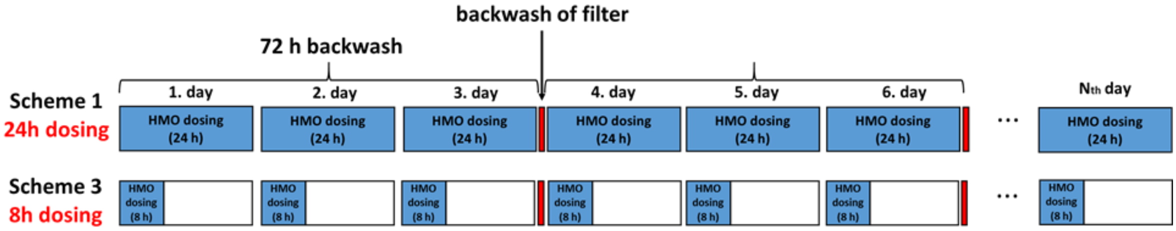

Figure 2.4 Graphical explanation of HMO dosage

In addition, the pilot plant was monitored in terms of volume of water used. Real consumptions of energy and consumables were also determined (Table 2.2).

Table 2.2 Pilot plant process parameters

Parameter	**Value**
Electricity consumption, kW per m^3 of treated water	1.9
Water flow, $L \cdot h^{-1}$	300
Total water produced (September 2018 – September 2020), m^3	4360
The rate of HMO slurry injection, $L \cdot h^{-1}$	0.1-0.2
MnO_2, g per m^3 of treated water	0.8-1.6

2.1.4 Backwashing procedure

Filter was regenerated using backwash to remove excess sludge from the filtration media. The pilot plant was programmed to maintain filter regeneration with 72 h cycles, i.e., the backwashing procedure was accomplished after each 72 h of operation (Figure 2.4). Equal intervals of 72 h were found to be optimal for avoiding of pressure drops in the filtration column. In the case of longer intervals, the filtration procedure would become slow due to accumulation of insoluble solids in the filter.

Backwashing procedure was accomplished with water (H_2O consumption of 370 L for one backwash cycle) and compressed air (maintained through the air compressor with a volume of 30 L, 1.5 kW, 350 L·min^{-1}; NARDI COMPRESSORI SRL) in accordance with sequence of actions presented in the Figure 2.5. Water collected from backwash was directed into the tank with a volume of 500 L (Cipax Eesti AS).

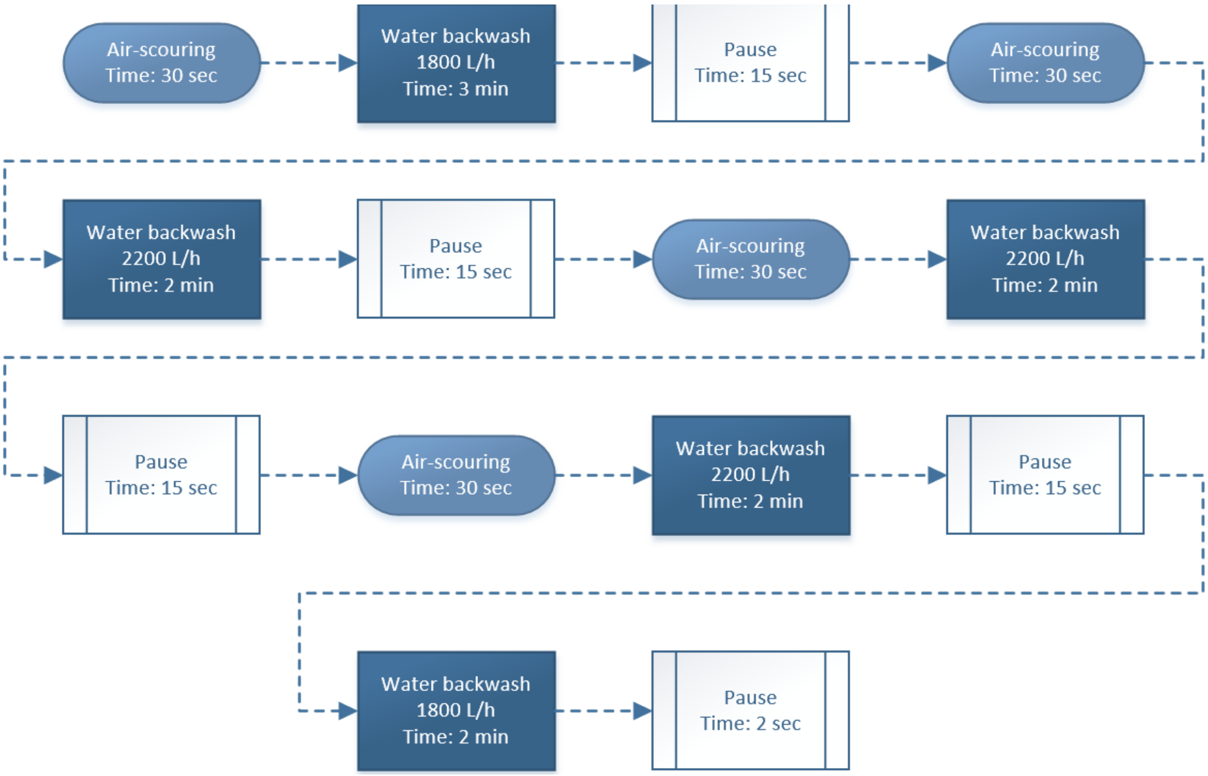

Figure 2.5 Backwashing mode

2.2 Sampling procedure

Aqueous samples were collected in plastic containers. Containers were filled with the water sample without leaving an ample air space. Depending on the type of analyses, different water samples were taken a) before the treatment (raw water), b) after the aeration, c) after the oxidation with HMO, d) after the final filtration (effluent), and e) from the backwash vessel. Determination of radionuclides was conducted only in raw water, the effluent, and the backwash water.

Generally, backwashing procedure was performed directly after the sampling. The filter samples, i.e., sand and anthracite, were collected using the sampling probe (piece of steel pipe). The probe was inserted into the filter column at the depth of ca 70 cm and 5 cm to withdraw sand and anthracite, respectively.

2.3 Measurements and analyses

The concentrations of iron, manganese, and ammonium cation were monitored twice per month, while concentrations of ^{226}Ra, ^{228}Ra, and ^{228}Th were observed monthly. Tallinn University of Technology was responsible for analyses of iron, manganese, ammonium cation, and other parameters except for radioactivity. The analysis of radionuclides was conducted by University of Tartu.

The pH was measured using a digital pH/ion meter (Seven Compact, Mettler-Toledo, Switzerland) equipped with a pH electrode (InLab® Routine & Routine Pro, Mettler-Toledo). The conductivity was measured using a conductometer (HQ430d flexi multi-parameter meter, Hach Co., USA) equipped with an IntelliCAL™ CDC401 standard conductivity probe.

2.3.1 Determination of Fe, Mn, and NH_4^+

The results on the iron and ammonium concentrations measured after certain period showed that the analyses as well as the treatment experiment should be performed within the first two or three hours from the moment of sampling.

The concentration of iron was measured using the o-phenanthroline method. For that purpose, water sample was mixed with a reagent solution containing o-phenanthroline. Iron was reduced to the ferrous state with hydroxylamine and reacted then with 1,10-phenanthroline at acidic conditions. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex, which obeys Beer's law. The iron concentration was determined photometrically at the wavelength of 492 nm using UV-Vis spectrophotometer (GENESYS™, Thermo Fisher Scientific, USA) [36].

Manganese was determined using the 1-(2-pyridylazo)-2-naphthol method (PAN). This method is highly sensitive towards the measurement of low levels of manganese. The ascorbic acid reagent reduces all oxidized forms of manganese to Mn(II). The alkaline-cyanide reagent masks potential interferences. PAN indicator forms an orange-coloured complex with Mn(II). The absorption of light was measured at the wavelength of 560 nm using UV-Vis spectrophotometer (GENESYS™, Thermo Fisher Scientific, USA) [52].

NH_4^+ was measured by the phenate method, where an intensively blue compound, indophenol, was formed by the reaction of ammonia, hypochlorite, and phenol catalysed by sodium nitroprusside. Complexing magnesium and calcium with citrate eliminated interference produced by precipitation of these ions at high pH. The blue-coloured compound is masked by the yellow colour from the excess reagent resulting in a green-coloured solution, which was then analysed photometrically at the wavelength of 610 nm using spectrophotometer (GENESYS™, Thermo Fisher Scientific, USA) [52].

In order to extract Fe and Mn from solid matrix (Figure 2.6), 10 mL of 1N HCl solution was added to a portion of sample. The mixture was boiled for 30 min. The resultant extract was diluted to 100 mL in volumetric flask, filtered, and then analyzed for the presence of Fe and Mn using methods described previously.

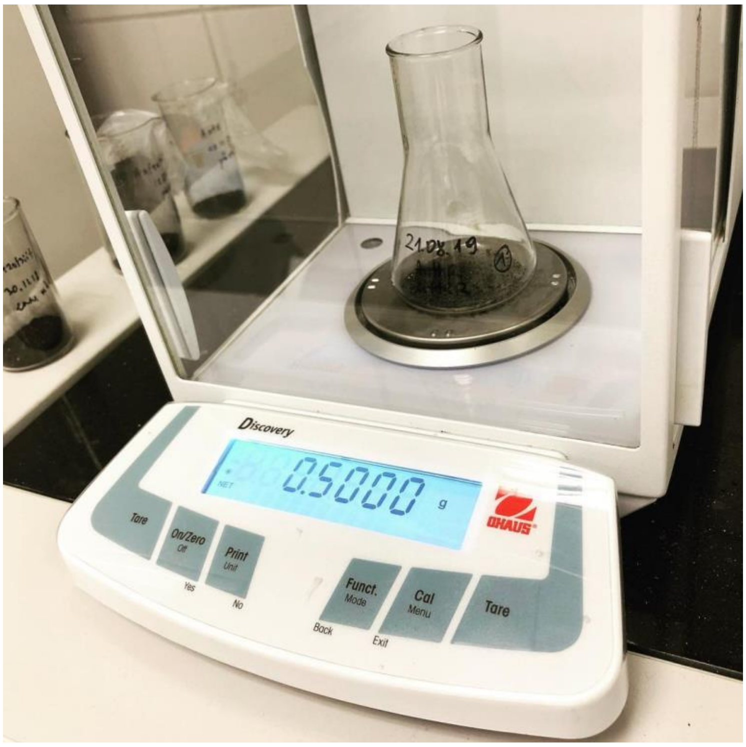

Figure 2.6 Solid samples (anthracite) measurement procedure

2.3.2 Determination of nitrates and anions

In addition to Fe, Mn, and NH_4^+, water samples were analysed for the presence of nitrates and other anions. For this purpose, investigated samples were initially filtrated using syringe filter (pore size of 0.45 µm; VWR®) and injected into ion chromatograph (Metrohm®, 761CompactIC) equipped with a suppressed conductivity detector and analytical ion separation column (150 x 4 mm inner diameter; Metrosep A Supp 5). The concentrations of investigated anions were determined through the integration of corresponding peaks on the chromatograms.

2.3.3 Determination of radionuclides

Radium isotopes (^{226}Ra and ^{228}Ra) in water were determined by an accredited methodology under the Testing Centre of University of Tartu. The Testing Centre holds an accreditation certificate provided by the Estonian Accreditation Centre, registration number L151. In addition to radium isotopes, ^{228}Th was analysed in solid samples (measurement of solid samples is not in the scope of accreditation in the Testing Centre of University of Tartu). The analysis procedure of radium-226, radium-228, and thorium-228 was based on gamma spectrometry.

For Ra isotope measurements in water, the collected sample was first acidified with concentrated HNO_3 to pH 1-2. Radium was co-precipitated with $Ba(SO_4)_2$. Then the precipitate was put into an aluminium can and homogenized with 5 g of epoxy resin. Epoxy was added in order to minimize ^{222}Rn and ^{220}Rn leakage from the sample [58]. It is a crucial step in sample preparation as daughter products of gaseous radon are used for ^{226}Ra [21].

Solid samples dried at 105 °C for 24 h were placed tightly into metal containers with a volume of 55 cm^3. The samples (both water samples and filter material samples) were measured after at least three weeks of waiting time on a high purity Germanium gamma spectrometer (coaxial type Ortec detector GEM 35200) with typical measurement time of one day. ^{226}Ra was determined according to its daughter nuclide ^{214}Pb (gamma peaks 242.00, 295.22, 351.93 keV). ^{228}Ra was analysed via the gamma peaks of ^{228}Ac (338.32, 911.20, 968.96 keV). The concentration of ^{228}Th measured through either the ^{212}Pb peak (238.63 keV) or the ^{224}Ra peak (240.99 keV) was corrected excluding the period from sample collection to measurement [21].

Calibration was performed with certified reference materials RGU-1 and RGTh-1 (IAEA). For this purpose, geometrically similar calibration sources were prepared and measured. In case of water samples, a few grams of the reference material were mixed with 5 g of epoxy resin in an aluminium can [21]. For the calibration of solid sample measurements, the reference materials were placed into the same type of containers, which were used for filter material samples (metal containers with the volume of 55 cm^3).

Subsequently, the radionuclide activity was calculated according to the Equation 2.4:

$$A = \frac{c}{t \cdot \varepsilon \cdot I_g}, \qquad (2.4)$$

where A – the radionuclide activity, Bq,

c – net surface area of the γ-peaks minus background, counts per s,

t – measurement duration (live time), s,

ε – γ-quantum detection efficiency,

I_g – γ-quantum emission probability.

Calibration is required in order to determine the efficiency (ε) as indicated in the Equation 2.5:

$$\varepsilon = \frac{c_{calib}}{t \cdot A_{calib} \cdot I_g}, \qquad (2.5)$$

where c_{calib} – net surface area of the γ-peak in the spectrum of a certified reference material used in calibration minus background, counts per s,

t – measurement duration of the certified reference material (live time), s,

A_{calib} – certified reference material's activity, Bq.

The Equation 2.6 was used to calculate the activity concentration (A_C) per mass unit (m); the activity concentration is expressed in Bq·kg^{-1}:

$$A_C = \frac{A}{m}, \qquad (2.6)$$

2.4 Chemicals and reagents

O-phenathroline monohydrate ($C_{12}H_{10}N_{2}O$, ≥99.5%), sulfuric acid (H_2SO_4, 96%) were purchased from Lach:Ner. Acetic acid glacial (CH_3COOH, ≥99%), ammonium acetate (CH_3COONH_4, ≥98%), ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$, ≥98%), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, ≥99%) were purchased from Sigma-Aldrich. Ascorbic acid powder pillows, Alkaline-Cyanide reagent, and PAN indicator solution (0.1%), ammonia tablet reagents №1 and №2 were obtained from Lovibond. All other reagents, e.g., NaOH, were of analytical grade at greater than 95% purity used without further purification.

All solutions for analyses were prepared using ultrapure water obtained from a Millipore ultrapure water UV-system (Simplicity®, EMD Millipore Corporation, Billerica, MA, USA).

3. RESULTS AND DISCUSSION

3.1 Influent quality parameters

Raw water quality parameters of the pilot plant were monitored throughout the experimental period (from October 2018 to February 2020). Table 3.1 demonstrates the average values of the parameters.

Table 3.1 Results of raw water analysis (average values; October 2018 – February 2020)

Parameter	Average value	Threshold limit
Fe, $mg \cdot L^{-1}$	0.197	0.200
Mn, $mg \cdot L^{-1}$	0.147	0.050
NH_4^+, $mg \cdot L^{-1}$	0.654	0.500
^{226}Ra, $Bq \cdot L^{-1}$	0.359	—
^{228}Ra, $Bq \cdot L^{-1}$	0.483	—
ID, $mSv \cdot year^{-1}$	0.317	0.100*
pH	8.12	6.5-9.5
Conductivity, $\mu S \cdot cm^{-1}$	883	2500

*ID is defined as a parametric value.

As it can be seen from the Table 3.1, the total manganese, ammonium, and ID exceed threshold limits set by the Regulation №61 of the Minister of Social Affairs (RT I, 26.09.2019, 2) on "Quality and monitoring standards and methods of analysis for drinking water"; Fe concentration is also close to its limit value [12].

3.2 The results of periodic and continuous dosing

The overall analysis conducted for both periodic and continuous dosing demonstrated no significant change in pH and conductivity in the effluent; hence, these parameters are not affected by implementation of HMO (Table 3.2).

Table 3.2 Comparison between influent and effluent (average values of pH and conductivity)

Parameter	Raw water	Filtrate
pH	8.12	8.09
Conductivity, $\mu S \cdot cm^{-1}$	883	877

In the pages below, the performance of only continuous and periodic dosing will be discussed as the implementation of additional zeolite filtration (Scheme 2) was not found technologically feasible.

In the early laboratory experiments, the presence of NH_4^+ in water became a serious issue since HMO technology is not intended for ammonium-nitrogen removal.

Based on the promising results obtained from the laboratory study on zeolite [29], the test of zeolite filtration was scheduled at the pilot plant scale. However, the pilot plant experiments revealed that the use of conventional HMO process was able to remove almost all NH_4^+ without any addition of zeolite.

From a scientific standpoint, effective ammonium removal remained curious because the identical experiments in laboratory indicated no sign of NH_4^+ concentration decrease. In the present case, the removal of ammonium may be explained by the possible development of nitrifying consortium of microorganisms, i.e., chemoautotroph bacteria, on the MBBR carriers packed in the aeration column (Figure 3.1). This type of microorganisms uses CO_2 as a carbon source and NH_4^+ as an electron donor for redox processes to occur in order to obtain energy [28]. The hypothesis on the presence of bio-oxidation of ammonium-nitrogen was supported by the significant rise of NO_3^- up to 0.820 $mg \cdot L^{-1}$ in filtrated water indicating the biochemical oxidation of NH_4^+ to NO_3^- by the activity of nitrifying bacteria. Following the threshold limit set for nitrates in drinking water [12], which is 50 $mg \cdot L^{-1}$, it should be mentioned here that the concentration of NO_3^- of the present case is significantly lower than the limit value and does not pose a risk to human health.

Figure 3.1 MBBR carriers during the operation in aerator

3.2.1 HMO process with periodic dosing (Scheme 3)

First, the periodic mode was examined at the pilot plant scale. To avoid the immediate clogging of the filter and prolong its lifecycle, it was agreed to inject HMO at the resultant concentration of 0.5 mgMn·L^{-1} in treated water. Considering the total water flow of 300 L·h^{-1}, the HMO slurry was injected into the oxidation tank at the rate of ca 0.1 L·h^{-1}. Under these conditions, the pilot setup was operated from October 2018 to February 2019.

The Figures 3.2-3.21 (except for 3.5, 3.10, 3.15, and 3.20) consist of boxplots, which represent the range of measured values from minimum to maximum; the dot inside the boxplot signifies the location of an average value (followed by a number), and the line represents the location of the median (measurement of the central tendency). The threshold limits, or a parametric value in case of ID, are shown with dashed lines marked in red.

The periodic dosing was effective in Fe, Mn, and NH_4^+ removal (Figures 3.2-3.4), whereas the removal of radionuclides has not yielded the expected results (Figure 3.5). The average ID (0.122 ± 0.029 mSv·year^{-1}; standard deviation calculated over all measurements of the studied mode) was above the parametric value of 0.1 mSv·year^{-1} (Figure 3.6). In addition, the injection of HMO slurry caused a small rise of total Mn in water after the oxidation with HMO. Observed phenomenon will be discussed later.

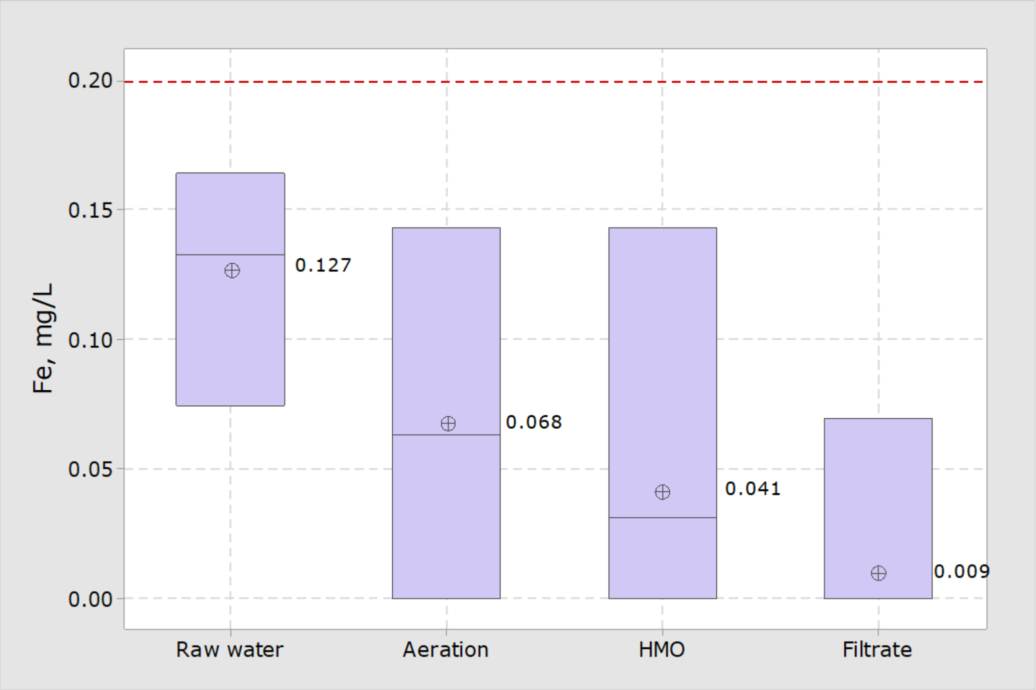

Figure 3.2 Fe concentration throughout the process (Scheme 3, 0.1 L·h^{-1})

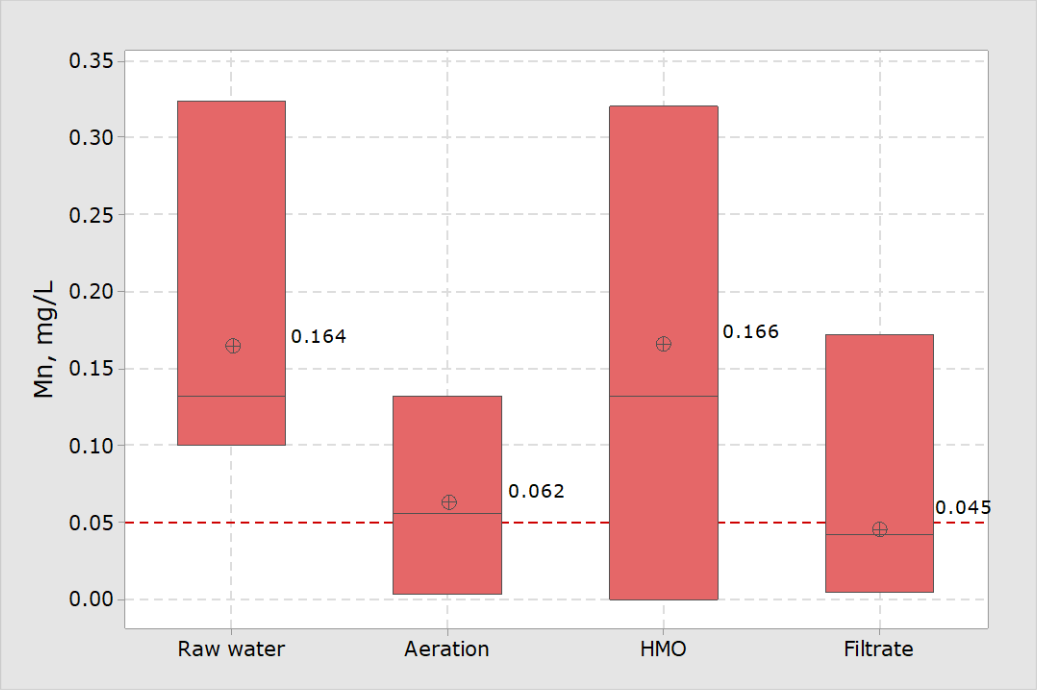

Figure 3.3 Mn concentration throughout the process (Scheme 3, 0.1 L·h^{-1})

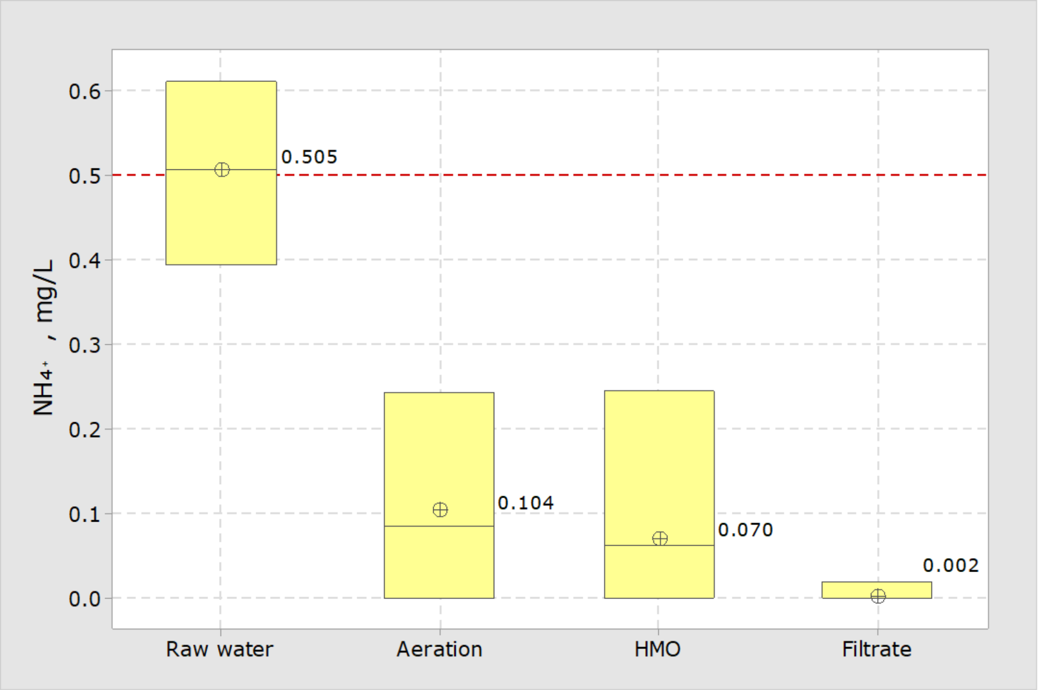

Figure 3.4 NH_4^+ concentration throughout the process (Scheme 3, 0.1 L·h^{-1})

The periodic dosing of preformed HMO seemed to have several advantages, e.g., reduction of operational costs due to the lower HMO consumption and the prolongation of filter material's lifecycle, as less precipitate is accumulated in the filter system [29].

Average removal efficiency of ^{226}Ra and ^{228}Ra (calculations are based on the activity concentrations of radium-226 and radium-228 (Table 3.3)) was 51% and 55%, respectively.

Under the conditions of Viimsi groundwater, such radium removal efficiency was not sufficient to reach an indicative dose of <0.1 mSv·year^{-1} in treated water. Therefore, periodic dosing was found to be insufficient, and experiments were conducted with continuous dosing.

Table 3.3 Activity concentrations (± measurement uncertainty, k=2) of ^{226}Ra and ^{228}Ra for the Scheme 3, 0.1 L·h^{-1}

Sample collection date	**Raw water** ***Bq·kg^{-1}***		**Filtrate** ***Bq·kg^{-1}***	
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
02.10.2018	0.302 ± 0.030	0.451 ± 0.065	0.193 ± 0.032	0.228 ± 0.033
16.11.2018	0.219 ± 0.024	0.413 ± 0.061	0.172 ± 0.019	0.262 ± 0.041
13.12.2018	0.280 ± 0.023	0.412 ± 0.057	0.129 ± 0.015	0.227 ± 0.043
09.01.2019	0.351 ± 0.034	0.487 ± 0.052	0.133 ± 0.012	0.182 ± 0.025
14.02.2019	0.334 ± 0.033	0.466 ± 0.059	0.095 ± 0.018	0.136 ± 0.038
22.02.2019	0.303 ± 0.028	0.386 ± 0.042	0.119 ± 0.020	0.138 ± 0.039

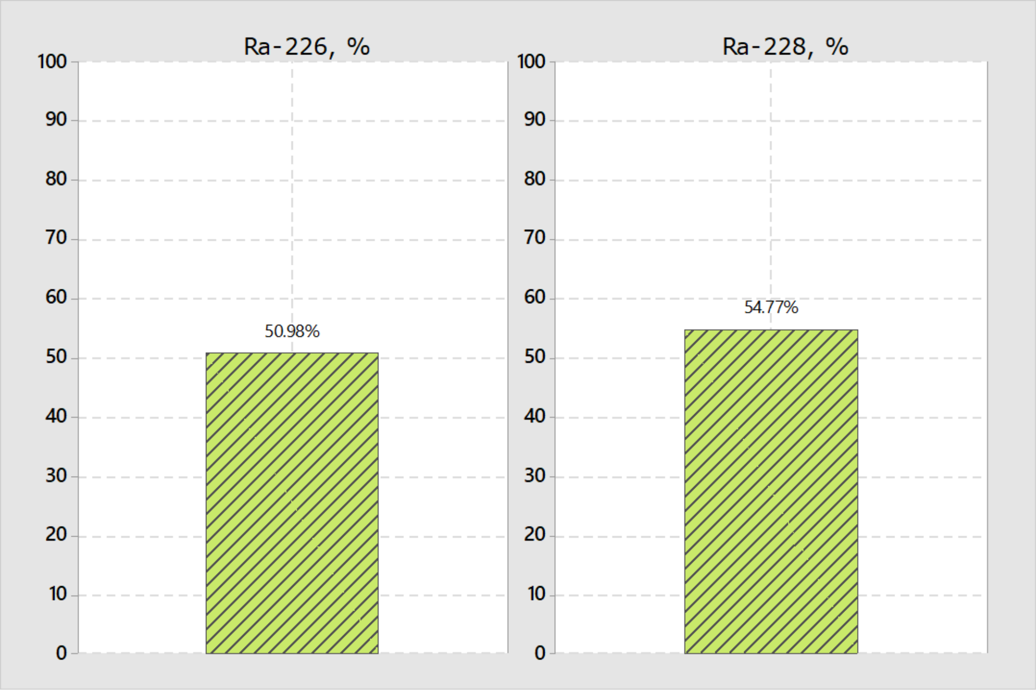

Figure 3.5 Average removal efficiency of ^{226}Ra and ^{228}Ra (Scheme 3, 0.1 L·h^{-1})

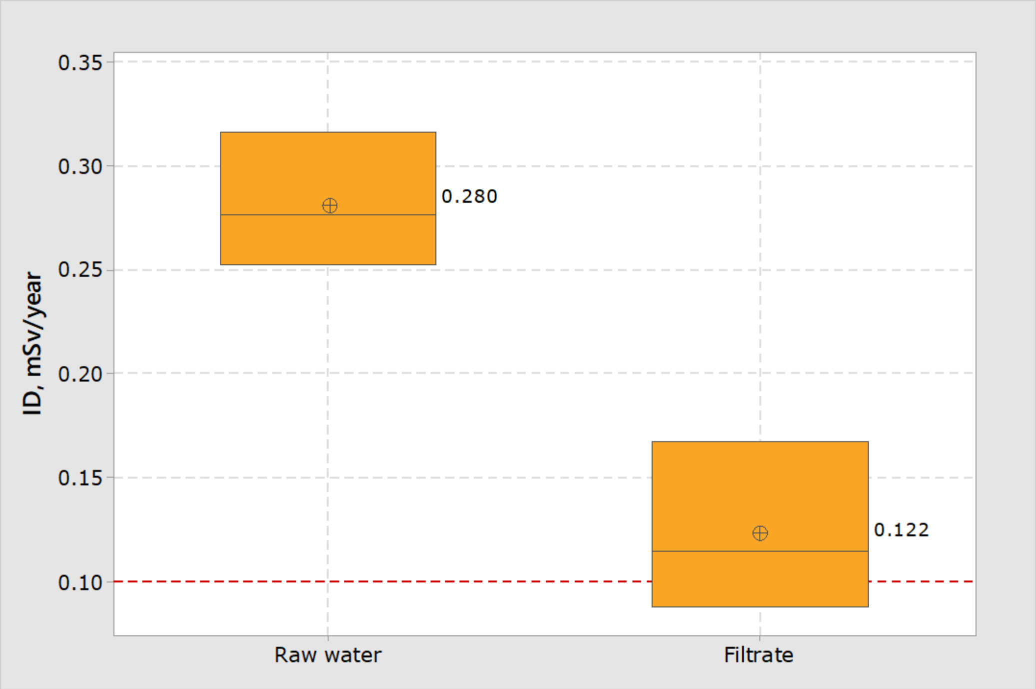

Figure 3.6 ID of raw and treated water (Scheme 3, 0.1 L·h^{-1})

3.2.2 HMO process with continuous dosing (Scheme 1)

The same injection rate (ca 0.1 L·h^{-1}) was tested with continuous dosing from March 2019 to May 2019. As it can be seen from the Figures 3.7-3.9, iron, manganese, and ammonium cation were almost completely removed meeting the threshold limits set by the Regulation №61 of the Minister of Social Affairs (RT I, 26.09.2019, 2).

Average removal efficiency of radium isotopes (Figure 3.10) was calculated using the activity concentrations of radium-226 and radium-228 in raw water and the filtrate (Table 3.4).

Table 3.4 Activity concentrations (± measurement uncertainty, k=2) of ^{226}Ra and ^{228}Ra for the Scheme 1, 0.1 L·h^{-1}

Sample collection date	**Raw water** ***Bq·kg^{-1}***		**Filtrate** ***Bq·kg^{-1}***	
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
06.03.2019	0.412 ± 0.035	0.539 ± 0.050	0.148 ± 0.021	0.193 ± 0.048
19.03.2019	0.471 ± 0.036	0.728 ± 0.076	0.063 ± 0.010	0.145 ± 0.025
09.04.2019	0.319 ± 0.024	0.470 ± 0.039	0.055 ± 0.017	0.122 ± 0.038
16.05.2019	0.335 ± 0.035	0.483 ± 0.074	0.089 ± 0.017	0.144 ± 0.043
29.05.2019	0.322 ± 0.034	0.439 ± 0.064	0.115 ± 0.023	0.132 ± 0.036
04.06.2019	0.410 ± 0.033	0.521 ± 0.061	0.123 ± 0.017	0.125 ± 0.037
06.06.2019	0.440 ± 0.040	0.519 ± 0.067	0.115 ± 0.022	0.142 ± 0.036
10.06.2019	0.402 ± 0.037	0.526 ± 0.068	0.088 ± 0.017	0.126 ± 0.027
12.06.2019	0.293 ± 0.034	0.385 ± 0.060	0.090 ± 0.018	0.088 ± 0.030
14.06.2019	0.318 ± 0.035	0.430 ± 0.059	0.070 ± 0.020	0.087 ± 0.032

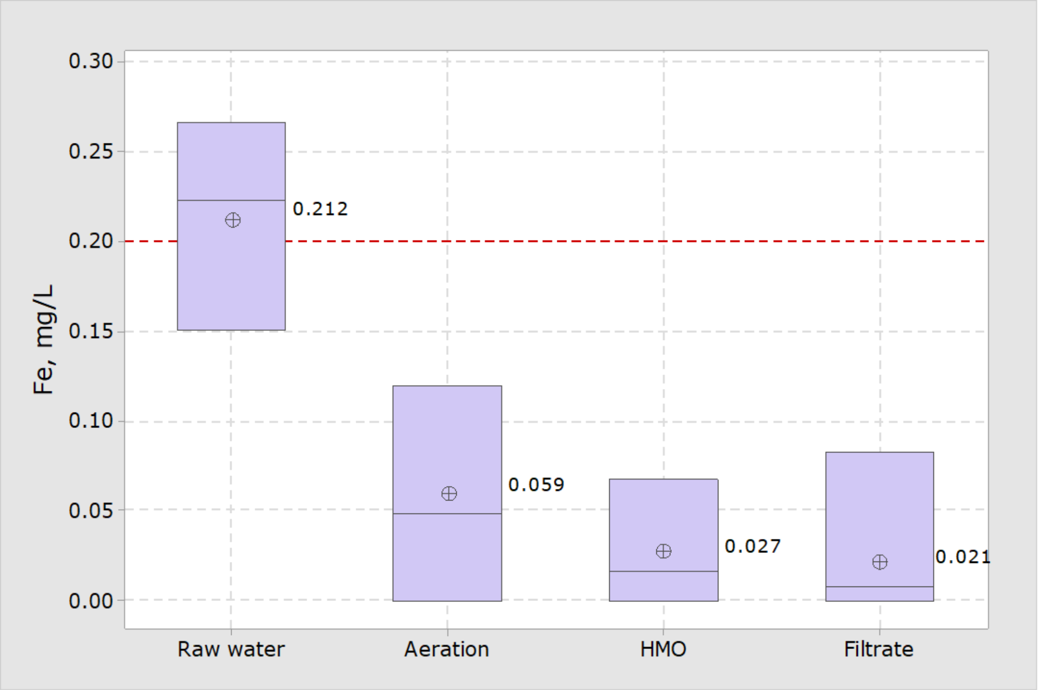

Figure 3.7 Fe concentration throughout the process (Scheme 1, 0.1 L·h-1)

Figure 3.8 Mn concentration throughout the process (Scheme 1, 0.1 L·h-1)

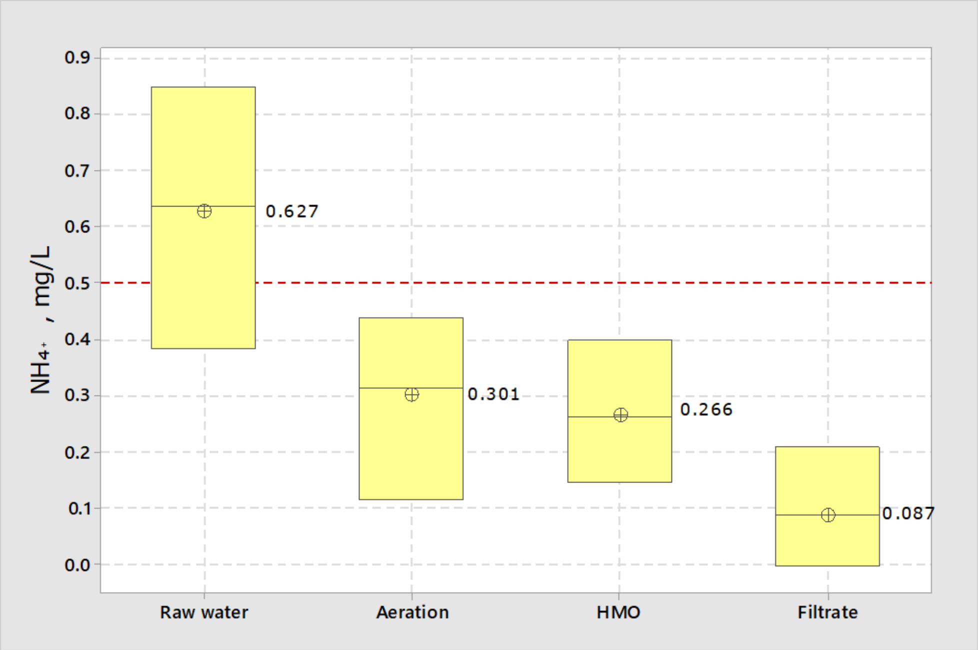

Figure 3.9 NH_4^+ concentration throughout the process (Scheme 1, 0.1 L·h^{-1})

According to the Figure 3.10, removal efficiency of ^{226}Ra and ^{228}Ra increased to 75% and 74%, respectively. This resulted in lower values of ID measured during the operational period established for the Scheme 1 at an injection rate of ca 0.1 L·h^{-1}.

Although the average ID (0.085 ± 0.019 mSv·year^{-1}; standard deviation calculated over all measurements of the studied mode) was below the parametric value of 0.1 mSv per year (Figure 3.11), it was proposed to double the HMO concentration.

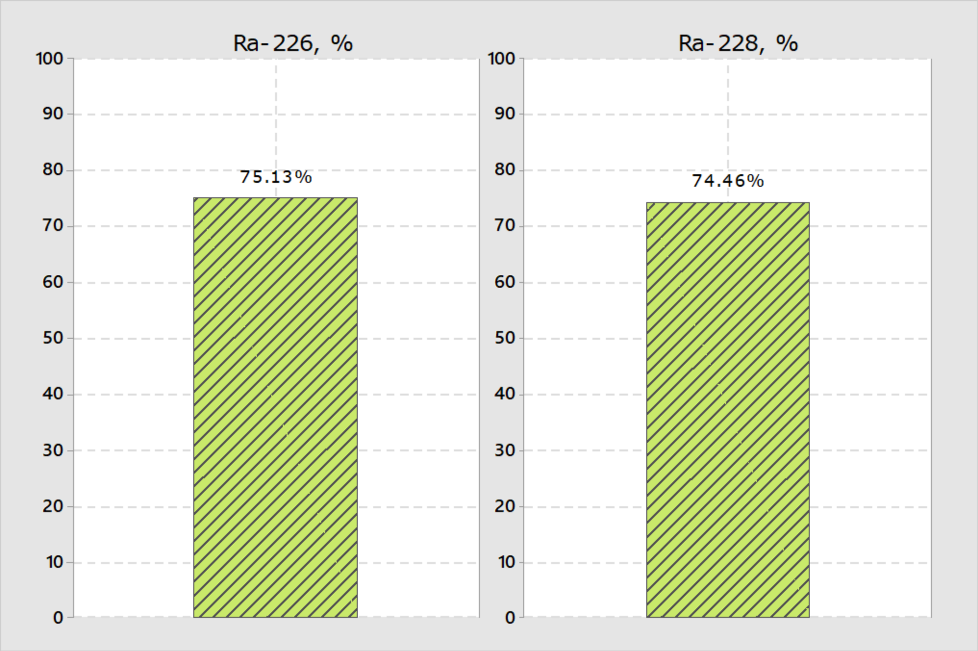

Figure 3.10 Average removal efficiency of ^{226}Ra and ^{228}Ra (Scheme 1, 0.1 L·h^{-1})

The main objective of this action was to develop conditions under which the water quality parameters would satisfy the requirements stated in the Regulation №61 of the Minister of Social Affairs (RT I, 26.09.2019, 2) as well as to provide larger margin between the parametric value and an average ID of drinking water.

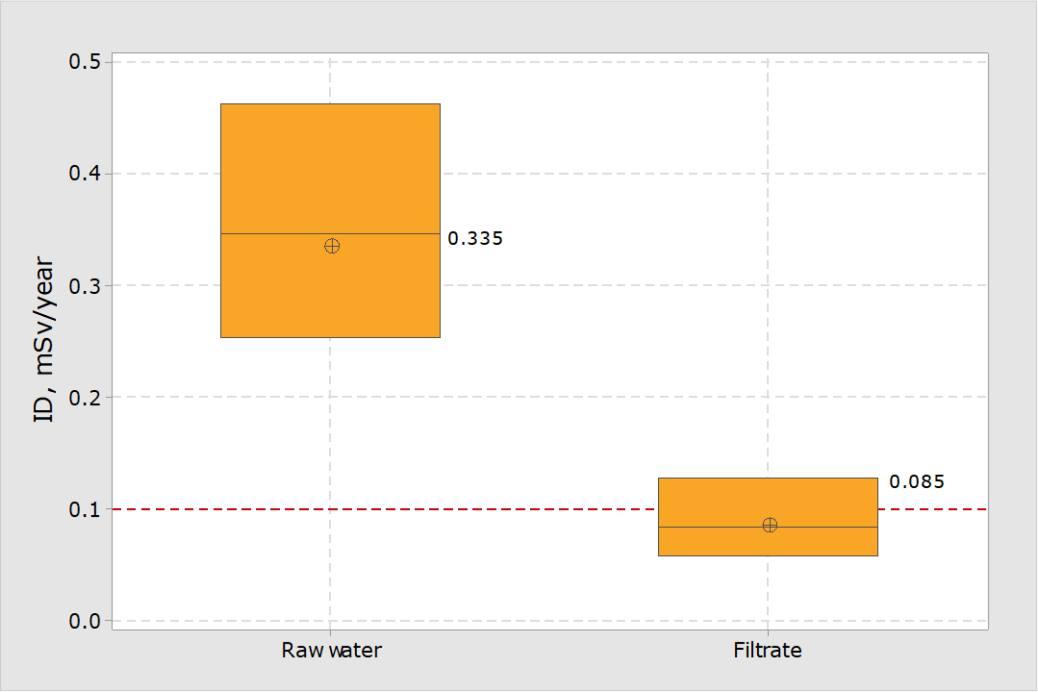

Figure 3.11 ID of raw and treated water (Scheme 1, 0.1 L·h^{-1})

Higher dosages of HMO were implemented in order to improve the radium removal efficiency. From September 2019 to December 2019, the HMO slurry was injected into the oxidation tank at the rate of ca 0.2 L·h^{-1}, which corresponds to 1.0 mgMn·L^{-1} in treated water.

As it can be seen from the Figures 3.12-3.14, increasing an injection rate had a beneficial impact on the treatment process. Following the drastic decrease of ID (Figure 3.16) with its average value of 0.043 ± 0.030 mSv·year^{-1} in the effluent (standard deviation calculated over all measurements of the studied regimen), concentrations of Fe, Mn, and NH_4^+ were also near the limits of detection (LOD). LOD for Fe, Mn, and NH_4^+ are 0.001, 0.003, and 0.002 mg·L^{-1}, respectively.

The average removal efficiency for both radium-226 and radium-228 (Figure 3.15) was calculated on the basis of radium activity concentrations (Table 3.5). As a result, the average removal efficiency reached 87% for ^{226}Ra and 86% for ^{228}Ra.

Table 3.5 Activity concentrations (± measurement uncertainty, k=2) of ^{226}Ra and ^{228}Ra for the Scheme 1, 0.2 L·h^{-1}

Sample collection date	**Raw water** ***Bq·kg^{-1}***		**Filtrate** ***Bq·kg^{-1}***	
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
02.09.2019	0.3800 ± 0.0305	0.4879 ± 0.0456	0.1095 ± 0.0163	0.1530 ± 0.0293
06.09.2019	0.2790 ± 0.0290	0.4260 ± 0.050	0.1182 ± 0.0157	0.1632 ± 0.0389
09.09.2019	0.4210 ± 0.0335	0.5457 ± 0.0546	0.0688 ± 0.0158	0.1019 ± 0.0335
13.09.2019	0.3700 ± 0.0268	0.5210 ± 0.0652	0.1075 ± 0.0151	0.1544 ± 0.0314
16.09.2019	0.4168 ± 0.0238	0.5432 ± 0.0382	0.0438 ± 0.0134	<LOD (U_A = 0.0172)
20.09.2019	0.2976 ± 0.0243	0.4155 ± 0.0404	0.0408 ± 0.0109	0.0744 ± 0.0302
23.09.2019	0.3881 ± 0.0275	0.5380 ± 0.0635	0.0725 ± 0.0096	0.0937 ± 0.0154
27.09.2019	0.3444 ± 0.0258	0.4857 ± 0.0446	0.0442 ± 0.0113	0.0408 ± 0.0228
30.09.2019	0.4025 ± 0.0301	0.5173 ± 0.0646	0.0257 ± 0.0118	0.0652 ± 0.0237
04.10.2019	0.3701 ± 0.0281	0.4946 ± 0.0595	0.0581 ± 0.0179	0.0894 ± 0.0268
07.10.2019	0.4411 ± 0.0301	0.5667 ± 0.0503	0.0291 ± 0.0059	0.0336 ± 0.0142
14.10.2019	0.3746 ± 0.0312	0.4953 ± 0.0605	<LOD (U_A = 0.0161)	0.0602 ± 0.0274
21.10.2019	0.3783 ± 0.0256	0.5139 ± 0.0469	0.0275 ± 0.0176	0.0406 ± 0.0293
01.11.2019	0.2998 ± 0.0283	0.4120 ± 0.0449	0.0324 ± 0.0163	0.0445 ± 0.0295
08.11.2019	0.3515 ± 0.0343	0.4830 ± 0.0634	<LOD (U_A = 0.0150)	0.0326 ± 0.0257
15.11.2019	0.3837 ± 0.0348	0.4865 ± 0.0459	0.0379 ± 0.0194	0.0375 ± 0.0245
22.11.2019	0.4086 ± 0.0237	0.5049 ± 0.0437	0.0281 ± 0.0147	<LOD (U_A = 0.0225)
29.11.2019	0.3748 ± 0.0268	0.4848 ± 0.0473	0.0243 ± 0.0131	<LOD (U_A = 0.0146)
06.12.2019	0.4021 ± 0.0288	0.4816 ± 0.0590	0.0182 ± 0.0068	0.0284 ± 0.0147

*LOD for ^{226}Ra and ^{228}Ra is 20 mBq·kg^{-1}.

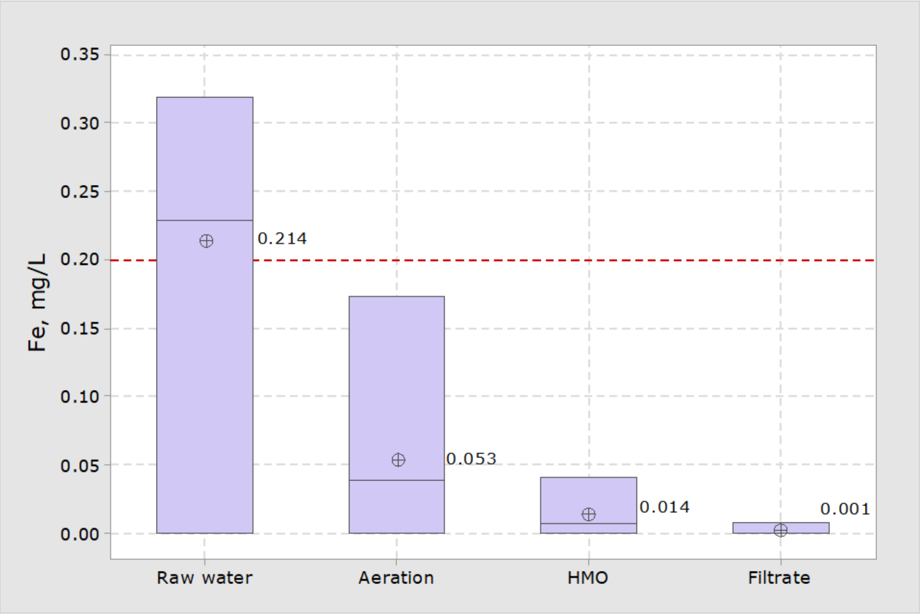

Figure 3.12 Fe concentration throughout the process (Scheme 1, 0.2 L·h^{-1})

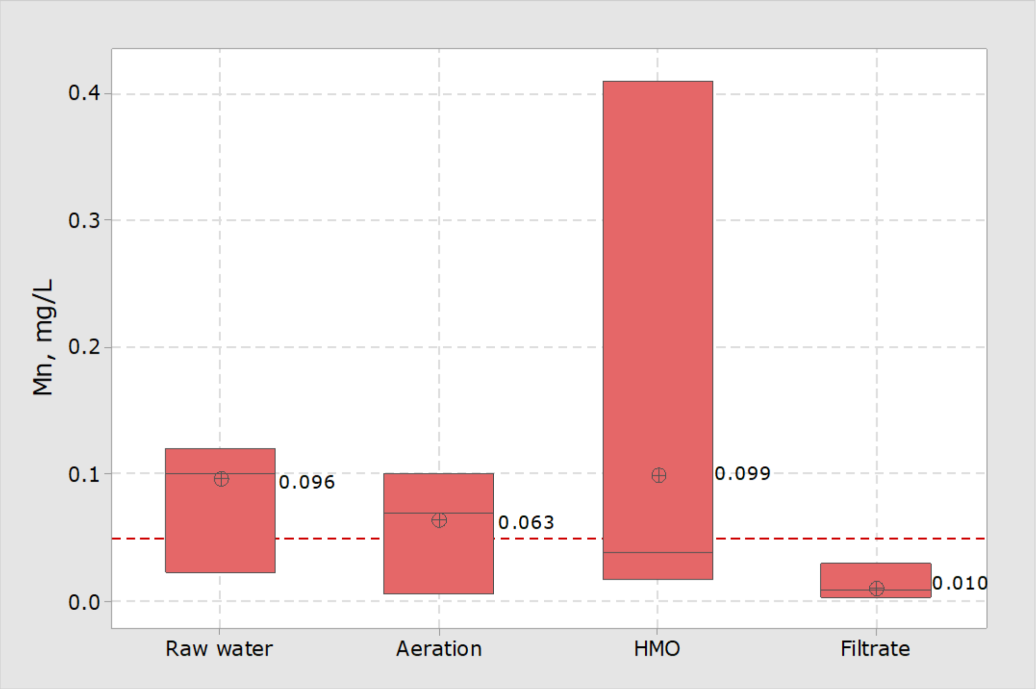

Figure 3.13 Mn concentration throughout the process (Scheme 1, 0.2 L·h^{-1})

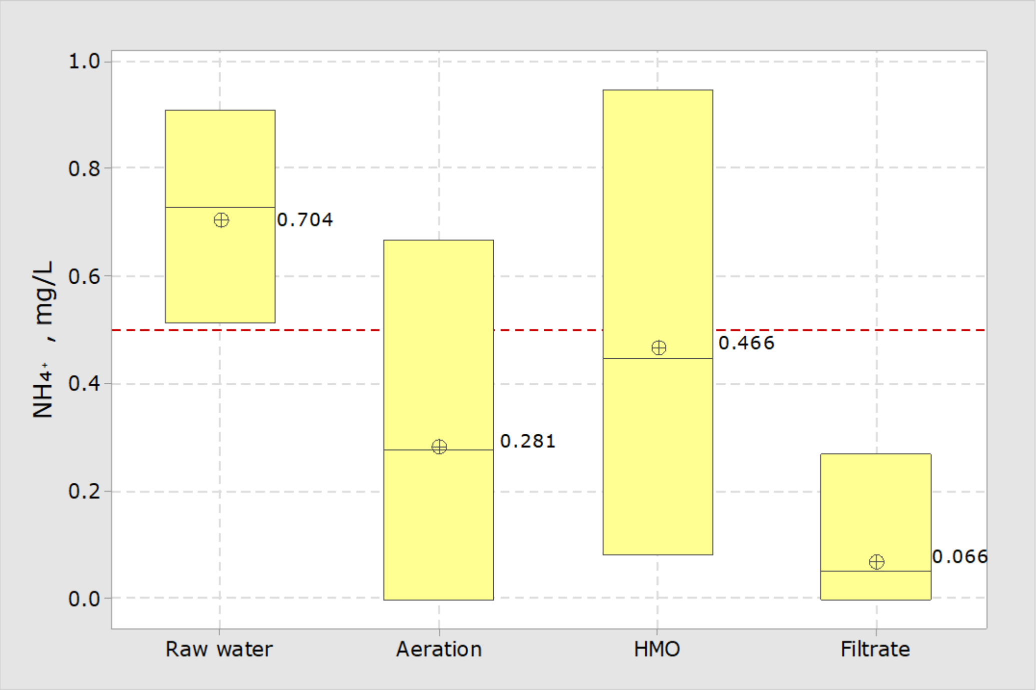

Figure 3.14 NH_4^+ concentration throughout the process (Scheme 1, 0.2 L·h^{-1})

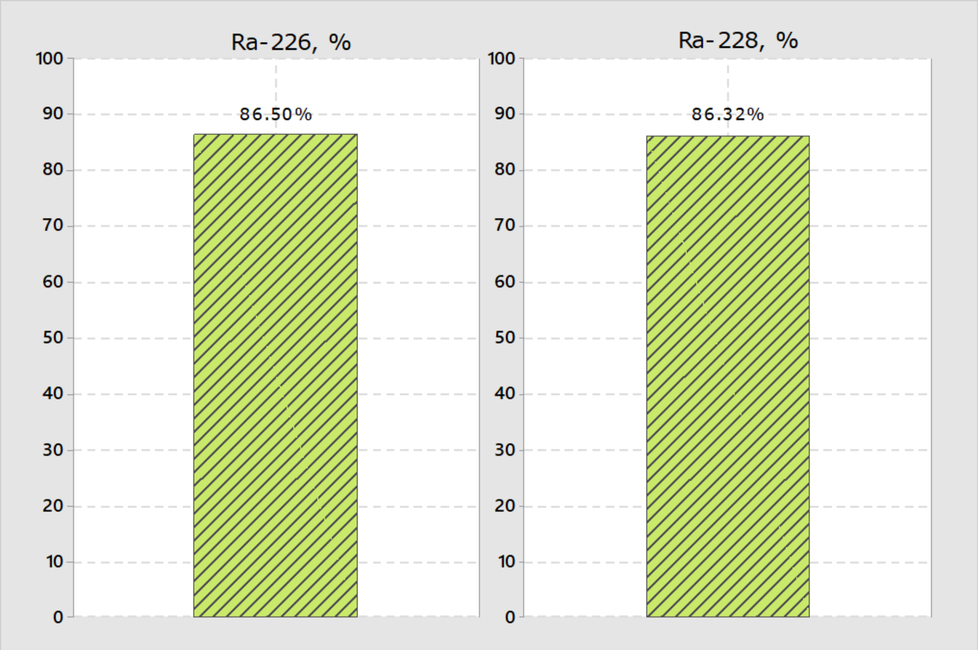

Figure 3.15 Average removal efficiency for ^{226}Ra and ^{228}Ra (Scheme 1, 0.2 L·h^{-1})

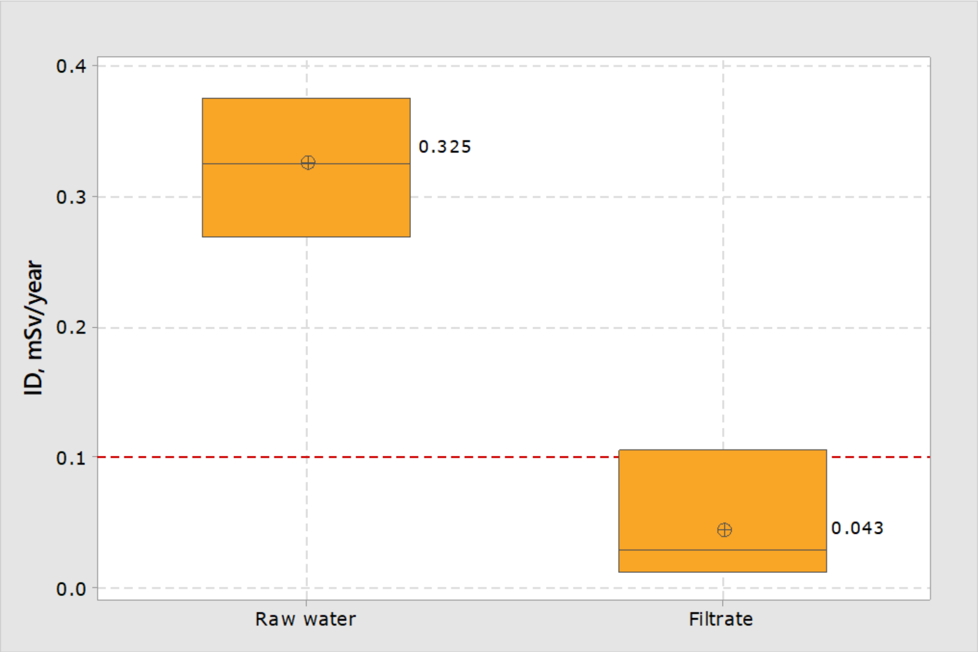

Figure 3.16 ID of raw and treated water (Scheme 1, 0.2 L·h^{-1})

Nevertheless, doubling the concentration of MnO_2 raised an already known issue of total manganese concentration increase after the oxidation with HMO. As it could be seen from the Figure 3.13, one of the measurements demonstrated high result of 0.410 mg·L^{-1}. This may be explained by the change of the mode, i.e., from injection rate of ca 0.1 to 0.2 L·h^{-1}, as the sampling was conducted on September 2, 2019 (the first date after the dosing switch).

It may be assumed that doubling the concentration of HMO during its preparation leads to the rise in total Mn concentration in treated water due to the presence of unreacted Mn(II).

It was discovered that $KMnO_4$ was not dissolved completely during the HMO preparation due to low temperatures inside the facility, where the pilot setup was installed. Thus, even the addition of $KMnO_4$ in 5% excess could not guarantee complete oxidation of Mn(II) during the preparation of HMO. Fortunately, excess of manganese was finally oxidized and removed via filtration.

Based upon the results conducted for an injection rate of ca 0.2 $L \cdot h^{-1}$, it may be assumed that the system requires certain time in order to be adapted to new conditions.

Further investigation was carried out at the HMO injection rate of ca 0.15 $L \cdot h^{-1}$, which corresponds to 0.75 $mgMn \cdot L^{-1}$ in treated water. Under these conditions, the pilot setup operated from January 2020 to February 2020. The results of examined treatment mode are presented in the Figures 3.17–3.21 with the average ID of 0.034 ± 0.014 mSv per year in the effluent (standard deviation calculated over all measurements of the studied mode).

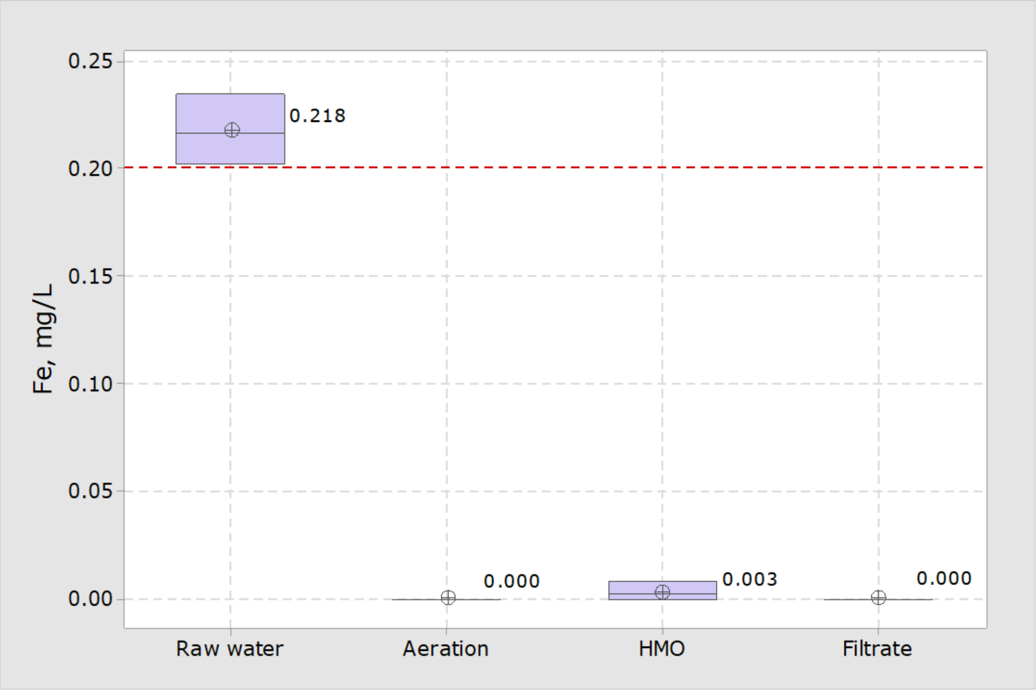

Figure 3.17 Fe concentration throughout the process (Scheme 1, 0.15 $L \cdot h^{-1}$)

Figure 3.18 Mn concentration throughout the process (Scheme 1, 0.15 L·h^{-1})

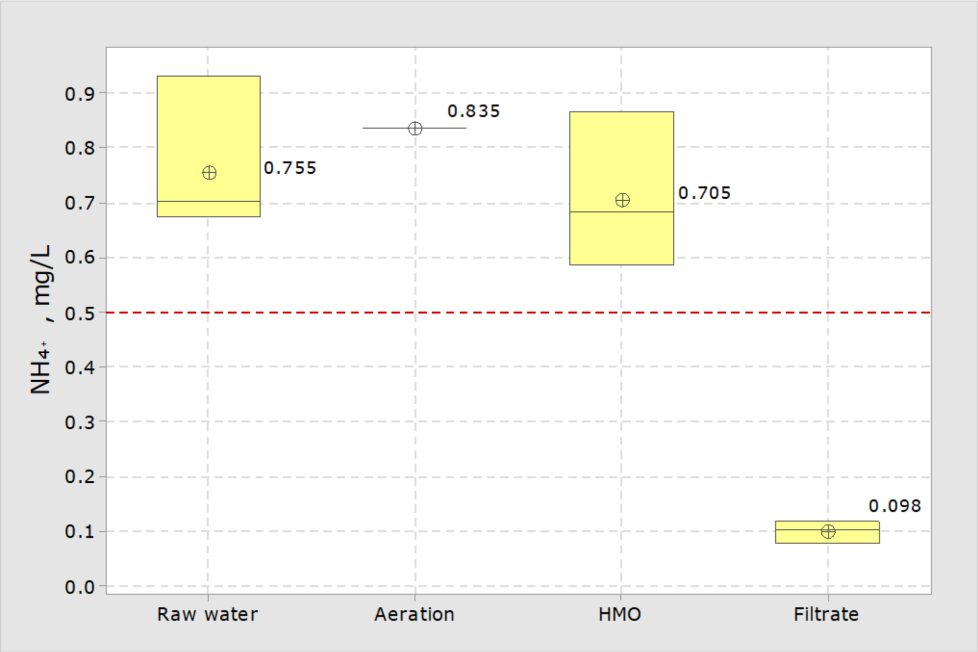

Figure 3.19 NH_4^+ concentration throughout the process (Scheme 1, 0.15 L·h^{-1})

The main objective of dosage reduction from 1.0 to 0.75 mgMn·L^{-1} was to optimize both the quantity of reagents implemented as well as the radium removal efficiency. Too high radium removal efficiency from groundwater leads to a higher accumulation of radioisotopes in the filtration media, which is among the issues of the present technology. The optimal solution, however, is not removing all the radionuclides from water, but achieving a radium removal efficiency that is just enough to reach ID below the parametric value of 0.1 mSv·year^{-1}.

The average removal efficiency for radium-226 and radium-228 based on the activity concentrations (Table 3.6) resulted in 86% for ^{226}Ra and 91% for ^{228}Ra (Figure 3.20), which was the highest result obtained throughout all the treatment modes tested. The reason for this could be described in terms of so-called "memory effect", where certain amount of HMO particulates remained in the filter even after thorough backwashing procedure. The cumulative effect resulted in the highest removal efficiency for both ^{226}Ra and ^{228}Ra contributing to the accumulation of radioisotopes in the filtration media.

Table 3.6 Activity concentrations (± measurement uncertainty, k=2) of ^{226}Ra and ^{228}Ra for the Scheme 1, 0.15 L·h^{-1}

Sample collection date	**Raw water** *Bq·kg^{-1}*		**Filtrate** *Bq·kg^{-1}*	
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
13.12.2019	0.3779 ± 0.0274	0.4862 ± 0.0590	0.0312 ± 0.0100	0.0441 ± 0.0291
20.12.2019	0.3767 ± 0.0239	0.4823 ± 0.0369	0.0297 ± 0.0160	0.0500 ± 0.0303
03.01.2020	0.3252 ± 0.0302	0.4463 ± 0.0575	0.0509 ± 0.0343	<LOD (U_A = 0.0142)
10.01.2020	0.3445 ± 0.0518	0.4410 ± 0.0595	0.0630 ± 0.0176	0.0837 ± 0.0351
17.01.2020	0.3205 ± 0.0328	0.4509 ± 0.0461	0.0546 ± 0.0218	0.0585 ± 0.0298
24.01.2020	0.4238 ± 0.0343	0.5278 ± 0.0565	0.0507 ± 0.0180	<LOD (U_A = 0.0134)
31.01.2020	0.3204 ± 0.0325	0.4331 ± 0.0613	0.0452 ± 0.0182	<LOD (U_A = 0.0143)
07.02.2020	0.3688 ± 0.0310	0.4816 ± 0.0511	0.0546 ± 0.0167	0.0702 ± 0.0339
21.02.2020	0.3980 ± 0.0368	0.5278 ± 0.0698	0.0368 ± 0.0163	0.0760 ± 0.0326
28.02.2020	0.3210 ± 0.0270	0.4275 ± 0.0444	0.0680 ± 0.0132	0.0495 ± 0.0223

*LOD for ^{226}Ra and ^{228}Ra is 20 mBq·kg^{-1}.

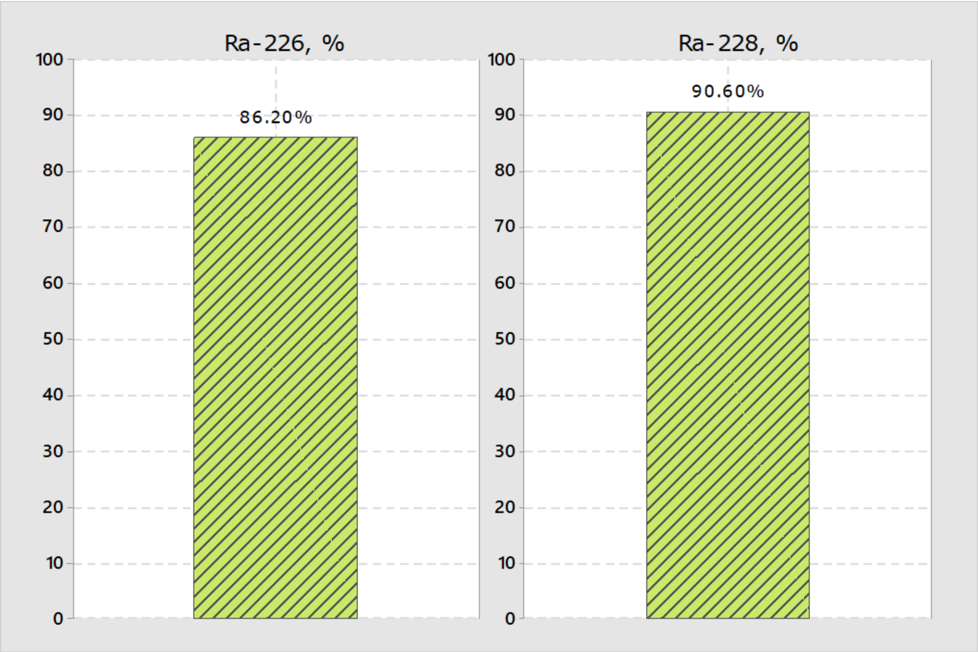

Figure 3.20 Average removal efficiency for ^{226}Ra and ^{228}Ra (Scheme 1, 0.15 L·h^{-1})

Figure 3.21 ID of raw and treated water (Scheme 1, 0.15 L·h^{-1})

Generally, the target water constituents tend to decrease as water passes through the system. Iron is easily oxidized by oxygen in aerator, whereas manganese concentration decreases below the threshold limit only after HMO oxidation and subsequent filtration. The process of oxidation of Mn to manganese oxyhydroxide, or manganite, that occurs inside the contact column may be described by the Equation 3.1 [19]:

$$Mn^{2+} + MnO_2 + 2H_2O \leftrightarrow 2MnOOH \downarrow + 2H^+, \qquad (3.1)$$

The continuous HMO dosing at an injection rate of ca 0.15 L·h^{-1} (0.75 mgMn·L^{-1} in treated water) was found to be optimal for removal of both the constituents and radionuclides. Still, the unexpected rise of Mn concentration was detected after mixing and reaction with HMO, as it was previously mentioned.

3.3 Accumulation of radionuclides in the filter material

Among the issues encountered during the treatment of groundwater is the formation of radioactive solid waste from the filtration column. The continuous separation of radionuclides from aqueous phase inevitably leads to their accumulation within the filter material. This process results in the formation of NORM and may constitute radiological consequences both for workers and the general public, if not managed properly.

It is known that radium-226 and radium-228 tend to adsorb onto the surface of MnO_2. In addition, thorium-228 is formed in the filter media as a product of the radium-228 decay chain becoming a relevant radionuclide in terms of NORM waste classification. It was observed that radioisotopes accumulate predominantly in the upper part of the filter media, i.e., onto the layer of anthracite, while quartz sand has relatively low properties of radionuclides sorption. The likelihood of divalent radionuclides to accumulate in anthracite as a part of HMO flocs was confirmed by activity concentrations measured in both anthracite and sand (Figure 3.22). The exemption value of 1 000 Bq·kg^{-1} set for ^{226}Ra, ^{228}Ra, and ^{228}Th is shown with dashed line marked in red.

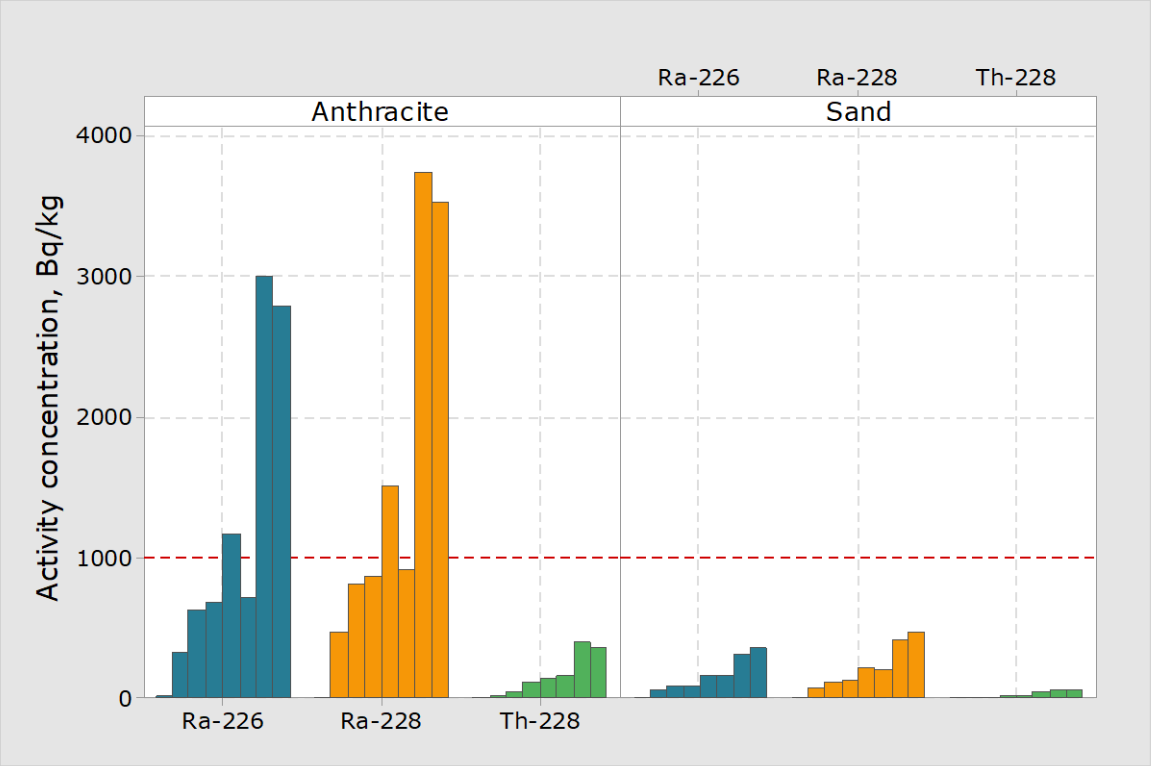

Figure 3.22 Activity concentrations of radium-226, radium-228, and thorium-228 in the filter media after the backwash

In addition, it was revealed that the anthracite separation from the sand layer may become rational during the disposal of the filter material. Since the activity concentrations of ^{226}Ra, ^{228}Ra, and ^{228}Th stay below the exemption level within the layer of sand (<1 000 Bq·kg^{-1}), it was proposed that the sand may be classified as non-hazardous waste. The anthracite, however, does not fall under the category of non-hazardous, and should be disposed as NORM-containing waste.

Furthermore, liquid obtained as a result of the backwashing procedure includes backwash water and HMO precipitate flushed out from the filter (the main components of which are Fe(III) hydroxide and manganese Mn(IV) oxide). It should be noted that activity concentrations of ^{226}Ra and ^{228}Ra as well as the total volume of water filter backwash (WFB) are relatively small, if compared to the overall input from sewer water. Consequently, any contamination from WFB, including radiological impact, will be diluted. Being a liquid waste, WFB may be discharged directly to the sewerage.

According to the general mechanism of contaminants removal by HMO (Figure 1.3), particles of Fe and Mn are formed with the subsequent trapping in the filter bed. Iron and manganese complexes as well as their Fe-Mn oxides are known to sorb radium from aqueous solution. At neutral pH values, the surface of such complexes becomes rich in negatively charged OH-groups enhancing the sorption of positively charged species, e.g., radium isotopes [39]. In other words, the higher is the Fe-Mn oxyhydroxides concentration in solid matrix, the higher should be radium content present there.

This phenomenon was confirmed by setting a correlation between the amount of manganese and radionuclides activity concentration of the solid matrix, i.e., anthracite and sand layers of the filtration column. The dependence appeared to follow a linear isotherm. The issue is illustrated by the Figure 3.23 on the example of radium-226 activity concentration, as radium-228 share the same sorption tendency.

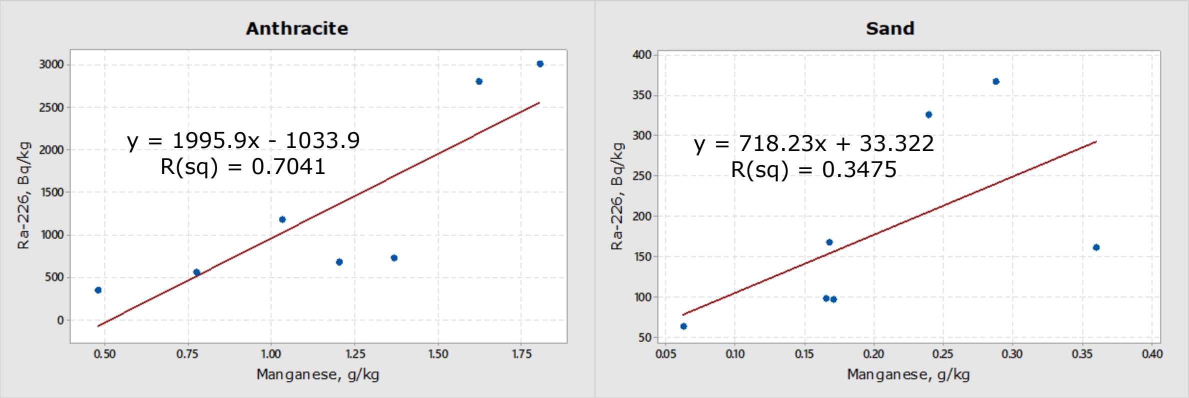

Figure 3.23 A correlation between Mn content and ^{226}Ra activity concentration of the solid matrix

It is important to mention that current industrial technology adopted at the Viimsi WTP utilizes a MnO_2 based catalytic filter material (FMH) and subsequent zeolite filtration, i.e., the IX technology, in order to remove iron, manganese, and radium from water [19].

From the year 2012 to 2016, research on the filter materials was conducted on the basis of conventional treatment used at the Viimsi WTP. It was observed that the current approach generates NORM-containing wastes in amounts higher than those produced by the implementation of HMO [21, 57]. Results of the comparison analysis are summarized in the Table 3.7.

Table 3.7 Annual accumulation rates of radionuclides in various materials

Scale	**Filter material**	**^{226}Ra** ***Bq·(kg·year)$^{-1}$***	**^{228}Ra** ***Bq·(kg·year)$^{-1}$***
Pilot plant scale (HMO)	Anthracite	686	895
	Sand	151	198
Industrial scale: current technology used at the Viimsi WTP	FMH	1400	1860
	Zeolite	3400	4760

SUMMARY

Water is a vital natural resource. Among all fields of application, water is used for drinking purposes; hence, contaminant concentrations of such water must satisfy the drinking water quality standards estimated by corresponding aspects of legislation. However, conventional water treatment technologies, such as reverse osmosis, ion-exchange, adsorption, etc., were found to be insufficient due to their high cost and accumulation of NORM.

Upon exploring the pilot project from multiple perspectives, it is safe to assume that implementation of HMO-technology demonstrates high results in removal of iron, manganese, ammonium cation, and radionuclides, i.e., radium-226 and radium-228. In the context of water treatment, the observed technology has a number of advantages, e.g., ease of maintenance, affordability of reagents implemented, and reduced generation of NORM-containing waste (if compared with the current technology used at the Viimsi WTP).

The overall removal efficiency for Fe, Mn, and NH_4^+ was 97%, 83%, and 92%, respectively. Nevertheless, the most optimal treatment mode was achieved upon the continuous HMO dosing at an injection rate of ca 0.15 $L \cdot h^{-1}$, which resulted in an average indicative dose of 0.034 ± 0.014 $mSv \cdot year^{-1}$. In addition, the unexpected removal of NH_4^+ eliminated the need for additional zeolite filtration.

However, several issues were left out of the thesis scope. For example, the pilot plant demonstrated high electricity consumption (1.9 kW per m^3 of treated water) throughout the entire operational period. Investigation revealed that the pump located between the aeration and oxidation columns is too powerful in terms of the pilot setup. Unfortunately, replacement of the pump was not possible, as the pump industry does not provide devices of lower capacity.

Furthermore, the presence of gaseous radon-222, which is generated by the decay of radium-226 in the filter, remains an open question. During the pilot study, it was unable to conduct appropriate experiments in order to determine the HMO-technology impact to an indoor air radon contamination in the facility because of the presence of other equipment responsible for radon exhalation into filtration hall (ten filter columns are present in there, apart from the HMO setup). Operators of drinking water treatment facilities should pay attention to the possible ^{222}Rn exhalation. It is highly recommended to measure gaseous radon-222 content in the indoor air and improve the ventilation system of the water treatment facility, if required.

In general, the pilot setup was able to produce water compliant with the requirements proposed for drinking water. However, further assessment of scale-up process is necessary before moving on to an industrial scale.

KOKKUVÕTE

Vesi on elutähtis loodusresurss. Vett kasutatakse joogiveena, seepärast peavad saasteainete kontsentratsioonid vastama veekvaliteedi standardile, mis on seadusega reguleeritud. Traditsioonilised veepuhastusmeetmed, nagu pöördosmoos, ioonvahetus, adsorptsioon jne, jäävad teatud olukordades ebapiisavaks oma kalliduse ja NORM-i akumulatsiooni tõttu.

HMO tehnoloogia rakendamine tagab hea tulemuse raua, mangaani, ammooniumi ja radionukliidide (raadium-226 ja raadium-228) eemaldamisel. Veepuhastustehnoloogiana omab antud meetod suuri eeliseid, näiteks teenindamise lihtsus, reagentide kättesaadavus ja NORM-jäätmete vähendamine (võrreldes praeguse Viimsi puhastusjaama seadmega).

Üldine puhastusefektiivsus Fe, Mn ja NH_4^+ puhul oli vastavalt 97%, 83% ja 92%. Kõige optimaalsem puhastusrežiim saavutati pideva HMO doseerimise juures, kui sissepritse oli ca 0,15 $L \cdot h^{-1}$. Seega langes keskmine indikatiivdoos alla seadusandluses kehtestatud viitetaseme, saavutati väärtus 0,034 ± 0,014 $mSv \cdot aasta^{-1}$. Lisaks sellele avaldus ka prognoosimatu efekt ammooniumi eemaldamise näol, mis elimineeris vajaduse lisada HMO tehnoloogiale täiendav tseoliitfilter.

Mõningad küsimused jäid lõputööst välja. Näiteks näitas pilootjaam suurt elektritarbimist (1,9 kW ühe kuupmeetri puhastatud vee kohta) kogu protsessi ulatuses. Uuringu käigus selgus, et pump, mis asub aeratsiooni ja oksüdatsiooni kolonnide vahel, on liiga võimas pilootseade kontekstis. Kahjuks ei olnud pumba vahetamine võimalik, kuna turul ei ole sellise rakenduse jaoks sobivat väiksema võimsusega pumpa saadaval. Seetõttu jäi pilootjaama täpne elektritarve välja selgitamata.

Peale selle, filtrisse akumuleerunud raadium-226 radioaktiivsel lagunemisel tekib radioaktiivne gaas radoon-222, mille tulemusena võib veetöötlusjaama siseõhu radoonisisaldus märkimisväärselt tõusta. HMO pilootjaama puhul ei olnud võimalik eksperimentaalselt mõõta, kui palju see ruumi õhu radoonisisaldust tõstis, sest pilootseade asus filtreerimishallis, kus on niigi kümme suurt filtrit, mis pidevalt radooni genereerivad. Siiski peaks veekäitleja, kes HMO tehnoloogiat rakendab, radooni küsimusele tähelepanu pöörama (veepuhastusjaamas siseõhu radoonisisaldust mõõtma) ning vajadusel ruumi ventilatsiooni parandama.

Kokkuvõtteks võib sedastada, et pilootseade võimaldas toota vett, mis vastab joogiveele sätestatud nõuetele. Selleks, et rakendada tehnoloogiat tööstuslikus mastaabis, on vaja teha lisauuringuid (sh tehnoloogia elektritarbe määramine, soodsate tingimuste tagamine Mn(II) oksüdeerumisel HMO suspensiooni valmistamise jooksul).

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