

SIIRI SUURSOO

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Groundwater – Analytical Procedures,
Monitoring of Drinking Water Treatment
Technology, and Associated Changes in
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Department of Bio- and Environmental Physics, Institute of Physics, Faculty of Science and Technology, University of Tartu.

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“Meie füüsik ja teoloog on sõbrad. Meie astronoom ja kiriku-
õpetaja on vennad. Nii et ei ole see asi sugugi võõras...”

Meenutades minu vanaonu, *prof. theol.* Evald Saag'i
(24.11.1912–20.10.2004)

*“Our physicist and theologian are friends. Our astronomer
and pastor are brothers. So there really is nothing new...”*

Recollecting the words of my great-uncle, *prof. theol.* Evald
Saag (24.11.1912–20.10.2004)

TABLE OF CONTENTS

LIST OF ORIGINAL PUBLICATIONS	9
AUTHOR'S CONTRIBUTION TO THE PUBLICATIONS	10
ABBREVIATIONS	11
ABSTRACT	12
INTRODUCTION	14
1. GENERAL BACKGROUND	16
1.1. Requirements for radiological parameters in drinking water	16
1.2. Assessment of ID in drinking water	17
1.3. Radioactivity of Estonian groundwater	18
2. MATERIAL AND METHODS	21
2.1. The Area and Object of Study	21
2.2. Sampling	25
2.2.1. Paper I	25
2.2.2. Paper II	25
2.2.3. Papers III, IV, and V	25
2.3. Analytical procedures	28
2.3.1. ²²⁶ Ra measurements in water by LSC	28
2.3.2. ²²⁶ Ra and ²²⁸ Ra measurements in water by gamma spectrometry	28
2.3.3. ²²² Rn in water	30
2.3.4. ²²⁶ Ra, ²²⁸ Ra and ²²⁸ Th in filter material	30
2.3.5. ²²⁶ Ra, ²²⁸ Ra and ²²⁸ Th in backwash samples	31
2.3.6. Other radiological parameters	31
2.3.7. <i>In situ</i> gamma spectrometry	32
2.3.8. Chemical parameters	33
2.3.8.1. Water samples taken from the treatment plant (V)...	33
2.3.8.2. Well waters (IV)	33
2.3.9. Analyses of oxygen and hydrogen isotope ratios (IV)	33
2.4. Indicative dose assessment	34
2.5. Data analysis tools	34
3. RESULTS AND DISCUSSION	35
3.1. Radionuclides of interest for radiation protection	35
3.2. The applicability of gross alpha and gross beta measurements for Cm-V groundwater	36
3.3. Validation of analytical procedures for radium measurement	37
3.4. Radium removal and accumulation in Viimsi Water Ltd. treatment plant	45
3.4.1. Purification efficiency of the treatment plant	45
3.4.2. Radionuclides' accumulation in filter columns	50
3.4.3. Filter backwash	51
3.5. Influence of the intensive water uptake on groundwater quality	55

5. CONCLUSIONS.....	60
REFERENCES	62
SUMMARY IN ESTONIAN.....	66
ACKNOWLEDGEMENTS.....	68
PUBLICATIONS	69
CURRICULUM VITAE	137
ELULOOKIRJELDUS	141

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications (full texts included at the end of the thesis) which are referred to in the text by Roman numbers:

- I** Suursoo, S., Kiisk, M., Jantsikene, A., Isakar, K., Koch, R., 2011. Applying gross alpha and beta measurements as an estimate to the total indicative dose of Cambrian-Vendian ground water in Estonia. *Radioprotection*, 46(6), pp. S125–S130.
<https://doi.org/10.1051/radiopro/20116868s>
- II** Suursoo, S., Kiisk, M., Semakalu, A., Isakar, K., 2014. Radon leakage as a source of additional uncertainty in simultaneous determination of ^{226}Ra and ^{228}Ra by gamma spectrometry – validation of analysis procedure. *Applied Radiation and Isotopes*, 87, pp. 447–451.
<https://doi.org/10.1016/j.apradiso.2013.11.031>
- III** Suursoo, S., Kiisk, M., Al-Malahmeh, A., Jantsikene, A., Putk, K., Lumiste, L., 2014. ^{226}Ra measurement by LSC as a tool to assess the efficiency of a water treatment technology for removing radionuclides from groundwater. *Applied Radiation and Isotopes*, 93, pp. 57–63.
<https://doi.org/10.1016/j.apradiso.2014.01.016>
- IV** Suursoo, S., Hill, L., Raidla, V., Kiisk, M., Jantsikene, A., Nilb, N., Czuppon, G., Putk, K., Munter, R., Koch, R., Isakar, K., 2017. Temporal changes in radiological and chemical composition of Cambrian-Vendian groundwater in conditions of intensive water consumption. *Science of the Total Environment*, 601–602, pp. 679–690.
<https://doi.org/10.1016/j.scitotenv.2017.05.136>
- V** Hill, L., Suursoo, S., Kiisk, M., Jantsikene, A., Nilb, N., Munter, R., Realo, E., Koch, R., Putk, K., Leier, M., Vaasma, T., Isakar, K., 2018. Long-term monitoring of a water treatment technology designed for radium removal – removal efficiencies and NORM formation. *Journal of Radiological Protection*, 38, pp. 1–24.
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AUTHOR'S CONTRIBUTION TO THE PUBLICATIONS

- I** Sample preparation, statistical data analysis, writing the full text of the article.
- II** Design of the methodology (validation experiments), gamma spectrometric analysis, statistical data analysis, writing the full text of the article.
- III** Planning the sampling and experiments, sample measurement and analysis, writing the full text of the article.
- IV** Planning the sampling, gamma spectrometric analysis, statistical data analysis, responsible person for writing the article.
- V** Planning the sampling, gamma spectrometric analysis, ^{226}Ra analysis of LSC samples, statistical data analysis, writing the respective parts of the article.

ABBREVIATIONS

BEGe	Broad energy germanium
BfS	<i>Bundesamt für Strahlenschutz</i> (German Federal Office for Radiation Protection)
Cm-V	Cambrian-Vendian aquifer system
EC	European Commission
EU	European Union
GDT	Gas-degas technology
HPGe	High purity germanium
IAEA	International Atomic Energy Agency
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICRP	International Commission on Radiological Protection
ID	Indicative dose
LoD	Limit of detection
LSC	Liquid scintillation counting
MDA	Minimum detectible activity concentration
NORM	Naturally occurring radioactive material
Stdev	Standard deviation
TalTech	Tallinn University of Technology
TID	Total indicative dose
UT	University of Tartu
V2gd	Cambrian-Vendian Gdov aquifer
V2vr	Cambrian-Vendian Voronka aquifer
WHO	World Health Organisation

ABSTRACT

The most important public water supply in North-Estonia – the Cambrian-Vendian (Cm-V) aquifer system – is the deepest aquifer system available for drinking water uptake in Estonian territory. It lies on the crystalline basement rock known to be rich in uranium and thorium. Cm-V groundwater is contaminated with naturally occurring radionuclides. According to estimations from 2009, approximately 18% of Estonian inhabitants (230 000 people) consume drinking water where radiological parameters exceed the parametric values given by international suggestions and local legislation.

The capacity to conduct radiological analysis of water in Estonia was very limited when the requirements for radiological parameters in drinking water were adopted into local legislation. In order to fill the gap, analytical procedures for radium measurement were developed and validated as a part of this thesis. Screening methods based on the measurement of gross alpha and beta activity, suggested by the World Health Organisation and European Commission, proved to be unsuitable for Cm-V water. Instead nuclide specific measurements should be preferred. Procedures based on simultaneous determination of ^{226}Ra and ^{228}Ra by gamma spectrometry were accredited, which now enable to offer a reliable measurement service for water treatment facilities.

Exceeding the parametric values for radiological parameters has pushed water treatment facility operators to search for options for radionuclide removal. However, the long term efficiency of the treatment technologies and the accumulation of naturally occurring radioactive material (NORM) in filtration media have not given enough attention.

In February 2012, the first water treatment plant specially designed for radium removal from iron- and manganese-containing groundwater started operation in Viimsi, Estonia. The facility was monitored for three years. The thesis demonstrated clearly that NORM generation is difficult to avoid when Cm-V groundwater is used for drinking water production. In addition to radium isotopes, which are the only radionuclides of concern in groundwater, ^{222}Rn and ^{228}Th become of interest in the water treatment facility because they are generated by the decay of ^{226}Ra and ^{228}Ra in the filter material.

As for now, the water treatment facility in Viimsi has been able to provide water compliant with the drinking water requirements. Yet the intensive use of groundwater brings about changes in the quality of the incoming water.

Changes in Cl and Ra concentrations are critical parameters to monitor for sustainable management of the Cm-V groundwater. Possible explanations for the increase of salinity are (a) intrusion of sea water into the aquifer or (b) inflow of highly saline water from the crystalline basement accompanied by inflow of meteoric water. Radium concentration may rise either because of migration of Ra into the system or by changes in geochemical conditions that may lead to desorption of Ra from sediment surface. The present study proved that the monitoring frequency set for radiological parameters in a local

regulation (“Quality and monitoring standards and methods of analysis for drinking water” by the Estonian Minister of Social Affairs) is not sufficient for ensuring stable drinking water quality in case of aquifer systems as sensitive as the Cm-V aquifer system.

INTRODUCTION

The Cambrian-Vendian (Cm-V) aquifer system is the deepest aquifer system available for drinking water uptake in Estonian territory (Vallner and Savitskaja, 1997). It lies on the crystalline basement rock known to be rich in thorium and uranium (Petersell *et al.*, 1991; Raudsep, 1997). In many places on the northern coast the Cm-V aquifer system is the only suitable source of public water supply. In North and North-East Estonia, Cm-V groundwater comprises about 75% of the total groundwater usage; in north-western part of the country, it gives 50% of the overall groundwater uptake (Raidla *et al.*, 2009).

The problem of high natural radioactivity in North Estonian groundwater has been known since the 1990s (as stated by the Estonian Radiation Protection Centre, 2005). Over the years, most of the monitoring programmes have concentrated on radium measurements in Cm-V waters (Estonian Radiation Protection Centre, 2005). However, there is still limited knowledge on other radionuclides in Estonian groundwater (Kiisk *et al.*, 2011) and hardly any information has been published on changes in radionuclide activity concentrations in the same location over a longer period of time. Intensive groundwater uptake from Cm-V may lead to water inflow either from the sea (a), from the underlying crystalline basement rock (b) or through ancient buried valleys (c) (Marandi *et al.*, 2012). This in turn may bring about many changes in water quality, including the alteration of radiological parameters.

Requirements for radiological parameters in drinking water were adopted into Estonian legislation in 2002 (Minister of Social Affairs, 2002). Since 2005 water treatment facility operators are obliged to determine the radiological parameters of every new water supply before using it (Minister of Social Affairs, 2005). A high demand for radionuclide measurements arose in 2008, when the requirement came into force for the water treatment facilities that had started their operation before 2005. However, back then, the capacity to conduct radiological analysis in water samples was limited and no accredited measurement services were available in Estonia.

Exceeding the parametric values for radiological parameters has pushed water treatment facility operators to search for options for radionuclide removal. Yet, the long term efficiency of the treatment technologies and the accumulation of naturally occurring radionuclides in filtration media have not been given enough attention. In February 2012, the first water treatment plant specially designed for radium removal from iron- and manganese-containing groundwater started operation in Viimsi, Estonia.

Motivated by the abovementioned shortcomings, the aims of this thesis were:

- To develop and validate a suitable approach for radionuclide determination in Cm-V groundwater (I, II, III).

- To assess the long-term performance of the technology in Viimsi along with the possible build-up of NORM (naturally occurring radioactive material) in the treatment process (III, V).
- To discover possible changes in radiological and chemical parameters of Cm-V groundwater in the condition of intensive water uptake using the wells of the Viimsi treatment plant as an example (IV).

1. GENERAL BACKGROUND

1.1. Requirements for radiological parameters in drinking water

From the viewpoint of radiation protection, intake of radionuclides by drinking water consumption can be classified as a *planned exposure situation* or as an *existing exposure situation* of the public.

- *Planned exposure situations* are defined as everyday situations involving the planned operation of radiation sources or a planned activity that results in an exposure to a radiation source (ICRP, 2007). For restricting individual doses in planned exposure situations International Commission on Radiological Protection (ICRP, 2007) has derived a dose limit (1 mSv/yr) and a dose constraint (0,1 mSv/yr). The former is a value of the effective dose that shall not be exceeded (ICRP, 2007). The latter – the dose constraint – is a restriction on the individual dose that ensures the appropriate level of protection (ICRP, 2007). The risk caused by an exposure equal to the dose constraint is low enough that it is not expected to give rise to any detectable adverse health effects (WHO, 2017).
- An *existing exposure situation* is a situation that already exists when a decision on control has to be taken (ICRP, 2007), for example natural background radiation and exposure to indoor radon (WHO, 2017). As existing exposure situations are often more difficult to control than planned exposure situations, reference levels are used instead of dose constraints or dose limits to restrict individual doses. ICRP (2007) defines a reference level as follows: “Reference level represents the level of dose or risk, above which it is judged to be inappropriate to plan to allow exposures to occur, and below which optimisation of protection should be implemented.” The value of a reference level should be decided depending on the circumstances of the exposure but is suggested to be between 1 and 20 mSv/year (ICRP, 2007).

The dose constraint, dose limit and reference levels are derived based on the linear-non-threshold model, which assumes that all radiation doses greater than zero will increase the risk of excess cancer (ICRP, 2007). The relationship between exposure and risk is linear (ICRP, 2007).

As a conservative approach, ICRP has suggested to use the dose constraint 0.10 mSv/yr as the guidance level for effective dose from drinking water consumption (ICRP, 1999). Drinking water is treated as a commodity that contains radionuclides as a result of natural processes (or human activities) and delivers prolonged exposures to the public (ICRP, 1999). Exceeding the dose constraint 0.10 mSv/yr should not be taken as an indication that the drinking water is unsafe, but as a trigger for further investigation (WHO, 2017).

The dose constraint 0.10 mSv/yr has been adopted as a parametric value for the indicative dose (ID) from drinking water consumption in the Council

Directive 2013/51/Euratom, which is the document laying down the quality standards for radioactivity in drinking water in the member states of the European Union (EU). Additionally, it sets a parametric value for tritium activity concentration (100 Bq/L), and radon activity concentration (100 Bq/L). In case of noncompliance with a parametric value, the member state shall assess whether it poses a risk to human health which requires action. Where necessary, the member state is obliged to take remedial actions to improve the quality of the water to a level which complies with the requirements for the protection of human health from the perspective of radiation protection (Council Directive 2013/51/Euratom).

Before the directive 2013/51/Euratom came into force the radiological parameters were regulated by the Drinking Water Directive (Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption). It included only two parameters – tritium and indicative dose, which was referred to as total indicative dose (TID)¹.

The requirements of the Drinking Water Directive and the directive 2013/51/Euratom have been adopted into Estonian legislation by the regulation of the Minister of Social Affairs “Quality and monitoring standards and methods of analysis for drinking water”. When the radiological parameters were first introduced to the regulation in 2002, the parametric values were misleadingly translated as permissible limits (Minister of Social Affairs, 2002). This led to a misinterpretation of the ID both by water treatment facility operators and regulatory bodies creating pressure to implement treatment technologies for radionuclide removal. At the same time, the fact that groundwater filtration facilities can be a source of NORM was often disregarded, although listed as an industrial sector involving NORM in the Basic Safety Standards Directive (Council Directive 2013/59/Euratom). When paper I was published, the misleading phrasing was still used in Estonian legislation. The inaccurate wording was corrected in 2015 (Minister of Health and Labour, 2015). Since then ID is clearly recognised as a parametric value.

1.2. Assessment of ID in drinking water

ID is defined as “the committed effective dose for one year of ingestion resulting from all the radionuclides whose presence has been detected in a supply of water intended for human consumption, of natural and artificial origin, but excluding tritium, potassium-40, radon and *short-lived radon decay products*” (Council Directive 2013/51/Euratom). The definition of TID given in the Drinking Water Directive differed slightly from ID by excluding tritium, potassium-40, radon and *radon decay products* from the dose estimation (Council Directive 98/83/EC). The enactment of directive 2013/51/Euratom has

¹ The old abbreviation TID was used in papers I, III, IV and V. However, in the dissertation, the new abbreviation ID is utilized.

added clarity to regulating the long-lived radon decay products – ^{210}Po and ^{210}Pb – acknowledging their possible contribution to the committed effective dose from water consumption.

Knowledge on which radionuclides are of interest from the viewpoint of radiation protection is a crucial input to develop a suitable approach for the assessment of ID. Nuclide specific analysis are often rather time-consuming and expensive. To optimise the time and resources spent on radiological analysis the World Health Organisation (WHO) and European Commission (EC) have proposed the use of gross alpha and beta measurements for initial screening of water samples to determine whether a nuclide specific analysis is needed or not (WHO, 1984, 1993, 2004, 2008, 2011, 2017; Council Directive 2013/51/Euratom). A nuclide specific analysis is required only if the gross alpha and beta screening levels are exceeded. In other cases it can be assumed that the ID is less than 0.10 mSv/yr.

Different recommendations can be found on what screening values to use for gross alpha and beta activity measurements. In the first and second edition of the Guidelines for Drinking Water Quality, WHO proposed the screening value of 0.1 Bq/L for gross alpha activity and 1.0 Bq/L for gross beta activity (WHO, 1984, 1993). In its third edition in 2004, WHO elevated the gross alpha screening level to 0.5 Bq/L stating that ID does usually not exceed 0.10 mSv/yr if the gross alpha activity is equal to or below 0.5 Bq/L (WHO, 2004). The same screening values – 0.5 Bq/L for gross alpha and 1.0 Bq/L for gross beta – are also recommended in the newest version of the Guidelines for Drinking Water Quality (WHO, 2017). The EU has taken a more conservative approach recommending 0.1 Bq/L and 1.0 Bq/L as the screening levels for gross alpha and beta activity, respectively (Council Directive 2013/51/Euratom).

On the other hand, multiple authors have expressed criticism on the usability of these screening methods (Schönhofer and Garcia-Tenorio, 2011; Chalupnik *et al.*, 2011; Jobbágy *et al.*, 2014, 2015). Jobbágy *et al.* emphasized the need to revise the gross alpha and beta methods (2015). Results of an interlaboratory comparison with 71 participants revealed that even application of the same analytical procedure in different laboratories does not guarantee comparable results (Jobbágy *et al.*, 2015). The suitability of the method for waters containing natural radionuclides has also been debated (Schönhofer and Garcia-Tenorio, 2011; Chalupnik *et al.*, 2011). Hence, the applicability analysis of gross alpha and beta measurements in case of the Cm-V groundwater needs critical consideration.

1.3. Radioactivity of Estonian groundwater

Earliest radium measurements in Estonian groundwater date back to 1961 (not published individually, summarized by Kiisk *et al.*, 2011). The first larger conclusive investigation based on the existing radiological data was conducted in 2005 by the Estonian Radiation Protection Centre. It estimated that

approximately 14% of Estonian inhabitants (184 000 people) consume drinking water with higher ID than 0.10 mSv/year (ID calculated according to ^{226}Ra and ^{228}Ra activity concentrations; Estonian Radiation Protection Centre, 2005). In 2009, another vast summarizing study – the Estonian-Italian Twinning project “Estimation of Concentrations of Radionuclides in Estonian Groundwaters and Related Health Risks” – was conducted giving a new assumption to the number of people consuming water with ID > 0.1 mSv/year. According to these results, 230 000 inhabitants (*circa* 18% of the Estonian population) drink water with higher radionuclides concentration than the parametric value (Forte *et al.*, 2010b).

The problem of high radionuclide content is mainly limited to Cm-V aquifer system (Estonian Radiation Protection Centre, 2005; Forte *et al.*, 2010b). The aquifer lies on the crystalline basement rock and is gradually sloped towards south. Along the North-Estonian coastline, its depth from surface is 60–70 m, which increases to 450–600 m in South Estonia. The water bearing formation consists of sand- and siltstones with interlayers of clay. In north-eastern part of Estonia, a layer of Kotlin clays divides the aquifer system into two sub-aquifers with different geochemical and isotopic composition – Voronka (V2vr, the upper) and Gdov (V2gd, the lower). (Perens and Vallner, 1997)

Cm-V aquifer is well confined from overlying aquifers, intrusion of meteoric water, and surface pollution by the Lontovo-Lükati aquitard. However, in some places in North Estonia the aquitard is cut by deep pre-Quaternary valleys filled with sediments with higher hydraulic conductivity. In these regions the Cm-V aquifer is exposed to upper groundwater horizons. (Raidla *et al.*, 2009)

Stable isotope studies ($\delta^{18}\text{O}$) reveal the ancient, glacial origin of the Cm-V groundwater dating back to the last ice age (Raidla *et al.*, 2009). Variations in the geochemical and stable isotope composition suggest that the current water in the Cm-V aquifer is a mixture of three components – glacial melt water, brine which was present in the aquifer before the intrusion of the glacial water, and recent meteoric water. Mixing has occurred in two stages. First, the intrusion of the glacial melt waters took place during Pleistocene glacial periods. The second stage – intrusion of meteoric water through deep buried valleys – occurs today. (Raidla *et al.*, 2009)

In North Estonia, where the Cm-V aquifer system is the most important source of public water supply (Perens and Vallner, 1997), the dominant component in the groundwater is the glacial melt water (Raidla *et al.*, 2009). In South Estonia the prevailing component is the brine (Raidla *et al.*, 2009), making the groundwater unsuitable for drinking.

In 2005, Estonian Radiation Protection Centre reported that 80% of the wells fed by Cm-V groundwater do not comply with the requirement of ID \leq 0.10 mSv/year. High indicative dose in Cm-V waters is caused by radium isotopes ^{226}Ra and ^{228}Ra (Estonian Radiation Protection Centre, 2005; Forte *et al.*, 2010b; Kiisk *et al.*, 2011).

The origin of radionuclides in Cm-V water is not exactly known. It is believed that the radioactivity comes from the underlying crystalline basement

rock (Savitskaja and Jaštšuk, 2001; Forte *et al.*, 2010a; Mokrik *et al.*, 2009), which is known to have relatively high concentrations of thorium and uranium (Petersell *et al.*, 1991; Raudsep, 1997). Therefore, it can be assumed that activities are higher in the Gdov sub-aquifer, as it is in direct contact with the basement rock. In regions of ancient buried valleys, lower concentrations of radionuclides can be expected because of the infiltration of meteoric water.

Mokrik *et al.* (2009) have also suggested another hypothesis. They proposed that the source rocks of radium may be related to clay minerals, radium-barium carbonates, and basement granites. Radium, soluble in reduced environment which exists in Cm-V aquifer, behaves similarly to bivalent cations, e.g. Ca and Ba. Two reactions were suggested as mechanisms controlling radium desorption from clay surfaces into groundwater: (1) an active cation (Na-Ca) exchange which took place during carbonate precipitation on the smectite-illite clay surface, and (2) the exchange of sodium to potassium on K-rich smectite-illite clays (Mokrik *et al.*, 2009).

Over the years, most of the monitoring programmes have concentrated on radium measurements in Cm-V waters. The data available about other natural radionuclides and other aquifers besides Cm-V is limited. Levels of radioactivity in non-Cm-V aquifers tend to be low; however, some elevated values have also been found (Forte *et al.*, 2010b). Non-compliances of ID have been detected in a few Ordovician-Cambrian wells (Estonian Radiation Protection Centre, 2005). In 2012-2014 the Estonian Health Board conducted a survey on South-Estonian groundwater. Measurement of radium isotopes in 230 samples (229 of which were from non-Cm-V aquifers) was ordered from the Nuclear Spectroscopy Laboratory in the Testing Centre of the University of Tartu (UT). ID was estimated according to ^{226}Ra and ^{228}Ra activity concentrations. A non-compliance with the parametric value of ID was found only in two mineral water samples originating from Cm-V and Ordovician-Cambrian aquifers (Estonian Health Board, 2014). However, the results of this survey tell little about the occurrence of other radionuclides, e.g. uranium, which has the opposite dissolution properties to radium (Clark and Fritz, 1997). Still, the sparse data that is available on ^{234}U , ^{235}U and ^{238}U activity concentrations (Kiisk *et al.*, 2011) suggests that these isotopes are not of interest from the viewpoint of radiation protection in Cm-V.

In 2008, Estonian Geological Survey published a report estimating the additional effective dose from ^{210}Po and ^{210}Pb in Cm-V groundwater (Savitskaja and Savva, 2008). ID values were calculated from the activity concentrations of ^{226}Ra , ^{228}Ra , ^{234}U , ^{238}U , ^{210}Po , and ^{210}Pb , assuming a yearly water consumption of 730 L and using dose contribution factors for the adult age group. The contribution of ^{210}Po and ^{210}Pb to ID ranged from 1.8–28.3%, the average value being *ca.* 10%. The authors suggested to continue monitoring ^{210}Po and ^{210}Pb concentrations, as the available data is not enough to make conclusions on the occurrence patterns of ^{210}Po and ^{210}Pb in Cm-V waters. Forte *et al.* (2010a) reached the same conclusion stating that the dose contribution from ^{210}Po and ^{210}Pb is not always negligible.

2. MATERIAL AND METHODS

2.1. The Area and Object of Study

Estonia's first water treatment facility designed for radionuclide removal and nine wells feeding it are situated in Viimsi, Estonia. Viimsi is a peninsula located approx. 15 km north-east from Tallinn, the capital of Estonia (Fig. 1). The surface of the peninsula consists of glacial and marine deposits from the Quaternary Period. The Cm-V aquifer system is the only significant source of drinking water on the peninsula. The water-bearing rocks in the aquifer system form a 70 m thick layer of silt- and sandstones. It is overlain by up to 40 m thick Cambrian clay layer (Lükati-Lontova regional aquitard; Fig. 1). Although a solid aquitard is lacking in the Cm-V aquifer system on the Viimsi peninsula, it is possible to distinguish two aquifers – the upper Voronka (V2vr) and the lower Gdov (V2gd). A siltstone layer forms a conditional aquitard (Kotlin aquitard) between the aquifers. The Voronka aquifer is located in the sandstones of the Lower-Cambrian (Lontova Formation) and Ediacaran time. The Gdov aquifer forms an intermediate layer consisting of sandstone and siltstone. The chemical composition of the deeper and upper parts of the aquifer system is fundamentally different. Groundwater in the Gdov aquifer is typically more saline than in the upper Voronka aquifer – 700 mg/L and 200 mg/L, respectively.

Viimsi is a popular residential area due to its vicinity to the capital city. During the last decades the population has tripled reaching 19 000 by 2017 (Statistics Estonia, 2017). This has created a growing demand for drinking water.

The water treatment plant, designed for iron, manganese, ammonia, and radium removal, was commissioned in February 2012. The plant is operated by Viimsi Water Ltd. and should be able to supply up to 15 000 consumers with drinking water. The maximum designed capacity of the plant is 6000 m³/day, but the average capacity stayed around 3000 m³/day in the study period (2012–2016).

The purification technology combines catalytic oxidation, co-precipitation, filtration and adsorption processes. The plant consists of five parallel treatment lines (Fig. 2). Each line comprises of units for oxidation, degassing and two-stage filtration (Fig. 3).

Water is first led through an aeration system, where it is enriched with oxygen and dissolved gasses are released. The aeration system consists of an air injector, an oxidation tank and a GDT separator (GDT – gas-degas technology). Thereafter the water is led through two gravitational filters.

The first filtration column contains gravel (h=150 mm), quartz sand (h=600 mm), and catalytic filter material FILTERSORB® FMH (h=1200 mm). The total weight of material in column 1 is 21.5 tons. Its main purpose is to remove iron, manganese, and ammonia, but it has also been proven to remove

radium. The removal mechanism is the following. Manganese and iron, naturally present in the groundwater, are oxidized to encourage radium adsorption and co-precipitation. MnO_2 coating the FILTERSORB® FMH grains acts as a catalyst for iron and manganese removal. The chemical reaction between metal ions (Fe^{2+} , Mn^{4+}) and MnO_2 takes place on the surface of MnO_2 (Burghardt and Kassahun 2005, Noubactep *et al.*, 2011) and the resulting precipitate is filtered out. Radium is adsorbed on the MnO_2 flakes formed in this process. Ra is also removed by iron hydroxide through co-precipitation or adsorption onto the surface of already formed iron hydroxide flakes.

The second filtration column is packed with gravel ($h=150$ mm), quartz sand ($h=400$ mm), and natural zeolite clinoptilolite ($h=1500$ mm) for the adsorption of excess ammonia and radium isotopes. Its total weight is 14.7 tons.

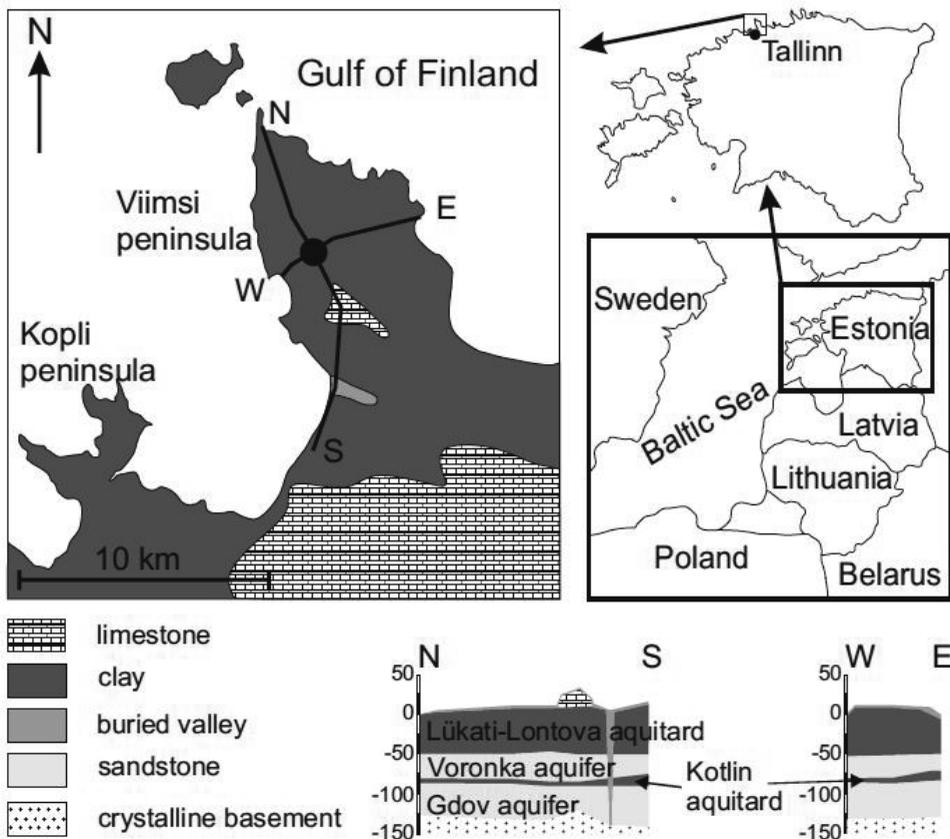


Fig. 1. Geological cross section of the Viimsi peninsula. The study area is marked by a black dot on the intersection of the cross-sections (Fig. 1 from IV).

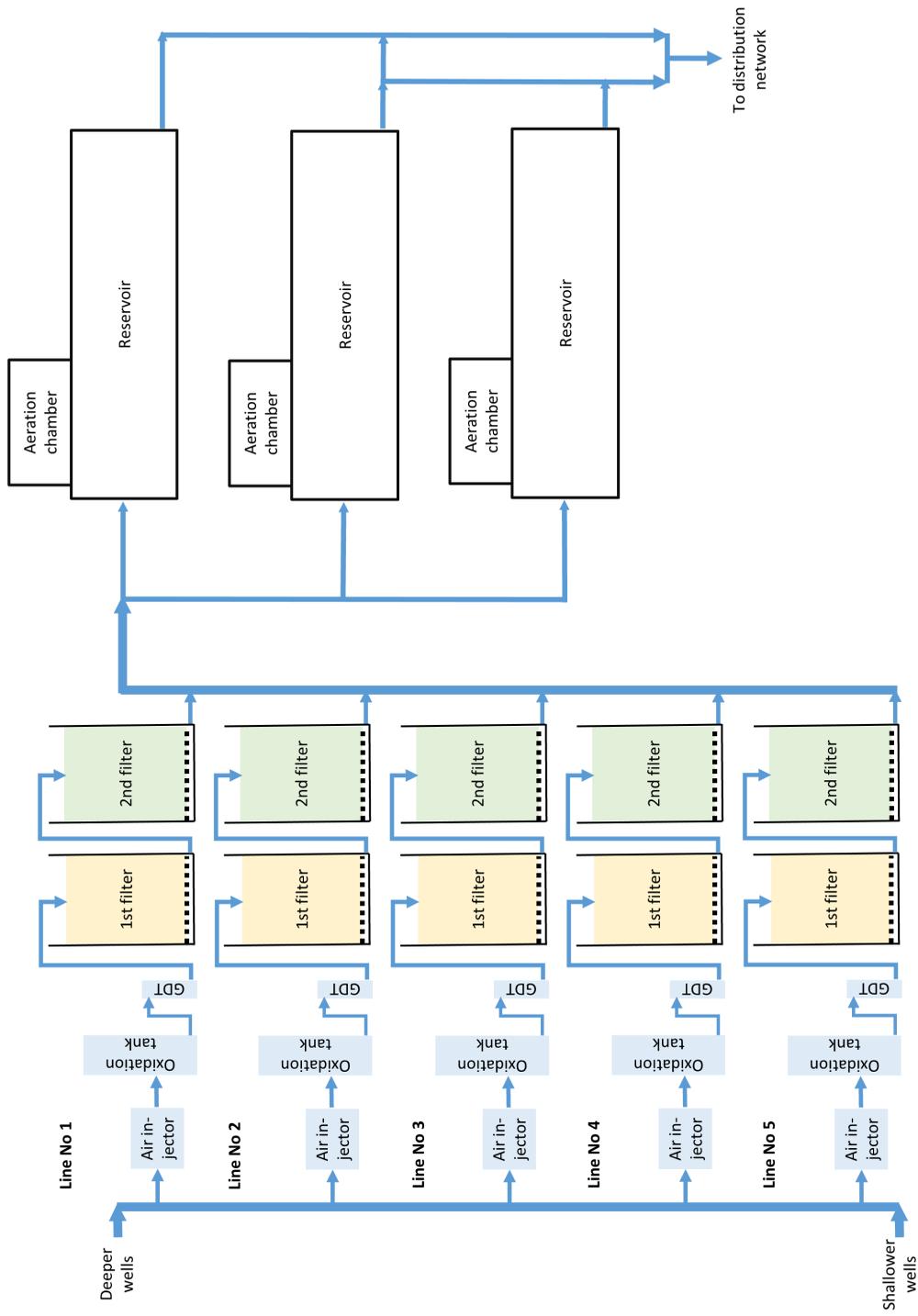


Fig. 2. Technological scheme of Viimsi Water Ltd. treatment plant (not in scale).

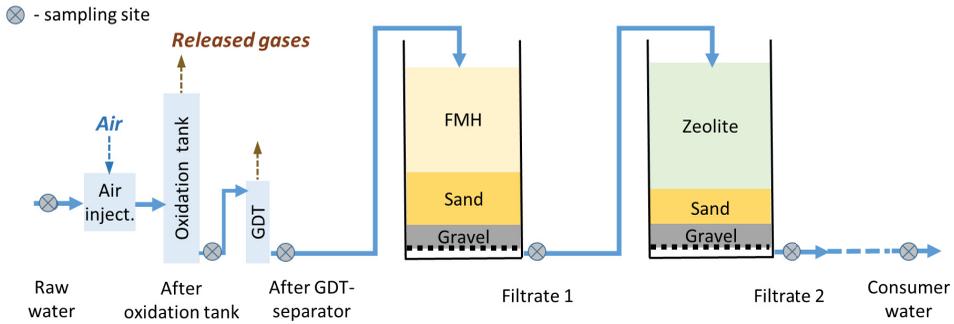


Fig 3. Technological scheme of a treatment line (not in scale) with sampling points for water.

Purified water is fed to consumers through three water reservoirs ($3 \times 2000 \text{ m}^3$). Therefore the consumer water is a mixture of water from different treatment lines.

The treatment lines were originally designed to obtain uniform raw water, but the monitoring results revealed that the groundwater from different wells does not mix in the inlet piping. Hence the quality of the incoming water was different for each treatment line. In November 2014, a raw water mixing system was added and all the lines started to get the same feed water. However, this brought about a contamination of iron bacteria which had so far been an issue only for the treatment lines getting water from shallower wells.

The filters are cleaned by an air-water backwash system. The backwash interval during the study period was 120 h for the first filtration stage and 336 h for the second stage. The amount of water used for each backwash was 35 m^3 for the first filter column, and 48 m^3 for the second. The backwash of the filter columns is an important maintenance procedure for the treatment technology. It enables the prevention of pressure loss caused by iron and manganese sludge which plugs the gravitational filter columns.

The water treatment plant is fed by nine wells located in a forested area in the plant's near vicinity. All of the wells get their water from the Cm-V aquifer system (Table 1). The wells are categorised into 5 groups according to their geographical setting. For the identification of wells Group No and Well No are used (Well No 1 denotes shallower boreholes and Well No 2 deeper ones). The wells were drilled in 2008–2009, but extensive groundwater uptake started in 2012 with the commissioning of the water treatment plant. All the nine wells are not used simultaneously. The combination of wells giving the feed water changes from one day to the next leading to fluctuations in incoming water quality.

Table 1. Wells feeding the water treatment plant.

<i>Well ID</i>	<i>Depth (m)</i>	<i>Sub-aquifer</i>	<i>Output capacity (m³/h)</i>
<i>Group 1 Well 1</i>	88.0	V2vr	30
<i>Group 1 Well 2</i>	124.5	V2gd	50
<i>Group 2 Well 2</i>	122.0	V2gd	50
<i>Group 3 Well 1</i>	82.0	V2vr	30
<i>Group 3 Well 2</i>	118.0	V2gd	50
<i>Group 4 Well 1</i>	85.0	V2vr	30
<i>Group 4 Well 2</i>	122.0	V2gd	50
<i>Group 5 Well 1</i>	90.0	V2vr	30
<i>Group 5 Well 2</i>	120.0	V2gd	50

2.2. Sampling

2.2.1. Paper I

For the applicability analysis of gross alpha and beta screening method a database of 44 groundwater samples from North and North-East Estonia was used. All the samples were analysed for ²²⁶Ra and ²²⁸Ra. In 30 samples, ⁴⁰K was also determined. The samples date back to 2008–2010.

2.2.2. Paper II

For the validation of the analytical procedure of ²²⁶Ra and ²²⁸Ra measurement by gamma spectrometry 90 litres of Cm-V groundwater was used. The water was taken into nine 10-litre canisters in May 2011.

2.2.3. Papers III, IV, and V

From 2012 to 2016 samples were taken regularly from the wells and from selected points in the water treatment plant to analyse a variety of radiological and chemical parameters.

A larger radiological inventory was carried out for selected wells in the beginning of the study in 2012 to make a well-informed decision on which radionuclides to include in the monitoring plan. Measurements of ²²⁶Ra, ²²⁸Ra, ²²⁸Th, and ²²²Rn were performed for all the wells. ²¹⁰Po and ²¹⁰Pb analyses were conducted for seven wells, U isotopes were measured in five wells. Some wells were not sampled for ²¹⁰Po, ²¹⁰Pb and U only because they were not in operation on the day of sampling. After obtaining the ²¹⁰Po, ²¹⁰Pb, and isotopic U results for the sampled wells it became evident that these radiological parameters are

not important from the perspective of radiation protection in both Voronka and Gdov aquifers. Therefore, the remaining wells (two shallow wells – Group 1 Well 1, Group 3 Well 1 – and two deep wells – Group 2 Well 2, Group 5 Well 2) were not further investigated.

In order to monitor the effect of extensive water uptake on the groundwater quality, all nine wells were analysed once a year for radium isotopes ^{226}Ra and ^{228}Ra and chemical parameters (Fe, Mn, Cl) during 2012–2015. Additionally, $\delta^{18}\text{O}$ was measured in six wells and $\delta^2\text{H}$ in four wells in 2012 and 2014. In 2015, all the wells were analysed for alkaline earth metals (Ba, Mg and Ca). The wells were sampled only in conditions when they were currently used for water uptake ensuring that the sample is representative of the groundwater. (IV)

The main aspects of the water treatment process – including the removal efficiency of radium, radon, iron and manganese; accumulation of radionuclides in the filtering media; and the backwash process – were observed through sampling water, filter materials and backwash water approximately every month (V).

In the beginning of plant operation, not all the treatment lines were constantly used. However, line no 5 was always in operation. Therefore it was chosen to be the main sampling site. The water samples were taken from raw water, after the first stage filter, after the second stage filter and from the consumer water (see Fig. 3). The following analytes were measured every month: ^{226}Ra , ^{228}Ra , ^{228}Th , dissolved oxygen, total iron, and manganese. Once every three months, the activity concentrations of ^{222}Rn were also observed. For the ^{222}Rn measurements, additional water samples were taken after the oxidation tank and GDT separator.

Filter material samples were taken from the surface layer of both filter columns in the fifth treatment line. Every month, two samples were taken from both filters – one before backwash and another one after it. The activity concentrations of ^{226}Ra , ^{228}Ra and ^{228}Th were determined.

Two backwash water samples were collected monthly from both filters – one at the beginning and one at the end of backwash. Due to limited measurement capacity, only ^{226}Ra was measured in the liquid phase of the backwash water. However, ^{226}Ra , ^{228}Ra , and ^{228}Th were analysed in the precipitate filtered out of the backwash water.

The need to sample other treatment lines besides line no 5 became evident by mid-2013 when the discrepancy between measured concentrations in filtrate 2 and consumer water revealed that the quality of incoming and output water differed for each line. Therefore all treatment lines were sampled for raw water, first stage filtrate, and second stage filtrate on October 30th 2013. ^{226}Ra activity concentration was analysed. The measurement was repeated on October 16th 2016, when all treatment lines were fed uniform quality incoming water. This time, ^{228}Ra activity concentration was also determined.

All the wells and sampling sites in the water treatment plant were equipped with taps, which simplified probing. Samples for radiological analysis, except for radon, were collected into five or ten litre plastic canisters. After sampling,

the water was acidified with concentrated HNO_3 to pH 1–2, with the exemption of backwash samples, which were first filtered and then acidified. For radon measurement, water was taken with a syringe and injected to a LSC-vial on site. For the analysis of Cl, Mn, total Fe, alkaline earth metals, dissolved oxygen, $\delta^{18}\text{O}$, and $\delta^2\text{H}$, water was first directed into a clean bucket and the samples were taken from the bucket to a plastic bottle. Filter material samples (a few hundred grams) were taken with a long handle scoop from the top layer of the filter column. The samples were put into plastic containers for transport to the laboratory.

Fig. 4 summarises the different sample types and analytes measured.

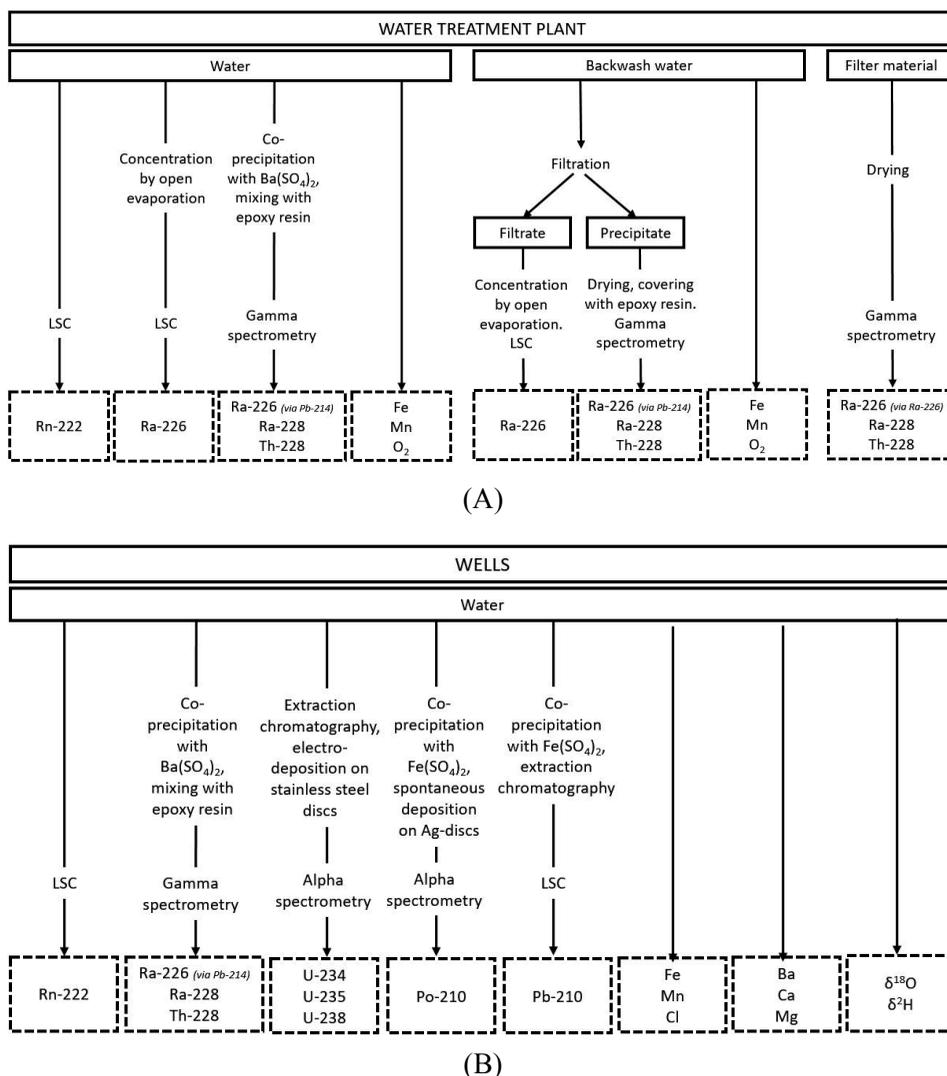


Fig. 4. An overview of sample types, measured analytes and analytical procedures from the treatment plant (A) and from the wells (B).

2.3. Analytical procedures

Different analytical procedures based on gamma spectrometry and liquid scintillation counting (LSC) were tested and validated to analyse radionuclides in water samples, filter material and backwash. The selection of measurement methods and sample preparation techniques was guided by instrumentation available in the laboratory of Environmental Physics, UT. At first, the equipment was limited to two high purity germanium (HPGe) gamma spectrometers (coaxial type Ortec detector GEM 35200 and planar BSI GPD 50400) and a one photomultiplier tube LSC device Triathler (Hidex). Later on, the instrumentation was enhanced by the addition of two gamma spectrometers (BEGe type Canberra BE3830P and coaxial BSI GCD 50200) and a two photomultiplier tube LSC device Quantulus (PerkinElmer). Opportunities for sample preparation were also significantly improved over the years.

2.3.1. ^{226}Ra measurements in water by LSC

LSC devices Triathler and Quantulus were used to measure ^{226}Ra in water samples (III, V). Measurements were performed in UT, Estonia.

Acidified water was concentrated up to six times using open evaporation on a hotplate. Ten mL of the sample was mixed with an equal amount of extractive scintillation cocktail Betaplate Scint (PerkinElmer). The samples were measured after a waiting time of at least three weeks which is necessary for the ingrowth of ^{222}Rn . Radium-226 activity concentration was determined through ^{222}Rn and its alpha decaying daughter nuclides ^{218}Po and ^{214}Po . A certified ^{226}Ra standard solution from the Czech Metrology Institute was used for calibrating the measurements. A vial of Betaplate Scint and deionized water acidified with HNO_3 was used as the background sample.

For paper III, the analysis were performed with Triathler. Samples were shaken 3 h before the measurement to enhance the transfer of gaseous radon to the cocktail phase. Measurement time ranged from a few hours to one day depending on the supposable activity of the sample. Typical minimum detectable activity concentration (MDA) ranged from 10 to 20 mBq/L.

The procedure was transferred to Quantulus after its purchase in 2013. Samples were measured in three cycles for 2 hours/cycle and not shaken prior the measurement (V). The activity concentration of ^{226}Ra was calculated as an average from the results of the three cycles. MDA of 40 mBq/L was achieved.

2.3.2. ^{226}Ra and ^{228}Ra measurements in water by gamma spectrometry

Gamma spectrometric measurements to determine ^{226}Ra and ^{228}Ra in water were performed in UT (I, II, III, IV, V). The following devices were used: coaxial type Ortec detector GEM 35200, coaxial BSI GCD 50200 or planar BSI GPD 50400.

Two different sample preparation procedures were applied. At first, sample preparation was based on evaporation. 3 litres of acidified water was evaporated to dryness. The residue was dissolved with ethanol (96% v/v), and transferred to the measurement beaker (aluminium alloy cans, diameter 61 mm, height 37 mm), where it was again evaporated to dryness under an infrared lamp. Typically, about 1–3 g of dry residue was left. Five gram of epoxy resin was added to the residue and stirred into a homogenous mass to achieve a comparable geometry for all the samples.

As there is no chemical separation, the procedure can also be used to determine other gamma emitting radionuclides in the sample, e.g. ^{40}K (according to its 1460.60 keV gamma peak, paper I) or ^{228}Th (detection via its progeny: the 240.99 keV peak of ^{224}Ra or the 238.63 keV peak of ^{212}Pb , papers IV and V).

From 2014 co-precipitation procedure became the dominant sample preparation technique. 2 litres of acidified water was taken for analysis. Ra was co-precipitated with $\text{Ba}(\text{SO}_4)_2$ by adding 8 mL of a barium carrier, 8 mL of a lead carrier, 16 mL of 9M sulfuric acid and 15 g of ammonium sulfate to the sample (details on the co-precipitation procedure can be found in IAEA, 2014). The barium carrier was a solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and HNO_3 in distilled water (barium concentration 0.22 M). The lead carrier was a solution of $\text{Pb}(\text{NO}_3)_2$ and HNO_3 in distilled water (lead concentration 0.22 M). The addition of the lead carrier brings about the precipitation of lead as PbSO_4 , with what thorium is co-precipitated (Cook and Kleinschidt, 2011). Therefore the presence or absence of Th in a sample can also be detected (papers IV and V), although the recovery rate for Th has not been determined. The precipitate was centrifuged, transferred to the aluminium measurement beaker, and dried under an infrared lamp. The procedure yielded about 0.5–1 g of fine-grained precipitate which was homogenised with 5 g of epoxy. A certified ^{226}Ra standard solution from the Czech Metrology Institute was used to determine the recovery rate of the procedure.

The samples, regardless of the preparation technique, were measured for about 24 h after a waiting time of at least three weeks.

Gamma spectrum analysis software GammaVision-32 (version 6.07, EG&G Ortec) was used for spectrum analysis. ^{226}Ra activity concentration was calculated according to ^{214}Pb peaks (242.00, 295.22, 351.93 keV). The calculation of ^{228}Ra activity concentration was done via ^{228}Ac peaks (338.32, 911.20, 968.97 keV).

Five gram of epoxy resin in an aluminium can was used as a background sample. Calibration samples were made of about 2 g of uranium or thorium-containing reference material (RGU-1 and RGTh-1 produced by the International Atomic Energy Agency (IAEA)) which were mixed with 5 g of epoxy resin in an aluminium can.

The MDA (calculated by GammaVision software according to the Traditional Ortec Method) of samples prepared with the evaporation procedure (3 L

of water) was 15 mBq/L for both Ra isotopes. In case of the co-precipitation procedure (2 L of water) the MDA of ^{226}Ra and ^{228}Ra was 20 mBq/L.

2.3.3. ^{222}Rn in water

Liquid scintillation counting with an extractive scintillation cocktail Betaplate Scint was used for the ^{222}Rn measurements (III, IV, V). To minimize losses of radon, the water was injected into LSC vials right on the sampling site. Ten mL of water was taken with a syringe and infused directly under 10 mL of Betaplate Scint in a 20 mL class vial which was then capped tightly. Radon-222 was determined according to the alpha decay of ^{222}Rn , ^{218}Po and ^{214}Po . A certified ^{226}Ra standard solution from the Czech Metrology Institute was used for calibration. The background was determined from a sample of deionized water and Betaplate Scint. Measurements were done with Triathler or Quantulus in UT. The typical MDA was about 150 mBq/L for both instruments.

2.3.4. ^{226}Ra , ^{228}Ra and ^{228}Th in filter material

Radionuclides in the filter material samples were analysed in UT using gamma spectrometry. Filter material was first dried and then put into a steal container (inner diameter 62 mm, height 19 mm). The container was sealed with a thin layer of plasticine covered with insulation tape. The samples were measured not sooner than three weeks after sealing. The measurements were performed with the following HPGe gamma spectrometers: coaxial Ortec GEM 35200, planar BSI GPD 50400 or BEGe type Canberra BE3830P. A measurement time of 0.5–1 h was usually enough to obtain sufficient counting statistics (statistical uncertainty around 5% or lower).

Certified reference materials RGU-1 and RGTh-1 (IAEA) were used for calibration. The calibration sources had the same geometry as the samples (cylindrical steel container). An empty steal container was measured for background.

Radium-226 was analysed according to its 186.21 keV gamma peak instead of doing the analysis according to ^{214}Pb . In case of the FILTERSORB® FMH samples (filter material from the first filter column), determination through ^{214}Pb would have led to an underestimation of the ^{226}Ra activity by 20% because of the partial loss of ^{222}Rn .

For the efficiency calibration the 186.21 keV peak of ^{226}Ra in RGU-1 spectrum was manually corrected to subtract the contribution from the ^{235}U 185.72 keV gamma rays. Additional correction of the 186.21 keV peak was not necessary in the samples, because uranium was not present in the raw water and no accumulation of uranium isotopes was observed in the filter materials.

Radium-228 calculations were performed the same way as for water samples (see chapter 3.3.2).

For ^{228}Th analysis, both the 238.63 keV peak of ^{212}Pb and the 240.99 keV peak of ^{224}Ra were used. The ^{224}Ra 240.99 keV peak has an emission probability of only 4.12(4) %, but was still applicable because of the high ^{228}Th activity concentrations in the filter material.

All the measured activity concentrations in the filter materials were orders of magnitude above the MDA values of ^{226}Ra , ^{228}Ra and ^{228}Th .

2.3.5. ^{226}Ra , ^{228}Ra and ^{228}Th in backwash samples

Backwash samples were analysed in UT. Five litres of backwash water was first filtered through Whatman Grade 1 qualitative filter paper to separate the undissolved sludge. Then, the filtrate was acidified with concentrated HNO_3 to pH 1–2.

A sample for gamma spectrometric analysis was prepared from the filter paper with the sludge. For that, the filter paper was put into an aluminium can, dried and then covered with a layer of epoxy resin. The determination of the activity concentration was done the same way as for the water samples (see chapter 3.3.2). Measurement time per sample was one day. The typical MDA values were in the range of 20 mBq/L for ^{226}Ra , and 50 mBq/L for ^{228}Ra and ^{228}Th .

The filtered backwash water was analysed for ^{226}Ra using LSC (see 3.3.1). Although the analytical procedure was the same, the MDA for backwash samples was higher (60 mBq/L), because the samples could not be concentrated as much as regular water samples.

2.3.6. Other radiological parameters

For the analysis of U isotopes, ^{210}Po , and ^{210}Pb in well waters, samples were taken to the laboratory of the German Federal Office for Radiation Protection (BfS), Berlin, Germany.

Water was sampled into 10 L plastic canisters and acidified with HNO_3 . Thereafter, an intensive air flow was created through the water in the canister with an aquarium pump for 1.5 h to allow emanation of dissolved radon. This is important because ^{222}Rn decays into ^{210}Po and ^{210}Pb and would therefore increase their concentrations. The emanation procedure was performed promptly after sampling. Then the samples were sent to BfS for analysis. The analytical procedures and limits of detection (LoD) are summarised in Table 2.

Table 2. Analytical procedures for isotopic U, ^{210}Po and ^{210}Pb measurements in BfS.

<i>Radio-nuclide</i>	<i>Principle of sample preparation</i>	<i>Measurement method</i>	<i>Recovery determination</i>	<i>Required sample volume</i>	<i>Limit of detection (Bq/L)</i>
^{210}Po	Co-precipitation with Fe-sulphate, spontaneous deposition on Ag-discs.	Alpha spectrometry (Ortec)	^{209}Po tracer	1 L	0.002
^{210}Pb	Co-precipitation with Fe-sulphate, extraction chromatography with Sr extraction column (Triskem). Pb eluate mixed with scintillation cocktail Ultima Gold AB (PerkinElmer) in a plastic vial.	LSC (Quantulus)	Spiking with stable lead, concentration measured with ICP-OES.	1 L	0.005
^{234}U ^{235}U ^{238}U	Extraction chromatography with UTEVA extraction column (Triskem), electrodeposition on stainless steel discs.	Alpha spectrometry (Ortec)	^{232}U tracer	300 mL	0.004-0.009

2.3.7. *In situ* gamma spectrometry

In order to investigate the accumulation profile of radionuclides in the filter columns of the Viimsi Water Ltd. treatment plant, *in situ* gamma spectrometry measurements were carried out on April 7th 2014. The height distribution of ^{226}Ra , ^{228}Ra and ^{228}Th in the filter columns of the fifth treatment line was determined.

The detector – coaxial Ortec Detective-DX with a 4 mm thick tungsten collimator, type DET-100-COL-W – was provided by the Radiation Safety Department, Estonian Environmental Board. Measurements were performed at different heights of the filter columns' outer walls in steps of 25 cm. The measurement time at each point ranged from 1 to 10 min depending on the activity of the layer. The following high intensity gamma peaks were used to determine the count rates of the three radionuclides of interest:

- ^{226}Ra – 609.31 keV peak of ^{214}Bi ;
- ^{228}Ra – 911.20 keV peak of ^{128}Ac ;
- ^{228}Th – 583.19 keV peak of ^{208}Tl .

2.3.8. Chemical parameters

2.3.8.1. Water samples taken from the treatment plant (V)

Dissolved oxygen was measured with an ion-selective electrode Marvet. A colorimeter MaxiDirect was used for determining total iron (1,10-Phenanthroline method, $\lambda=530$ nm, tolerance ± 0.05 mg/L Fe), and manganese (PAN method, $\lambda=560$ nm, tolerance ± 0.3 mg/L Mn). The measurements were performed *in situ* at the water treatment plant in Viimsi by its personnel.

2.3.8.2. Well waters (IV)

Cl, Mn, and total Fe analyses were conducted in an independent commercial laboratory in Tallinn, Estonia using the following measurement methods: Cl^- – titration (according to the standard ISO 9297), Fe_{total} – spectrophotometry (GOST 4011-4), Mn^{2+} – atomic absorption spectrometry (ISO 8288).

In addition to the measurements mentioned in paper IV all the wells were analysed for three alkaline earth metals (Ba, Mg and Ca) on the last year of the observation period (2015). The measurements were ordered from the Department of Geology, Tallinn University of Technology (TalTech). Barium, magnesium and calcium concentrations were analysed by a Dionex ICS-1000 ion chromatograph. For cation analyses, CS12A 4×250 mm analytical column and CG12A 4×50 mm guard column were used with 20mM methanesulfonic acid eluent at flow rate of 1 mL/min.

2.3.9. Analyses of oxygen and hydrogen isotope ratios (IV)

Stable isotope ratios of oxygen and hydrogen were measured in the Institute for Geological and Geochemical Research in Budapest, Hungary (7 samples) and in the Department of Geology, TalTech, Estonia (2 samples).

$\delta^2\text{H}$ and $\delta^{18}\text{O}$ were determined simultaneously and expressed in δ -notations (‰) relative to Vienna Standard Mean Ocean Water (VSMOW) standard.

The measurements in Hungary were performed using the liquid water isotope analyser manufactured by Los Gatos Research Ltd. (LWIA-24d). The reproducibility of the measurements was better than 1.0‰ for hydrogen and 0.15‰ for oxygen.

In TalTech, the measurements were done using the cavity ring-down laser spectroscopy (CRDS) Picarro L2120-i Isotopic Water Analyzer (Brand *et al.*, 2009). The reproducibility of stable isotope measurements was ± 0.1 ‰ for $\delta^{18}\text{O}$ and ± 1 ‰ for $\delta^2\text{H}$.

Previous inter-comparisons have shown that the results of the two laboratories are in good agreement, therefore the results were treated as one set in paper IV.

2.4. Indicative dose assessment

The indicative dose ID (mSv/yr) from radionuclides in water was assessed according to Equation 1 (I, IV, V).

$$ID = \sum A_i \cdot f_i \cdot V \quad (\text{Eq. 1})$$

A_i – the activity concentration of radionuclide i in water (mBq/L);

f_i – the effective dose coefficient (Sv/Bq) for an adult member of the public for ingestion of radionuclide i (values taken from ICRP, 2012);

V – yearly water consumption of 730 L (2 litres per day).

In situations where the activity concentration of a radionuclide was below the MDA, a “worst case scenario” of dose estimation was applied and the MDA value was used in the ID calculation.

The expanded uncertainty of the indicative dose ($U(ID)$, $k=2$) was estimated by Equation 2.

$$U(ID) = \sqrt{\sum (U(A_i) \cdot f_i \cdot V)^2} \quad (\text{Eq. 2})$$

$U(A_i)$ – the expanded uncertainty (at $k=2$ level, in mBq/L) of the activity concentration for radionuclide i .

2.5. Data analysis tools

MS Excel was used to generate the regression models in paper I and perform the statistical analysis of validation experiments in paper II.

Statistical computing software R, version 3.2.4, was used in paper IV to analyse correlations (Pearson correlation coefficients) between the activity concentrations of Ra isotopes, Cl, Mn and Fe concentrations, total well production (m^3), and annual production rate (m^3/yr) as well as compose linear regression models.

3. RESULTS AND DISCUSSION

3.1. Radionuclides of interest for radiation protection

Results of the radiological inventory of well waters are given in paper IV: Table 2 (^{222}Rn , ^{210}Po , ^{210}Pb , U isotopes) and Appendix A (^{226}Ra and ^{228}Ra). The activity concentrations of ^{210}Po , ^{210}Pb , and U isotopes were either below LoD or slightly above LoD. In the worst case, the additional indicative dose from ^{210}Po , ^{210}Pb and U would be 0.005 mS/yr, which is low enough to be considered nonsignificant from the viewpoint of radiation protection (III, IV).

Likewise, ^{228}Th activity concentrations proved to be insignificant in the investigated groundwater samples (IV), staying in the range of MDA (50 mBq/L). This is supported by the literature: Th concentrations in natural groundwaters are usually low (Jia *et al.*, 2009; Chau *et al.*, 2011; Lauria *et al.*, 2012) due to its low solubility and poor environmental mobility (Cook *et al.*, 2003). Nevertheless, ^{228}Th was measured in water samples from the water treatment plant, because ^{228}Ra accumulated in filter columns acts as a ^{228}Th generator (V). If thorium is not strongly bound to the filter material, some of it may leach into the water. Still, the measurement results demonstrated, that ^{228}Th activity concentrations were insignificant in water samples throughout the purification process (V). Therefore, ^{210}Po , ^{210}Pb , U, and ^{228}Th were not further investigated in water samples.

Radon-222 activity concentrations in well waters were detectible (Table 2 in IV) but stayed well below the parametric value for drinking water (100 Bq/L as laid down by the directive 2013/51/Euratom). All the results were below 20 Bq/L, hence ^{222}Rn was not of radiological significance in the well waters. Per contra, ^{222}Rn concentrations were routinely monitored in water samples throughout the treatment process (Fig. 6 in V), as ^{226}Ra accumulated in the filter columns generates additional ^{222}Rn , which may dissolve in water during the filtration process, consequently contaminating the water with radon.

Taking the abovementioned into consideration, the following radiological parameters were focused on:

- in groundwater samples, ^{226}Ra and ^{228}Ra activity concentrations were determined;
- in water samples from the purification plant, ^{226}Ra , ^{228}Ra , ^{222}Rn were monitored;
- the indicative dose was defined as the dose from ^{226}Ra and ^{228}Ra ingestion with water;
- in filter material, ^{226}Ra , ^{228}Ra , ^{228}Th were monitored;
- in backwash samples, ^{226}Ra was measured in the liquid phase and ^{226}Ra , ^{228}Ra , ^{228}Th were determined in the solid phase (precipitate from filtration).

3.2. The applicability of gross alpha and gross beta measurements for Cm-V groundwater

The aim of gross alpha and beta measurements is to be a tool for initial screening of water samples to determine whether the parametric value for ID is met or not (WHO, 2017; Council Directive 2013/51/Euratom). WHO proposes the screening levels of 0.5 Bq/L for alpha activity and 1.0 Bq/L for beta activity. The directive 2013/51/Euratom has set the levels to 0.1 Bq/L and 1.0 Bq/L for gross alpha and beta, respectively. An applicability analysis of gross alpha and beta measurements in case of the Cm-V groundwater was done in paper I.

One of the main reasons why gross alpha and beta measurements have been criticized is the inadequacy of these screening methods in case of water samples containing high amounts of natural radionuclides, especially the alpha emitter ^{226}Ra and the beta emitter ^{228}Ra . These radionuclides have high dose coefficients. If only ^{226}Ra was present in the water, its concentration of 0.5 Bq/L would give rise to an indicative dose of 0.10 mSv/yr. In case of ^{228}Ra the same indicative dose would be caused by a concentration of 0.2 Bq/L which is five times lower than the gross beta screening level.

The presence of potassium in the water may significantly interfere the interpretation of gross beta measurement results. In nature, stable potassium is always accompanied by its beta-decaying isotope potassium-40. The latter is not considered in indicative dose estimations, as ^{40}K does not accumulate in the body and its level maintains constant regardless of the intake (Argonne National Laboratory, 2007). WHO suggests to subtract the contribution of ^{40}K from the beta activity, but this needs a separate determination of total potassium (WHO 2004, 2017).

The directive 2013/51/Euratom gives EU member states the opportunity to set their own alternative screening levels for gross alpha and beta activity when compliance with the requirement of $\text{TID} = 0.10 \text{ mSv/yr}$ is demonstrated. An attempt to find suitable screening levels for Cm-V groundwater was made in paper I. Based on a regression model between ^{226}Ra and ^{228}Ra , the following conservative screening levels were derived: 0.065 Bq/L for gross alpha and 0.170 Bq/L for gross beta activity. These values are so low, that they are exceeded in nearly all Cm-V groundwater samples. In addition, the high variability of ^{40}K activity concentration in the water makes the gross beta measurement result uninterpretable without an additional potassium determination (I).

The possible occurrence of other uranium series radionuclides in Cm-V groundwater is briefly discussed in paper I. Subsequent research has indicated that the potential of ^{210}Po , ^{210}Pb , and U being present in detectable amounts is reasonably low (see chapter 4.1). In principle this simplifies the derivation of alternative screening values. Nevertheless, the conclusion of paper I still applies: gross alpha and beta measurements have a high potential of being misleading screening tools in case of water containing natural radionuclides

with high dose coefficients like ^{226}Ra and ^{228}Ra . It is cheaper and more efficient to turn to a nuclide specific analytical procedure without prior screening.

3.3. Validation of analytical procedures for radium measurement

As ^{226}Ra and ^{228}Ra were proven to be the most important radionuclides from the viewpoint of radiation protection, emphasis was given to find a robust and reliable analytical procedure for determining the activity concentration of radium isotopes in water.

The simplest procedure tested was ^{226}Ra measurement by LSC (see 3.3.1 for the description of the analytical procedure). The main arguments why this procedure was taken into consideration were its non-laborious sample preparation, small quantity of water needed (approx. 100 mL), and the simplicity of spectrum analysis. In principle, the measurements can be performed with a very simple and affordable LSC device like Triathler. The analyst needs only a basic training on sample preparation and spectrum analysis techniques. Therefore employing this procedure could be feasible for a water treatment company to do its own routine radium monitoring on site.

Unfortunately, validation of the ^{226}Ra LSC procedure with Triathler did not give promising results (III). Validation experiments revealed problems with the stability of measurement efficiency, which was either caused by instabilities of the samples or variations in measurement conditions. Unwanted changes in the sample are illustrated in Fig. 4 of paper III which compares the alpha spectra of two calibration samples measured at different times after sealing. One of the calibration samples was acidified with HNO_3 and concentrated six times, the other one was not acidified nor concentrated. In case of the concentrated sample the spectrum shifted notably towards lower energies with each re-measurement. This is caused by the quench effect – the interference of converting the decay energy to photons emitted from the sample vial (L'annunziata and Kessler, 2003). Two main mechanisms of quench are distinguished: chemical and colour quench (L'annunziata and Kessler, 2003). The former is produced by substances in the scintillation vial that absorb the decay energy before it produces light in a scintillation process. In case of the latter, the colour quench, scintillation photons are produced, but get absorbed in the scintillation vial before being detected by the photomultiplier tube. As can be assumed by the name of the effect, colour quench occurs when colour is visible in the sample. In the validation experiments described in paper III visual change in sample colour was not apparent. Therefore it can be concluded that quench is caused by the HNO_3 used for acidifying the sample to prevent precipitation of radium during sample concentration. The shift of spectrum did not occur in non-concentrated samples even after 205 days from sealing. Nevertheless, measuring the samples without any pre-treatment (no acidification nor concentration) is not a viable

option, because that would mean a MDA of 60 mBq/L for a 24 h measurement. This is not in line with the requirements of the directive 2013/51/Euratom, which sets 40 mBq/L as the minimum limit of detection for determining ^{226}Ra in drinking water. The required MDA can be achieved by concentrating the sample twice and measuring it for 3 hours. As most of the samples in paper III were concentrated more and measured for a longer time, the typical MDA ranged from 10 to 20 mBq/L.

The shift in peak location towards lower energy was not present either in real samples or in non-concentrated calibration samples after similar waiting periods (III). One of the reasons why pre-concentrated calibration samples and real samples differed so much might lie in shaking. Pre-concentrated calibration samples were shaken each time before the measurement and multiple measurements were performed. Real samples were shaken and measured only once. Shaking enhances significantly the contact between the cocktail phase and the water phase containing HNO_3 . Therefore, the cocktail phase of the calibration samples might be more damaged and consequently more quenched (III).

Shaking the sample before the measurement has a notable effect on radon transfer from the water phase to the cocktail phase (III). This is demonstrated by the fact that calibration sample measurements without shaking yielded systematically lower efficiencies than calibration samples which were shaken before the measurement (Fig. 5 in III). However, the standard deviations (stdev) of the efficiency values with and without shaking were comparable. Therefore, not shaking the samples does not introduce a larger measurement uncertainty. Further investigations on the effect of shaking done on Quantulus revealed that the standard deviation of the efficiency was lower in case of not shaking the sample. Thus, shaking was not applied for samples measured for paper V.

For the uncertainty estimation the following components were taken into account: the statistical uncertainty of counting the sample, the calibration source and the background, and the uncertainty of the activity of the calibration source. The uncertainty of sample mass was discarded as its contribution to the total uncertainty budget was negligible. The relative combined uncertainty of the ^{226}Ra activity concentrations was between 6–15%, $k = 2$, but the poor results of comparison measurements with gamma spectrometry (III) indicate this might be an underestimation.

The possible reasons why the ^{226}Ra analytical procedure with Triathler described in paper III did not give satisfactory results may be the following (III):

- aging of the samples,
- differences in the matrices of real samples and calibration samples,
- variations in measurement conditions – Triathler does not have a temperature control system and is therefore affected by fluctuations in room temperature. This might influence the solubility of radon in the cocktail phase.

The accuracy of the procedure is not sufficient enough for a quantitative analysis. The results can only be used for giving a rough estimation of the radium removal efficiency in a water treatment process (III).

Testing of the ^{226}Ra LSC procedure continued after purchasing Quantulus. This stationary device has an automatic temperature control, which minimises variations in measurement conditions. As mentioned above, the routine of shaking the samples before the measurement was discarded to reduce the effect of sample aging and quenching. The measurement regime was also altered: instead of one measurement of up to 24 hours, sample was measured in three cycles for 2 hours/cycle. A similar measurement arrangement would have not been possible with a Triathler, because it enables the measurement of only one sample at once and samples have to be changed manually. Measurement in cycles enabled to get a better estimate of the uncertainty of the determination process. When the standard deviation of the three measurements was higher than the combined uncertainty, the former was used as the estimation of the measurement uncertainty of the ^{226}Ra activity concentration.

To compensate for the differences in the matrices of real samples and calibration samples, real samples were spiked with a certified ^{226}Ra solution to determine the measurement efficiency. The stability of the efficiency in time was monitored using an X-type control chart. In each path of samples prepared, a spiked control sample of one of the samples was made to monitor the efficiency. By these means the temporal stability of efficiency was verified. The value of 255% (standard uncertainty 9%) was used in calculations.

The MDA of 40 mBq/L required by the directive 2013/51/Euratom was achieved with a sample concentration level of 2.5. Although Quantulus is a more powerful tool, its MDA for ^{226}Ra or ^{222}Rn does not differ much from Triathler because the alpha background of the two instruments does not vary significantly. The situation would be different for beta measurements, where the background count rate for Quantulus is considerably lower than for Triathler.

The combined uncertainty was estimated from the statistical uncertainty of the sample and background measurement, and the uncertainty of efficiency. Typical relative combined uncertainty of the measurement ranged from 15–30%, $k = 2$.

The abovementioned adjustments made the ^{226}Ra LSC procedure with Quantulus reliable and applicable for the purposes of paper V.

A more sophisticated LSC procedure, which enables simultaneous determination of ^{226}Ra and ^{228}Ra (IAEA, 2014) was also given careful consideration. Sample preparation of the analytical procedure described in the document IAEA/AQ/39 is based on chemical separation of radium by coprecipitation with barium sulphate. ^{210}Pb , which can cause interference in the beta-spectrum, is removed from the sample in order to increase the accuracy of ^{228}Ra measurement. This is achieved by adding a lead carrier and lowering the pH of the solution by acetic acid in which lead sulphate is soluble but barium(radium) sulphate is not. Then the barium sulphate precipitate is suspended in a solution of ethylenediaminetetraacetic acid (EDTA), which acts

as a complexing agent. The suspension is transferred to a HDPE vial and scintillation cocktail Optiphase Hisafe 3 (PerkinElmer) is added. The samples are measured right away on a LSC device for 1 h. ^{226}Ra is determined from the alpha spectrum and ^{228}Ra from the beta spectrum. This analytical procedure has also been discussed by Cook and Kleinschmidt (2011).

The procedure seemed promising because it enables to get the results with only two days instead of one month which is usual for analytical procedures where ^{226}Ra is determined indirectly from its progeny. The amount of water needed is only 0.5 L which would ease the transport of samples significantly. However, the validation experiments did not demonstrate the same performance characteristics as reported by Cook and Kleinschmidt (2011) and IAEA (2014). IAEA (2014) achieved an overall efficiency (sum of chemical recovery and detection efficiency) of 0.908 with a relative stdev of 6.6% for ^{226}Ra and 0.516 with a relative stdev of 18.9% for ^{228}Ra . Validation experiments in UT resulted the following overall efficiency values: for ^{226}Ra 0.659, relative stdev 10.0%; for ^{228}Ra 0.212, relative stdev 28.6%.

Due to lower overall efficiencies, the MDA of the validation experiments in UT differed from results reported by IAEA (2014). MDA values 0.02 Bq/L and 0.43 Bq/L were achieved for ^{226}Ra and ^{228}Ra respectively instead of 0.01 Bq/L and 0.06 Bq/L. The MDA for ^{226}Ra is in line with the requirements of the directive 2013/51/Euratom whereas the MDA for ^{228}Ra is insufficient. Due to the high dose coefficient of ^{228}Ra , its limit of detection is set at 0.02 Bq/L when the ID of a water source is screened for the first time (Council Directive 2013/51/Euratom). For routine ^{228}Ra measurements the limit of detection can be increased to 0.08 Bq/L when the expected effective dose caused by ^{228}Ra does not exceed 20% of the parametric value of ID (Council Directive 2013/51/Euratom).

Another problematic issue was the large combined uncertainty of the measurement results – UT validation experiments yielded an average relative combined uncertainty of 22%, $k = 2$ for ^{226}Ra and 38%, $k = 2$ for ^{228}Ra . An uncertainty that high would not enable to notice changes in radium content of a water source or determine purification efficiency of a water treatment technology. An example uncertainty calculation given by IAEA (2014) demonstrates a relative combined uncertainty of 13%, $k = 2$ for ^{226}Ra and 33%, $k = 2$ for ^{228}Ra .

The reason behind the poor performance characteristics might be the difficulty to prepare a homogenous sample. Cook and Kleinschmidt (2011) reported that a sample should be usable for counting within 24 h. This was not achieved in UT. Instability of the suspension in the LSC-vial was noticeable – often, precipitation started to occur within a few hours after sample preparation. Consequently, if a larger batch of samples is prepared at once, samples cannot be measured under the same conditions.

Another well-known measurement method that enables simultaneous measurement of ^{226}Ra and ^{228}Ra is gamma spectrometry. An in-house analytical procedure for determining ^{226}Ra via ^{214}Pb and ^{228}Ra via ^{228}Ac by gamma spectrometry was developed and validated in UT (II). A rather time consuming

sample preparation includes evaporation of 3 litres of water to dryness and mixing the residue with epoxy resin (see chapter 3.3.2 for more details). Epoxy, as many authors have demonstrated (Anagnostakis *et al*, 1996, Bollhöfer *et al*, 2011; Ryan *et al.*, 2008), reduces the exhalation rate of radon, which is critical when ^{226}Ra is determined via the daughter products of gaseous ^{222}Rn (^{214}Pb or ^{214}Bi). However, the repeatability study still revealed unexpected instabilities in the radon holding capacity of the epoxy resin (II). Repeatability was assessed by comparing standard deviation and pooled uncertainty of ^{226}Ra and ^{228}Ra measurement results in 17 samples. The pooled uncertainty (u_{pooled}) was calculated from samples' combined uncertainties according to Eq. (3):

$$u_{pooled} = \sqrt{\frac{\sum u_i^2}{n}} \quad (\text{Eq. 3})$$

n – the number of samples

u_i – the combined standard uncertainty of sample i .

Combined uncertainty, calculated automatically by GammaVision, takes into account the following uncertainty components: statistical uncertainty of sample counting, uncertainties of gamma-ray emission probabilities, uncertainty of calibration sample activity, and uncertainty of the efficiency calibration curve (calibration fit).

In the case of ^{226}Ra , the pooled uncertainty at $k = 1$ level is lower than the standard deviation (0.0074 Bq/L versus 0.0180 Bq/L, respectively), indicating that the combined uncertainty does not describe all the variability that might influence the sample. The same cannot be said for ^{228}Ra (pooled uncertainty 0.0120 Bq/L, $k = 1$; stdev 0.0099 Bq/L).

As the standard deviation was larger than the pooled uncertainty only in case of ^{226}Ra , the most probable explanation for the differences is leakage of radon from the sample container (II). There is also the possibility that radon did not leak out from the container, but was exhaled from the epoxy resin into the air layer. In this case, ^{222}Rn progeny were redistributed on the inner surface of the measurement beaker or on top of the epoxy resin which changes the geometry of the sample and therefore influences the detection efficiency (II).

The larger variations in activity concentration results of ^{226}Ra compared to ^{228}Ra suggests that Rn does not always escape at the same rate and the Rn holding capacity of the epoxy resin varies from sample to sample (II). A qualitative estimate to the additional uncertainty component caused by radon leakage was given by comparing the relative standard deviation and relative pooled uncertainty (Table 1 in II). The relative pooled uncertainty describes only 4.6% of the variances, while the relative standard deviation of ^{226}Ra activity concentration measurement was 11.0%. The additional uncertainty component not described by the uncertainty calculation was estimated to be 6.5%, $k = 1$ (II).

After the inclusion of the new uncertainty component the average relative combined uncertainty of a sample with an activity concentration of *ca.* 200 mBq/L for both Ra isotopes was assessed at 16%, $k = 2$ for ^{226}Ra and 13%, $k = 2$ for ^{228}Ra (Tabel 2 in II). The MDA of the procedure is approximately 15 mBq/L for both radium isotopes which is well in line with the directive 2013/51/Euratom. The analytical procedure was found to be fit for purpose and was accredited in 2011 according to the ISO 17025 standard by Estonian Accreditation Centre. Nevertheless, the labour intensity and time consumption of the sample preparation motivated to search for more efficient solutions.

A co-precipitation principle used in the analytical procedure for simultaneous determination of ^{226}Ra and ^{228}Ra by LSC (IAEA, 2014) was tested for preparing the samples for gamma spectrometry. Unlike in the procedure described by IAEA (2014), sample preparation was limited to co-precipitation of radium as Ba(Ra)-sulphate and did not include the chemically more advanced re-dissolving of the precipitate (see chapter 3.3.2 for details on sample preparation). This significantly shortened the sample preparation time compared to the evaporation technique.

As a part of the validation the repeatability study was repeated to investigate the emanation of radon from the samples. The comparison of pooled uncertainty and standard deviation of ^{226}Ra and ^{228}Ra measurement results revealed that $u_{pooled} \approx Stdev$ for both isotopes (Table 3). This indicates that radon losses are negligible, wherefore there is no need to use a separate uncertainty component to describe the variability of radon leakage. The difference in radon emanation from samples prepared by co-precipitation can be due to the different texture of the precipitate or smaller precipitate/epoxy ratio compared to the evaporation residue.

Table 3. The results of the repeatability study for co-precipitation technique – average activity concentrations, standard deviations and pooled uncertainties of ^{226}Ra and ^{228}Ra measurements.

<i>Repeatability of co-precipitation (8 samples)</i>	^{226}Ra (Bq/kg)	^{228}Ra (Bq/kg)
Average activity concentration	0.518	0.675
Stdev	0.015	0.028
Pooled u, $k = 1$	0.017	0.029

The recovery rate of the co-precipitation procedure was determined by spiking seven samples with a certified ^{226}Ra solution. These results were the basis of creating an X-chart for continuous the monitoring of the recovery rate (Fig. 5). The recovery rate has not fluctuated significantly being 0.96 as an average (stdev 0.023). In routine measurements a moving average of the last year's recovery rates is used.

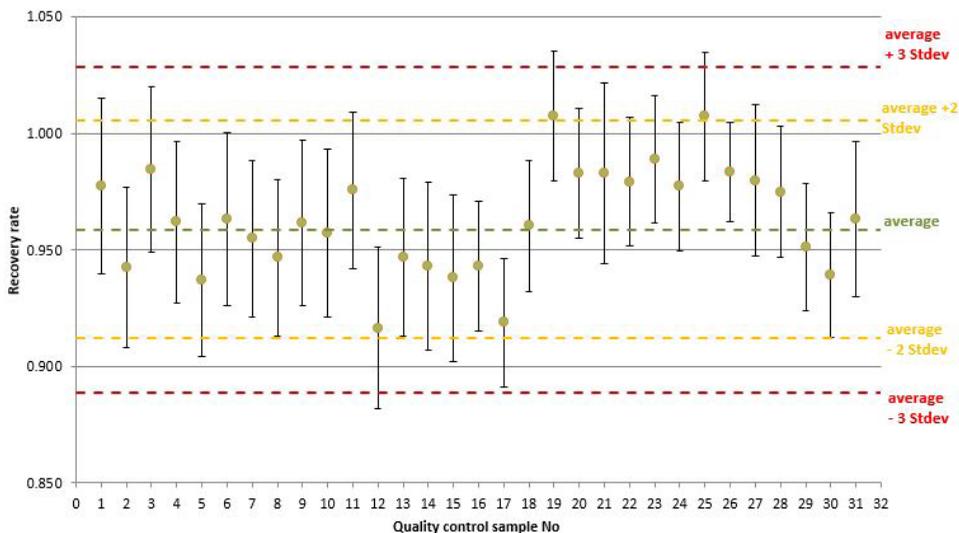


Fig. 5. X-chart for monitoring the recovery rate of the co-precipitation procedure (quality control samples from 2014-2019). The uncertainty bars represent combined uncertainty ($k = 2$).

The uncertainty budget was re-evaluated. In addition to the statistical uncertainty of sample counting, uncertainties of gamma-ray emission probabilities, uncertainty of calibration sample activity, and uncertainty of the efficiency calibration curve, the uncertainty of the recovery rate is taken into account. The standard deviation of the recovery (calculated from the X-chart data) is used as the estimate of its uncertainty. Typical relative combined uncertainties ($k = 2$) of ^{226}Ra and ^{228}Ra for a sample containing *ca.* 200 mBq/L of both isotopes would be 11% and 20%, respectively.

Sample preparation by co-precipitation gives a slightly higher MDA than the evaporation technique due to smaller sample volume – 20 mBq/L versus 15 mBq/L, respectively. However, MDA of 20 mBq/L is sufficient for ^{228}Ra and twice as low as required for ^{226}Ra (Council Directive 2013/51/Euratom). The procedure has been accredited according to the requirements of the ISO 17025 standard since 2014.

Table 4 gives an overview of the analytical procedures tested. For a better comparison of the different procedures, the relative combined uncertainty is given for a sample with ^{226}Ra and/or ^{228}Ra activity concentration of 200 mBq/L.

Due to the need to determine both radium isotopes for assessing ID, the gamma spectrometric measurement of samples prepared by co-precipitation became the standard analytical procedure. Sample preparation still takes about 2–3 days, but the recovery is easily traceable. As the number of gamma spectrometers in UT is limited, measurement of ^{226}Ra by Quantulus has been used as a substitute in cases when the relative change of radium content is observed and the trends of measured ^{226}Ra activity concentrations are able to predict the ^{228}Ra content.

Table 4. Comparison of the tested analytical procedures for radium measurement.

Analytical procedure	LSC ^{226}Ra Triathler	LSC ^{226}Ra Quantulus	LSC ^{226}Ra and ^{228}Ra Quantulus	^{226}Ra and ^{228}Ra evaporation, gamma spectrometry	^{226}Ra and ^{228}Ra co-precipitation, gamma spectrometry
Sample preparation	Non-laborious, fast	Non-laborious, fast	Requires advanced skills in chemistry, takes 1.5 days	Laborious, time consuming (4–5 days)	A little less time consuming (2–3 days)
Amount of water needed	Ca. 100 mL	Ca. 100 mL	0.5 L	3 L	2 L
Waiting time	At least 3 weeks	At least 3 weeks	-	At least 3 weeks	At least 3 weeks
Measurement time	Up to 24 h	3 x 2 h	1 h	Ca. 24 h	Ca. 24 h
MDA	2x conc., 3 h measurement → 40 mBq/L 6x conc., 24 h measurement → 10 mBq/L	2.5x conc. → 40 Bq/L 5x conc. → 20 mBq/L	^{226}Ra – 20 mBq/L ^{228}Ra – 430 mBq/L	^{226}Ra – 15 mBq/L ^{228}Ra – 15 mBq/L	^{226}Ra – 20 mBq/L ^{228}Ra – 20 mBq/L
Typical combined U_{reb} $k = 2$ **	10%*	20%	^{226}Ra – 22% ^{228}Ra – 38%	^{226}Ra – 16% ^{228}Ra – 13%	^{226}Ra – 11% ^{228}Ra – 20%
Conclusion of validation experiments	Failed validation	Fit for purpose	Failed validation	Fit for purpose	Fit for purpose

* Combined uncertainty underestimated.

** Relative uncertainty for a sample with activity concentration in a range of a few hundred mBq/L.

3.4. Radium removal and accumulation in Viimsi Water Ltd. treatment plant

From the point of view of a consumer, the most important feature to monitor in a water treatment facility is the quality of the output water. Yet, for the facility operator knowing the characteristics of the waste the technology produces is also important. Waste is not limited to the backwash water that is led to sewerage. Once the filter material has lost its properties of removing contaminants from the water, it too has to be handled as waste. If the exemption level for radionuclides in the filter material is exceeded, it has to be treated as NORM waste. This brings about several difficulties as at the time of writing this thesis Estonia did not have a clear strategy for NORM management (Vaasma *et al.*, 2019). Every water treatment facility is treated case by case creating costs and time expenditure which are hard to predict in advance.

Knowing the risks that may arise from water treatment (NORM production, elevated radon concentration in the treatment plant, etc.) is also important for justification of the activity – the risks arising from radionuclide removal must remain smaller than the risk caused by drinking untreated water. Ideally, justification should be done before the commissioning of a treatment facility, but this is hard to comprehend when a NORM management strategy is missing.

The processes observed in Viimsi treatment plant are an example of challenges what water purification with a filtration system may bring about and what details the technology operator needs to consider.

3.4.1. Purification efficiency of the treatment plant

During the observation period from May 2012 to June 2015, the activity concentration of radium isotopes in raw water of the 5th treatment line have ranged from 0.240 to 0.622 Bq/L for ^{226}Ra and from 0.356 to 0.842 Bq/L for ^{228}Ra depending on the combination of wells used (V). To achieve the 0.10 mSv/yr dose recommendation in purified water even in the worst situations, the plant needs a purification efficiency over 80%. Here, a $^{228}\text{Ra}/^{226}\text{Ra}$ ratio of 1.3 is assumed which was the average ratio of these isotopes in the raw water of the 5th treatment line during the period of observation.

Fig. 6 represents the radium purification efficiencies of the 5th treatment line from May 2012 to May 2015. ^{228}Ra activity concentrations have been used in purification efficiency calculations because it results in slightly smaller uncertainties.

Total purification efficiency describes the difference of the ^{228}Ra activity concentration in the purified water (2nd stage filtrate) and in the raw water:

$$Eff_{total} = \frac{\text{raw water} - \text{2nd stage}}{\text{raw water}} \quad (\text{Eq. 4})$$

Purification efficiency of the first stage filter is calculated from ^{228}Ra activity content in the 1st stage filtrate and in raw water:

$$Eff_{1st} = \frac{\text{raw water} - \text{1st stage}}{\text{raw water}} \quad (\text{Eq. 5})$$

Purification efficiency of the second stage filter is estimated by subtracting the efficiency of the 1st stage filter from the total purification efficiency:

$$Eff_{2nd} = Eff_{total} - Eff_{1st} \quad (\text{Eq. 6})$$

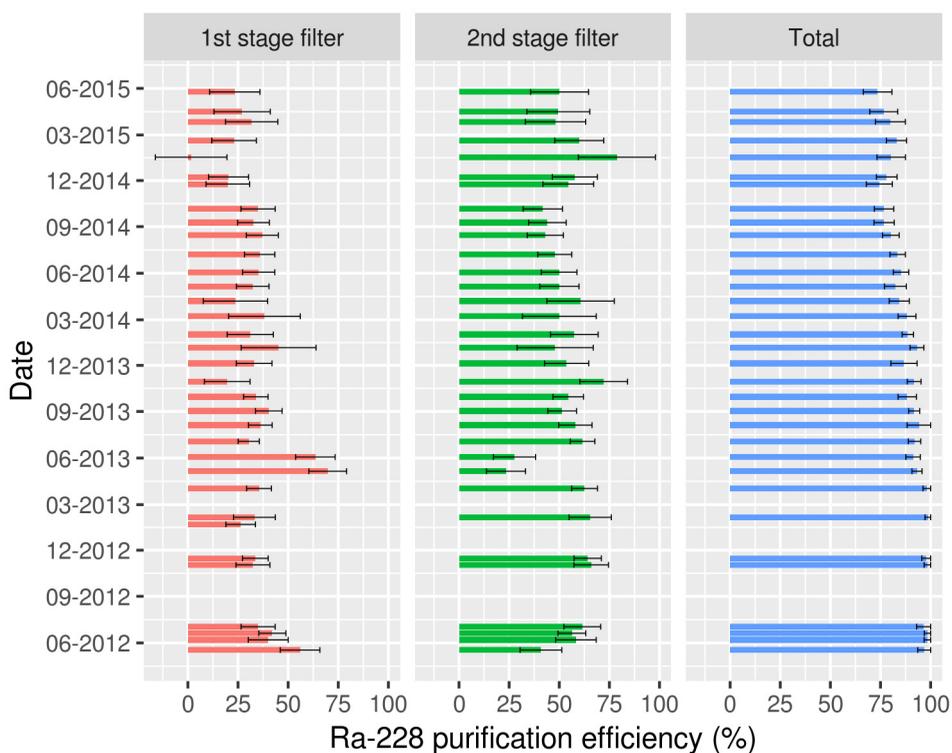


Fig. 6. Radium purification efficiency (calculated based on ^{228}Ra measurement results) in the 1st and 2nd filter column and in the 5th treatment line as total.

For the first year of plant operation (until May 2013), the total purification efficiency stayed close to 100% and the 2nd stage filter compensated for the fluctuations of the purification efficiency of the 1st filter. This is in line with the initial design of the treatment plant – the zeolite filter was planned as a polishing step of the treatment process. Changes in the raw water (in November 2014) led to lowering of the purification efficiency of the first stage filter. The

total purification efficiency has been gradually declining from nearly 100% to about 75%. However, as the consumer water is a mixture of purified water from different treatment lines, the requirement of 0.1 mSv/yr was not yet exceeded by May 2015.

Radon-222 activity concentrations in the well water proved to be insignificant from the perspective of radiation protection (see section 4.1). Nevertheless, ^{222}Rn was still monitored in the treatment process because ^{226}Ra accumulating in the filter columns generates additional ^{222}Rn , which may dissolve in water during filtration (V). This hypothesis was confirmed by the observations of the fifth treatment line (see Fig. 6 in V). A two- to threefold increase of ^{222}Rn activity concentrations with a growing trend in time was detected in the second stage filtrate. Radon-222 concentration dropped again in the consumer water because water from all five treatment lines mixes while passing through the reservoirs where radon is partly exhaled (see the scheme of the of the treatment plant in Fig. 2). Although radon contamination caused by the filtration process is an undeniable fact, ^{222}Rn activity concentrations in any step of the purification have not yet reached levels where it becomes a critical issue (V). All the measured ^{222}Rn activity concentrations stayed below the parametric value of 100 Bq/L suggested by WHO and EC (WHO, 2017; Council Directive 2013/51/Euratom).

In addition to being ^{222}Rn generators, the filter columns might be a source of thorium contamination because ^{228}Th is generated by the decay of ^{228}Ra accumulated in the filter material. Hence, at first, ^{228}Th was also monitored in the water samples but its concentrations proved to be insignificant (V). This can be explained by the low solubility of thorium in water (Cook *et al.*, 2003).

The discrepancy of radionuclides' concentrations in the second stage filtrate and consumer water led to the need to study purification efficiencies of each treatment line. The purification efficiency does not only change in time but it also varies for different treatment lines. It was first clearly demonstrated in October 2013 when raw water, filtrate 1 and filtrate 2 of all five treatment lines were sampled. ^{226}Ra activity concentration of the samples was analysed by LSC (Fig. 7). The treatment lines did not operate uniformly because of the different composition of raw water (V). The purification efficiency of the first stage filter is the highest in treatment line no 5 (45%) while it has hardly any effect in lines no 2 and no 4. At the same time, the purification efficiency of filter 2 is more comparable in different treatment lines.

Sampling of all treatment lines was repeated in October 2016 when both of the radium isotopes were determined (Fig. 8 (A) and (B)). By that time, the lines had been fed by uniform raw water for nearly two years. However this did not assure a uniform output. Unlike three years earlier the 1st stage filters operate more consistently with radium purification efficiencies ranging from 30% in line no 3 to 47% in line no 5. On the contrary, the performance of the second stage filter (zeolite) has started to vary more. Its purification efficiency has declined to only 10% in lines no 4 and 5, while being nearly 60% in line no 3.

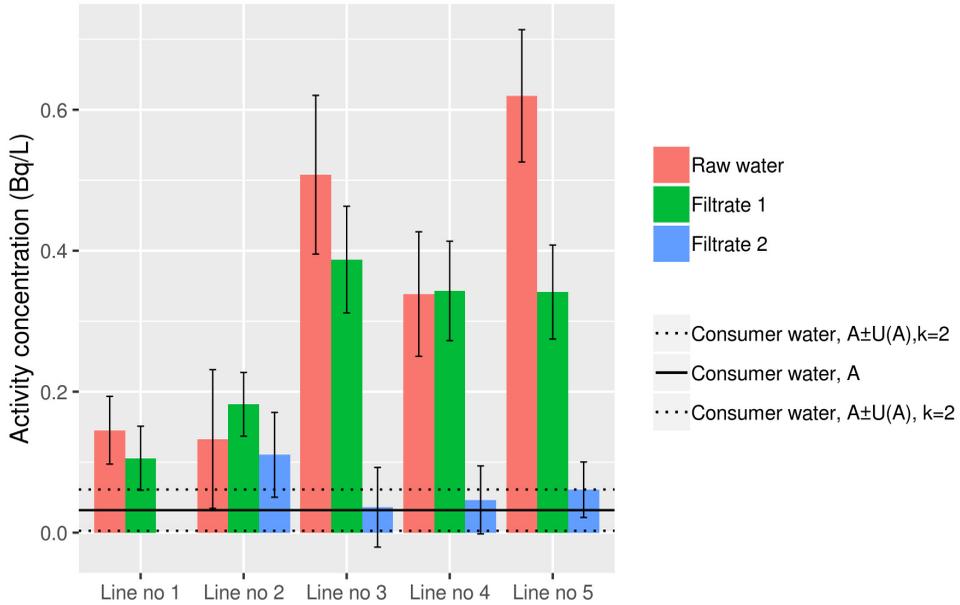
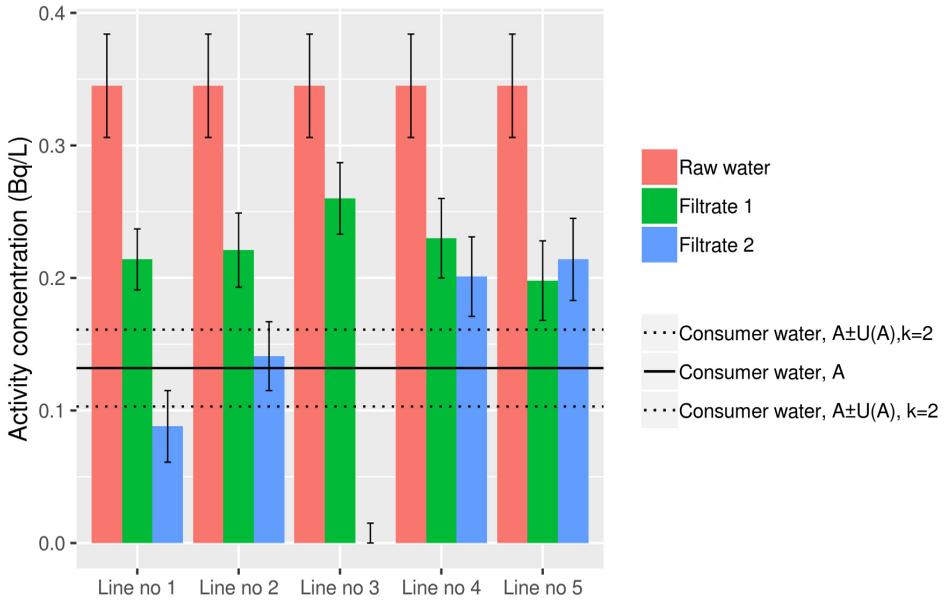


Fig. 7. ²²⁶Ra activity concentration with combined uncertainty ($k = 2$) in all treatment lines, sampled on October 30th 2013 (Fig. 5 from V). Continuous line represents ²²⁶Ra activity concentration in consumer water on the same date (dashed lines are the activity concentration \pm uncertainty, $k = 2$).

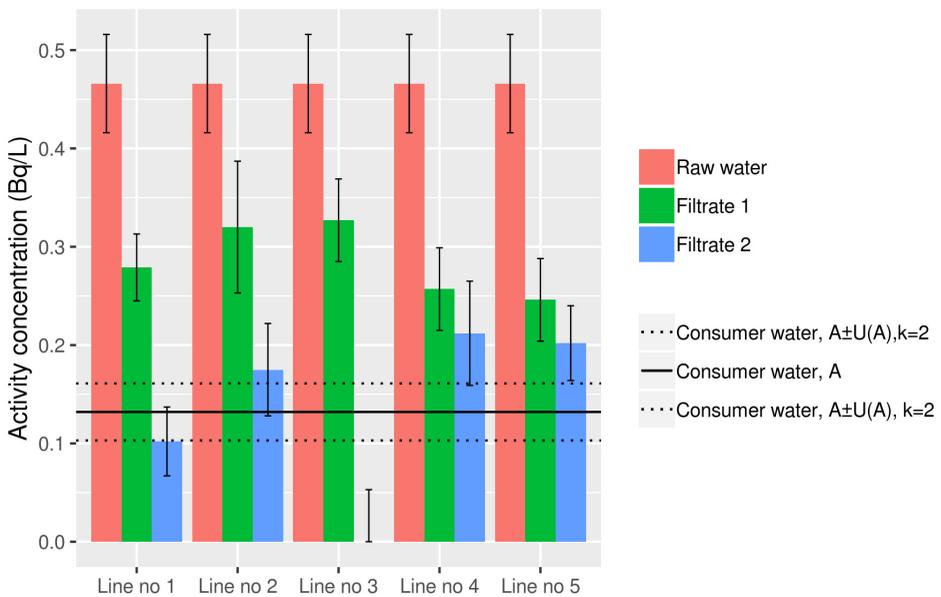
The steady increase of radium activity concentrations and the decline of purification efficiency indicates changes in the filtration system unseen in the planning phase of the technology (V).

The average iron removal rate was 80% (V). Iron concentrations in the output water were well below the parametric value of 200 $\mu\text{g/L}$ required by the Drinking Water Directive (Council Directive 98/83/EC). Usually, Fe concentrations between 20–50 $\mu\text{g/L}$ were achieved in treated water with a few exemptions caused by insufficient amount of air introduced to the treatment system (see Fig. 7 and 8 in V). Iron is oxidised by the oxygen in the injected air and removed by filtration in the first filter column. The second filter column has very little effect on Fe concentrations.

The removal rate for manganese was permanently high (approx. 90%) throughout the study period leaving the Mn concentration in treated water between 20–30 $\mu\text{g/L}$ (see Fig. 9 in V). The parametric value for Mn is 50 $\mu\text{g/L}$ (Council Directive 98/83/EC). Manganese is removed by oxidation and adsorption in filter 1, the role of the second filtration stage is insignificant (V). The oxygen in air alone is not sufficient for manganese oxidation. The catalytic filter material FILTERSORB® FMH is capable of aiding the oxidation process only in an excess of oxygen, which was not achieved in the treatment process (Fig. 8 in V). Therefore, oxidation is partial and contributes to 10% of manganese removal, while the rest of the manganese is removed by adsorption onto negatively charged MnO_2 in the first filter column (V). This influences negatively radium adsorption onto these same possible sites due to much higher concentration of manganese cations in water compared to radium cations (V).



(A)



(B)

Fig. 8. ²²⁶Ra (A) and ²²⁸Ra (B) activity concentration with combined uncertainty ($k = 2$) in all treatment lines, sampled on October 16th 2016. Continuous line represents activity concentration in consumer water on the same date (dashed lines are the activity concentration \pm uncertainty, $k = 2$).

3.4.2. Radionuclides' accumulation in filter columns

Both filters accumulate radium to an extent which exceeds clearance and exemption levels, and therefore need to be treated as NORM (V). The Basic Safety Standard directive sets 1000 Bq/kg as the exemption and clearance level for natural radionuclides from the ^{238}U and ^{232}Th series, when the daughter products of the decay chain are in secular equilibrium with the mother nuclide. However, if the chain is not in equilibrium with the parent radionuclide, higher values may be applied (Council Directive 2013/59/Euratom). At the time of conducting this study the following exemption levels were used in Estonia: ^{226}Ra – 10 000 Bq/kg, ^{228}Ra – 10 000 Bq/kg, ^{228}Th – 1000 Bq/kg (Regulation No 96 of the Estonian Government, 2016).

Radium accumulation was the fastest in the second stage filter material – zeolite. The exemption levels for ^{226}Ra and ^{228}Ra (10 000 Bq/kg) were exceeded in a sample taken from the top layer of the filter column already by the time of the first sampling in June 2012 (see Fig. 11 in V), when the plant had operated for less than half a year. In the first stage filter material, FILTERSORB® FMH, exemption levels were reached after two years of plant operation (Fig. 10 in V).

As a result of the radioactive decay of ^{228}Ra in the filter material, ^{228}Th is produced. It makes a significant contribution to the absolute activity of the filters. ^{228}Th activity concentration rose above its exemption level (1000 Bq/kg) with less than a year in zeolite and with 1.5 years in FILTERSORB® FMH.

It should be stressed that the filter material samples were taken from the top layer of the filter columns. This may not be representative for the entire filter material because a gravitational filtration system may easily lead to the formation of a height distribution of elements removed from water. Sampling with a sediment corer was tested but failed because of the dense packaging of material in the filter columns. Therefore *in situ* gamma spectrometry was used instead to determine the count rates of ^{226}Ra , ^{228}Ra , and ^{228}Th and assess the height distribution of these radionuclides in the filters (Fig. 16 and 17 in V). A clear height dependence was discovered in zeolite. For FILTERSORB® FMH, the backwash cycles mix the material more intensively resulting in a more homogenous distribution.

Knowing the height distribution of the radionuclides enables to estimate the average activity concentration of the filtering media. This becomes important when choosing waste management options for the filter material or assessing the annual accumulation rates of radionuclides. In paper V, the annual addition of ^{226}Ra and ^{228}Ra to the first stage filter was estimated to be 30 MBq and 40 MBq, respectively. For the second filter column, the accumulation rates are 50 MBq/yr for ^{226}Ra and 70 MBq/yr for ^{228}Ra (Table 2 in V).

Leier *et al.* (2018) have proven that NORM production cannot always be avoided by using a simpler water treatment technology not intended for radium removal. In the study by Leier *et al.* 18 water treatment plants in North-Estonia, fed by Cm-V groundwater, were sampled for filter material. Only six treatment plants in the selection implemented a radium removal system, but the

exemption level for ^{228}Th (1000 Bq/kg) was exceeded in 11 plants. ^{226}Ra and ^{228}Ra activity concentrations exceeded 1000 Bq/kg in 15 and 16 cases, respectively. In three treatment facilities the concentration of radium isotopes was above 10 000 Bq/kg (Leier *et al.*, 2018). Unintentional water purification from radium is a consequence of iron and manganese removal – radium is co-precipitated when iron and manganese are oxidised and the precipitate accumulates in filtration media. Poor awareness of water treatment facility operators on NORM-related issues may easily lead to uncontrolled disposal of NORM waste.

It is important to emphasise that exceeding exemption levels does not automatically indicate the need to change the filter material. The purification efficiency for iron, manganese and radium is not greatly influenced by the amount of radionuclides that has accumulated in the filtering media. If feasible options for NORM management would be available and radiation protection needs are taken into account in the water treatment facility, the filter material can still be used for drinking water production. (V)

3.4.3. Filter backwash

The backwash process proved to be rather inefficient in reducing the activity concentrations of the filter materials. No correlation can be seen between the activity concentration of radionuclides in the filter material and in the backwash samples (V). This applies for both FILTERSORB® FMH and zeolite, and can be explained by the fact that the amounts of radionuclides released by the backwash water are negligible compared to the activity that accumulates in the filters. Only about 6% of the incoming radium (activity of radium isotopes in raw water) was removed from the first filter column by backwash (see Table 2 in V). The effect was even lower for the zeolite filter, where less than 1% of the incoming radium was released by backwash (V).

In case of FILTERSORB® FMH the activity concentrations in filter material samples taken after the backwash were sometimes higher than in samples taken before the backwash (Fig. 10 in V). This can be explained by the formation of sludge containing insoluble Fe-compounds (and, in a smaller amount, MnO_2) with co-precipitated or adsorbed Ra. Most likely some of the sludge is trapped between and on the FILTERSORB® FMH grains. The backwash is not able to completely remove it from the filter. Instead, pieces of sludge are moved around with the movement of water and air and some of this material ends up in the top layer of the column (V).

Analyses of the backwash samples showed that the majority of radium removed from the filter columns was attached to an undissolved phase, the backwash sludge (Fig. 9). The amount of radium that dissolved in the backwash water was modest and did not change much in time. The major factor causing lower ^{226}Ra concentrations in backwash samples taken at the end of the process was the smaller amount of undissolved matter per sample. (V)

A sudden drop in the sludge-bound ^{226}Ra activity concentrations was detected in samples taken at the beginning of the backwash cycle from the first filter column in the end of 2014 (Fig. 9(A)). This could be explained by changes in raw water quality accompanied by the intrusion of iron bacteria. In November 2014, the raw water mixing system was added and treatment line no 5 started to get incoming water with a lower radium content. Radium gets into the sludge when it is co-precipitated by iron hydroxide or adsorbed onto iron hydroxide flakes. The sludge consists mostly of iron hydroxide but may also contain manganese in a form of a dioxide, which is formed in a catalytic reaction in the presence of FILTERSORB® FMH. Adsorption to manganese dioxide is another mechanism how radium is incorporated into the sludge. After the iron bacteria contamination, a portion of iron and manganese was oxidised by the bacteria, and became bound to the bacterial slime. Slime-bound iron hydroxide and manganese dioxide are less efficient in removing radium from the water phase (V). This caused a decrease of the purification efficiency in filter 1 (Fig. 6). The bacterial slime is not easily removed from the filter by the backwash, as illustrated by the sharp decline of Fe content in the backwash samples of the first stage filter in the end of 2014 (see Fig. 13(A) in V).

Manganese concentrations in the backwash samples of the first filter column were significantly lower than Fe concentrations. This is due to the different removal mechanisms of Fe and Mn: iron is mostly oxidised and filtered, while manganese is mostly adsorbed onto FILTERSORB® FMH because the concentration of dissolved oxygen in the treatment process was too low to allow complete oxidation of Mn (see Fig. 8 in V). In case of complete oxidation, Mn should be released from the surface of FILTERSORB® FMH grains and filtered out of the column as a solid MnO_2 precipitate. In treatment line no 5, 90% of the manganese removed from the water remained in the filter, while only 10% was washed out.

Although the amount of radionuclides removed from the filter columns is rather irrelevant compared to the amounts that accumulate in the filter media, there is still notable difference in the activity concentrations of backwash samples taken at the beginning and at the end of the backwash cycle from the first filter (Fig. 9 (A) and (B)). Therefore, the backwash process is more or less optimised in terms of radionuclide washout. A longer or more frequent backwash process would not significantly improve radium removal, and would just increase waste water (V). In principle, radium washout may increase when the oxygen dissolution rate is increased in the aeration step of the treatment process. During most of the operation period, the concentration of dissolved oxygen in water was lower than the theoretical concentration needed for complete oxidation of Fe and Mn (Fig. 8 in V). When the amount of dissolved oxygen is high enough to achieve complete oxidation, more radium cations are able to co-precipitate with and adsorb to Fe hydroxides and MnO_2 . The sludge that forms as a result of complete oxidation is not attached to the filter material grains and should be removable by an optimised water backwash. However, the radium that is adsorbed to the filter material grains would still not be washed

out because backwash with purified water is not able to desorb cations from FILTERSORB®FMH.

The activity concentration of ^{226}Ra and the amount of sludge were much lower in backwash samples of the second filter (Fig. 9 (C) and (D)). The removal of significant amounts of radium from zeolite by water backwash can be considered unlikely as radium is adsorbed onto zeolite's surface. Backwash mainly works as mechanical removal of undissolved media plugging the filters. Chemical treatment would be needed to remove radium from zeolite. Increasing the oxygen dissolution rate in the aeration step would influence positively the performance of the zeolite filter. Complete oxidation of Mn and Fe would enhance the radium purification efficiency of the first filter column leaving less radium into the water to be removed by the second filter.

In principle, radium and other contaminants can be desorbed from the surface of FILTERSORB®FMH and zeolite grains with chemical agents. Regeneration of these filter materials by potassium permanganate and potassium chloride has been tested on a lab scale by Goi *et al.* (2017). FILTERSORB®FMH regeneration by KMnO_4 , which was preceded and followed by water backwash, resulted in 63% radium removal (Goi *et al.*, 2017). For zeolite, a 34% radium removal was accomplished with the following experimental setup: water backwash, followed by KCl regeneration, followed by water backwash (Goi *et al.*, 2017). The functionality of the filter materials was not affected by regeneration. However, the feasibility of regeneration on an industrial scale is questionable due to the big amount of filter material and the large volume of liquid waste that would be produced.

On the basis of activity concentrations measured in backwash samples an average amount of radionuclides released by each backwash cycle from treatment line no 5 can be estimated. Fig. 10 illustrates the different influence the backwash has on sludge and radionuclide release from the two filter columns. It should be kept in mind that the backwash of the first filter is nearly three times as frequent as the backwash of the second filter (every 5 days versus every 14 days, respectively). Hence, the contribution of radionuclides released from the first filter is even higher in the total waste flow. Approximately nine times more radium isotopes are washed out from the FILTERSORB®FMH filter than from the zeolite filter.

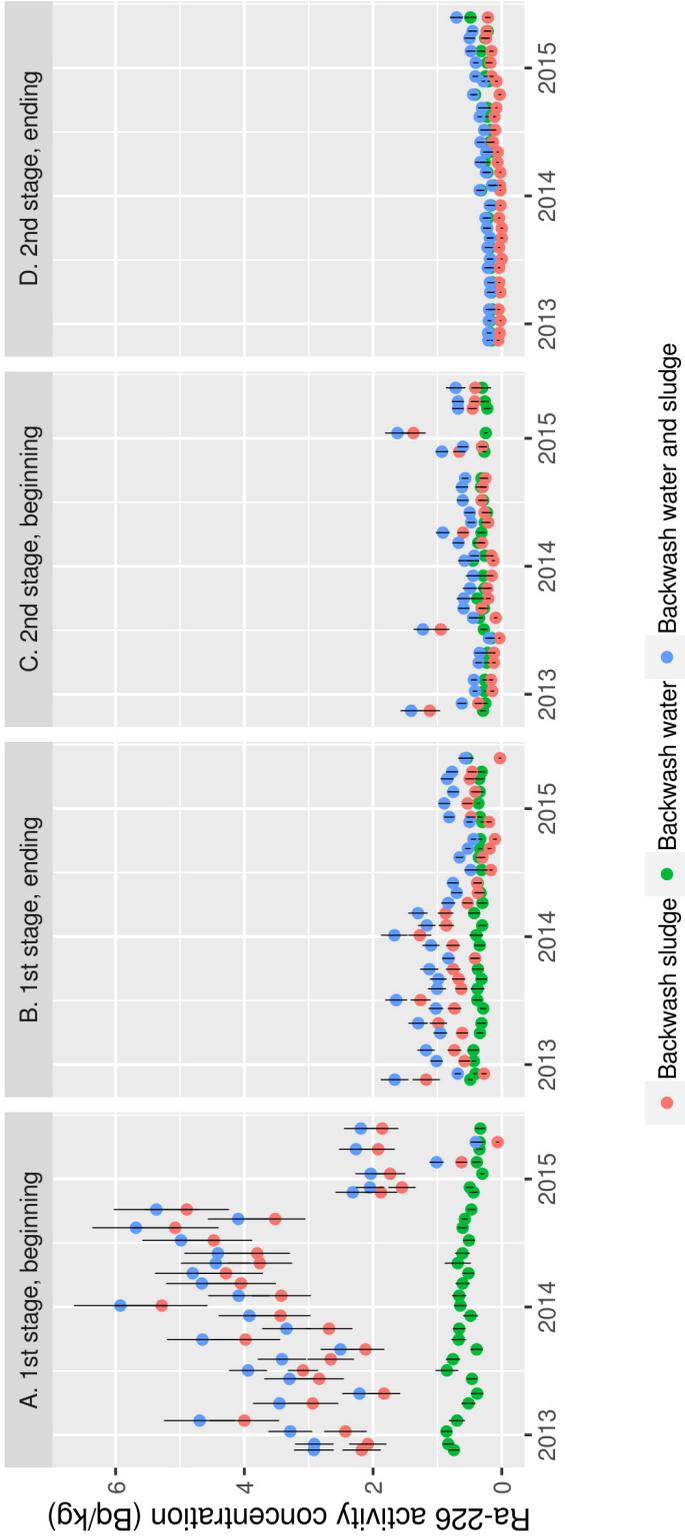


Fig. 9. ^{226}Ra activity concentrations in backwash samples of the first (A, B) and second filter column (C, D) (Fig. 12 from V)

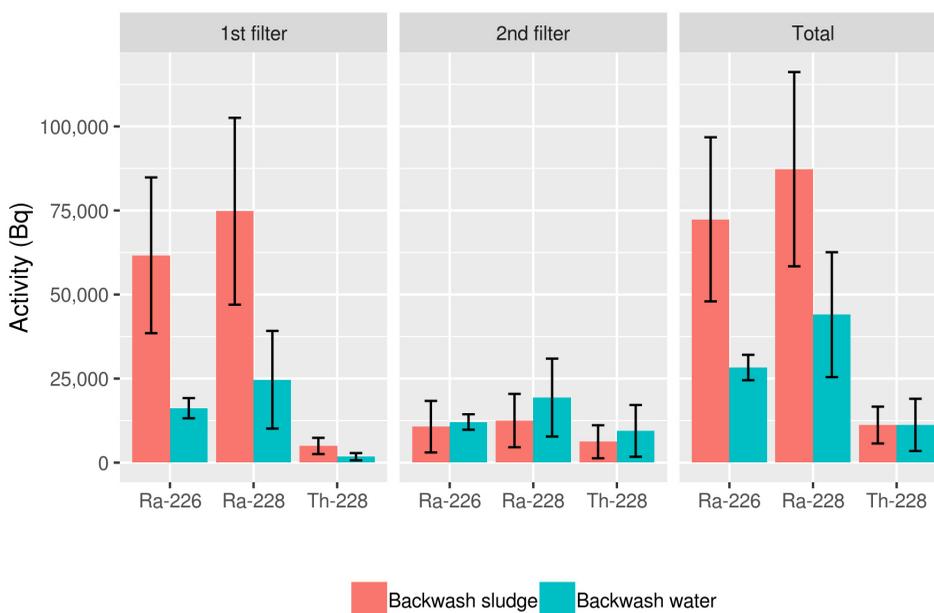


Fig. 10. Absolute activities of ²²⁶Ra, ²²⁸Ra and ²²⁸Th washed out from treatment line no 5 by one backwash cycle (calculated based on average values throughout the observation period 2012–2015).

3.5. Influence of the intensive water uptake on groundwater quality

The choice of a water treatment technology should be guided by the properties of the feed water. Hence, the possible changes in the quality of the feed water should be acknowledged in order to guarantee a consistent quality of treated water.

Wells feeding the Viimsi Water Ltd. treatment plant were monitored for four years (V). The activity concentration of radium isotopes rose steadily in the deeper wells, which open to the Gdov aquifer (see Fig. 2 (A) and (B) in IV). The same trend appeared in case of chloride (Fig. 4 (A) in IV) with the fastest increase in wells which were used more intensively. For manganese, a minor growing tendency in the deeper wells was observed, while Mn concentrations in the shallower wells stayed stable (Fig. 4 (C) in IV). Fe concentrations had larger fluctuations, but the changes were not dependent on the aquifer (Fig. 4 (B) in IV). The concentrations of all the measured parameters were lower in wells opening to the Voronka aquifer. The only well with a different pattern was Group 5 Well 1, which is a few meters deeper than the rest of the wells fed by the Voronka aquifer (Table 1). It can be assumed from the documentation of the borehole that the aquitard between the Voronka and Gdov aquifers was pierced when the well was drilled and it opens in a range of 1.5 m to the deeper aquifer. The proportion of water from the Gdov aquifer has increased in time in the production of Group 5 Well 1. This has caused rising trends in Ra, Cl, Fe, and Mn concentrations.

The fact that water of Group 5 Well 1 is a mixture of water from two aquifers is supported by measurement results of alkaline earth metals. Scatter plots of radium isotopes and alkaline earth metals (Mg, Ca, Ba) with fitted regression lines are presented in Fig. 11. Deeper and shallower wells form two clearly distinguishable sets with Group 5 Well 1 in between. Consequently, Group 5 Well 1 was discarded from further data analysis.

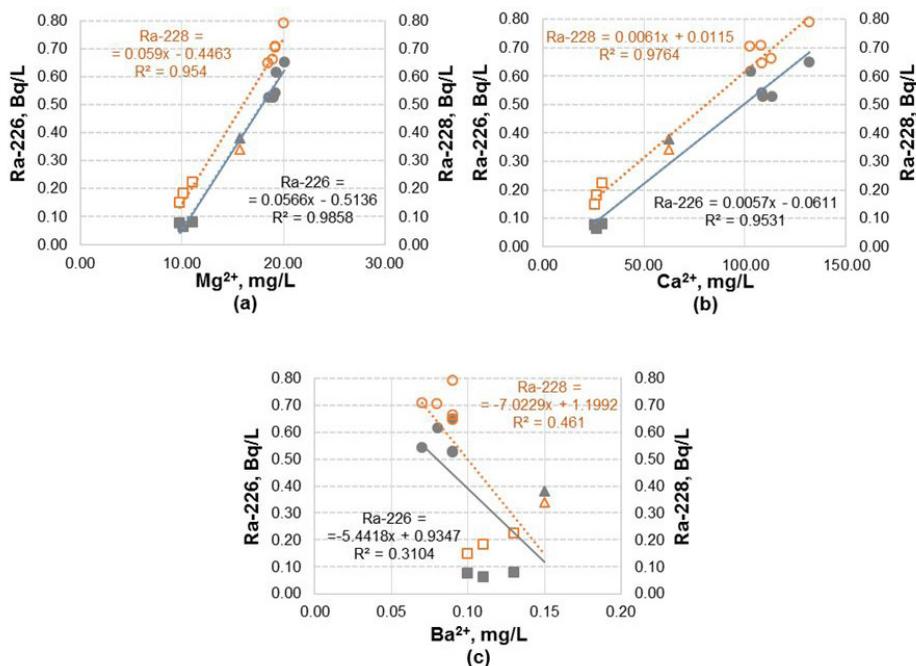


Fig. 11. Scatter plots of ^{226}Ra and ^{228}Ra activity concentrations and Mg (A); Ca (B); Ba (C) with fitted regression lines. Filled symbols correspond to ^{226}Ra activity concentrations:

■ – shallow wells (Voronka); ▲ – Group 5 Well 1; ● – deep wells (Gdov).

Hollow symbols denote ^{228}Ra activity concentrations:

□ – shallow wells (Voronka); Δ – Group 5 Well 1; ○ – deep wells (Gdov).

Correlations between radium isotopes, Mn, Fe, Cl, and well production were studied separately for wells fed by Voronka and Gdov, because treating the data as one set led to artificially well-suited regressions (IV).

Figures 12 and 13 present the Pearson correlation coefficients, linear regression models (blue line), best fit models (best suited polynomial, red line), and probability distribution histograms of the measured values and well production for the deep (Gdov) and shallow wells (Voronka, excluding Group 5 Well 1), respectively.

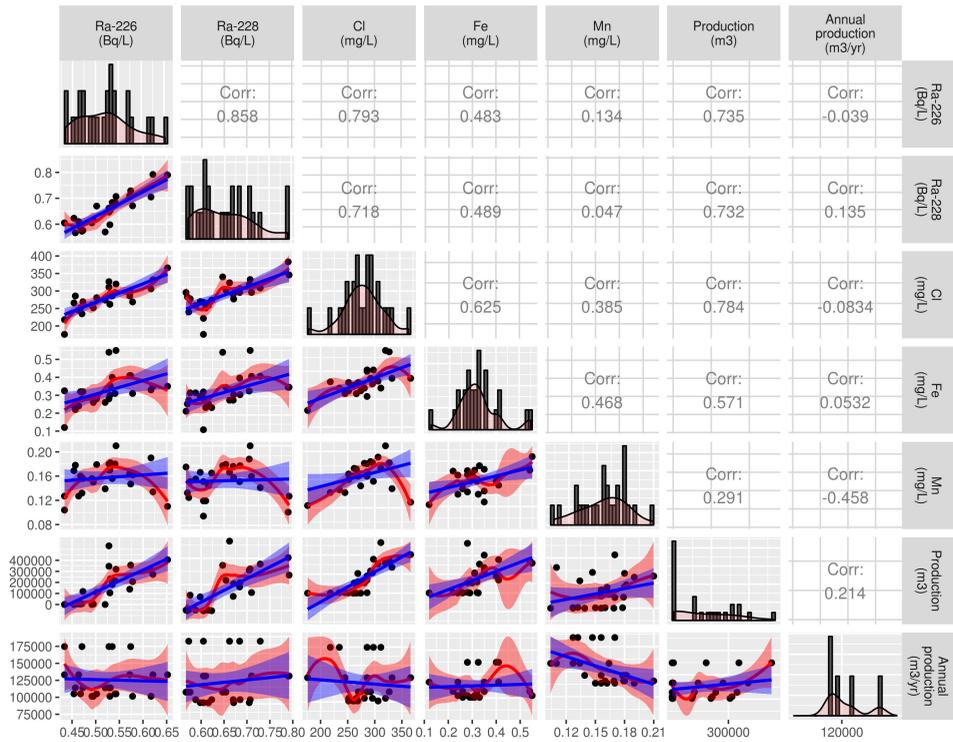


Fig. 12. Correlation matrix, deep wells (Gdov) only.

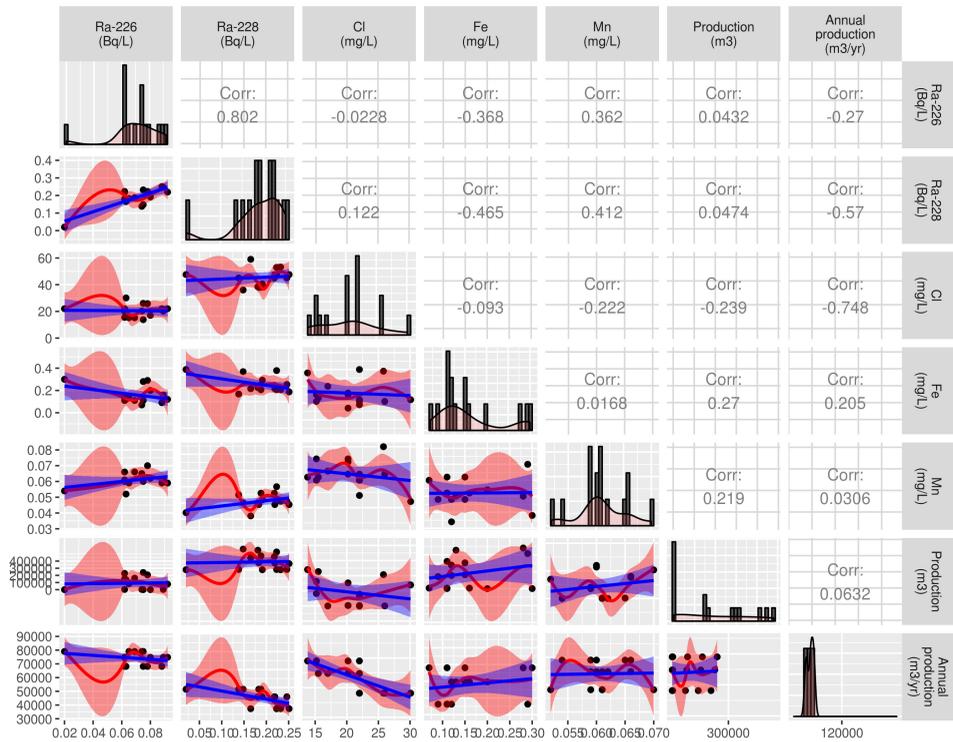


Fig. 13. Correlation matrix, shallow wells (Voronka, without Group 5 Well 1) only.

Ra and Cl have a strong correlation in Gdov groundwater while the elements do not correlate in Voronka groundwater. Instead a weak positive correlation between Ra and Mn and a weak negative correlation between Ra and Fe appear in shallower wells.

There is hardly any correlation between the annual production rate and Ra or Cl concentrations in the deep wells, but the total production seems to influence the Ra and Cl content of the water. In case of the shallower wells, neither annual production rate nor total production of the well have a significant influence on the chemical or radiological parameters.

Due to the strong correlation of Ra and Cl in Gdov groundwater, Cl can be used as a marker to predict changes in radium concentrations. Chloride measurements are much faster and cheaper than radium measurements. Additionally, Cl has to be monitored more frequently (four times a year in case of the wells feeding the Viimsi Water Ltd. treatment facility).

The monitoring frequency of radionuclides is not that clearly stated in international guidelines and legislative acts. The Guidelines for Drinking-Water Quality (WHO, 2017) suggests the following principles:

“/.../ if sources of potential radionuclide contamination exist nearby or are expected to be changing rapidly with time, then the sampling should be more frequent. /.../ A graded approach to sampling frequency should be developed commensurate with the degree of contamination, the source of supply (i.e. surface water or groundwater), the size of the population served, the expected variability of radionuclide concentrations and the availability and results of historical monitoring records.”

In the third edition of the Guidelines for Drinking-Water Quality (WHO, 2004, 2008) an indicative time period was also given:

“Once measurements indicate the normal range of the supply, then the sampling frequency can be reduced to, for example, every 5 years. However, if sources of potential radionuclide contamination exist nearby (e.g., mining activity or nuclear reactors), then sampling should be more frequent. Less significant surface and underground drinking-water sources may be sampled less frequently.”

The directive 2013/51/Euratom sets the minimum sampling and analysis frequencies for drinking water monitoring from distribution networks based on the volume of water produced daily. However, the directive gives the member states the opportunity to decide their own monitoring frequency based on previous results on the stability of radionuclide activity concentrations. The requirement has been transposed to Estonian legislation by the Regulation No 82 of the Minister of Social Affairs, which obliges the water facility operators to monitor the indicative dose from drinking water every ten years (Minister of Social Affairs, 2019).

Regression models predicting Ra activity concentrations in deep wells based on total well production (Table 8 in IV) estimate a significant growth in Ra concentrations indicating the need for a more frequent ID monitoring. The wells were not utilised at their maximum allowed output capacity. If the production of the wells were increased to the maximum capacity the changes in radium content would be several times higher (Table 9 in IV) and annual monitoring of ID would be adequate.

A similar growth was predicted for chloride (Table 9 in IV). The parametric value for Cl is set at 250 mg/L (Council Directive 98/83/EC; Minister of Social Affairs, 2019). Its concentrations were above 250 mg/L in most deep wells already in the beginning of the study (Fig. 4 (A) in IV). An increase in Ra and Cl concentrations in Gdov groundwater may create a need to adjust the existing water treatment technology to still be able to meet the requirements for drinking water. The water treatment facility in Viimsi does not have a system for chloride removal; Cl concentration is reduced only through mixing the water from different wells. The facility operator should pay attention on which wells are working simultaneously to get an appropriate dilution, or consider additional treatment for Cl removal (IV). A rise in the radium content will increase the absolute activity accumulating in the filter materials. This requires the facility operator to pay more attention to NORM related issues, e.g. generation of ^{228}Th and ^{222}Rn in the filtering media, and NORM waste management.

Understanding the causes of the growth of salinity and Ra content in the Gdov groundwater is a key question for sustainable groundwater management. Oxygen and hydrogen isotope ratios were used to trace the changes in the groundwater system (IV). Comparison of the isotopic ratios of the wells (Table 6 in IV) alongside with the changes in Ra and Cl concentrations led to the following hypotheses (IV):

- a) Cl concentrations may rise because of sea water intrusion as a result of water uptake from the Gdov aquifer;
- b) two compensation mechanisms may exist simultaneously – Cl concentrations may increase because of the penetration of highly saline water from the crystalline basement rock; at the same time, inflow of meteoric water through ancient buried valleys in the southern part of the peninsula causes the $\delta^{18}\text{O}$ values to be higher.

The increase of Ra activity concentrations may arise from the inflow of water from the crystalline basement. This water has a higher content of radionuclides (Savitskaja and Viigand, 1994) because of the contact with the crystalline basement rich in thorium and uranium (Petersell *et al.*, 1991; Raudsep, 1997). However, the increase in the radium content in the Gdov aquifer could not be caused by migration of Ra into the system but by changes in geochemical conditions that may lead to desorption of Ra from sediment surface. The increase in Cl concentrations in the Gdov aquifer has brought about a rise in Ca concentrations (Savitskaja and Viigand, 1994; Raidla *et al.*, 2012) which in turn could cause desorption of Ra (IV).

5. CONCLUSIONS

The results of this thesis support the conclusions of earlier research (Estonian Radiation Protection Centre, 2005) that the most important dose contributors in Cm-V groundwater are ^{226}Ra and ^{228}Ra . Gross alpha and beta screening methods suggested by WHO and EC are not suited for this kind of water (I). It is practical to skip the screening step and start with a nuclide specific measurement instead. The most suitable measurement method turned out to be gamma spectrometry, as it enables the determination of both radium isotopes in one sample. The MDA values of the gamma spectrometric analytical procedures, which were validated as a part of this thesis, meet the requirements set by the directive 2013/51/Euratom. Validation provided a precise overview of all the uncertainty components (II). Implementation of the gamma spectrometric analytical procedure for determination of radium isotopes has filled a gap in the provision of radiological measurements in Estonia and created a possibility to do accredited measurements.

NORM generation is difficult to avoid when Cm-V groundwater is used for drinking water production (V). Monitoring of the Viimsi Water Ltd. water treatment technology revealed serious NORM accumulation in the filter materials (V). In addition to radium isotopes, which are the only radionuclides of concern in groundwater, ^{222}Rn and ^{228}Th become of interest in the water treatment facility (V). Gaseous ^{222}Rn is generated by the decay of ^{226}Ra in the filter columns. Radon dissolves partly back to water (V). The decay of ^{228}Ra in the filter columns produces ^{228}Th . As the exemption level for ^{228}Th is an order of magnitude lower than the levels for ^{226}Ra and ^{228}Ra , it often becomes the first criteria why the filter media needs to be treated as NORM (V).

Radium remains in the filters not because of an inefficient backwash but because of adsorption onto the filter material (V). A more efficient aeration which would allow more oxygen to dissolve in the water and enable complete oxidation of Fe and Mn may reduce the accumulation of radium in the filter columns. More Ra would be co-precipitated with Fe and adsorbed on the Fe-hydroxide and MnO_2 flakes formed in the oxidation process.

As for now, the water treatment facility has been able to provide water compliant with the requirements set for drinking water. Yet the intensive use of groundwater may bring about changes in the quality of the incoming water.

Radionuclide activity concentrations in groundwater are often considered rather stable, minimum monitoring frequency of the total indicative dose from drinking water is set at once every ten years in local legislation (Minister of Social Affairs, 2019). The present study demonstrates that this is not sufficient for ensuring stable drinking water quality in case of aquifer systems as sensitive as the Cm-V aquifer system (IV).

Analysis of radionuclides is often time consuming and rather expensive. Therefore, a stable marker element can be searched for which would indicate the changes in radionuclides. This can act as a tool of early notification to detect

changes in radiological parameters of the water. In the case of studied wells fed by Gdov aquifer, the stable marker element is Cl (IV). Changes in Cl and Ra concentrations are critical parameters to monitor for sustainable management of the Cm-V groundwater (IV). Possible explanations for the increase of salinity are intrusion of sea water into the Gdov aquifer as a consequence of increased consumption or simultaneous existence of two compensation mechanisms – inflow of highly saline water from the crystalline basement accompanied by inflow of meteoric water. Increase of Ra in the Gdov aquifer may either be caused by migration of Ra into the system or by changes in geochemical conditions that may lead to desorption of Ra from sediment surface.

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SUMMARY IN ESTONIAN

Looduslik radioaktiivsus Kambrium-Vendi põhjavees – mõõtemetoodikad, veetötlustehnoloogia seire ja veekasutusega kaasnevad muutused põhjavee kvaliteedis

Kambrium-Vendi (Cm-V) põhjaveekiht on üks peamisi joogiveeallikaid Põhja-Eestis. See asub kõrge uraani- ja tooriumisisaldusega kristalse aluskorra peal ja on Eesti aladel kõige sügavam põhjaveekiht, mis sobib joogivee tootmiseks. Cm-V põhjavesi on saastunud looduslikult esinevate radioaktiivsete elementidega. 2009. a hinnangute põhjal tarbib seetõttu ligi 18% Eesti elanikkonnast (230 000 inimest) joogivett, mille radioloogilised näitajad ületavad Eesti ja Euroopa Liidu seadusandluses kehtestatud viitetaset.

2000-ndate keskpaigas, kui nõuded joogivee radioloogiliste näitajate kohta Eesti seadusandlusesse üle võeti, oli Eestis vähe võimalusi radioloogiliste parameetrite määramiseks veeproovides. Lünga täitmiseks arendati ja valideeriti käesoleva doktoritöö raames meetodikaid raadiumi isotoopide aktiivsuskontsentratsioonide määramiseks. Kuna kõrge indikatiivdoosi põhjustajateks Cm-V põhjavees on raadium-226 ja raadium-228, ei osutunud sobilikuks Maailma Tervise Organisatsiooni ja Euroopa Komisjoni soovitatud summaarse alfa- ja beetakiirguse mõõtmisel põhinev skriiningmetoodika. Selle asemel tuleb keskenduda raadiumi isotoopide määramisele nukliidspetsiifiliste mõõtemetoodikatega. Kõige sobivamaks osutus gammaspetsimeetiline analüüs, mis võimaldab samaaegselt määrata kahe raadiumi isotoobi aktiivsuskontsentratsiooni. Meetodika akrediteerimine tekitab võimaluse teostada akrediteeritud mõõtmisi Eestis kohapeal ja pakkuda veetötlusettevõtetele usaldusväärset analüüsiteenust.

Seadusandluse nõuded on survestanud veekäitlejaid otsima võimalusi joogivee radionukliididest puhastamiseks. Esimesena Eestis avas sellelaadse veetötlusjaama AS Viimsi Vesi veebruaris 2012. Veetötlustehnoloogiat jälgiti kolme aasta vältel. Seiretulemused näitavad selgelt, et Cm-V põhjavee kasutamise puhul on väga keeruline vältida NORM-jäätmete teket (NORM – *Naturally Occurring Radioactive Material*, looduslik radioaktiivne materjal), kuna radionukliidid akumuleeruvad vee puhastamisel kasutatavatesse filtermaterjalidesse. Kuigi põhjavee puhul on ainsad kiirguskaitse seisukohast muret tekitavad isotoobid ^{226}Ra ja ^{228}Ra , tuleb vee töötlemise protsessis tähelepanu pöörata ka radionukliididele radoon-222 ja toorium-228, mis tekivad filtermaterjalides ^{226}Ra ja ^{228}Ra radioaktiivse lagunemise tulemusena. Kuna ^{228}Th väljaarvamistase on suurusjärgu võrra madalam kui raadiumi isotoopidel, on tihti just ^{228}Th sisaldus kriitiline näitaja, mis dikteerib vajaduse käidelda veetötlusjaama filtermaterjali NORM-jäätmena.

Viimsis kasutatav tehnoloogia on tänaseni suutnud tagada joogivee kvaliteedinõuetele vastava vee, kuid intensiivne põhjavee kasutus võib kutsuda esile muutusi sisendvee kvaliteedis. Võtmenäitajateks Cm-V põhjavee kvaliteedi

jälgimisel osutusid kloriidid ja raadiumi isotoobid. Intensiivse veevõtu tulemusel võib põhjavee kloriidisisaldus muutuda kas (a) merevee sissetungi tagajärjel või (b) kristalses aluskorras sisalduva kõrge soolsuse ja radionukliidisisaldusega vee sissetungi tõttu, millega kaasneb tänapäevase meteoorse vee sissetung läbi mattunud uhtorgude. Raadiumisisalduse kasvu taga võib olla kas raadiumirikka vee sissetung või muutused põhjaveekihi geokeemilistes tingimustes, mis põhjustavad raadiumi lahustumist setete pinnalt põhjavette. Doktoritöö tulemused näitavad, et sotsiaalministri määrusega „Joogivee kvaliteedi- ja kontrollinõuded ning analüüsimeetodid“ kehtestatud seiresagedus radioloogilistele näitajatele – kord kümne aasta jooksul – ei ole piisav, et tagada stabiilset joogivee kvaliteeti nii tundlike põhjaveekogumite puhul nagu seda on Cm-V.

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I am grateful for my supervisor, Madis Kiisk, PhD, for trusting my ideas and initiatives and for treating me as an equal colleague ever since the beginning of my studies. The author is indebted to dr. Enn Realo who sparked my interest for natural radioactivity and radiation protection.

My sincere appreciation goes to my dear colleagues and co-authors, especially Liie (Lumiste) Hill. Collaboration with the following institutions is deeply acknowledged: Viimsi Water Ltd. (Nele Nilb); Department of Geology, Tallinn University of Technology (Valle Raidla, PhD and Tõnu Martna, PhD); Department of Materials and Environmental Technology, Tallinn University of Technology (Anna Goi, PhD). Special thanks to Kadri Isakar, Taavi Vaasma, Alar Jantiskene and Banu Özden for their cheerful companionship. The encouragement of my good friend Jasper Adamson is greatly acknowledged.

I cannot thank enough my parents, Liivi and Jüri Suursoo, who are my role models for patience and support. Last but foremost, I am grateful for my family – my son Oskar and my partner Rauno, who has not only been a great mental support, but also an excellent help with statistical analysis and data visualisation.

PUBLICATIONS

CURRICULUM VITAE

I Personal information

Name Siiri Suursoo
Date of birth 17.06.1985, Tallinn
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Education

2009– University of Tartu, PhD candidate in Environmental Technology
2007–2009 University of Tartu, Master of Science in Natural Sciences
(Environmental Monitoring Technology), *cum laude*
2004–2007 University of Tartu, Bachelor of Science in Natural Sciences
(Environmental Technology)

Language skills

Estonian – mother tongue
English – fluent in speech and writing
German – intermediate level
Russian – basic level

Professional employment

2016– Estonian Environmental Board, Radiation Safety Department,
adviser
2012– University of Tartu, Institute of Physics, Lab. of Environ.
Physics, specialist
2010–2012 University of Tartu, Institute of Physics, Lab. of Environ.
Physics, engineer
2008–2010 University of Tartu, Institute of Physics, Lab. of Environ.
Physics, laboratory assistant
2006–2007 Foundation for Science and Liberal Arts Domus Dorpatensis,
project assistant

II Research and development work

Main fields of research

Environmental radioactivity, naturally occurring radioactive material (NORM).
Nuclear spectroscopy measurement methods (gamma spectrometry, liquid
scintillation counting). Validation and accreditation of analytical procedures.

List of scientific publications

1. Leier, M., Kiisk, M., Suursoo, S., Vaasma, T., Putk, K., 2019. Formation of radioactive waste in Estonian water treatment plants. *Journal of Radiological Protection*, 39, pp. 1–10.

2. Vaasma, T., Kiisk, M., Leier, M., Suursoo, S., Jantsikene, A., Putk, K., 2019. NORM-related industrial activities in Estonia – Establishing national NORM inventory. *Journal of Sustainable Mining*, 18(2), pp. 86-93.
3. Raidla, V., Pärn, J., Aeschbach, W., Czuppon, G., Ivask, J., Kiisk, M., Mokrik, R., Samalavičius, V., Suursoo, S., Tarros, S., Weissbach, T., 2019. Intrusion of Saline Water into a Coastal Aquifer Containing Palaeogroundwater in the Viimsi Peninsula in Estonia. *Geosciences*, 9(1), 47; <https://doi.org/10.3390/geosciences9010047>.
4. Hill, L., Suursoo, S., Kiisk, M., Jantsikene, A., Nilb, N., Munter, R., Realo, E., Koch, R., Putk, K., Leier, M., Vaasma, T., Isakar, K., 2017. Long-term monitoring of a water treatment technology designed for radium removal – removal efficiencies and NORM formation. *Journal of Radiological Protection*, 38(1), pp. 1-24.
5. Suursoo, S., Hill, L., Raidla, V., Kiisk, M., Jantsikene, A., Nilb, N., Czuppon, G., Putk, K., Munter, R., Koch, R., Isakar, K., 2017. Temporal changes in radiological and chemical composition of Cambrian-Vendian groundwater in conditions of intensive water consumption. *Science of the Total Environment*, 601–602, pp. 679–690.
6. Goi, A., Nilb, N., Suursoo, S., Putk, K., Kiisk, M., Bolobajev, J., 2017. Regeneration of filter materials contaminated by naturally occurring radioactive compounds in drinking water treatment plant. *Journal of Water Process Engineering*, Corrected proof, in press, available online: <https://doi.org/10.1016/j.jwpe.2017.08.002>
7. Isakar, K., Kiisk, M., Realo, E., Suursoo, S., 2016. Lead-210 in the atmospheric air of North and South Estonia: long-term monitoring and back-trajectory calculations. *Proceedings of the Estonian Academy of Sciences*, 65, 4, pp. 442–451.
8. Jantsikene, A., Kiisk, M., Suursoo, S., Koch, R., Lumiste, L., 2014. Groundwater as a source of indoor air. *Applied Radiation and Isotopes*, 93, pp. 70–75.
9. Suursoo, S., Kiisk, M., Al-Malahmeh, A., Jantsikene, A., Putk, K., Lumiste, L., 2014. ^{226}Ra measurement by LSC as a tool to assess the efficiency of a water treatment technology for removing radionuclides from groundwater. *Applied Radiation and Isotopes*, 93, pp. 57–63.
10. Suursoo, S., Kiisk, M., Semakalu, A., Isakar, K., 2014. Radon leakage as a source of additional uncertainty in simultaneous determination of ^{226}Ra and ^{228}Ra by gamma spectrometry – Validation of analysis procedure. *Applied Radiation and Isotopes*, 87, pp. 447–451.
11. Suursoo, S., Kiisk, M., Jantsikene, A., Isakar, K., Koch, R. 2011. Applying gross alpha and beta measurements as an estimate to the total indicative dose of Cambrian-Vendian ground water in Estonia. *Radioprotection*, 46(6), pp. S125–S130.
12. Kiisk, M., Suursoo, S., Isakar, K., Koch, R. 2011. Relevant radionuclides in Estonian drinking and ground waters – measurement techniques and activity concentrations. *Radioprotection*, 46(6), pp. S107–S112.

Participation in scientific projects

- 2017–2020 LIFE ALCHEMIA: Towards a smart & integral treatment of natural radioactivity in water provision services (funded by EU LIFE programme).
- 2016–2017 Optimization of radiation protection – development of methods for health risk assessment in drinking water industry (funded by Environmental Investment Centre KIK).
- 2012–2015 Optimisation of radionuclides removal technology from ground waters, investigation of radioactive waste production and estimation of related radiation risks from water purification plants (funded by Archimedes Foundation).
- 2010–2012 Determination of Ra-226 and Ra-228 activity concentrations in 110 groundwater samples (funded by the Estonian Health Board through KIK).
- 2009–2010 Development of the methodology for the detection of radionuclides concentration in ground- and drinking waters (funded by KIK).

III Teaching

Courses

- “Experimental Methods in Nuclear Physics” (LOFY.01.015, 3EAP) – a course for bachelor students in physics in the University of Tartu.
- “Radiation safety training for radiation workers” – a training course.

Supervised dissertations

1. Kaisa Putk, 2016. *Veeproovide ettevalmistamismetoodika valideerimine raadiumi isotoopide aktiivsuse kontsentratsioonide gammaspektromeetria liseks määramiseks* (Validation of a sample preparation procedure for determining activity concentrations of radium isotopes in water by gamma spectrometry). Master thesis in environmental technology, supervisors Siiri Suursoo and Madis Kiisk, University of Tartu, Faculty of Science and Technology.
2. Tarvo Metspalu, 2013. *Süsiniknanotorude funktsionaliseerimine ning radiomarkerimine Ra226 aatomitega* (Functionalization and radio-labelling of carbon nanotubes with Ra-226 atoms). Bachelor thesis in physics, supervisors Madis Kiisk and Siiri Suursoo, University of Tartu, Faculty of Science and Technology.
3. Amer Jamil Aref Al-Malahmeh, 2013. *Methodological development and validation of sample treatment and source preparation procedures and liquid scintillation counting measurements for determination of ²²⁶Ra in drinking water*. Master thesis in applied measurement science, supervisors Siiri Suursoo and Madis Kiisk, University of Tartu, Faculty of Science and Technology.
4. Birgit Arujõe, 2012. *Raadiumi isotoopide ja radooni eemaldamise efektiivsus Viimsi Spa joogivee puhvermahutis* (Removal efficiency of radium

- isotopes and radon in a water buffer tank at Viimsi SPA) Bachelor thesis in environmental technology, supervisors Siiri Suursoo and Madis Kiisk, University of Tartu, Faculty of Science and Technology.
5. Kaisa Putk, 2012. *Radooni emanatsiooni ja ekshalatsiooni mõju Ra-226 määramisele gammaspекtrometrilisel meetodil* (Validation of an analysis procedure for gammaspectrometrical determination of Ra-226 content in water – effects of radon emanation and exhalation and spiking experiments). Bachelor thesis in environmental technology, supervisors Siiri Suursoo and Madis Kiisk, University of Tartu, Faculty of Science and Technology.
 6. Antonio Semakalu, 2012. *Gamma spectrometric measurement of radium content in water – validation of analysis procedure*. Master thesis in applied measurement science, supervisors Madis Kiisk and Siiri Suursoo, University of Tartu, Faculty of Science and Technology.

IV Administrative duties

2014– Testing Centre of the University of Tartu, Head of the Nuclear Spectroscopy Laboratory

V Professional development

- 20.–24.02.2017 Participation in a training course „Environmental Impact Assessment (EIA) for Decommissioning and Environmental Remediation (D&ER) Projects“ (IAEA TC Project INT9183), Lancaster, United Kingdom.
- 19.–23.10.2015 Participation in a training course „Regional Training Course on Quality Management Systems for Technical Services“ (IAEA TC Project RER/9/128), Vilnius, Leedu.
- 15.–19.06.2015 Participation in a training course „Train the Trainers Workshop for Radiation Protection Officers“ (IAEA TC Project RER/9/109), Lisbon, Portugal.
- 13.–15.11.2012 Participation in a training course „Training workshop on applications of gamma-ray spectrometry to environmental samples“, Belgrade, Serbia.
- 16.04.–21.09.2012 Traineeship at German Federal Office for Radiation Protection, Berlin, Germany. Determination of naturally occurring radionuclides (^{226}Ra , ^{228}Ra , ^{210}Po , ^{210}Pb , U isotopes) in water samples using liquid scintillation counting, alpha and beta spectroscopy.

VI Public and social activities

Member of sorority korp! Indla since 2004.

Member of the organizing committee of a student science conference “WinterAcademy” in 2007, 2008 and 2010.

ELULOOKIRJELDUS

I Üldandmed

Nimi: Siiri Suursoo
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Haridus

2009– Tartu Ülikool, doktoriõpe keskkonnatehnoloogia erialal
2007–2009 Tartu Ülikool, loodusteaduse magistri kraad (keskkonnaseire tehnoloogia), *cum laude*
2004–2007 Tartu Ülikool, loodusteaduse bakalaureuse kraad (keskkonnatehnoloogia)

Keelteoskus

eesti keel – emakeel
inglise keel – sorav kõnes ja kirjas
saksa keel – kesktase
vene keel – algtase

Teenistuskäik

2016– Keskkonnaamet, Kiirgusosakond, nõunik
2012– Tartu Ülikooli Füüsika Instituut, Keskkonnafüüsika labor, spetsialist
2010–2012 Tartu Ülikooli Füüsika Instituut, Keskkonnafüüsika labor, insener
2008–2010 Tartu Ülikooli Füüsika Instituut, Keskkonnafüüsika labor, laborant
2006–2007 SA Domus Dorpatensis, projektijuhi abi

II Teadus- ja arendustegevus

Peamised uurimisvaldkonnad

Keskkonna radioaktiivsus, looduslikult esinevad radioaktiivsed materjalid (NORM). Tuumaspektroskoopia meetodid (gamm-spektromeetria, vedelikstsin-tillatsioon-spektromeetria). Mõõtemetoodikate valideerimine ja akrediteerimine.

Teaduspublikatsioonide loetelu

1. Leier, M., Kiisk, M., Suursoo, S., Vaasma, T., Putk, K., 2019. Formation of radioactive waste in Estonian water treatment plants. *Journal of Radiological Protection*, 39, pp. 1–10.

2. Vaasma, T., Kiisk, M., Leier, M., Suursoo, S., Jantsikene, A., Putk, K., 2019. NORM-related industrial activities in Estonia – Establishing national NORM inventory. *Journal of Sustainable Mining*, 18(2), pp. 86-93.
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4. Hill, L., Suursoo, S., Kiisk, M., Jantsikene, A., Nilb, N., Munter, R., Realo, E., Koch, R., Putk, K., Leier, M., Vaasma, T., Isakar, K., 2017. Long-term monitoring of a water treatment technology designed for radium removal – removal efficiencies and NORM formation. *Journal of Radiological Protection*, 38(1), pp. 1-24.
5. Suursoo, S., Hill, L., Raidla, V., Kiisk, M., Jantsikene, A., Nilb, N., Czuppon, G., Putk, K., Munter, R., Koch, R., Isakar, K., 2017. Temporal changes in radiological and chemical composition of Cambrian-Vendian groundwater in conditions of intensive water consumption. *Science of the Total Environment*, 601–602, pp. 679–690.
6. Goi, A., Nilb, N., Suursoo, S., Putk, K., Kiisk, M., Bolobajev, J., 2017. Regeneration of filter materials contaminated by naturally occurring radioactive compounds in drinking water treatment plant. *Journal of Water Process Engineering*, Corrected proof, in press, available online: <https://doi.org/10.1016/j.jwpe.2017.08.002>
7. Isakar, K., Kiisk, M., Realo, E., Suursoo, S., 2016. Lead-210 in the atmospheric air of North and South Estonia: long-term monitoring and back-trajectory calculations. *Proceedings of the Estonian Academy of Sciences*, 65, 4, pp. 442–451.
8. Jantsikene, A., Kiisk, M., Suursoo, S., Koch, R., Lumiste, L., 2014. Groundwater as a source of indoor air. *Applied Radiation and Isotopes*, 93, pp. 70–75.
9. Suursoo, S., Kiisk, M., Al-Malahmeh, A., Jantsikene, A., Putk, K., Lumiste, L., 2014. ^{226}Ra measurement by LSC as a tool to assess the efficiency of a water treatment technology for removing radionuclides from groundwater. *Applied Radiation and Isotopes*, 93, pp. 57–63.
10. Suursoo, S., Kiisk, M., Semakalu, A., Isakar, K., 2014. Radon leakage as a source of additional uncertainty in simultaneous determination of ^{226}Ra and ^{228}Ra by gamma spectrometry—Validation of analysis procedure. *Applied Radiation and Isotopes*, 87, pp. 447–451.
11. Suursoo, S., Kiisk, M., Jantsikene, A., Isakar, K., Koch, R. 2011. Applying gross alpha and beta measurements as an estimate to the total indicative dose of Cambrian-Vendian ground water in Estonia. *Radioprotection*, 46(6), pp. S125–S130.
12. Kiisk, M., Suursoo, S., Isakar, K., Koch, R. 2011. Relevant radionuclides in Estonian drinking and ground waters – measurement techniques and activity concentrations. *Radioprotection*, 46(6), pp. S107–S112.

Osalemine teadusprojektides

- 2017–2020 LIFE ALCHEMIA: parima veetööstlustehnoloogia rakendamine põhjavee kõrgele loodusliku radioaktiivsuse korral (rahastaja: EL LIFE programm).
- 2016–2017 Joogivee radionukliidide sisaldusest põhjustatud terviseriskihinnangu meetodika väljatöötamine ning NORM-vaba veetööstluse teostatavuse uuringud (rahastaja: Keskkonnainvesteeringute keskus (KIK)).
- 2012–2015 Radionukliidide põhjaveest eraldamise tehnoloogia optimeerimine, tekkivate radioaktiivsete jäätmetüüpide ja koguste väljaselgitamine ning veepuhastusjaama kiirgusriskide hindamine (rahastaja: SA Archimedes).
- 2010–2012 110 põhjaveeproovi Ra-226 ja Ra-228 aktiivsuse kontsentratsiooni analüüsimine (rahastaja: Terviseamet KIK-i toel).
- 2009–2010 Põhja- ja joogivee radionukliidide sisalduse määramise meetodika väljatöötamine (rahastaja: KIK)

III Õppetöö

Õppetöö läbiviimine

- „Tuumafüüsika eksperimentaalmeetodid“ (LOFY.01.015, 3EAP) – kursus füüsika bakalaureuseõppe tudengitele Tartu Ülikoolis.
- „Kiirgusohutuse koolitus kiirgustöötajatele“ – täiendõppekoolitus.

Juhendamine

1. Kaisa Putk, 2016. *Veeproovide ettevalmistamismetoodika valideerimine raadiumi isotoopide aktiivsuse kontsentratsioonide gammaskintillatsioonmeetodiliseks määramiseks*. Magistritöö keskkonnatehnoloogia erialal, juhendajad Siiri Suursoo ja Madis Kiisk, Tartu Ülikool, Loodus- ja täppiseaduste valdkond.
2. Tarvo Metspalu, 2013. *Süsiniknanotorude funktsionaliseerimine ning radiomarkerimine Ra226 aatomitega*. Bakalaureusetöö füüsika erialal, juhendajad Madis Kiisk ja Siiri Suursoo, Tartu Ülikool, Loodus- ja tehnoloogiateaduskond.
3. Amer Jamil Aref Al-Malahmeh, 2013. *Methodological development and validation of sample treatment and source preparation procedures and liquid scintillation counting measurements for determination of ²²⁶Ra in drinking water* (Joogivee Ra-226 sisalduse määramise meetodika arendamine ja valideerimine – proovide ettevalmistus ning vedelikskintillatsioonmõõtmiste teostamine). Magistritöö rakendusliku mõõteteaduse erialal, juhendajad Siiri Suursoo ja Madis Kiisk, Tartu Ülikool, Loodus- ja tehnoloogiateaduskond.
4. Birgit Arujõe, 2012. *Raadiumi isotoopide ja radooni eemaldamise efektiivsus Viimsi Spa joogivee puhvermahutis*. Bakalaureusetöö keskkonnatehnoloogia erialal, juhendajad Siiri Suursoo ja Madis Kiisk, Tartu Ülikool, Loodus- ja tehnoloogiateaduskond.

5. Kaisa Putk, 2012. *Radooni emanatsiooni ja ekshalatsiooni mõju Ra-226 määramisele gammaspetspektromeetrilisel meetodil*. Bakalaureusetöö kesk-konnatehnoloogia erialal, juhendajad Siiri Suursoo ja Madis Kiisk, Tartu Ülikool, Loodus- ja tehnoloogiateaduskond.
6. Antonio Semakalu, 2012. *Gamma spectrometric measurement of radium content in water – validation of analysis procedure* (Vee raadiumisisalduse gammaspetspektromeetriline määramine – analüüsimetoodika valideerimine). Magistritöö rakendusliku mõõteteaduse erialal, juhendajad Madis Kiisk ja Siiri Suursoo, Tartu Ülikool, Loodus- ja tehnoloogiateaduskond.

IV Administratiivtöö

2014– Tartu Ülikooli Katsekoda, Tuumaspektroskoopia labori juhataja.

V Erialane enesetäiendus

20.–24.02.2017 Osalemine koolitusel „Environmental Impact Assessment (EIA) for Decommissioning and Environmental Remediation (D&ER) Projects“ (IAEA TC Project INT9183), Lancaster, Suurbritannia.

19.–23.10.2015 Osalemine koolitusel „Regional Training Course on Quality Management Systems for Technical Services“ (IAEA TC Project RER/9/128), Vilnius, Leedu.

15.–19.06.2015 Osalemine koolitusel „Train the Trainers Workshop for Radiation Protection Officers“ (IAEA TC Project RER/9/109), Lissabon, Portugal.

13.–15.11.2012 Osalemine koolitusel „Training workshop on applications of gamma-ray spectrometry to environmental samples“, Belgrad, Serbia.

16.04.–21.09.2012 Praktika Saksamaa Kiirguskaitseameti laboris, Berliin, Saksamaa. Erinevate looduslike radionukliidide (^{226}Ra , ^{228}Ra , ^{210}Po , ^{210}Pb , U isotoobid) määramine veeproovides kasutades vedeliktsintillatsiooni, alfa- ja beetaspetspektroskoopiat.

VI Ühiskondlik tegevus

Korporatsioon Indla liige alates 2004.

Üliõpilaste teaduskonverentsi „TalveAkadeemia“ korraldustoimkonna liige aastatel 2007, 2008, 2010.

DISSERTATIONES GEOPHYSICALES UNIVERSITATIS TARTUENSIS

1. **Andres Kuusk.** The hot-spot effect in plant canopy reflectance. Tartu, 1991.
2. **Tiit Nilson.** Radiative transfer in non-homogeneous plant canopies. Tartu, 1991.
3. **Helgi Arst.** Atmosfääri ja mere kiirguskarakteristikud looduskeskkonna seisundi informaatoritena (vene keeles). Tartu, 1991.
4. **Juha Sarkkula.** Measuring and modelling water currents and quality as a part of decision making process for water pollution control. Tartu, 1992.
5. **Piia Post.** On the two radiatively effective cloud parameters. Tartu, 1993.
6. **Aadu Mirme.** Electric aerosol spectrometry. Tartu, 1994.
7. **Aare Luts.** Mathematical simulation of the evolutions of air ions. Tartu, 1995.
8. **Tiit Kutser.** Estimation of water quality in turbid inland and coastal waters by passive optical remote sensing. Tartu, 1997.
9. **Ülle Kikas.** Atmospheric aerosol in the Baltic region. Tartu, 1998.
10. **Tarmo Kõuts.** Processes of deep water renewal in the Baltic sea. Tartu, 1999.
11. **Anu Reinart.** Underwater light field characteristics in different types of Estonian and Finnish lakes. Tartu, 2000.
12. **Marko Kaasik.** Parameterisation of atmospheric boundary layer in the numerical model of air pollution transport. Tartu, 2000.
13. **Janek Laanearu.** Topographically constrained deep-water flows in channels. Tartu, 2001.
14. **Urmas Raudsepp.** Wind-driven circulation in the gulf of Riga. Tartu, 2001.
15. **Urmas Hõrrak.** Air ion mobility spectrum at a rural area. Tartu, 2001.
16. **Marko Vana.** Formation and evolution of atmospheric aerosol size spectrum by the occurrence of nucleation burst events in the atmospheric boundary layer; transport of the climatically active particulate air pollution. Tartu, 2002.
17. **Veljo Kimmel.** Analysis of methods of air quality assessment. Applications in Estonia. Tartu, 2002.
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19. **Aarne Männik.** Implementation and validation of the nonhydrostatic adiabatic core of the numerical weather prediction model hirlam. Tartu, 2003.
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23. **Erko Jakobson.** Spatial and temporal variability of atmospheric column humidity. Tartu, 2009, 125 p.
24. **Sander Mirme.** Development of nanometer aerosol measurement technology. Tartu, 2011, 118 p.
25. **Hannes Keernik.** Estimating methods and variability of atmospheric humidity over the Baltic Region and the Arctic. Tartu, 2015, 105 p.
26. **Martin Kannel.** Development of Broadband Aerosol Optical Depth Models. Tartu, 2016, 168 p.
27. **Krista Alikas.** From research to applications: monitoring optically complex waters with MERIS/ENVISAT data. Tartu, 2016, 172 p.
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29. **Margit Aun.** Dependence of UV radiation on climate factors. Reconstruction of UV doses in Estonia for past years. Tartu, 2017, 124 p.