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ABSTRACT

TENAWA project (Treatment Techniques for Removing Natural Radionuclides from Drinking Water) was carried out on a cost-shared basis with the European Commission (CEC) under the supervision of Directorate-General XII, Radiation Protection Unit. TENAWA project was started because in several European countries ground water supplies may contain high amounts of natural radionuclides. During the project both laboratory and field research was performed in order to test the applicability of different equipment and techniques for removing natural radionuclides from drinking water. The measurable objectives of the project were:

- to give recommendations on the most suitable methods for removing radon (^{222}Rn), uranium ($^{238, 234}$U), radium ($^{226, 228}$Ra), lead (^{210}Pb) and polonium (^{210}Po) from drinking water of different qualities (i.e. soft, hard, iron-, manganese- and humus-rich, acidic)

- to test commercially available equipment for its ability to remove radionuclides
- to find new materials, adsorbents and membranes effective in the removal of radionuclides
- to issue guidelines for the treatment and disposal of radioactive wastes produced in water treatment.

Radon could be removed efficiently (>95%) from domestic water supplies by both aeration and granular activated carbon (GAC) filtration. Defects in technical reliability or radon removal efficiency were observed in some aerators. The significant drawback of GAC filtration was the elevated gamma dose rates (up to 120 µSv/h) near the filter and the radioactivity of spent GAC. Aeration was found to be a suitable method for removing radon at waterworks, too. The removal efficiencies at waterworks where the aeration process was designed to remove radon or carbon dioxide were 67–99%. If the aeration process was properly designed, removal efficiencies higher than 95% could be attained.

Uranium could best be removed (>95%) with strong basic anion exchange resins and radium by applying strong acidic cation exchange resins. Also, weak acidic cation resin, zeolite A, sodium titanate and manganese dioxide were found efficient in radium removal. Hydroxyapatite removed both uranium and radium. Simultaneous removal (>95%) of uranium, radium, lead and polonium could be carried out by nanofiltration and reverse osmosis. The side-effect of RO-technique was the quality of the effluent; the water becomes almost totally demineralized and therefore corrosive. Commercially available iron and manganese removal equipment removed variable amounts of radon (0–90%), uranium, radium, lead and polonium (0–100%) depending on the operation principle.

Lead and polonium could be removed only fairly well by ion exchange and GAC filtration (35–100%). The presence of lead and polonium in particles of different sizes in groundwater was determined in the laboratory. Only in one type of water, with relatively high NaCl concentration and rich in humus material, was a considerable fraction, about 20%, of both radionuclides found to be present in the soluble form. In the other types of water only from 1 to 2% of lead and polonium was soluble. It is expected that neither lead nor, especially polonium would form intrinsic precipitates but they would be adsorbed on colloidal minerals and organics.

When different kinds of treatment methods are used to remove natural radioactivity from drinking water, wastes containing natural radioactivity will be produced. It is recommended that the annual dose to inhabitants from external gamma radiation of a GAC filter should not exceed 0.1 mSv. It is also recommended that the dose rate at a distance of 1m from the GAC filter should not exceed 1 µSv/h. To achieve these aims the GAC filter should be equipped with special shielding to attenuate gamma radiation. It is also recommended that the wastes containing natural radioactivity in solid form be discharged into communal dumps, and wastes containing natural radioactivity in liquid form be discharged into the sewer.

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Avainsanat luonnon radioaktiivisuus, vedenkäsittely, pohjavesi, juomavesi, uraani, radium, radon, lyijy, polonium, ilmastus, aktiivihiili, raudanpoisto, mangaaninpoisto, ioninvaihto, adsorptiosuodatus, käänteisosmoosi, nanosuodatus, spesiaatio.

TIIVISTELMÄ

TENAWA-projekti (Treatment Techniques for Removing Natural Radionuclides from Drinking Water) toteutettiin yhteisrahoitteisesti Euroopan komission (CEC) kanssa, sen kahdennentoista pääosaston (DGXII) Säteilysuojeluyksikön valvonnassa. TENAWA-projekti käynnistettiin, koska useiden Euroopan maiden pohjavesissä on havaittu esiintyvän korkeita määriä luonnon radionuklideja. Projektin aikana tehtiin laboratorio ja –kenttäkokeita, joilla testattiin eri laitteiden ja tekniikoiden soveltuvuutta luonnon radionuklidien poistamiseen juomavedestä. Projektilla oli seuraavat päätavoitteet:

- antaa suosituksia menetelmistä, joilla voidaan poistaa radon 222 , uraani 238, uraani 234, radium 226, radium 228, lyijy 210 ja polonium 210 erilaatuisista juomavesistä (esim. pehmeä vesi, kova vesi, rauta-, mangaani-, humus- tai hiilidioksidipitoinen vesi)
- testata kaupallisten laitteiden toimivuutta radionuklidien poistossa
- löytää uusia materiaaleja, adsorbantteja ja kalvoja, jotka tehokkaasti poistavat radionuklideja

- antaa suosituksia vedenkäsittelyssä syntyneiden jätteiden käsittelyyn ja hävittämiseen.

Radon voitiin poistaa tehokkaasti (>95 %) kotitalouksien vedestä sekä ilmastamalla että aktiivihiilisuodatuksella. Jotkin ilmastimet eivät kuitenkaan toimineet teknisesti odotetulla tavalla. Puutteita havaittiin myös radonin poistotehokkuudessa. Aktiivihiilisuodatuksen haittapuolena oli korkea gammasäteilyn annosnopeus (jopa 120 µSv/h) suodattimien pinnalla ja käytetyn hiilen radioaktiivisuus. Ilmastuksen todettiin soveltuvan hyvin radoninpoistoon myös vesilaitoksilla. Mikäli ilmastusprosessi oli suunniteltu radonin tai hiilidioksidin poistoon, radonin poistumat olivat 67–99 %. Kun ilmastusprosessi on oikein suunnitteltu, voidaan yli 95 prosenttia radonista poistaa.

Vahva anioninvaihtohartsi soveltui parhaiten uraanin poistoon ja vahva kationinvaihtohartsi radiumin poistoon. Radium poistui tehokkaasti myös heikolla kationinvaihtohartsilla, zeoliitti A:lla, natriumtitanaatilla ja mangaanidioksidilla. Hydroksiapatiitti adsorboi tehokkaasti sekä uraania että radiumia. Samanaikainen uraanin, radiumin, lyijyn ja poloniumin poisto (> 95 %) voitiin toteuttaa nanosuodatuksella ja käänteisosmoosilla. Käänteisosmoosin haittana on puhdistetun veden laatu. Demineralisoituna se ei sellaisenaan kelpaa talousvedeksi, vaan tarvitsee veden jälkikäsittelyn. Vesi on lähes täysin demineralisoitu ja siten syövyttävää. Kaupalliset raudan- ja mangaaninpoistolaitteet poistivat toimintaperiaatteesta riippuen vaihtelevia määriä radonia (0–90 %), uraania, radiumia, lyijyä ja poloniumia (0–100 %).

Lyijy ja polonium voitiin poistaa ioninvaihdolla ja aktiivihiilisuodatuksella vain osittain (35–100 %), koska näiden nuklidien kemialliset muodot pohjavesissä vaihtelevat. Lyijyn ja poloniumin sitoutuminen erisuuruisiin partikkeleihin tutkittiin laboratoriossa. Vain yhdessä tutkituista vesistä lyijyn ja poloniumin liukoisen muodon osuus oli merkittävä, noin 20 %. Tässä vedessä oli myös korkeahko NaCl-pitoisuus. Muissa vesissä liukoisen muodon osuus oli 1–2 %. Oletettavaa on, etteivät lyijy ja erityisesti polonium saostu puhtaina yhdisteinä, kuten esim. hydroksideina, vaan adsorboituvat mineraalisten ja orgaanisten kolloidien pinnoille.

Eri puhdistusmenetelmiä käytettäessä syntyy jätteitä, jotka sisältävät luonnon radioaktiivisia aineita. Suosittelemme, että aktiivihiilen lähettämän ulkoisen gammasäteilyn aiheuttama vuosiannos ei saa ylittää 0,1 mSv asukasta kohden. Suosittelemme myös, ettei annosekvivalenttinopeus ylitä arvoa 1 µSv/h yhden metrin päässä suodattimesta. Näiden tavoitteiden toteuttamiseksi suodattimet pitää varustaa gammasäteilyä vaimentavilla suojilla. Lisäksi suosittelemme, että käsittelyssä syntyvät kiinteät jätteet voidaan viedä kaatopaikalle ja nestemäiset jätteet laskea viemäriin.

CONTENTS

PREFACE

The shared-cost research project “Treatment Techniques for Removing Natural Radionuclides from Drinking Water” (TENAWA) was carried out in the fourth Framework Programme 1994–98 of research and training funded by the European Commission in the sector of Nuclear Fission Safety. The aim of the TENAWA project was the evaluation of treatment techniques for removing natural radionuclides from drinking water. It was carried out by the following partners, who were responsible for the scientific work and for writing this report:

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The TENAWA project was divided into 13 work packages:

WP 1.1:	General Considerations: Literature Survey on Natural Radioactivity in Drinking Water and Treatment Methods in European Countries
WP 1.2:	General Considerations: Intercomparison of Analysis Methods
WP 1.3:	General Considerations: Definition and Classification of Different Water Types and Experimental Conditions
WP 2.1:	Removal of Radon by Aeration: Testing of Commercially Available Equipment for Domestic Use
WP 2.2:	Removal of Radon by Aeration: Testing of Various Aeration Techniques for Small Waterworks
WP 3.1:	Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of Radon
WP 3.2:	Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of U, Ra, Pb and Po
WP 4:	Removal of Radioactivity by Methods Used for Fe- and Mn-removal from Private Wells
WP 5.1:	Removal of U, Ra, Pb and Po by Ion Exchange Methods. Removal of U and Po from Private Ground Water Wells using Anion Exchange Resins
WP 5.2:	Removal of U, Ra, Pb and Po by Ion Exchange Methods. Removal of Ra and Pb from Private Ground Water Wells using Cation Exchange Resins
WP 6:	Removal of U, Ra, Pb, and Po with Adsorptive or Membrane Filters
WP 7:	Speciation of U, Ra, Pb and Po in Water
WP 8:	Disposal of Radioactive Wastes from Water Treatment Methods: Recommendations for EC.

1 INTRODUCTION

The reason for the TENAWA project was the fact that in several European countries ground water, especially bedrock water, may contain high amounts of natural radioactivity. Elevated levels of natural radionuclides in ground waters are mainly associated with uranium- and thorium-rich soil and rock minerals, or with uranium, thorium or radium deposits in soil or bedrock.

Nation-wide surveys of natural radioactivity in drinking water have been conducted in several European countries. The surveys made, e.g., in the Nordic countries, in Finland, Sweden and Norway, indicate that high concentrations of ^{222}Rn and other radionuclides usually occur in water from wells drilled in bedrock. In surface waters the concentrations are usually low, as well as in ground waters occurring in soil. Data on natural radioactivity in drinking and mineral waters have also been published, e.g., for Austria, Denmark, France, Germany, the United Kingdom, Ireland, Italy, Portugal, and Spain. High concentrations of natural radionuclides have been reported in some areas.

In most European countries ground water is used as drinking water. There is also an increasing tendency to replace surface water with water originating from various types of ground water aquifers. However, this involves an increased risk of finding natural radionuclides in the water.

Elevated levels of natural radionuclides in drinking water accompany potential health risks for the population because of the increase in the radiation dose. Therefore, the waters should be purified before use. Various processes based on different principles can be applied to removing radionuclides from water. Aeration is a method that can be applied to removing high levels of radon (^{222}Rn) from drinking water. GAC filtration can be used when the radon concentration of water is not exceptionally high. Ion exchangers are applied to removing uranium (^{238}U, ^{234}U) and radium (^{226}Ra). Lead (^{210}Pb) and polonium (^{210}Po) may sometimes be removed by ion exchange techniques as well. Membrane techniques, such as reverse osmosis (RO) or nanofiltration (NF), are used to remove uranium, radium, lead and polonium. Fe- and Mn-removal equipment also removes natural radionuclides from water.

When different kinds of treatment methods are used to remove natural radioactivity from drinking water, wastes containing natural radioactivity will be produced. The wastes are in liquid or solid form. Liquid wastes are produced when materials used to accumulate radioactivity are regenerated or backwashed. Solid wastes are formed in cases where regeneration or backwashing are not used or cannot be used.

2 OBJECTIVES

The overall objective of the TENAWA project was to study equipment currently available for removing natural radionuclides from drinking water. There is a definite need for well-tested methods and equipment both in small and large waterworks and in private dwellings. The measurable objectives of the TENAWA project were as follows:

- to make recommendations on the most suitable methods for removing ^{222}Rn, ^{238}U, ^{234}U, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po from drinking water of different qualities (soft, hard, Fe-, Mn- and humus-rich, acidic, etc.)
- to test commercially available equipment for its ability to remove radionuclides
- to find new materials, absorbers and membranes effective in the removal of radionuclides
- to issue guidelines for the treatment and disposal of radioactive wastes produced in water treatment.

The aims of the different WPs of the TENAWA project were as follows:

- to gain a European perspective for the TENAWA project as well as to find the potential risk areas for further studies and to point out areas where radionuclide removal techniques are most needed
- to ensure that the analysis methods used in the laboratories owned by the partners produce reliable and comparable results
- to make sure that different research groups produce results under comparable and pertinent experimental conditions
- to provide data which can be used when choosing an aerator capable of removing radon and of producing sufficient amounts of water from ground water wells
- to implement a cheap, easy-to-use aeration technique (e.g. spray aeration, diffused bubble method or packed column aeration) for various types of small water works and to write guidelines on how to build aeration systems
- to provide information and recommendations as to which types of waters GAC filtration can be safely used with
- to find out the usability of GAC filtration for removing uranium, radium, lead and polonium from various types of waters

- to test the removal efficiency of Fe- and Mn-removal equipment for different radionuclides
- to test the removal efficiency of anion exchange resins for uranium and polonium, to study the capacity and regeneration of the resins and necessary prefilters and to study cation exchange resins for radium and lead removal
- to study adsorbents for their efficiency in removing uranium and radium and reverse osmosis (RO) for its efficiency in removing uranium, radium, lead and polonium
- to make a literature survey of speciation of uranium, radium, lead and polonium in ground waters and to determine the oxidation states (IV, VI) and chemical forms of uranium in different groundwaters
- to estimate the effect of oxidation states and chemical form on the removal of these radioelements from ground waters
- to recommend guidelines for treatment and disposal of radioactive wastes produced by various water treatment methods.

3 PROGRESS AND RESULTS

3.1 Survey of Literature on Natural Radioactivity in Drinking Water and Treatment Methods in European Countries

A literature review was prepared with the title: “Natural radionuclides in drinking water in Europe and treatment methods for their removal”. The review presents the fundamental hydrochemical processes which are responsible for the mobility of natural radionuclides in water. The main potential risk areas for the occurrence of high contents of natural radionuclides in ground and surface water in Europe are pointed out and data concerning contents in drinking, mineral, ground and surface water from 17 European countries are presented. An overview of treatment methods to remove natural radionuclides from drinking water is given, and human health aspects and regulations regarding natural radionuclides in drinking water are summarised.

3.2 Intercomparison of Analysis Methods

Six intercomparison runs were performed for quality assurance of the analytical results produced in the TENAWA project. Both natural water samples and spiked samples were distributed among the partners in the project for analysis of radon (^{222}Rn), radium (^{226}Ra), uranium-isotopes and -total content and in one intercomparison, thorium-isotopes and -total content, lead (^{210}Pb) and polonium (^{210}Po).

3.3 Definition and Classification of Different Water Types and Experimental Conditions

Experimental conditions, including the way of planning experiments, the type and frequency of the analysis to be made, documentation of results and the interchange of information between the project partners were defined regarding the different treatment technologies to be tested and the type of experiments.

Water types to be selected for the experiments were fixed for each treatment technology. The selection was based on the water quality parameters which were assumed to have relevant influence on the treatment technologies, and on surveys regarding water quality in the areas with elevated natural radionuclides in water.

The ftp-server, the communication platform and database for the whole TENAWA project was established at IWGA and was continuously serviced. A WWW page on the TENAWA project was implemented on the IWGA server and regularly up-dated (`http://iwga-sig.boku.ac.at/tenawa1_e.htm`).

3.4 Removal of Radon by Aeration: Testing of Commercially Available Equipment for Domestic Use

There are three basic water treatment methods that can be used to remove radon from water supplies, namely decay storage, aeration and granular activated carbon (GAC) filtration. In this study different types of aerators were tested for their performance in radon removal.

Because of its relatively high Henry's law constant, radon can be removed from water by aeration. Basically two different principles can be applied: water can be released into air or air can be released into the water. A common way to release water into air is to spray untreated water into a tank with a fine mist spray nozzle. To reach a radon reduction of 70%, theoretically one litre of air is mixed with one litre of atomised water. With diffused bubble aeration a high pressure blower forces air through a fine bubble diffuser located at the bottom of the tank. Commercial aeration systems usually use combinations of both principles.

Radon is released from the water at an increasing rate as the air to water ratio is increased. The radon diffuses from the water into the air and the air is then ventilated into the outdoor air. Most commercial systems work under atmospheric pressure and a re-pressurisation pump is therefore needed after the aeration tank. Further radon reduction can be achieved by increasing the amount of air, either by using more air or by recirculating the water several times through ejector mouth-pieces.

Eleven installations of equipment for radon removal by aeration supplied by four commercial companies were studied. Seven units were selected for long-term monitoring. The main criteria for the selection of the households where aerators were installed were the concentrations of radon (^{222}Rn), iron (Fe), manganese (Mn) and organic matter (TOC, total organic carbon) (Table I).

Different types of installation were also studied (Figure 1). Basically, there are two ways to carry out the installation of an aerator. The aerated water can either be directed into a pressure tank (type A) or a storage tank (type B). The pressure tank maintains the hydraulic pressure in the household water line. When a storage tank is applied, the booster pump starts up every time water is taken from the taps. An additional pressure tank before the aerator, piping and three valves are needed to by-pass the system. The types of installation presented in the figure are largely simplified.

Table I. *Water quality data at the selected test locations. The concentrations of ^{222}Rn, Fe, Mn and TOC may have varied, the maximum values are presented. The installation types A and B are set out in Figure 1.*

Test Location	Company	Model	Install. Type	Volume (L)	^{222}Rn (Bq/L)	Fe (μg/L)	Mn (μg/L)	TOC (mg/L)
1A	Overcraft	Radox	B	290	510	69	3	-
1B		Radox	B	690	18 900	410	240	2.0
1C		Radox	B	300	17 000	130	59	3.4
2A	Vartiainen	modified	B	200	9 000	18	43	1.5
2B		RA 300/35	B	300	27 500	21	11	1.2
2C		RA 300/35	B	300	14 200	170	77	0.8
3A	WatMan	RF-150/KR6	A	150	22 200	65	95	0.9
3B		RF-150/KR6	A	150	15 200	390	170	7.6
3C		RF-150/3R	A	150	1 200	170	92	-
3D		Rn-A1	A/B	300	670	64	22	-
4A	Sarholms	Radonett	A	100	42 000	45	3	1.1

- not available or determined.

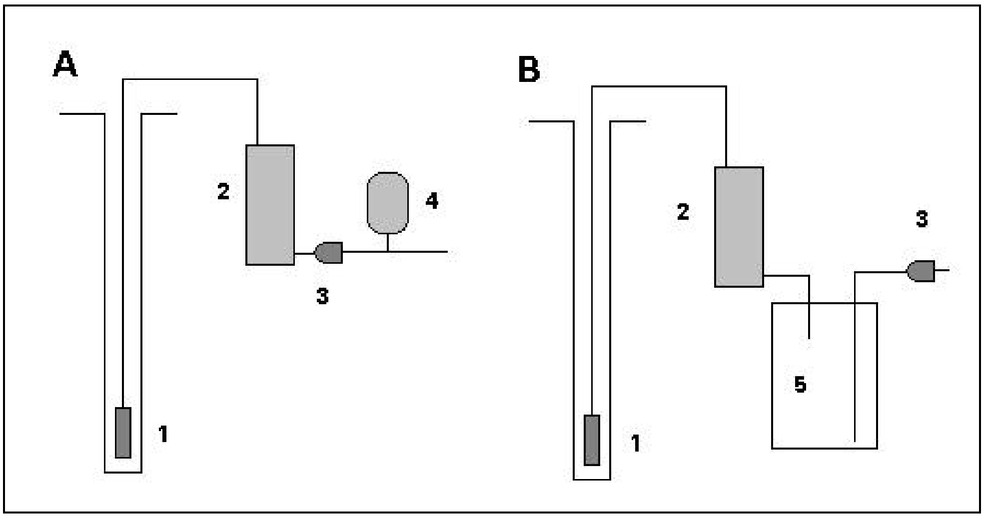

Figure 1. *Two types of installation of a treatment system based on aeration. In the figure, number 1 corresponds to the (submersible) well pump, 2 to the aerator, 3 to the booster pump, 4 to the pressure tank and 5 to the storage tank. In type A, the water is stored under pressure (normally 1.5–5 bar) whilst in type B the storage tank operates under atmospheric pressure.*

Radon concentration as well as the relevant water quality parameters (Fe, Mn, TOC, pH, CO_2, Redox, O_2, alkalinity and temperature) were monitored in both influent and effluent at approximately three month intervals. Respectively, the microbiological quality of the water was studied by determining the heterotrophic plate count (HPC in 22°C and 35°C). At an early stage in the study it was noticed that the radon removal efficiency of an individual unit is not always constant. The concentration of radon in the aerated water varied with the volume of water flowing, with the flow rate, and with the water usage prior to sampling. Furthermore, the installation (e.g. the power of the well pump and the booster pump) had an effect on the removal efficiency. One radon sample taken from the effluent did not provide sufficient information on the removal efficiency and therefore a standard test protocol was developed. This test protocol revealed malfunctions that could not be detected with conventional sampling where only one or two samples taken were from the effluent (Figure 2).

The flow rate was adjusted to a constant value (4, 8, 12 L/min). Samples were taken every 10–20 litres. If the flow rate did not remain constant (installation type A, Fig. 1) the flow rate was measured with a stop-watch and a measuring cylinder after each sample was collected. When more than

100 litres of water had flowed the sampling was stopped (time recorded) and a second sample of the influent was taken.

The radon concentrations (Bq/L) were plotted against the volume of water that had flowed. The removal efficiency for the water sample that was first taken, was calculated according to the equation

(1) $$R_0 = (1 - \frac{C_0}{C_{i0}}) \cdot 100\% ,$$

where R_0 is the *initial removal efficiency*, C_0 is the radon concentration in the first effluent sample, and C_{i0} is the concentration in the first influent sample.

The *average removal efficiencies* for 50 and 100 litres were calculated according to the equation

(2) $$R_e = \frac{(C_0 \cdot V_0) + \sum_n \left[½ \cdot (C_n + C_{n-1}) \cdot (V_n - V_{n-1}) \right]}{V_{tot} \cdot \frac{C_{io} + C_{if}}{2}} \cdot 100\% ,$$

where C_0 is the radon concentration in the first effluent sample, V_0 is the volume of water that had flowed before the first sample was taken, C_n is the radon concentration of the effluent sample n, V_n is the volume of water that had flowed when sample n was taken, C_{io} and C_{if} are the radon concentrations in the initial and final influent samples respectively, and V_{tot} is the volume at the last sampling, for which the efficiency was calculated (50 or 100 litres).

The *minimum removal efficiency* during the sampling run was calculated according to the equation

(3) $$R_{\min} = (1 - \frac{2C_{\max}}{C_{i0} + C_{if}}) \cdot 100\% ,$$

where C_{max} is the maximum radon concentration measured in effluent. C_{io} and C_{if} are the radon concentrations in the initial and final influent samples, respectively.

Removal type	Efficiency (%)
R_0	93.9
R_e, 50 L	95.5
R_e, 50 L	95.2
R_{min}	81.9

Flow rate: 4–5 L/min

C_{i0}: not measured

C_{if}: 19 700 Bq/L

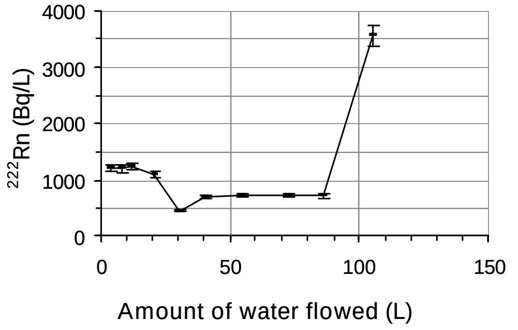

Figure 2. *The results obtained at test location 3A. The O-ring of a solenoid valve was broken and insufficiently aerated water was released into the waterline.*

The rate of radon removal from water was also determined. A high removal efficiency may naturally be attained if the aeration time is prolonged, but by doing this less water is produced. The rate of removal will ultimately control the throughput of the system. Since radon removal by aeration is a random process, the rate of removal can be modelled by first-order kinetics. The kinetics equation can be presented in the form of

(4) $$K_s = \frac{-\ln(\frac{C_t}{C_0})}{t}$$, where

C_t is the radon concentration in the treated water after the aeration (processing) time, t has passed, C_0 is the radon concentration in the raw water and K_s is the *(first-order kinetics) stripping constant*, which represents the rate of removal. As such, the K_s constant is not sufficient to be used when comparing the capacity of different aerators. The size of the aerator must also be considered, because various volumes of water (batches) are treated by different aerators. Since a removal efficiency of 99% is sufficient in most cases, a new parameter, the *effective flow rate*, Q_{eff} is introduced. The Q_{eff} is the flow rate by which the aerator attains the removal efficiency of 99%. It is calculated by the following equation:

(5) $$Q_{eff} = 0.217 \cdot K_s \cdot V_{batch}\ ,$$

where K_s is the stripping constant of the aerator and V_{batch} the volume of the water (batch) that is aerated in one go.

The aerator “Radonett” (4A) had the highest removal rate. Radon was released from water rapidly and only short aeration times were needed to mitigate even extremely high levels of radon. The Radox aerator (1A–1C) was also very efficient and the removal rate was high. The aerator needs longer aeration times than Radonett, but larger volumes of water are aerated in one batch in the corresponding time. Radonfällan RF-150 (3A–3C) had a good removal efficiency but it required rather long aeration times, and only a small batch of water could be aerated in one go. The Orwa aerator (2A–2C) had problems with both the removal efficiency and the removal rate. Even during low consumption, radon laden water could get into the plumbing. A summary of the radon removal performance of the aerators studied is presented in Table II.

Table II. *The removal efficiencies, rates of removal and effective flow rates calculated for different aerators.*

Test location	R_0 (%)	R_e, 50L (%)	R_e, 100L (%)	R_{min} (%)	K_s (min^{-1})	Q_{eff} (L/min)
1A	97.0	97.0	97.0	97.0	0.7	44
1B	99.2–99.7	99.2–99.7	99.2–99.7	99.2–99.7	0.25	37
1C	94.7–99.0	94.7–99.0	94.7–99.0	94.7–99.0	0.6	39
2A	87.1–92.0	81.3–99.4	85.8–99.5	60.7–98.9	0.2	9
2B	>99.9	95.9	91.2	77.0	0.2	11
2C	62.5–95.4	62.0–95.0	61.2–93.0	59.4–76.7	0.2	11
3A	93.9–99.9	95.5–99.4	95.2–99.5	81.9–91.2	0.6	14
3B	96.3–98.5	94.4–98.4	95.1–98.4	86.1–98.1	0.5	12
4A	>99.9	>99.9	>99.9	>99.9	3.7	48

The water quality remained good. Some iron may precipitate as ferric hydroxide during aeration. The precipitates can settle down on the bottom of the aeration tank, be removed by a sediment filter installed after the aerator, or be released in the water line. Therefore, the concentrations of iron are usually different in raw and aerated water. Manganese may co-precipitate with ferric hydroxide. Iron and manganese precipitates can cause fouling of the treatment system. Water becomes virtually saturated with oxygen during aeration. This improves the taste of the drinking water, and reduces its corrosiveness. Carbon dioxide is removed, which causes a rise in pH value. Water with a higher pH value is less corrosive for the plumbing. Other water quality parameters change only slightly. No clear trends could be observed in their results.

3.5 Removal of Radon by Aeration: Testing of Various Aeration Techniques for Small Waterworks

The aim of this study was to design and test different aeration techniques for radon removal, to compare their cost-effectiveness and to write guidelines on how to build aeration systems. For that purpose one waterworks, where radon removal was based on spray and diffused bubble aeration, was designed and installed in Finland and experiments were made in Germany with a counter current packed tower column in half technical scale to evaluate its ability to remove radon and carbon dioxide.

The aim of this study was also to compare the different aeration techniques already applied for radon removal at waterworks in Finland, Germany and Sweden. The data on the radon removal efficiencies, on the descriptions of the aeration principles and on the other water treatments applied simultaneously with radon removal were gathered from several waterworks in these countries. The most important water quality parameters were determined in raw and treated water at the Finnish waterworks to see the effect of the water treatment on its quality. In most of the waterworks studied here, aeration was applied together with other water treatments. In Finland and Sweden typical treatments are the removal of iron, manganese or humus or the alkalisation of too acidic and soft waters. In Germany the typical water treatment in the areas where increased radon levels occur in groundwater, is de-acidifying, but iron and manganese removal is also necessary.

The aim of this project was also to collect data on radon removal efficiencies in those waterworks which apply aeration for removing Fe, Mn, CO_2 or H_2S. For this purpose water samples from the raw and treated water were collected at several Finnish waterworks.

A number of radon measurements were carried out at Finnish, Swedish and German waterworks which apply different aeration techniques either for radon removal or in other water treatment processes, with the aim of surveying their radon removal capabilities.

A water treatment plant for the removal of radon (^{222}Rn), uranium ($^{238,234}U$), manganese and hardness was designed and installed at one Finnish waterworks supplying water to 350 people. Its radon removal is based on combined spray and diffused aeration. Water is sprayed into a cylindrical basin through four spray nozzles located about 30 cm above water level. Four diffusers are placed at the bottom of the basin to accomplish aeration by diffused bubble aeration having an air-to-water ratio of 11. After aeration the water is discharged into a storage basin. At this waterworks uranium, manganese and hardness are removed with separate anion and cation exchangers before aeration. Thus raw water first enters the cation exchanger, where manganese and hardness are removed and then the water flows through the anion exchanger for uranium removal. The ion exchangers are regenerated automatically every night with saturated sea salt solution.

Additionally, six other Finnish waterworks where radon is removed by various aeration methods, were located and their radon removal efficiencies were determined. Radon removal efficiencies in these seven waterworks varied between 67% and 98% and were sufficient in all waterworks to attain the limit for radon (300 Bq/L) set in the Finnish regulations. The concentration of radon in the raw water varied from 330 to 5 800 Bq/L and at some waterworks they varied greatly at different sampling times. Practically all uranium was removed by an anion exchanger.

Radon removal efficiencies were compiled from 18 small Swedish waterworks where various types of commercial aerators had been installed for radon removal. The results showed that the removal efficiencies varied between 93% and 99%. All these aerators were efficient enough to reduce the radon levels (in raw waters between 400–4 000 Bq/L) below the limit of 100 Bq/L set in Sweden and to supply water even to dozens of households.

Radon removal efficiencies were determined at nine Finnish waterworks where various types of aeration or oxidation techniques were applied in the removal processes for iron and manganese. The radon levels in the raw waters were quite low (8–110 Bq/L) but the water treatment capacities varied largely (24-5 600 m^3/d). The radon reduction varied greatly (from 13% to 94%). It seems that better rates of removal are attained by applying packed tower or drip aeration (from 72% to 94%) than by using spray aeration or cascade gravitation (from 13% to 58%). Aeration removed radon and carbon dioxide at a very similar rate. The radon reduction was usually a little higher than that of carbon dioxide. Iron and manganese were removed efficiently at all of these waterworks.

Radon removal efficiencies were studied at 11 German waterworks where conventional water treatment methods are applied mainly for de-acidification or for iron and manganese removal. Due to the geological situation elevated levels of radon in ground waters are not so common in Germany as in Scandinavia, and also the concentrations of radon are lower in German raw waters which are used for the production of drinking water (max. about 1500 Bq/L). The radon reductions at these waterworks varied from 0% to 98%.

At one of the German waterworks (water consumption 700 m^3/d) a Venturi water aeration device was installed as a first treatment step to remove carbon dioxide and radon (300 Bq/L in raw water) and to add oxygen. The aeration process takes place in the container room of the waterworks at a water flux of approximately 30 m^3/h. The removal efficiency of radon was always from 70% to 80%. The transfer of radon from water to air leads to a strong enrichment of radon in the indoor air. To attain a continual exchange of the indoor air with outdoor air, ventilation windows were set into the outer walls. Nevertheless, average indoor radon level of 62 000 Bq/m^3 was found in the container room during a four-day measurement period.

At another German waterworks (water throughput 1200 m^3/d) shallow bed cross-flow aeration equipment was installed as a first treatment step to remove carbon dioxide and radon (130 Bq/L in raw water) and to add oxygen. The equipment is operated at a water throughput of approximately 50 m^3/h and an air-to-water ratio of 16. Water passes through the equipment on a slightly inclined bed while air is blown through many nozzles set into the bed in a cross-flow direction. To avoid radon and carbon dioxide enrichment in the indoor air of the waterworks, the process-air is led out of the building through a pipe. The radon reduction was above 98%. Average indoor air radon levels were only 500 Bq/m^3 because the aerator was equipped with the ventilation pipe.

Experiments were made in Germany with a counter-current packed tower column in half-technical scale to compare the removal behaviour of radon and carbon dioxide from water during its aeration. In a packed tower column water flows downstream while air is blown upstream. The filling rings inside the equipment form a large surface where dissolved gases transfer from the liquid to the gaseous phase. The process-air can be led out of the equipment by a pipe.

Water with a radon content of 1000 Bq/L and a carbon dioxide content of 1 mmol/L was used for the experiments. The column was 150 cm high and had a diameter of 19 cm. In several experiments it was filled with four different filling rings made of metal or polypropylene. The filling height of the column was 1 m. By using throughputs of 1 to 4 m³/h (specific fluxes: 35 to 140 $m^3m^{-2}h^{-1}$) and air/water ratios of up to 40, removal efficiencies up to 85 % were achieved (Figure 3 and Figure 4).

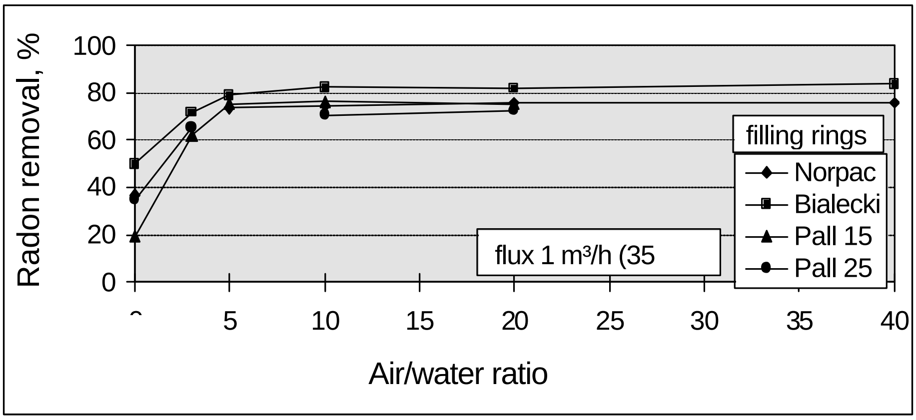

Figure 3. *Radon removals attained by various filling rings as a function of air-to-water ratio.*

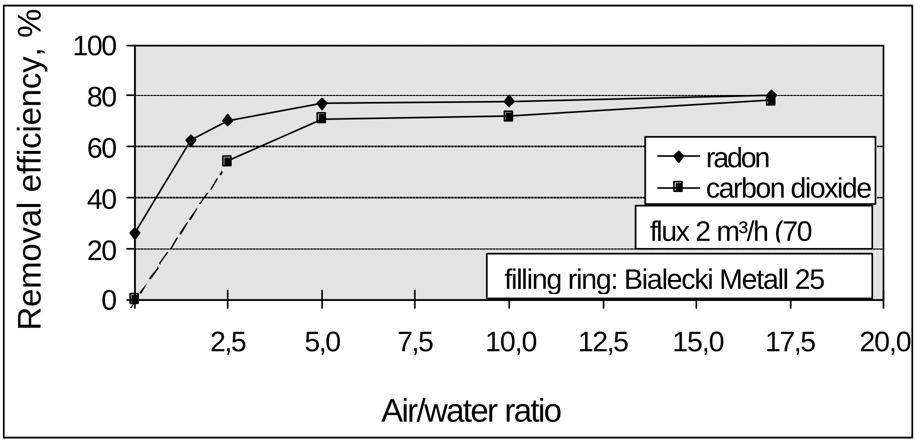

Figure 4. *Radon and carbon dioxide removals as a function of air-to-water ratio.*

From a packed tower column radon or carbon dioxide-rich air can be diverted directly out of a waterworks building. The tested column in half-technical scale removed 85% of the water-dissolved radon. By using a typical filling ring heights of two to three metres in a practical application at waterworks a removal efficiency of 95% can be expected. Additionally the experiments showed that high radon removal efficiencies were attained by using air-to-water ratios as low as five and that carbon dioxide and radon showed very similar removal behaviour.

3.6 Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of Radon

In drinking water treatment GAC filtration has been primarily used for removing taste, odour, colour and synthetic organic chemicals. Activated carbon removes effectively low or trace concentrations of impurities occurring in water by adsorption. The adsorption capacity of GAC is directly related to the extremely high internal surface area within the porous structure, which consists of macropores and micropores.

Radon (^{222}Rn) can be effectively adsorbed by a GAC filter. Since radon is chemically inert and radon does not form bonds, the adsorption process is one of purely physical adsorption. Also the short-lived decay products of radon are retained on GAC. As a consequence the filter matrix will emit gamma radiation. The dose rate in the vicinity of the filter can approach 100 µSv/h. The radioactivity in the GAC masses can be a problem when they are disposed of.

The main objective of this study was to investigate radon removal by GAC filtration in everyday household use. Test locations were selected so that the water types most typically found in bedrock were covered. The classification of water types was based on the concentration of radon, iron (Fe), manganese (Mn), organic matter (TOC) and the long-lived radionuclides of the uranium series (U, ^{226}Ra, ^{210}Po and ^{210}Pb). Their removal and effect on the GAC filter’s performance and the effect of pre-filters were also studied. Other aspects considered in this study were: the effect of GAC filtration on water quality parameters (including microbiological quality), gamma radiation levels on the surface of the filter and in its vicinity, necessary shielding, and waste disposal of spent carbon.

Two commercial companies installed GAC filters at several test locations (Table III). Most GAC filters were installed as such, without having any pre-treatment units prior to GAC filtration. Two GAC filters were equipped with both a sediment filter and a backwash system and one GAC filter was equipped with a sediment filter. In addition, two test locations had a 21-litre anion exchange unit for removing uranium installed before the GAC filter. Flow meters and sampling taps for influent water were installed in most test locations. In Table III test location C(b) is the same household as test location C(a) but with a new filter combination and the GAC batch changed. All GAC filters operated under normal plumbing pressure in the down-flow mode.

Table III. *Installation data and the main water quality parameters in raw water from the first sampling at the selected test locations. Test locations marked with an asterisk (*) are vacation residences.*

Test location	BV (L)	Flow meter	Back-wash	Pre-filter	Anion exch.	^{222}Rn (Bq/L)	Fe (mg/L)	Mn (mg/L)	TOC (mg/L)	U (mg/L)
A	39	-	-	-	-	2 000	0.021	0.018	n/d	0.052
B	40	x	x	x	-	4 000	0.410	0.120	1.5	0.013
C(a)	39	x	-	-		3 000	0.016	0.064	2.3	0.21
C(b)	39	x	-	x	x	3 000	0.016	0.064	2.3	0.21
D	39	x	-	-	-	3 700	0.089	0.270	3.4	0.035
E*	40	x	x	x	-	910	0.032	0.011	1.1	0.017
F*	63	-	-	-	-	3 000	0.019	0.024	2.4	0.046
G	63	x	-	-	-	5 100	0.033	0.027	1.5	0.070
H	39	x	-	-	x	1 800	0.034	0.002	2.5	0.26
I	63	x	-	-	-	2 000	n/d	n/d	n/d	n/d
J	63	x	-	-	-	4 600	n/d	n/d	n/d	n/d
K	63	x	-	-	-	1 300	0.70	n/d	n/d	n/d
L*	63	x	-	x	-	5 800	0.16	0.066	2.1	0.007

n/d—not determined.

- not installed.

At approximately three-month intervals sampling from influent and effluent was carried out. ^{222}Rn, U, ^{226}Ra, ^{210}Pb, ^{210}Po, gross-alpha, Fe, Mn, TOC, pH, temperature and heterotrophic plate count were monitored regularly. SiO_2, redox potential, O_2, CO_2, colour, $KMnO_4$, acidity, PO_4^{3-}, NO_3^- and NH_4^+ were occasionally determined. Radon removal efficiencies were calculated. Since the removal efficiency of radon depends on the bed size of the filter and the daily water usage, the rates of adsorption (independent of those parameters) were also determined. The rate of adsorption is utilised when studying the negative effects of water quality parameters on the adsorption. The rate of adsorption was determined by calculating the K_{ss} constants according to the first-order kinetics model:

(6) $C_t = C_0 \cdot e^{-K_{ss} \cdot t}$, where

C_t is the ^{222}Rn concentration in effluent in Bq/L,
C_0 the concentration in influent in Bq/L,
K_{ss} the adsorption-decay steady-state constant in h^{-1}, and
t is the empty bed detention time. It is defined as

(7) $t = \frac{V_b}{Q}$, where

V_b is the volume of the GAC bed in L and
Q is the average volumetric flow rate in L/h.

Dose equivalent rates of gamma radiation were measured on the surfaces of the GAC filters and at different horizontal distances from the filters. Attenuation of gamma radiation in the vicinity of the filters was studied applying lead, aluminium, concrete and water shields. Two batches of spent GAC were investigated in order to determine the activity of radionuclides accumulated in the carbon. The spent carbon was either cored or homogenised, then dried and measured with an n-type HPGe detector.

Radon was removed efficiently by most filter combinations (Table IV). Six units out of thirteen were capable of removing more than 99.9% of radon. The lowest removal efficiency observed was approx. 90%.

Table IV. *The ranges of radon concentration in influent and effluent during the operating period of the filters, the radon reduction at the most recent sampling and the corresponding treated water volume (in bed volumes).*

Test location	^{222}Rn Influent (Bq/L)	^{222}Rn Effluent (Bq/L)	Time in service (months)	Water treated (BV)	Radon reduction(%)
A	1 900–2 850	1.2 – 41	27	~8 000	98.5
B	3 500–4 200	12 – 190	11	5 350	98.9
C(a)	2 600–2 700	150 – 340	13	4 050	92.9
C(b)	1 850–3 100	<0.4 – 31	11	4 460	98.6
D	2 750–4 100	<0.4 – 15	23	3 030	> 99.9
E	910–1 100	<0.4 – 3.1	8	150	> 99.9
F	1 700–3 000	0.9 – 2.2	13	~400	> 99.9
G	5 100–7 400	<0.4 – 2.2	23	3 790	> 99.9
H	1 600–2 200	1 – 37	21	4 860	97.8
I	1 300–2 200	1 – 5.3	15	1 501	99.7
J	4 100–4 600	1.2 – 2.6	17	4 440	> 99.9
K	1 300–1 600	<0.4 – 0.5	23	5 550	> 99.9
L	3 040–6 400	45 – 99	9	389	98.5

The calculated K_{ss} constants differed significantly between different test locations, but remained quite constant at an individual test location. The best adsorption rate was obtained at test location B (3.4 h^{-1} on average) while test location I had the poorest adsorption rate (1.1 h^{-1} on average). The effect of water quality on the rate of adsorption was studied by plotting the K_{ss} constants against different water quality parameters (gross-alpha, U, Fe, Mn, TOC, $KMnO_4$, HPC 22°C, HPC 35°C and pH). Only gross-alpha, uranium and TOC had a clear negative correlation with the calculated K_{ss} constants (Figure 5). These substances are also partly removed by GAC filtration, which suggests that they have the potential to clog the micropores of GAC where radon removal occurs.

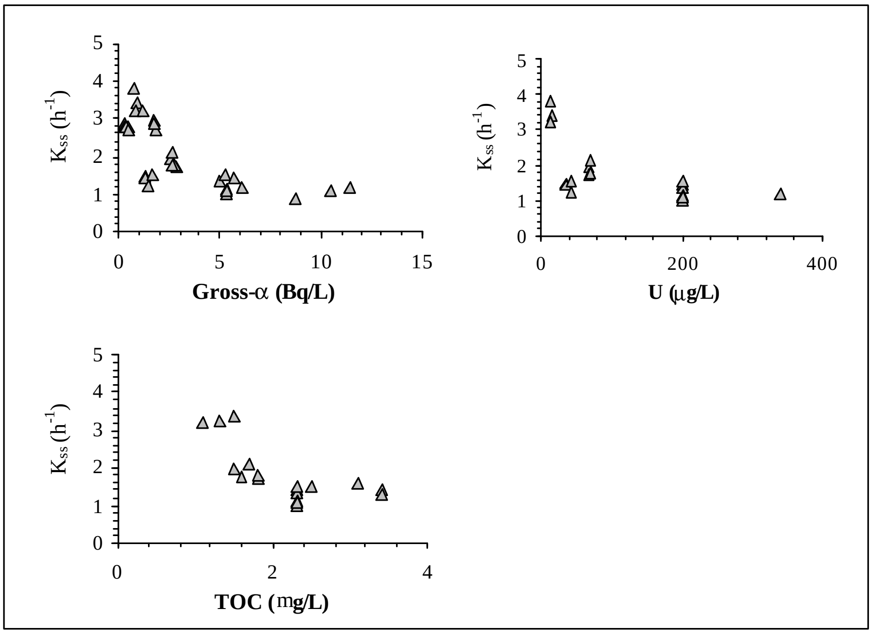

Figure 5. *The rate of adsorption (K_{ss} constant) as a function of gross-alpha, uranium and total organic carbon (TOC) concentration of the influent. A negative correlation was obtained.*

To investigate the effect of uranium on radon removal in more detail, the GAC filter at test location C(a) was loaded with a fresh batch of GAC. An additional sediment filter and an anion exchange unit (removes most of the uranium and some of the humic substances) were installed before the GAC filter. Following this installation, the filter removed nearly 99% of the radon and the K_{ss} constant increased from value 1.2 h^{-1} to 2.8 h^{-1}. It is evident that the interfering substance in the water was some anionic species, most probably uranium or humus.

Iron was usually removed efficiently by GAC filtration (>50%). High concentrations were removed most effectively. The concentration of manganese did not significantly change during filtration. Organic matter was removed fairly well when less than 1 000 BV's was treated. The reduction efficiency decreased gradually and after 2 000 BV's reduction efficiency was less than 70%. The pH value may increase for a few weeks after a new filter has been commissioned. Turbidity decreased and the correlation between iron reduction and decrease in turbidity was observed. Electric conductivity increased for a couple of weeks after a new filter had been commissioned. No significant changes were observed later on. The concentration of phosphate (PO_4^{3-}) may increase significantly when less than 400 BV's have been filtered. No significant changes were observed for alkalinity, total hardness, nitrate (NO_3^-), ammonium (NH_4^+), redox potential, silica (SiO_2) and heterotrophic plate counts (HPC in 22°C and 35°C).

Along with radon, GAC filters were capable of retaining various amounts of uranium, radium, and radon progeny. The activity of radionuclides in spent GAC determined gamma-spectrometrically indicated 100% retention of ^{210}Pb formed in the decay of radon. Therefore, spent GAC batches may contain several hundred kilobecquerels of ^{210}Pb. The specific activity of other radionuclides was low.

Radon and its daughters build up in the GAC unit. The short-lived daughters of radon (^{218}Po, ^{214}Pb, ^{214}Bi, and ^{214}Po) come into secular equilibrium with radon in about four hours. ^{214}Pb, ^{214}Bi are beta emitters but also emit gamma photons. Because the daughter nuclides are totally retained in the GAC bed, the filter becomes a source of gamma radiation.

The external gamma dose rate depends on the radon concentration in the influent water, on daily water usage, and on the dimensions of the GAC filter. Due to these factors gamma dose rates varied at different test locations. At two test locations the GAC filter was placed in a cupboard, inside the house. Therefore, radiation shields were installed. The filter was encased in three 1mm-thick sheets of lead. Lead attenuated the gamma radiation efficiently. At the other test locations GAC filters were installed either in a cellar, in a technical room, or in a separate shed where the shields were not needed.

During this study no breakthrough of radon occurred at any of the test locations. Theoretically, a GAC filter is constantly regenerated in respect of radon due to radioactive decay, and can therefore remain in service for several years. When competitive substances occupy the active sites of the carbon, radon removal efficiency may decrease. This, however, largely depends on the other water parameters.

3.7 Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of U, Ra, Pb and Po

The objective of this study was to investigate the removal efficiency for natural radionuclides in adsorption processes by filter systems based on different activated carbon types. Measurements were focused on the following adsorption parameters:

- adsorption capacity
- adsorption velocity
- influence of the granular size
- interaction with ions (variation of hardness)
- influence of the pH value
- poisoning of active centres.

The study consisted of laboratory experiments and field research. The laboratory experiments started as batch experiments with seven different activated carbons derived from hard coal, brown coal, peat, wood and coconut. The carbon type that exhibited the best adsorptive properties for the radionuclides was selected for column experiments.

The field research was performed on the GAC units that were studied for radon removal. For the field tests test locations were selected such that the water types most typically found in Finnish bedrock were covered. The effect of water quality on the performance of the GAC filter was also studied. Other aspects considered in the field experiments were the changes in water quality due to filtration and the microbiological quality of treated water.

Batch experiments were carried out with spiked water. Two water types with different degrees of hardness were used. Seven different coal types were studied. The granular size was =0.1 mm for all of them. The experiments showed that lead and polonium were quantitatively adsorbed by every coal type studied. Significant differences appeared in batch experiments with uranium and radium. One coal type adsorbed uranium from 97% to 100%. The lowest adsorption efficiency noted was approximately 50%. All the other coal types were in the range from 70% to 85%. For radium the highest adsorption efficiency was achieved with one coal type, which adsorbed radium nearly totally. The lowest adsorption capability noticed was 70%. All the other coal types were in the range from

86% to 94%. The experiments indicated high efficiency of activated carbons in the removal of radionuclides from water.

The granular size of the activated carbon had a tremendous effect on uranium and radium adsorption, which was reduced substantially with increasing granular size. For lead and polonium only a slight influence in the same direction is recognisable.

As a standard water type a pH value of 7 and a water hardness of 5.0°dH were adjusted. To investigate the influence of water hardness on adsorption efficiency a second water type with a hardness of 2.5°dH was involved in a test series at the same pH value. In comparison with the standard type an increase of adsorption efficiency was found for uranium, indicating an interaction between various ions in the adsorption process. For radium, too, an increased adsorption efficiency with the soft water type was indicated. For lead and polonium no difference was noticeable. For both water types nearly total adsorption was achieved.

Three different pH values were adjusted: pH 6, pH 7 and pH 8. Lead and polonium were not effected by pH value changes. Measurement for uranium ions indicated a strong but not uniform influence of the pH value. For radium, too, no uniform influence was detectable.

A water type with a DOC content of 1.5 mg/L was used to show the influence of organic contaminants in the adsorption process. For lead and polonium no influence could be detected. For uranium and radium a significant reduction of adsorption for most coal types was found.

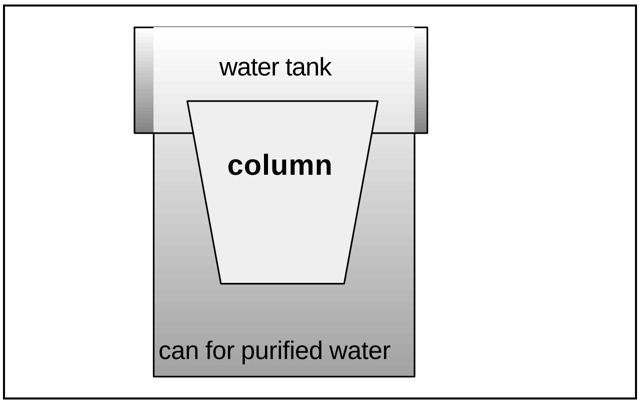

Figure 6. *Filter system for the removal of radionuclides from drinking water.*

For the column experiments a commercially available filter system was used (Figure 6). The experiments were focused on the influence of granular size, on interaction with ions and on poisoning of activated centres. The previous experiments showed that the pH value did not have a significant influence on the adsorption capacity. The batch experiments showed that even small variations in granular size influence adsorption capacity. Large differences in granular size between 0.8–1.4 mm and 0.5–0.8 mm for polonium and radium were noted. When the granular size was degraded of 0.2 mm, the flow rate dropped to 3 L/h. For a granular size between 0.4–0.8 mm the flow rate was 4 L/h. As a result of the above-mentioned, a granular size of >1 mm and 0.5-1 mm was adopted. The flow rate of >1 mm was 30 L/h and for 0.5–1.0 mm it came to a total of 15 L/h.

Column experiments were carried out with the two granular sizes. Waters exhibiting two different levels of water hardness (10.066 °dH and 2.517 °dH) and two concentrations of DOC, dissolved organic compounds (0 and 1.47 mg/L) were used. It is clearly seen that smaller granular size has greater adsorption capacity than larger granular size (Table V). Uranium was adsorbed approximately 30% more efficiently from water that was soft, for the other nuclides the effect of water hardness was smaller (Table VI). The adsorption capacity decreases when the DOC concentration increases (Table VII).

Table V. *Influence of granular size for a water hardness of 10.066°dH.*

Granular size (mm)	**Adsorption (%)** **U**	**Ra**	**Pb**	**Po**
>1	37.2	33.6	61.2	37.1
0.5–1	57.4	83.7	93.2	66.9

Table VI. *Influence of water hardness, with a granular size >1 mm and 0.5-1 mm.*

Water hardness **(°dH)**	Size >1 mm, adsorption **(%)**				Size 0.5–1 mm, adsorption **(%)**			
	U	Ra	Pb	Po	U	Ra	Pb	Po
10.066	37.2	33.6	61.2	37.1	57.4	83.7	93.2	66.9
2.517	68.1	38.3	86.9	56.9	85.0	85.2	100	85.9

Table VII. *Influence of DOC (1.47 mg/L) on the adsorption process, with a granular size >1 mm*

Water Type	Size >1 mm, adsorption **(%)**				Size 0.5–1 mm, adsorption **(%)**			
	U	Ra	Pb	Po	U	Ra	Pb	Po
standard	68.1	38.3	86.9	56.9	85.0	85.2	100	85.9
with DOC	29.4	28.6	65.9	55.0	62.9	73.3	95.8	100

The test locations selected for field research in Chapter 3.6 were also studied in terms of uranium (^{238}U, ^{234}U), radium (^{226}Ra), lead (^{210}Pb) and polonium (^{210}Po) removal. At seven test locations the radionuclides were determined by radiochemical separation (Table VIII), at the rest gross-alpha screening (the total activity of U, Ra and Po, ^{226}Ra separately) was applied (Table IX).

Table VIII. *Concentration of U, ^{226}Ra, ^{210}Pb and ^{210}Po in influent and effluent at the test locations where regular sampling was carried out. The volume of water that had been treated is referred to as bed volumes (BV): One BV corresponds to the volume of the GAC material inside the filter.*

Test Location	BV	U (μg/L) inf.	U (μg/L) eff.	^{226}Ra (Bq/L) inf.	^{226}Ra (Bq/L) eff.	^{210}Pb (Bq/L) inf.	^{210}Pb (Bq/L) eff.	^{210}Po (Bq/L) inf.	^{210}Po (Bq/L) eff.
B	741	12.9	8.5	0.20	0.04	0.283	0.009	0.122	0.007
	1786	14.8	14.8	0.17	0.07	0.371	0.014	0.102	0.015
	3518	13.0	13.7	0.20	0.07	0.328	0.005	0.154	0.012
	5348	–	–	0.20	0.10	0.660	0.005	0.454	0.013
C	431	207	181	0.21	0.15	0.375	0.040	0.266	0.045
	1274	202	212	0.23	0.22	0.640	0.045	0.126	0.042
	2670	200	211	0.25	0.22	0.228	0.031	.109	0.051
	4051	–	–	0.24	0.26	0.132	0.015	0.104	0.033
D	202	–	15.9	–	0.40	–	0.117	–	0.027
	528	35.9	12.8	0.28	0.24	0.354	0.234	0.169	<0.002
	1069	42.9	31.8	0.26	0.27	0.313	0.195	0.520	0.045
	1565	–	–	0.54	0.43	0.477	0.162	0.134	0.039
E	41	18.9	1.4	0.05	<0,01	0.461	0.003	0.416	0.003
	151	21.7	0.2	0.05	<0,01	0.014	0.001	0.033	0.006
F	~150	47	34	0.22	0.07	–	–	–	–
	~400	115	112	0.13	0.11	0.075	0.017	0.137	0.047
G	75	70	40	0.30	0.11	–	–	0.455	0.018
	555	67	65	0.32	0.25	0.517	0.149	0.461	0.043
	903	67	68	0.32	0.26	0.616	0.151	0.360	0.031
	1586	–	–	0.29	0.26	0.451	0.200	0.206	0.047
L	23	–	–	0.19	0.01	0.417	0.085	1.92	0.133
	181	6.5	0.3	0.14	0.14	–	–	–	–

– not determined

Table IX. *Gross alpha and* ^{226}*Ra concentrations in influent and effluent at the test locations where regular sampling was not performed.*

Test Location	BV	Gross-α (Bq/L)		^{226}Ra (Bq/L)	
		influent	effluent	influent	effluent
I	142	6.85	5.90	0.29	0.19
	509	6.09	5.51	0.19	0.20
	878	10.6	8.12	0.23	0.25
	1 501	8.78	9.81	0.19	0.17
J	943	1.64	1.01	0.09	0.06
	1 649	1.81	1.54	0.08	0.07
	3 434	1.73	1.45	0.08	0.07
	4 438	1.80	1.03	0.09	0.07
K	184	0.58	0.23	0.08	0.07
	1 656	0.45	0.33	0.15	0.07
	3 180	0.38	0.20	0.14	0.11
	4 087	0.40	0.25	0.11	0.11
	5 545	0.38	0.39	0.13	0.09
L	23	2.32	0.13	0.19	0.01
	181	2.63	0.18	0.14	0.14
	389	1.67	0.46	0.29	0.26

\- not determined

Efficient reduction of uranium was obtained only when less than 200 BV's of water was filtered, though most filters showed a low reduction even then. There seemed to be no particular breakthrough volume for uranium: rather, the retention decreased gradually. When a large amount of water had been treated, the uranium concentration in the effluent was the same or slightly higher than in the influent.

The adsorption efficiency for radium (^{226}Ra) varied considerably. Two of the filters removed radium fairly well (from 67% to 53%). Radium mostly occurs as a hydrated cation in ground water. Part of the retention observed, however, may be due to the complexes which radium can form with humus and fulvic acids because no breakthrough could be observed. Some retention may also occur by adsorption onto ferric hydroxide precipitates that are formed in the filter vessels during filtration. Ion exchange reaction may also be possible. The best adsorption was observed at the test location where the highest concentrations of iron occurred.

Lead (^{210}Pb) was removed quite efficiently (from 80% to 100%) at two permanent residences and two vacation residences. At one permanent residence the removal efficiency was only fair, from 30% to 60%. Polonium removal was mostly over 80%. Lead, as well as ^{210}Po, is readily adsorbed on particles, surfaces and colloids. Therefore, it can be expected that the mechanism by which these radionuclides are removed is particle filtration. The ratio between particulate species and dissolved species may vary in natural waters, which explains the different removal efficiencies obtained.

3.8 Removal of Radioactivity by Methods Used for Fe- and Mn-removal from Private Wells

The main aims of this study were to find equipment which is able to remove natural radionuclides simultaneously with iron and manganese and to find the highest concentrations of these radionuclides which can be removed.

Most of the iron and manganese removal equipment commercially available on the Finnish market was tested. The commercial iron and manganese removal equipment is based on three main principles:

- aeration-filtration
- greensand filters regenerated with $KMnO_4$
- ion exchange

All iron and manganese removal units are installed so that they treat all household water (point-of-entry). They are regenerated or backwashed at certain intervals depending on the quality of the effluent water and on daily water usage.

Fourteen test locations in Finland and six in Sweden were selected for field tests. The criterion for selection was the adequate concentration of natural radionuclides in the water and the possibility of sampling raw and treated water separately. The concentration of radon, uranium, radium, lead and polonium in influent and effluent was determined two or three times at the Finnish test locations and twice at the Swedish ones. The sampling interval was 4–10 months. In addition to the radionuclides, pH, electric conductivity, $KMnO_4$ value and the concentration of iron and manganese were analysed once at the test locations in Finland and twice in Sweden. External gamma dose rates on the surface of the filter were also measured.

The removal efficiencies for the different radionuclides varied within a large range. For radon, aeration-filtration was the most efficient (reduction from 12% to 89%). Uranium and radium were best removed by ion exchange techniques (reduction from 50% to 99%) when both anion and cation resins were applied. Removal of lead and polonium varied within a large range by various equipment mainly due to their speciation.

With the aim of improving the removal efficiency of radionuclides, alterations were made in two units in co-operation with the company. The company added new carbon-based and more oxidising masses to the filters studied. The radon removal efficiency of one type of equipment improved on average from 30% to 80%. In the other type of equipment the improvement was on average from 35% to 65%.

The aeration-filtration equipment removed from 83% to 98% of the iron and manganese. Organic matter was usually not removed by the aeration-filtration units, although sometimes fair removal rates (from 39% to 45%) were recorded. In the case of the greensand filters regenerated with $KMnO_4$, iron removal was efficient (from 67% to 99%), but most of the units failed to remove manganese.

Cation exchangers removed iron and manganese efficiently (from 77% to 99%). Organic matter was removed only when anion exchange resin had been added to the resin bed. Cation exchange increases the corrosiveness of the water. Since Ca and Mg ions are removed, the water usually becomes too soft. Therefore, re-hardening is nearly always necessary. If anion exchange resin is also used in the exchanger, the chloride concentration in the treated water increases and thus also amplifies the corrosiveness of the water.

3.9 Removal of U and Po from Private Ground Water Wells Using Anion Exchange Resins and Removal of Ra and Pb from Private Ground Water Wells Using Cation Exchange Resins

An ion exchange reaction may be defined as the reversible interchange of ions between a solid phase (the ion exchanger or ion exchange resin) and a solution phase, the ion exchanger being insoluble in the medium in which the exchange is carried out. The exchange unit can be installed as a point-of-entry, point-of-use or small pour-through unit.

The aim of this study was

- to summarise the available information about ion exchange for the removal of natural radionuclides, uranium ($^{238,234}U$), radium (^{226}Ra), lead (^{210}Pb) and polonium (^{210}Po) from drinking water
- to test commercially available equipment for the removal of natural radionuclides from drinking water
- to study the influence of different raw water qualities on the removal process
- to optimise ion exchange technology with respect to resin, and to undesirable influences on the product water quality and on the quantity and quality of waste produced.

These tasks were covered by a literature study, by conducting batch and small column experiments and by testing commercial ion exchange systems in Finnish households as well as in the laboratory.

3.9.1 Literature study

The high efficiency of ion exchange for the removal of radium and uranium was found to be well proven in the US-American laboratory and in bench scale tests as well as in full scale field studies. Concerning the removal of lead and polonium, only single or even no results, respectively, are published. Only sparse literature was found concerning European experiences under European conditions.

Some special questions arose with poor documentation in literature: regenerability of resins, hygienic problems (with domestic treatment devices in particular), the change of water composition by ion exchange treatment (conflicts with drinking water regulations), radioactivity in waste water, the accumulation of radionuclides on the filters (conflicts with radiation protection regulations), and the waste problem (used brine solution).

3.9.2 Batch and column experiments with different resins regarding exchange capacity

Batch and small column experiments using spiked waters and different types of ground-waters were conducted to find ion exchange resins having a high capacity for the removal of uranium, radium, lead and polonium.

The ion exchangers which were selected for testing had earlier been studied for decontamination of metallurgical waste effluents and the removal of radionuclides from nuclear waste solutions. A total of eleven ion exchange materials (six organic resins and five inorganic ion exchangers) were evaluated with respect to their ability to remove U and Ra from three different groundwater simulants.

In batch experiments the highest distribution coefficient (K_D) values were obtained by the strong basic anion resin (SBA) in the case of all water simulants studied. The synthetic mica, Na-4-mica, was the only inorganic ion exchanger which was found to take uranium quite well. The highest K_D values for radium ($K_D > 10^6$ mL/g_{dry}) were obtained by the inorganic ion exchangers, sodium titanate and manganese dioxide.

Using the results of these batch experiments two inorganic and five organic ion exchangers were selected for the column experiments with the real groundwater having high uranium content (200 Bq/L). The breakthrough levels of uranium, radium, lead and polonium were determined to evaluate decontamination factors. The best decontamination factor for uranium was with the strong basic anion resin, being between 20 and 120. The best exchangers for removal of ^{226}Ra from the groundwater were the weak and the strong acidic cation resins (WAC and SAC) and zeolite A. The decontamination factors (*DF*) for WAC, SAC and zeolite A were 2–26, 2–4 and 4–5. The better *DF*s were obtained for the weak acidic cation resin rather than for the strong acidic cation resin with a slow flow rate (15 BV/h).

The best results for removal of ^{210}Po and ^{210}Pb from water were received with the strong and weak basic anion exchangers. However, the mechanism of removing these nuclides is not an ion exchange process. Polonium and lead are probably mainly bound in particles and adsorbed on the surface of the anion resins.

3.9.3 Batch and column experiments with different resins regarding regeneration

Detailed regeneration studies were performed for ^{226}Ra, ^{210}Pb, ^{210}Po (cation exchange) and uranium (anion exchange). Cation exchange studies were performed for comparison of regeneration with NaCl and $CaCl_2$ solutions. In anion exchange studies various resins were compared for their regenerative abilities. In addition, regeneration kinetics, the influence of concentration and stoichiometry of the regenerate were studied.

Under conditions which were typical for the concentration and stoichiometric ratio of a water softening device, the result of ^{226}Ra regeneration was very poor (about 6% and 22% regeneration efficiency for sodium and calcium as regenerate, respectively). Results for ^{210}Pb and ^{210}Po were much higher. The difference between the extent of regeneration using NaCl and $CaCl_2$ solutions as regenerate is greatest for ^{226}Ra, less for ^{210}Pb and very small for ^{210}Po.

The influence of the stoichiometric ratio between regenerate and total resin capacity is linear for ^{226}Ra, whereas ^{210}Po behaves indifferently to variations of stoichiometry between one and three. In contrast to ^{226}Ra, variation of the concentration of the regenerate between 1 and 2.4 had no influence on ^{210}Po regeneration. Repeated regeneration after one uptake or after repeated uptakes showed for ^{226}Ra a constant partition coefficient, whereas the ratio between regenerated ^{210}Po to ^{210}Po on the resin decreased with each regeneration step. This is important for the accumulation of radionuclides on ion exchange units with regular regeneration, because ^{210}Po does not reach the limit of a geometrical series such as ^{226}Ra.

Batch tests for the regeneration of uranium from strong basic anion exchange resins showed a clear influence of regenerate concentration and stoichiometric ratio on the extent of regeneration, when both parameters were relatively low. Regeneration kinetics were similar to ^{226}Ra, the gel-type resins achieving a slightly higher efficiency for regeneration than the macroporous resin, the best result being achieved by a nitrate selective resin.

A small column test was carried out to study the efficiency of uranium regeneration from a strong basic anion resin using a concentrated sea salt solution. Uranium recovery efficiency was 99.4%. Uranium was mostly desorbed in the first few bed volumes of regenerant. At 5.6 bed volume of regenerant the recovery efficiency was 98.5%.

3.9.4 Influence of water composition – small column tests and simulation

The influence of the nuclide activity, competing ions and pH value on the removal of uranium, radium and lead was evaluated by conducting small column tests (mixed bed exchangers containing 80% SAC resin and 20% SBA resin) with six different water types.

Studies conducted earlier show that the feed water composition has an important effect on the possible run-length of an anion exchanger for removing uranium. Especially the strong effect of pH and the sulphate concentration is pointed out. Concerning the influence of water quality on the removal of the other natural radionuclides, no information was found.

Commercially available ion exchangers are usually regenerated at short intervals (e.g. weekly) to suppress bacteria growth and to avoid the accumulation of huge amounts of radioactivity. Usually the capacity for removing radionuclides is only partly exhausted during this interval. With smaller columns, the capacity could be used more effectively and regenerant agent could be saved. Since for reasons of convenience a certain water flow is necessary in a household (10 to 20 litres/minute) this would result—if, as is common practice, no storage tank is used—in higher filter velocities and small contact times between the water to be treated and the resin. It is not clear which minimum contact times are necessary to remove radionuclides effectively.

The aim of the study was

- to check whether high flow rates/small empty bed contact times (EBCT) can be used
- to examine the influence of the feed water quality on the removal of radium, lead and uranium by ion exchange by conducting small column tests
- to check whether the results of the tests can be calculated using a simulation programme
- to extrapolate the results for a wider range of feed water qualities, if possible.

Pre-tests showed that high flow rates result in an initial breakthrough of the ions to be removed and make the breakthrough curve flatter. This reduces the effective run-length of an ion exchanger, when a limit for the effluent concentration must be set. A flow rate of 200 BV/h (related to the SAC resin volume) is an acceptable value for the removal of radium and lead, as the tests demonstrated. The resulting 800 BV/h in the mixed bed exchanger for the SBA portion were too high to remove uranium effectively, the effluent concentration being about 20% of the feed value at the very beginning. For practical application this means that either the maximum flow rate for the simultaneous removal of radium, lead and uranium by mixed bed exchangers must be far lower than the tested 160 BV/h (related to the total bed volume) or the portion of SBA resin must be increased (resulting in a minimum use of the capacity for uranium removal till regeneration induced by lead or radium breakthrough starts). Small bed volumes and the optimal use of the resin capacity for radionuclide removal resulting in minimum regeneration agent consumption on the one hand and short regeneration intervals for hygienic reasons on the other hand are only possible with low flow rates. As a consequence ion-exchangers with constant flow rate followed by a storage tank should be preferred to an in-line installation.

Filter geometry had only a small impact on the form of the effluent curve, a slightly later breakthrough being observed with the more compressed filter form (lower ratio of height to diameter). This could be explained by the lower real velocity of the water in the filter bed.

Two ion exchange simulation programs were tested as to their applicability for calculating radionuclide removal. A comparison with experiments reported in the literature on radium removal showed a good correspondence of calculated and measured data. This was also true for our own radium experiments, but not for lead and uranium. The reasons for this are supposed to be the partly particle-bound portion of lead in natural waters (which was proved), the change of lead speciation with pH and other water quality parameters resulting in the variation of the affinity value, and the initial breakthrough of uranium caused by the high flow rate which was not reproducible by the simulation programme.

Radium broke through to 10% of the feed concentration after 1 000 to 2 000 BV had been treated. The largest reduction of radium removal capacity was observed with high total hardness followed by elevated sodium values; this was also confirmed by the extrapolation using a simulation programme. pH or radium concentration in feed water had no significant influence.

Lead broke through from the beginning to about 20% of feed concentration, except the low pH water type, which reached the 10% breakthrough only when about 1 000 BV had been treated. For the other water types the 100% breakthrough occurred already after 200 to 500 BV. As previously mentioned, a pH of 7 improved the removal efficiency enormously compared to the pH 8 water types. Little impact was also observed from hardness (earlier breakthrough with high hardness), the sodium and the lead concentration having no significant influence.

The measured uranium effluent curves look very flat; an initial breakthrough of more than 20% occurred because of the high flow rate. Even after more than 40 000 BV was treated, when the experiments were stopped, there was still about 60% of the uranium in the feed water removed. Contrary to the results reported in the literature, the greatest impact on the effluent concentration was observed from chloride and not from sulphate concentration. For final conclusions experiments with lower flow rates and a longer investigation time are necessary.

For practical application this means that feed water quality has an important influence on the capacity of ion exchangers for radionuclide removal. Water quality must be considered when fixing the regeneration intervals; capacities should be given by the manufacturers dependent on the content of competing ions and the pH of the feed water.

3.9.5 Tests of commercially available equipment

Several water treatment systems for domestic or laboratory use based on ion exchange technique are commercially available. Most of them are primarily developed to reduce hardness or iron and manganese (cation exchangers), to reject nitrate (anion exchangers) or to de-mineralise water (mixed bed exchangers).

Field and laboratory tests with several types of equipment were conducted to evaluate the efficiency of such commercially available ion exchange systems for removing radionuclides. The effect of the treatment process on other water quality parameters was studied and the quantity and quality of waste produced was determined.

Regeneration tests with the commercial systems and batch and column experiments simulating field conditions were conducted.

3.9.6 Field tests

Ion exchange units were installed in six private homes to treat either all the household water or the water for human consumption only. Because of the excellent results of earlier studies ORWA strong basic anion (SBA) or strong acidic cation (SAC) resins were used in all ion exchange units.

ORWA strong basic anion resin removed uranium very effectively from drinking water. The removal was over 95% at all the test places and independent of the filter type, water quality and bed volume. The removal of radium by the ORWA cation resin was over 94%. The anion resin also retained from 35% to 65% of radium (possibly by anionic radium compounds). Removal of lead and polonium was uneven mainly due to their speciation.

The main water quality improvement caused by the ion exchange was attained by removing organic matter simultaneously with radionuclides. The hygienic quality did not seem to deteriorate. No coliform bacteria were found in any of the test places. The number of heterotrophic colony forming bacteria either slightly increased or decreased during the treatment. The other improvements were achieved by the decrease of turbidity, phosphate, sulphate and nitrate (with anion resins).

The external gamma dose equivalent rate varied from 0.13 to 11.3 µSv/h in various test places. Mixed bed resins had the highest values because cation resin retained radium, which generated radon and its daughters in the unit. The dose rates on the surface of the anion exchangers were low, near the background value. Dose rate measurements on the surface of the unit and also at various distances from the unit indicated that the ion exchangers do not expose residents to any dose if the filters are properly located.

The regeneration studies in the laboratory indicated that about 70% of uranium could be regenerated, when water contained a lot of organic matter. When water quality was more innocuous (no organic matter) better regeneration efficiency could be achieved (near 100%). Both sea salt and NaCl removed uranium equally efficiently. The empty bed contact time (EBCT) did not have significant influence on regeneration efficiency. The regeneration of a tap filter was carried out in the laboratory after six month’s use in the private house. The results obviously indicated near 100% reduction efficiency for uranium. For a system with automatic regeneration which had been in domestic use before regeneration efficiency by using saturated sea-salt solution was over 96%. It can be assumed that the uranium is regenerated almost completely by the normal regeneration procedures applied for these types of commercial units.

3.9.7 Laboratory tests

In the laboratory two types of systems were tested for their capability in removing natural radionuclides by using ground water simulants: countertop pour-through filters and domestic water softeners.

Countertop pour-through filters, point-of-use-systems for treating only the small amount of water intended for human consumption, usually consist of a jug, a filter holder and exchangeable filter cartridges. The cartridges are aimed to improve the taste and quality of drinking water. After exhaustion of the filter capacity the cartridges are centrally recycled or disposed with household waste. The aim of the experiments was

- to determine the efficiency of a widely used commercially available filter system for the removal of uranium, radium and lead
- to study the influence of the treatment on other water quality parameters (mineralisation, hygienic quality)
- to modify the filter cartridges to optimise radionuclide removal and to minimise the influence on other water quality parameters.

Two commercially available cartridges and 5 modified cartridges were tested. The commercially available cartridges have not been developed for the special purpose of reducing radionuclides in drinking water. The experiments showed that with modified cartridge fillings radionuclides can be removed more selectively and more efficiently; the influence on the ionic composition of the feed water can be minimised.

Tests simulating the household use of pour-through filters showed that severe deterioration of the hygienic water quality can occur. The exhausted filter cartridges are solid waste with an activity of up to several 100 Bq/g. A summary of the radionuclide rejections achieved with the tested cartridges is set out in Table X.

Table X. *Average rejection of radionuclides by pour-through filters.*

Filter cartridge	**Average rejection of radionuclides (100 L filtered)**		
	Ra-226	**Pb-210 / Pb**	**U-nat.**
Brita standard	80%	60%	80%
Brita anti-nitrate	80%	95%	90%
SAC/Na	97%	20%	0%
SAC/Ca	95%	20%	0%
SAC/Ca + SBA/Cl	97%	40%	55%
SAC/Ca + NSS/Cl	98%	-	60%
WAC/Ca + SBA/SO_4	85%	80%	40%

Two typical domestic water softeners, both of them with automatic regeneration, were tested for their capability in removing radium and lead. In detail the aim of the experiments was

- to determine the efficiency of the systems in removing radium and lead
- to study regeneration efficiency and accumulation of the radionuclides on the ion exchange resin over several cycles
- to describe the influence of the treatment on other water quality parameters (ionic composition , hygienic quality).

For the removal of ^{226}Ra and ^{210}Pb the operational mode recommended by the manufacturer for softening was followed. Lead removal was in the range of hardness reduction, from 90% to 95% at the start of a cycle decreasing to about 80% to 90% just before regeneration started. Some cycles with bad reduction showed that the removal of lead is unreliable; small changes in water quality might influence the speciation and cause this variation. ^{226}Ra reduction exceeded hardness removal, beginning at about 95% and decreasing to about 90% at the end of a cycle. Higher values in the first bed volumes of a cycle were caused by insufficient backwashing of the filter after regeneration.

Simultaneously with ^{226}Ra and ^{210}Pb, Ca and Mg causing hardness of water are almost completely exchanged for Na, resulting in corrosive water. Electrical conductivity and pH was nearly unchanged, a high increase being observed for the heterotrophic plate count. This shows that even with short regeneration intervals a deterioration in hygienic quality cannot be excluded.

The regeneration efficiencies measured were only about 11% for ^{226}Ra and 37% for ^{210}Pb. Due to the limited regeneration efficiency accumulation of ^{226}Ra and ^{210}Pb occurs on the resin. This is not a linear process but a maximum value is reached dependent on feed water concentration, the regeneration interval and regeneration efficiency. A model developed for simulating this process was successfully verified with experimental data.

The use of $CaCl_2$ was tested for regeneration instead of NaCl to avoid an undesirable reduction in water hardness. Unfortunately, the $CaCl_2$ crystallised in the salt container and blocked the system. Modifications in the design of the water softeners is necessary to use this alternative.

The waste produced by these systems is used regeneration brine. The volume of this liquid, high in salinity, with a radionuclide concentration of 10 to 30 times the feed value, is in the range from 3% to 10% of the treated water volume.

3.10 Removal of U, Ra, Pb and Po with Adsorptive or Membrane Filters

Methods employing adsorptive filters, reverse osmosis (RO) and nanofiltration (NF) to remove natural radionuclides from drinking water were studied. Part of the study was to investigate if new adsorptive materials can be found and established for the adsorption of the non-volatile elements uranium (^{238,234}U), radium (^{226}Ra), lead (^{210}Pb) and polonium (^{210}Po).

3.10.1 Adsorptive filters (mineral materials)

Mineral materials are known to be selective in removing natural radionuclides from water under various conditions. Depending on the type of material and the compound to be removed different removal processes may be involved. Common to these materials is that they are not yet widely used for the treatment of drinking water.

The two main processes which may take place and which are responsible for the removal of radionuclides by mineral materials are adsorption and ion exchange. Zeolites in particular, which are actually synthetic clay minerals, act as ion exchangers like ordinary organic resins. Also, hydroxyapatite acts as an ion exchanger.

Adsorption is a phenomenon that takes place at the surface boundary between two phases, a liquid phase (drinking water) and a solid phase (mineral material). Radionuclides can be collected on the surface of the adsorptive material, leading to an enrichment of these substances at the surface. Adsorptive mineral materials are porous and have a rather large surface area (some 100 m^2/g adsorbents). When the adsorbent is fully covered, the material has to be replaced.

Spiked water was used in the experiments. The water consisted of deionized water with varying amounts of calcium, magnesium and sodium salts.

After batch experiments with several materials such as zeolites (Na-Y zeolite, Wessalith XD® and H-ZSM5 M28), tin dioxide, titanium dioxide, calcium sulphate, barium sulphate and silica gel, two mineral materials, hydroxyapatite and manganese dioxide, were selected for more detailed studies in column experiments as well as a commercially available ion exchange unit (BRITA®).

Field experiments were carried out in order to evaluate the effectiveness of hydroxyapatite in removing natural radionuclides under normally occurring conditions. Hydroxyapatite was tested in a pour-through filter.

The laboratory experiments showed that hydroxyapatite has a good capability for adsorbing uranium and radium. The field experiments with very small flow rates showed the same phenomenon. The high adsorption at slow flow indicate that a strong interaction between the feed water and the surface of hydroxyapatite is necessary to gain good results. Therefore a new granular form has to be developed to obtain smaller and perhaps more porous particles to increase the surface area and contact time.

Results of the experiments with manganese dioxide as adsorbent showed that the adsorption yield of uranium decreases with increasing pH value and that the adsorption is smaller if the water hardness is high.

3.10.2 Membrane filters

A membrane can be defined as a thin film separating two phases and acting as a selective barrier to the transport of matter. In membrane operation a feed stream is divided into two streams: a permeate containing material which has passed through the membrane, and a retentate (or concentrate) containing the non-permeating species.

The driving force for the separation is either difference in pressure, concentration, temperature or electrical potential across the membrane. The majority of radionuclides occurring in natural waters (radium and uranium in particular) are not fixed to particles but are dissolved as ions. Therefore only membranes with very small pore sizes (“molecular sieves”) are able to remove these radionuclides effectively. Reverse osmosis (RO) and nanofiltration (NF) are pressure-driven membrane processes.

Osmosis occurs when two aqueous solutions of different concentrations are separated by a semi-permeable membrane. Since the osmotic pressures of the two solutions are different and therefore out of balance, water will flow from the solution of lower concentration, through the membrane, to dilute the solution having higher concentration. The transport of water increases the osmotic pressure of the dilute side, while reducing the osmotic pressure on the concentrate side. Eventually permeation (water flow) will cease, and the system will be in balance.

RO is the reversal of this natural process. By applying pressure (exceeding the difference of osmotic pressure) on the more concentrated solution in contact with the membrane, the feed water is divided in a permeate with low salt concentration passing the membrane (product water) and the concentrated solution, called retentate (waste water). The particle size range for applications of RO is approximately 0.1 nm to 1 nm; the mechanisms of separation of species are based on processes relating to their size and shape, their ionic charge and their interactions with the membrane itself.

NF is similar to RO and is applied in the area between the separation capabilities of RO membranes and ultrafiltration (UF) membranes. NF systems typically operate at lower pressures than RO but yield higher flow rates of water despite the different quality of RO. NF is used when high sodium rejection, typical of RO, is not needed, but where other salts such as Mg or Ca (i.e. divalent and higher valent ions, also the natural radionuclides concerned) are to be removed. The basic principles for the NF operation are the same as for RO.

Five different reverse osmosis (RO) and nanofiltration (NF) systems, typical of the great number of commercially available ones, were tested in the laboratory. Three of them were POU-RO units, one a POE-RO unit and one a POE-NF device (POU: point-of-use, POE: point-of-entry). Except for the last one, all of them are commercially available. Two different RO units were studied in the field. The units were installed for test purposes only and the water was not used as drinking water. Both of the units were POU-RO units. The practicability of the membranes was studied for a period of seven months.

In NF experiments at a plate module pilot plant the five most important uranium species for the mobilisation of uranium in natural water, $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $UO_2\ (HPO_4)_2^{2-}$ and UO_2^{2+} were generated in different model waters. Their rejection was determined at six NF membranes, which represent a broad spectrum of commercially available NF membranes, and at two open reverse osmosis (RO) membranes.

The single operational unit into which membranes are engineered for use is referred to as a module. The module consists of the membranes, pressure support structures, feed inlet and concentrate outlet ports and permeate draw-off points. For RO and NF two major types of modules are found on the market: the spiral wound and the hollow fibre type.

The common membrane materials are cellulose acetate (spiral wound), polyamide (hollow fibre, spiral wound) and thin film composites. Cellulose acetate membranes are chlorine tolerant, more tolerant to foulants than others but with an increased danger of biological attack, especially with warm feeds. Better salt rejection but no chlorine tolerance are characteristics of polyamide membranes. Thin film composites have the best performance (high flux at low pressure, high salt rejection, not biodegradable) but their tolerance to fouling is lower than cellulose acetate.

Expected problems with the use of RO or NF systems for drinking water treatment are demineralisation and pH-lowering, resulting in a lack of essential minerals for human health, corrosiveness of the water and infraction of drinking water regulations and deterioration in hygienic quality.

3.11 Speciation of U, Ra, Pb and Po in Water

The aim of this study was

- to make a literature survey of speciation of U, Ra, Po and Pb in ground waters
- to determine ^{210}Po and ^{210}Pb in particles in ground waters
- to determine the oxidation states of uranium in ground waters.

A literature survey on speciation and the behaviour of uranium, radium, lead and polonium in ground waters was performed. As a result of this literature survey and due to the first experimental results obtained from other studies made in the TENAWA project, it became evident that most information was needed on the speciation of lead and polonium in ground water. For this reason the speciation of these two radionuclides was chosen for more detailed investigation. As the second step of this study the division of ^{210}Po and ^{210}Pb in ground water into soluble and particle-bound fractions of different size was studied.

The ground water samples were taken from four different locations, which were previously known to contain high concentrations of natural radionuclides. The ground water samples were filtered with five membranes with pore sizes ranging from 0.8 µm to 5 kD and retention of ^{210}Po by these membranes was determined. The same was done for ^{210}Pb with three membranes with pores between 0.45 µm and 5 kD. The percentage proportions of ^{210}Po and ^{210}Pb bound in various particle fractions are given in Figure 7 and 8.

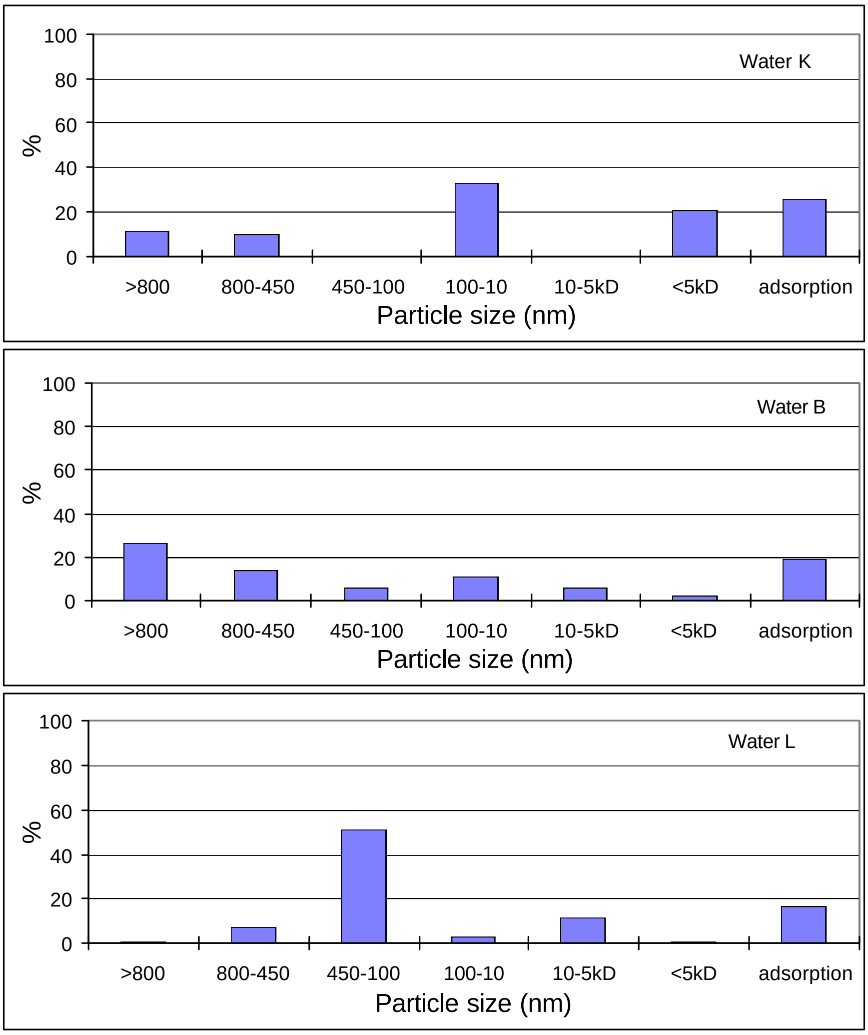

Figure 7. *Percentage proportions of ^{210}Po in the total activity bound in various particle size fractions from ground waters K, B and L.*

In waters B and I ^{210}Po and ^{210}Pb are mainly bound in particles with sizes greater than 0.45 µm, especially in water I this fraction containing ^{210}Pb comprises more than 80% of total activity. In water L and K, however, the intermediate size fraction, around 0.1 µm, containing ^{210}Pb is prevalent. ^{210}Po in these waters is more evenly distributed in various particle size fractions (Figures 7 and 8). Only in one water (water K), with relatively high NaCl concentration and rich in humus material, was a considerable fraction, about 20 % of both radionuclides found to be present in the soluble form, i.e.

passing through the membrane with the smallest pore size (5 kD). It was also found that large fractions of both radionuclides were adsorbed in the filtration system, filters and vessels. The fractions adsorbed on filters are also shown in these figures.

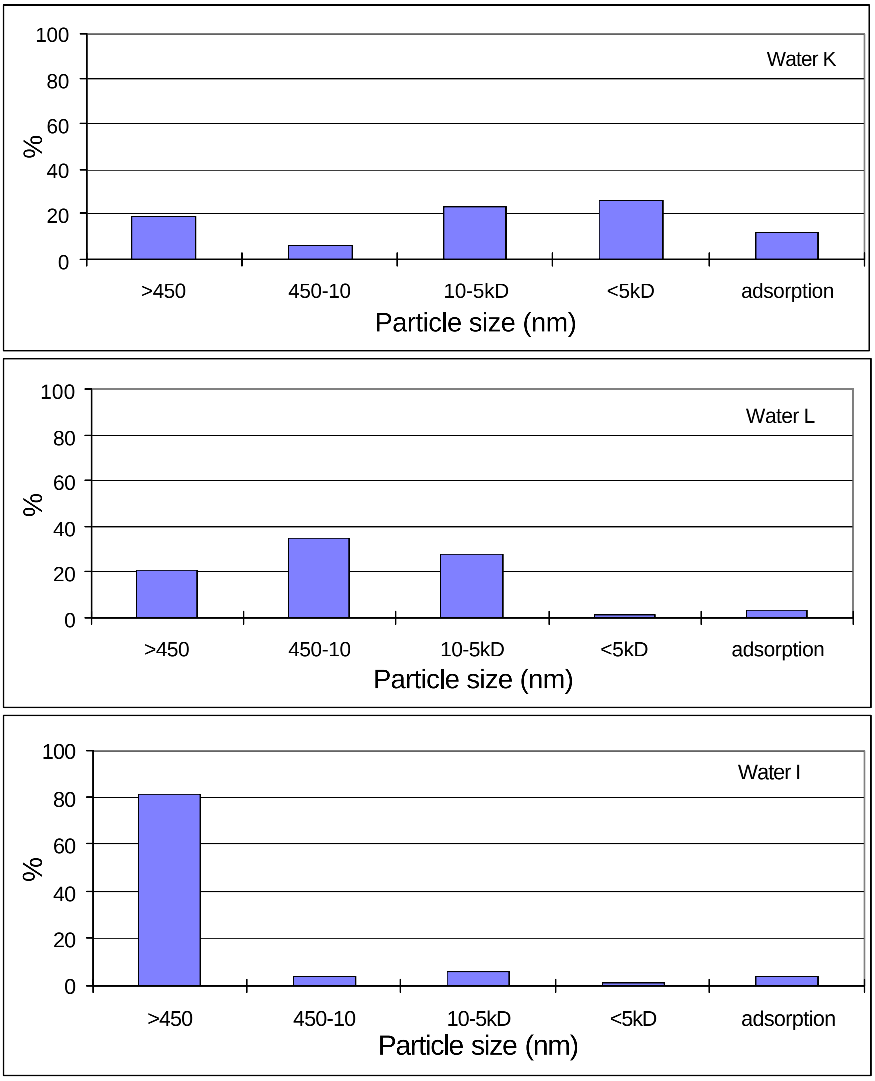

Figure 8. *Percentage proportions of* ^{210}*Pb in the total activity bound in various particle size fractions from ground waters K, L and I.*

One further objective of this study was to investigate the possible effect of the oxidation state of uranium on its speciation in ground water. The separation of the oxidation state U(IV) from the oxidation state U(VI) was carried out in two different ground waters. The ratio of the U(IV) form having a low solubility to the highly soluble U(VI) form and the radioactivity concentrations of the uranium isotopes ^{234}U and ^{238}U as well as the total uranium concentration were determined. The results of the uranium analyses are set out in Table XI.

Table XI. *The concentrations of U(IV), U(VI) and total uranium as well as the radioactivity ratio of* $^{234}U/^{238}U$ *in unfiltered drilled well water samples. The statistical error (1d) of radioassay is indicated.*

Sample	**^{238}U (mBq/l)**	**^{238}U (µg/l)**	**$^{234}U/^{238}U$**
Water K U_{tot}	500 ± 16	40.5 ± 1.3	1.71 ± 0.07
Water K U(IV)	10.5 ± 0.4	0.85 ± 0.04	1.83 ± 0.09
Water K U(VI)	312 ± 8	25.3 ± 0.6	1.63 ± 0.05
Water L U_{tot}	6720 ± 180	545 ± 15	1.28 ± 0.05
Water L U(IV)	179 ± 6	14.5 ± 0.5	1.27 ± 0.06
Water L U(VI)	6510 ± 180	528 ± 15	1.26 ± 0.05

The radioactivity ratio of U(IV) to U(VI) in the waters K and L were 0.034 and 0.027, respectively. Practically all uranium in both ground waters was in the highly soluble U(VI)– form. The ratio of $^{234}U/^{238}U$ is higher in water K than in water L. In both cases the ratio is >1. The solubility of ^{234}U from the rock to the ground water is higher than that of ^{238}U, which is due to the recoil energy formed by the radioactive decay of the ^{238}U isotope.

3.12 Disposal of Radioactive Wastes from Water Treatment Methods. Recommendations for the EC

When different kinds of treatment methods are used to remove natural radioactivity from drinking water, wastes containing natural radioactivity will be produced. The wastes are in liquid or solid form. Liquid wastes are produced when materials used to accumulate radioactivity are regenerated or backwashed. Solid wastes are formed in cases where regeneration or backwashing are not used or cannot be used, and when the materials are taken out of service.

GAC filters emit gamma radiation when they are in service. The higher the radon concentration and the larger the water usage, the more intense the external gamma dose rate around the filter. Furthermore, GAC filters also accumulate lead (^{210}Pb). In addition to retaining radon, GAC filters to some extent also retain uranium, radium (^{226}Ra), lead and polonium (^{210}Po).

Depending on the Fe- or Mn-removal system, high amounts of radionuclides may be accumulated by the equipment. Backwashing or regeneration at regular intervals, however, enables a safe daily use of these units because then radionuclides are rinsed out of the fixed bed and drained into the sewer. The regeneration interval is in most cases frequent enough to prevent this technique from causing a problem of waste disposal.

In connection with ion exchangers different operation principles and exchange materials can be utilised. Organic ion exchangers (resins) can usually be regenerated. The properties of many inorganic exchangers (mineral based) cannot be restored by regeneration and therefore they must be discharged after the exhaustion.

The radioactive wastes produced by membrane techniques are not accumulated into fixed matrices. The concentrate containing radionuclides, is constantly drained into the sewer as the unit operates. The concentrations of radionuclides in concentrate, however, are low and therefore are not considered as radioactive waste.

The water treatment methods that potentially produce radioactive wastes were identified. The amounts of radioactive wastes produced by different techniques were assessed on the basis of the average water consumption habits and the estimated concentrations of the radionuclides that are removed (Table XII).

Table XII. *The water treatment methods that potentially produce radioactive wastes and the estimated average amounts of the waste produced. The average was estimated for a family of three people consuming water 570 L/d (total consumption, POE) and 10 m^3/a (food and drink, POU).*

Technique	**Specification**	**Type of waste**	**U (mg/kg)**	**^{226}Ra (Bq/g)**	**^{210}Pb (Bq/g)**	**^{210}Po (Bq/g)**
GAC filtration	POE, carbon used for 3 a	solid	100	0.5–3	15–75	15–75
Ion exchange	POE, regeneration weekly	liquid	1–10	10–50	6–50	6–50
	POE, no regeneration, 1 a	solid	1000–5000	10–50	5–30	5–30
	POU, no regeneration, 1 a	solid	100–1500	1–5	0.2–2	0.2–2
	Pour-through, 100 L	solid	100–1000	0.2–1	0.05–0.2	0.05–0.2
Adsorptive techniques	POU or pour-through	solid	1–1000	0.2–50	0.05–50	0.05–50

A questionnaire was sent to all the Member Countries in order to gather information on the existing national regulations and guidelines on treatment and disposal of radioactive wastes produced by water treatment. The availability of national surveys on natural radioactivity in drinking water and estimates of population doses were also asked in the questionnaire (Table XIII). No answers were received from Belgium, Greece, the Netherlands and Portugal.

Regulations against a private person possessing material containing radioactivity have been issued in Austria and Sweden. In most countries solid wastes produced by water treatment can be disposed of at the municipal dumps and liquid wastes discharged into the sewer system. In some cases, however, this depends on the activity of the waste.

Table XIII. *The feedback from the questionnaire sent to all the Member States.*

Question 1 ***(Q1)****:"Is there a nation-wide or partly nation-wide survey on natural radionuclides in drinking water made in your country?"*

Question 2 ***(Q2)****:"Is there an estimate of the population dose due to natural radioactivity in drinking water made in your country?"*

			Maximum permissible concentration					Other information about natural radioactivity in drinking water
State	**Q1**	**Q2**	**^{222}Rn (Bq/L)**	**U (Bq/L)**	**^{226}Ra (Bq/L)**	**^{210}Pb (Bq/L)**	**^{210}Po (Bq/L)**	
Austria	yes	yes	-	7.4	0.123	-	-	-
Denmark	yes	no	-	-	-	-	-	No regulations
Finland	yes	yes	300	20	3	0.5	3	^{228}Ra: 2 Bq/L, effective dose $<$ 0.5 mSv/a
France	yes	yes	-	160 µg/L	1	-	0.1	^{3}H: 100 Bq/L
Germany	yes	yes	-	-	-	-	-	-
Ireland	yes	yes	-	-	-	-	-	No regulations
Italy	local surveys	no	-	-	-	-	-	No regulations
Luxembourg	under prep.	no	-	-	-	-	-	No regulations
Spain	yes	yes						Gross alpha 0.1 Bq/L, gross beta 1 Bq/L
Sweden	yes	yes	100	-	-	-	-	If ^{222}Rn$>$1000 Bq/L, unfit for consumption
U.K.	yes	yes	-	-	-	-	-	No regulations

4. MAIN ACHIEVEMENTS

4.1 Survey of Literature on Natural Radioactivity in Drinking Water and Treatment Methods in European Countries

The literature study presents the main hydrochemical processes which are responsible for the solution transport of natural radionuclides in water. The main areas for potentially elevated contents of natural radionuclides in European ground water are pointed out (Figure 9) and data about the contents in drinking, mineral, ground and surface waters of 17 European countries are presented.

Further, an extended literature overview on treatment methods suitable for removing natural radionuclides is given and results from pilot and full-scale studies are discussed. Finally, human health aspects are mentioned and nation-wide and internationally accepted regulations regarding natural radionuclides in drinking water are summarised.

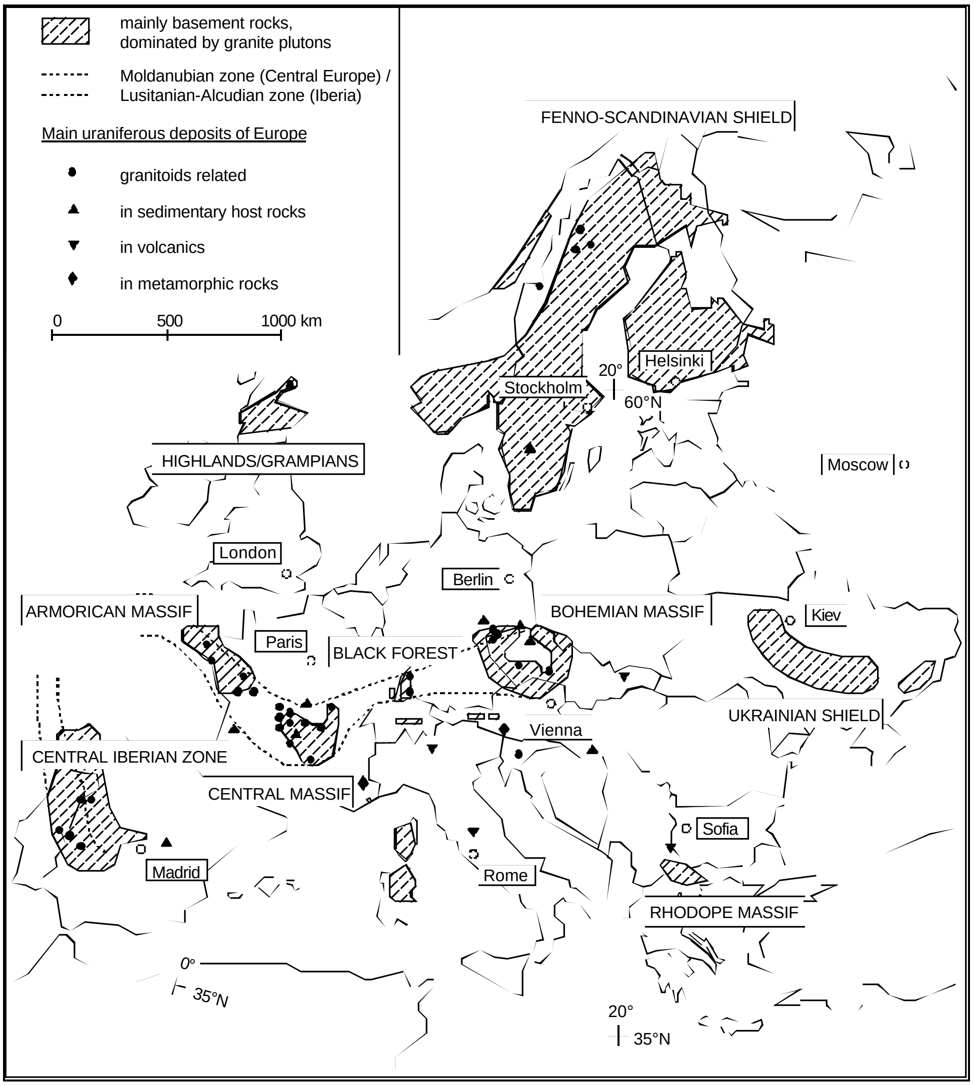

Figure 9. *Main uraniferous deposits of Europe and zones dominated by basement rocks as areas with potentially elevated contents of natural radionuclides in ground water.*

4.2 Intercomparison of Analysis Methods

The importance of having intercomparison exercises and proficiency tests accompanying the analytical work of the project is obvious from the improvement in the quality of the data converging from exercise to exercise. For radon the problems encountered in the first intercomparison run were overcome in later intercomparison runs where the data reported by the participating laboratories were in excellent agreement.

For uranium and radium there was also a clear improvement in the consecutive intercomparison runs. Moreover, laboratories not specialised in the radium analysis of water samples on a routine basis had a chance to adapt their methods in order to improve the quality of their results. The improvement can be attributed to the information gathered from the intercomparison runs, the analytical experience acquired in the course of the project as well as the extensive discussions about measurement methods going on at the meetings.

4.3 Definition and Classification of Different Water Types and Experimental Conditions

Two internal TENAWA reports ("Definition of Water Types" and "Experimental Conditions") were delivered; the content was accepted by all partners. The water types to be selected for tests as well as the experimental conditions were controlled using the reports delivered by the partners.

4.4 Removal of Radon by Aeration: Testing of Commercially Available Equipment for Domestic Use

The most efficient aerator in this study was "Radonett" manufactured by Sarholms Ab (4A). The removal rate of radon was also the best. "Radox" aerator made by Overcraft Oy (1A–1C) attained nearly as high an effective flow rate as "Radonett". The removal efficiencies were also good. The RF series sold by Oy WatMan Ab (3A–3C) attained generally good removal efficiencies but the removal rate and the effective flow rate were low. "Orwa" made by Vartiainen Oy (2A–2C) attained both poor removal efficiencies and low effective flow rates.

During the study, the technical reliability of the aerators was monitored. Several technical failures occurred. The most important factors that must be considered when installing an aerator, were found to be

- the type and model of the aerator should be selected according to the water consumption and radon concentration
- radon concentration in raw water may vary and therefore the aeration time should always be set a couple of minutes longer than needed at the time of sampling
- the volume of the pressure tanks should be large enough to avoid shortage of water during peak consumption
- storage tanks or “dummy wells” were found to be a good solution to guarantee sufficient water supply
- by installing a small pressure tank before the aerator a better removal efficiency, shorter aeration time and a possibility of by-passing the system is attained
- a system by-pass is essential in most cases
- integration of the aerator to the other treatment units should be done so that one control unit regulates all the system components
- ion exchangers and iron and manganese removal equipment should be installed before the aerator
- if no other treatment is applied, a sediment filter should be placed before the aerator to protect the solenoid valves
- the room where the aerator is installed should be cool, dark and equipped with a floor drain. The building materials should be water-resistant. The air used for the aeration should be clean and the exhaust air ventilated outdoors efficiently. The outlet of the ventilation channel should be designed in such a way that no freezing or developing of mould can occur.
- an aerator should be equipped with an overflow pipe so that in case of malfunction no water damage can occur.
- the manufacturer should provide customers with an operation and maintenance manual. An unequivocal description of the installation (taps, by-pass valves, air filters, etc.) should also be provided. The manual should include a section “troubleshooting” in case something goes wrong.

Another important result of this study was the development of a standard testing protocol. Previously used conventional tests do not provide enough information either about the effective capacity of the aerators or about the real removal efficiency. With the new protocol developed the aerators can be compared even-handedly. Also, malfunctions such as leaking solenoid valves can be detected.

A consumer guide was prepared. The guide is intended to be used by the water utility owner to enable one to define the problem and to evaluate the possible solutions in case the water contains excessive levels of natural radioactivity.

4.5 Removal of Radon by Aeration: Testing of Various Aeration Techniques for Small Waterworks

The study showed that only water aeration technology is able to produce extensive radon removal in waterworks. Other water treatment techniques were unable to remove more than 25% of radon. Venturi aeration equipment, installed in a German waterworks, removed from 70% to 80% of the water-dissolved radon. The disadvantage of Venturi aeration was that it causes high radon levels in the indoor air of the aeration room or reservoir.

Almost complete radon removal was achieved by shallow bed aeration. Additionally the process-air could be diverted without a greater effect on the radon content of the indoor air. At a packed tower column the process-air can also be diverted directly out of a waterworks building. The tested column in half-technical scale removed 85% of radon. At typical filling ring heights of two to three metres, as common in practical use, 95% can be expected.

Diffused bubble aeration combined with the spray aeration was efficient at removing radon in a new waterworks especially designed for the purpose. Diffused bubble aeration and spray aeration alike can be good alternatives to a packed tower aeration, especially in waterworks, where they can easily be combined with other existing water treatment processes. Water can be sprayed directly onto the filtration basins, which are needed in many treatment processes. Also, diffused bubble aeration can be easily applied in the existing basins. In such waterworks these two aeration methods are more economical than installing a packed tower aerator. The situation is the same when a packed tower is too high to be installed in an existing building.

Most of the various types of packed tower aerators removed radon very efficiently when installed in waterworks or tested in a pilot plant. Even small units applied in a number of waterworks were efficient enough to supply water to dozens of households. Various types of commercial aerators originally designed for radon removal in domestic use can also be efficiently applied in small waterworks.

The results from waterworks which apply aeration in their iron or manganese removal processes, indicate that most of the radon was also removed. Aeration can be improved easily if better radon removal is acquired.

The experiments showed that already low air-to-water ratios of five cause high radon removal efficiencies and that carbon dioxide and radon show very similar removal behaviour. This was proved by the pilot plant tests as well as by the field measurements from waterworks.

The physico-chemical and microbiological water qualities at waterworks where measurements were carried out, remained good. The various water treatment processes rather improved the qualities when iron, manganese and carbon dioxide were removed.

A waterworks guide was prepared. The aim of the guide is to provide basic information on different aeration techniques, which can be applied for radon removal in small waterworks.

4.6 Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of Radon

The results of this study were mainly in good agreement with those obtained in studies in the USA over the last 20 years. Radon removal efficiency was very high (>99.9%) at many test locations. It seems that GAC filtration can be applied to mitigate unacceptably high concentrations of radon in ground waters that are most typically found in Finnish and Swedish bedrock. The water types studied were

- water that is soft and low in mineral content
- iron- and manganese-rich water (Fe 0.7 mg/L, Mn 0.26 mg/L)
- humus-rich water (TOC 3.4 mg/L) and
- slightly saline water.

It is possible that high concentrations of uranium, and possibly organic matter, lower the adsorption rate of radon. Uranium, as a toxic heavy metal, is harmful to human health and therefore high concentrations (>0.1 mg/L) should always be removed from drinking water. The combination of an anion exchanger installed before a GAC filter, worked well and was capable of removing both uranium and radon efficiently. High concentration of iron and manganese and the sediment filters installed before a GAC unit had no effect on the performance of the GAC filters. The GAC units were technically reliable. No loss of hydraulic pressure or water leakage was reported.

The intensity of gamma radiation originating from GAC units in permanent use was high. With the proper shielding, instructions and placement of the unit, elevated doses to the residents can, however, be avoided. The water quality at the test locations remained good.

A consumer guide was prepared. The guide is intended to be used by the water utility owner to enable one to define the problem and to evaluate the possible solutions in case the water contains excessive levels of natural radioactivity.

Two commercial companies installed GAC filters at several test locations (Table III). Most GAC filters were installed as such, without having any pre-treatment units prior to GAC filtration. Two GAC filters were equipped with both a sediment filter and a backwash system and one GAC filter was equipped with a sediment filter. In addition, two test locations had a 21-litre anion exchange unit for removing uranium installed before the GAC filter. Flow meters and sampling taps for influent water were installed in most test locations. In Table III test location C(b) is the same household as test location C(a) but with a new filter combination and the GAC batch changed. All GAC filters operated under normal plumbing pressure in the down-flow mode.

Table III. *Installation data and the main water quality parameters in raw water from the first sampling at the selected test locations. Test locations marked with an asterisk (*) are vacation residences.*

Test location	BV (L)	Flow meter	Back-wash	Pre-filter	Anion exch.	^{222}Rn (Bq/L)	Fe (mg/L)	Mn (mg/L)	TOC (mg/L)	U (mg/L)
A	39	-	-	-	-	2 000	0.021	0.018	n/d	0.052
B	40	x	x	x	-	4 000	0.410	0.120	1.5	0.013
C(a)	39	x	-	-		3 000	0.016	0.064	2.3	0.21
C(b)	39	x	-	x	x	3 000	0.016	0.064	2.3	0.21
D	39	x	-	-	-	3 700	0.089	0.270	3.4	0.035
E*	40	x	x	x	-	910	0.032	0.011	1.1	0.017
F*	63	-	-	-	-	3 000	0.019	0.024	2.4	0.046
G	63	x	-	-	-	5 100	0.033	0.027	1.5	0.070
H	39	x	-	-	x	1 800	0.034	0.002	2.5	0.26
I	63	x	-	-	-	2 000	n/d	n/d	n/d	n/d
J	63	x	-	-	-	4 600	n/d	n/d	n/d	n/d
K	63	x	-	-	-	1 300	0.70	n/d	n/d	n/d
L*	63	x	-	x	-	5 800	0.16	0.066	2.1	0.007

n/d—not determined.

\- not installed.

At approximately three-month intervals sampling from influent and effluent was carried out. ^{222}Rn, U, ^{226}Ra, ^{210}Pb, ^{210}Po, gross-alpha, Fe, Mn, TOC, pH, temperature and heterotrophic plate count were monitored regularly. SiO_2, redox potential, O_2, CO_2, colour, $KMnO_4$, acidity, PO_4^{3-}, NO_3^- and NH_4^+ were occasionally determined. Radon removal efficiencies were calculated. Since the removal efficiency of radon depends on the bed size of the filter and the daily water usage, the rates of adsorption (independent of those parameters) were also determined. The rate of adsorption is utilised when studying the negative effects of water quality parameters on the adsorption. The rate of adsorption was determined by calculating the K_{ss} constants according to the first-order kinetics model:

(6) $$C_t = C_0 \cdot e^{-K_{ss} \cdot t}$$, where

C_t is the ^{222}Rn concentration in effluent in Bq/L,
C_0 the concentration in influent in Bq/L,
K_{ss} the adsorption-decay steady-state constant in h^{-1}, and
t is the empty bed detention time. It is defined as

(7) $$t = \frac{V_b}{Q}$$, where

V_b is the volume of the GAC bed in L and
Q is the average volumetric flow rate in L/h.

Dose equivalent rates of gamma radiation were measured on the surfaces of the GAC filters and at different horizontal distances from the filters. Attenuation of gamma radiation in the vicinity of the filters was studied applying lead, aluminium, concrete and water shields. Two batches of spent GAC were investigated in order to determine the activity of radionuclides accumulated in the carbon. The spent carbon was either cored or homogenised, then dried and measured with an n-type HPGe detector.

Radon was removed efficiently by most filter combinations (Table IV). Six units out of thirteen were capable of removing more than 99.9% of radon. The lowest removal efficiency observed was approx. 90%.

Table IV. *The ranges of radon concentration in influent and effluent during the operating period of the filters, the radon reduction at the most recent sampling and the corresponding treated water volume (in bed volumes).*

Test location	^{222}Rn Influent (Bq/L)	Effluent (Bq/L)	Time in service (months)	Water treated (BV)	Radon reduction(%)
A	1 900–2 850	1.2 – 41	27	~8 000	98.5
B	3 500–4 200	12 – 190	11	5 350	98.9
C(a)	2 600–2 700	150 – 340	13	4 050	92.9
C(b)	1 850–3 100	<0.4 – 31	11	4 460	98.6
D	2 750–4 100	<0.4 – 15	23	3 030	> 99.9
E	910–1 100	<0.4 – 3.1	8	150	> 99.9
F	1 700–3 000	0.9 – 2.2	13	~400	> 99.9
G	5 100–7 400	<0.4 – 2.2	23	3 790	> 99.9
H	1 600–2 200	1 – 37	21	4 860	97.8
I	1 300–2 200	1 – 5.3	15	1 501	99.7
J	4 100–4 600	1.2 – 2.6	17	4 440	> 99.9
K	1 300–1 600	<0.4 – 0.5	23	5 550	> 99.9
L	3 040–6 400	45 – 99	9	389	98.5

The calculated K_{ss} constants differed significantly between different test locations, but remained quite constant at an individual test location. The best adsorption rate was obtained at test location B (3.4 h^{-1} on average) while test location I had the poorest adsorption rate (1.1 h^{-1} on average). The effect of water quality on the rate of adsorption was studied by plotting the K_{ss} constants against different water quality parameters (gross-alpha, U, Fe, Mn, TOC, $KMnO_4$, HPC 22°C, HPC 35°C and pH). Only gross-alpha, uranium and TOC had a clear negative correlation with the calculated K_{ss} constants (Figure 5). These substances are also partly removed by GAC filtration, which suggests that they have the potential to clog the micropores of GAC where radon removal occurs.

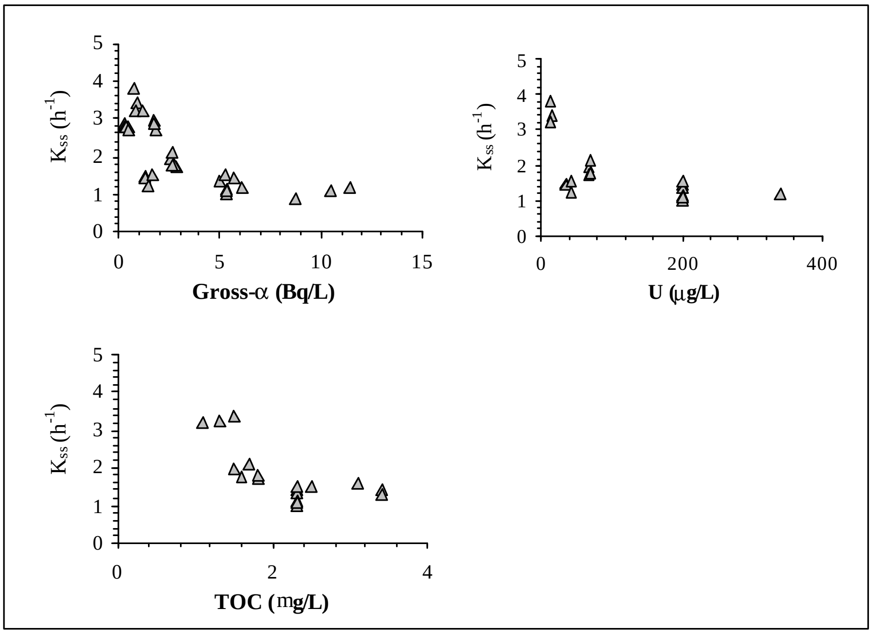

Figure 5. *The rate of adsorption (K_{SS} constant) as a function of gross-alpha, uranium and total organic carbon (TOC) concentration of the influent. A negative correlation was obtained.*

To investigate the effect of uranium on radon removal in more detail, the GAC filter at test location C(a) was loaded with a fresh batch of GAC. An additional sediment filter and an anion exchange unit (removes most of the uranium and some of the humic substances) were installed before the GAC filter. Following this installation, the filter removed nearly 99% of the radon and the K_{ss} constant increased from value 1.2 h^{-1} to 2.8 h^{-1}. It is evident that the interfering substance in the water was some anionic species, most probably uranium or humus.

Iron was usually removed efficiently by GAC filtration (>50%). High concentrations were removed most effectively. The concentration of manganese did not significantly change during filtration. Organic matter was removed fairly well when less than 1 000 BV's was treated. The reduction efficiency decreased gradually and after 2 000 BV's reduction efficiency was less than 70%. The pH value may increase for a few weeks after a new filter has been commissioned. Turbidity decreased and the correlation between iron reduction and decrease in turbidity was observed. Electric conductivity increased for a couple of weeks after a new filter had been commissioned. No significant changes were observed later on. The concentration of phosphate (PO_4^{3-}) may increase significantly when less than 400 BV's have been filtered. No significant changes were observed for alkalinity, total hardness, nitrate (NO_3^-), ammonium (NH_4^+), redox potential, silica (SiO_2) and heterotrophic plate counts (HPC in 22°C and 35°C).

Along with radon, GAC filters were capable of retaining various amounts of uranium, radium, and radon progeny. The activity of radionuclides in spent GAC determined gamma-spectrometrically indicated 100% retention of ^{210}Pb formed in the decay of radon. Therefore, spent GAC batches may contain several hundred kilobecquerels of ^{210}Pb. The specific activity of other radionuclides was low.

Radon and its daughters build up in the GAC unit. The short-lived daughters of radon (^{218}Po, ^{214}Pb, ^{214}Bi, and ^{214}Po) come into secular equilibrium with radon in about four hours. ^{214}Pb, ^{214}Bi are beta emitters but also emit gamma photons. Because the daughter nuclides are totally retained in the GAC bed, the filter becomes a source of gamma radiation.

The external gamma dose rate depends on the radon concentration in the influent water, on daily water usage, and on the dimensions of the GAC filter. Due to these factors gamma dose rates varied at different test locations. At two test locations the GAC filter was placed in a cupboard, inside the house. Therefore, radiation shields were installed. The filter was encased in three 1mm-thick sheets of lead. Lead attenuated the gamma radiation efficiently. At the other test locations GAC filters were installed either in a cellar, in a technical room, or in a separate shed where the shields were not needed.

During this study no breakthrough of radon occurred at any of the test locations. Theoretically, a GAC filter is constantly regenerated in respect of radon due to radioactive decay, and can therefore remain in service for several years. When competitive substances occupy the active sites of the carbon, radon removal efficiency may decrease. This, however, largely depends on the other water parameters.

3.7 Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of U, Ra, Pb and Po

The objective of this study was to investigate the removal efficiency for natural radionuclides in adsorption processes by filter systems based on different activated carbon types. Measurements were focused on the following adsorption parameters:

- adsorption capacity
- adsorption velocity
- influence of the granular size
- interaction with ions (variation of hardness)
- influence of the pH value
- poisoning of active centres.

The study consisted of laboratory experiments and field research. The laboratory experiments started as batch experiments with seven different activated carbons derived from hard coal, brown coal, peat, wood and coconut. The carbon type that exhibited the best adsorptive properties for the radionuclides was selected for column experiments.

The field research was performed on the GAC units that were studied for radon removal. For the field tests test locations were selected such that the water types most typically found in Finnish bedrock were covered. The effect of water quality on the performance of the GAC filter was also studied. Other aspects considered in the field experiments were the changes in water quality due to filtration and the microbiological quality of treated water.

Batch experiments were carried out with spiked water. Two water types with different degrees of hardness were used. Seven different coal types were studied. The granular size was =0.1 mm for all of them. The experiments showed that lead and polonium were quantitatively adsorbed by every coal type studied. Significant differences appeared in batch experiments with uranium and radium. One coal type adsorbed uranium from 97% to 100%. The lowest adsorption efficiency noted was approximately 50%. All the other coal types were in the range from 70% to 85%. For radium the highest adsorption efficiency was achieved with one coal type, which adsorbed radium nearly totally. The lowest adsorption capability noticed was 70%. All the other coal types were in the range from

86% to 94%. The experiments indicated high efficiency of activated carbons in the removal of radionuclides from water.

The granular size of the activated carbon had a tremendous effect on uranium and radium adsorption, which was reduced substantially with increasing granular size. For lead and polonium only a slight influence in the same direction is recognisable.

As a standard water type a pH value of 7 and a water hardness of 5.0°dH were adjusted. To investigate the influence of water hardness on adsorption efficiency a second water type with a hardness of 2.5°dH was involved in a test series at the same pH value. In comparison with the standard type an increase of adsorption efficiency was found for uranium, indicating an interaction between various ions in the adsorption process. For radium, too, an increased adsorption efficiency with the soft water type was indicated. For lead and polonium no difference was noticeable. For both water types nearly total adsorption was achieved.

Three different pH values were adjusted: pH 6, pH 7 and pH 8. Lead and polonium were not effected by pH value changes. Measurement for uranium ions indicated a strong but not uniform influence of the pH value. For radium, too, no uniform influence was detectable.

A water type with a DOC content of 1.5 mg/L was used to show the influence of organic contaminants in the adsorption process. For lead and polonium no influence could be detected. For uranium and radium a significant reduction of adsorption for most coal types was found.

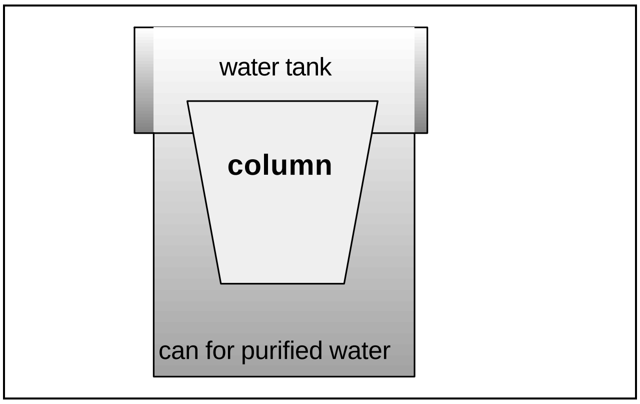

Figure 6. *Filter system for the removal of radionuclides from drinking water.*

For the column experiments a commercially available filter system was used (Figure 6). The experiments were focused on the influence of granular size, on interaction with ions and on poisoning of activated centres. The previous experiments showed that the pH value did not have a significant influence on the adsorption capacity. The batch experiments showed that even small variations in granular size influence adsorption capacity. Large differences in granular size between 0.8–1.4 mm and 0.5–0.8 mm for polonium and radium were noted. When the granular size was degraded of 0.2 mm, the flow rate dropped to 3 L/h. For a granular size between 0.4–0.8 mm the flow rate was 4 L/h. As a result of the above-mentioned, a granular size of >1 mm and 0.5-1 mm was adopted. The flow rate of >1 mm was 30 L/h and for 0.5–1.0 mm it came to a total of 15 L/h.

Column experiments were carried out with the two granular sizes. Waters exhibiting two different levels of water hardness (10.066 °dH and 2.517 °dH) and two concentrations of DOC, dissolved organic compounds (0 and 1.47 mg/L) were used. It is clearly seen that smaller granular size has greater adsorption capacity than larger granular size (Table V). Uranium was adsorbed approximately 30% more efficiently from water that was soft, for the other nuclides the effect of water hardness was smaller (Table VI). The adsorption capacity decreases when the DOC concentration increases (Table VII).

Table V. *Influence of granular size for a water hardness of 10.066°dH.*

Granular size (mm)	**Adsorption (%)** **U**	**Ra**	**Pb**	**Po**
>1	37.2	33.6	61.2	37.1
0.5–1	57.4	83.7	93.2	66.9

Table VI. *Influence of water hardness, with a granular size >1 mm and 0.5-1 mm.*

Water hardness **(°dH)**	Size >1 mm, adsorption **(%)**				Size 0.5–1 mm, adsorption **(%)**			
	U	Ra	Pb	Po	U	Ra	Pb	Po
10.066	37.2	33.6	61.2	37.1	57.4	83.7	93.2	66.9
2.517	68.1	38.3	86.9	56.9	85.0	85.2	100	85.9

Table VII. *Influence of DOC (1.47 mg/L) on the adsorption process, with a granular size >1 mm*

Water Type	Size >1 mm, adsorption **(%)**				Size 0.5–1 mm, adsorption **(%)**			
	U	Ra	Pb	Po	U	Ra	Pb	Po
standard	68.1	38.3	86.9	56.9	85.0	85.2	100	85.9
with DOC	29.4	28.6	65.9	55.0	62.9	73.3	95.8	100

The test locations selected for field research in Chapter 3.6 were also studied in terms of uranium (^{238}U, ^{234}U), radium (^{226}Ra), lead (^{210}Pb) and polonium (^{210}Po) removal. At seven test locations the radionuclides were determined by radiochemical separation (Table VIII), at the rest gross-alpha screening (the total activity of U, Ra and Po, ^{226}Ra separately) was applied (Table IX).

***Table VIII.** Concentration of U, ^{226}Ra, ^{210}Pb and ^{210}Po in influent and effluent at the test locations where regular sampling was carried out. The volume of water that had been treated is referred to as bed volumes (BV): One BV corresponds to the volume of the GAC material inside the filter.*

Test Location	BV	U (µg/L)		^{226}Ra (Bq/L)		^{210}Pb (Bq/L)		^{210}Po (Bq/L)	
		inf.	eff.	inf.	eff.	inf.	eff.	inf.	eff.
B	741	12.9	8.5	0.20	0.04	0.283	0.009	0.122	0.007
	1786	14.8	14.8	0.17	0.07	0.371	0.014	0.102	0.015
	3518	13.0	13.7	0.20	0.07	0.328	0.005	0.154	0.012
	5348	–	–	0.20	0.10	0.660	0.005	0.454	0.013
C	431	207	181	0.21	0.15	0.375	0.040	0.266	0.045
	1274	202	212	0.23	0.22	0.640	0.045	0.126	0.042
	2670	200	211	0.25	0.22	0.228	0.031	.109	0.051
	4051	–	–	0.24	0.26	0.132	0.015	0.104	0.033
D	202	–	15.9	–	0.40	–	0.117	–	0.027
	528	35.9	12.8	0.28	0.24	0.354	0.234	0.169	<0.002
	1069	42.9	31.8	0.26	0.27	0.313	0.195	0.520	0.045
	1565	–	–	0.54	0.43	0.477	0.162	0.134	0.039
E	41	18.9	1.4	0.05	<0,01	0.461	0.003	0.416	0.003
	151	21.7	0.2	0.05	<0,01	0.014	0.001	0.033	0.006
F	~150	47	34	0.22	0.07	–	–	–	–
	~400	115	112	0.13	0.11	0.075	0.017	0.137	0.047
G	75	70	40	0.30	0.11	–	–	0.455	0.018
	555	67	65	0.32	0.25	0.517	0.149	0.461	0.043
	903	67	68	0.32	0.26	0.616	0.151	0.360	0.031
	1586	–	–	0.29	0.26	0.451	0.200	0.206	0.047
L	23	–	–	0.19	0.01	0.417	0.085	1.92	0.133
	181	6.5	0.3	0.14	0.14	–	–	–	–

– not determined

Table IX. *Gross alpha and ^{226}Ra concentrations in influent and effluent at the test locations where regular sampling was not performed.*

Test Location	**BV**	**Gross-a (Bq/L)**		**^{226}Ra (Bq/L)**	
		influent	**effluent**	**influent**	**effluent**
I	142	6.85	5.90	0.29	0.19
	509	6.09	5.51	0.19	0.20
	878	10.6	8.12	0.23	0.25
	1 501	8.78	9.81	0.19	0.17
J	943	1.64	1.01	0.09	0.06
	1 649	1.81	1.54	0.08	0.07
	3 434	1.73	1.45	0.08	0.07
	4 438	1.80	1.03	0.09	0.07
K	184	0.58	0.23	0.08	0.07
	1 656	0.45	0.33	0.15	0.07
	3 180	0.38	0.20	0.14	0.11
	4 087	0.40	0.25	0.11	0.11
	5 545	0.38	0.39	0.13	0.09
L	23	2.32	0.13	0.19	0.01
	181	2.63	0.18	0.14	0.14
	389	1.67	0.46	0.29	0.26

\- not determined

Efficient reduction of uranium was obtained only when less than 200 BV's of water was filtered, though most filters showed a low reduction even then. There seemed to be no particular breakthrough volume for uranium: rather, the retention decreased gradually. When a large amount of water had been treated, the uranium concentration in the effluent was the same or slightly higher than in the influent.

The adsorption efficiency for radium (^{226}Ra) varied considerably. Two of the filters removed radium fairly well (from 67% to 53%). Radium mostly occurs as a hydrated cation in ground water. Part of the retention observed, however, may be due to the complexes which radium can form with humus and fulvic acids because no breakthrough could be observed. Some retention may also occur by adsorption onto ferric hydroxide precipitates that are formed in the filter vessels during filtration. Ion exchange reaction may also be possible. The best adsorption was observed at the test location where the highest concentrations of iron occurred.

Lead (^{210}Pb) was removed quite efficiently (from 80% to 100%) at two permanent residences and two vacation residences. At one permanent residence the removal efficiency was only fair, from 30% to 60%. Polonium removal was mostly over 80%. Lead, as well as ^{210}Po, is readily adsorbed on particles, surfaces and colloids. Therefore, it can be expected that the mechanism by which these radionuclides are removed is particle filtration. The ratio between particulate species and dissolved species may vary in natural waters, which explains the different removal efficiencies obtained.

3.8 Removal of Radioactivity by Methods Used for Fe- and Mn-removal from Private Wells

The main aims of this study were to find equipment which is able to remove natural radionuclides simultaneously with iron and manganese and to find the highest concentrations of these radionuclides which can be removed.

Most of the iron and manganese removal equipment commercially available on the Finnish market was tested. The commercial iron and manganese removal equipment is based on three main principles:

- aeration-filtration
- greensand filters regenerated with $KMnO_4$
- ion exchange

All iron and manganese removal units are installed so that they treat all household water (point-of-entry). They are regenerated or backwashed at certain intervals depending on the quality of the effluent water and on daily water usage.

Fourteen test locations in Finland and six in Sweden were selected for field tests. The criterion for selection was the adequate concentration of natural radionuclides in the water and the possibility of sampling raw and treated water separately. The concentration of radon, uranium, radium, lead and polonium in influent and effluent was determined two or three times at the Finnish test locations and twice at the Swedish ones. The sampling interval was 4–10 months. In addition to the radionuclides, pH, electric conductivity, $KMnO_4$ value and the concentration of iron and manganese were analysed once at the test locations in Finland and twice in Sweden. External gamma dose rates on the surface of the filter were also measured.

The removal efficiencies for the different radionuclides varied within a large range. For radon, aeration-filtration was the most efficient (reduction from 12% to 89%). Uranium and radium were best removed by ion exchange techniques (reduction from 50% to 99%) when both anion and cation resins were applied. Removal of lead and polonium varied within a large range by various equipment mainly due to their speciation.

With the aim of improving the removal efficiency of radionuclides, alterations were made in two units in co-operation with the company. The company added new carbon-based and more oxidising masses to the filters studied. The radon removal efficiency of one type of equipment improved on average from 30% to 80%. In the other type of equipment the improvement was on average from 35% to 65%.

The aeration-filtration equipment removed from 83% to 98% of the iron and manganese. Organic matter was usually not removed by the aeration-filtration units, although sometimes fair removal rates (from 39% to 45%) were recorded. In the case of the greensand filters regenerated with $KMnO_4$, iron removal was efficient (from 67% to 99%), but most of the units failed to remove manganese.

Cation exchangers removed iron and manganese efficiently (from 77% to 99%). Organic matter was removed only when anion exchange resin had been added to the resin bed. Cation exchange increases the corrosiveness of the water. Since Ca and Mg ions are removed, the water usually becomes too soft. Therefore, re-hardening is nearly always necessary. If anion exchange resin is also used in the exchanger, the chloride concentration in the treated water increases and thus also amplifies the corrosiveness of the water.

3.9 Removal of U and Po from Private Ground Water Wells Using Anion Exchange Resins and Removal of Ra and Pb from Private Ground Water Wells Using Cation Exchange Resins

An ion exchange reaction may be defined as the reversible interchange of ions between a solid phase (the ion exchanger or ion exchange resin) and a solution phase, the ion exchanger being insoluble in the medium in which the exchange is carried out. The exchange unit can be installed as a point-of-entry, point-of-use or small pour-through unit.

raw water is very important in this context. The combined effects of the environment of the installation, for instance indoors in a warm cellar, the material of the equipment, for instance transparent or semi-transparent plastic, the technical design of the system, the quality of the air that is mixed with the water and the quality of the raw water. All these are factors that affect the hygienic quality of the water treated. More research is needed to investigate the risks involved.

5.5 Removal of Radon by Aeration: Testing of Various Aeration Techniques for Small Water Works

The investigations showed that aeration is a highly effective method for removing radon from water. Removal efficiencies of more than 98% can be achieved, for example, with a fine bubble shallow bed aerator. Various types of aeration equipment are manufactured. All of them benefit from the same physical principle: gas exchange takes place at the interface of the phases of air and water. Therefore, each aeration method intends to create as large an interface as possible. The usability of a certain type of aeration equipment for removing radon, as well as CO_2, is very much dependent on several operation parameters, especially the amount of water to be treated, the available space and the degassing target. Most aeration facilities can be constructed to achieve radon removal efficiencies of more than 95% or even more than 99%. In most modern aeration facilities, where an active use of air takes place, high gas exchange rates are mainly a question of the throughput of air, which means a question of operation costs.

It was further recognised that radon and carbon dioxide show a very similar removing behaviour during aeration, which can be explained by the similar Henry's law constants for both gases (radon: $2.26 \cdot 10^3$ bar and CO_2: $1.51 \cdot 10^3$ bar; at 20°C water temperature and atmospheric pressure). Therefore, it is possible to estimate the radon removal efficiency of aeration equipment from its carbon dioxide removal efficiency. The latter has to be known by the manufacturer, since water aeration is a widespread treatment method for the de-acidification of water.

Finally, the study showed that water aeration is a very effective tool for radiation protection in waterworks. By operating water aeration equipment it is possible to reduce the radon degassing potential (from the treated water into the air) to a minimum and to reach moderate indoor air radon levels. To achieve this, it is necessary though that the process-air is led out of the aeration equipment and out of the waterworks completely.

5.6 Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of Radon

GAC filtration can be considered an inexpensive and easy way of mitigating high concentrations of radon in household water.

The longevity of a GAC batch was not discovered, because most filters exhibited constant removal efficiency for radon throughout the study. Therefore, no recommendations regarding the effective lifetime of a GAC batch can be given.

It was obvious that some anionic species reduced the adsorption rate of radon on GAC. According to the results, this could be either humus or uranium. The data, however, were too limited. At present there are some 50 GAC filters installed for radon removal in Finland. In order to give recommendations concerning the maximum levels of the interfering substances more water quality data are needed from these filters.

One of the main concerns in applying GAC filtration in domestic use is the external gamma radiation that can cause radiation exposure for the residents. An external dose rate as measured on the surface of a GAC unit installed in permanent use could exceed the normal background level even by a factor of one thousand. With proper shielding, instructions and placement of the unit in a non-residential area, elevated doses to the residents, however, can be avoided.

In order to minimise exposures different types of radiation shields have been studied. Lead attenuates gamma radiation most efficiently. A lead shield, however, may be expensive and it is made of toxic metal, which must be considered a potential health risk. Bricks and concrete can be applied, but the thickness of the shield must be considerably greater than for lead. A water jacket can be built. Water attenuates gamma rays, and is cheap. However, residential radiation exposure cannot always be eliminated sufficiently, especially when the influent radon activity is high. Therefore radon removal applying GAC filtration often remains a viable treatment method only when the radon concentration is low.

5.7 Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of U, Ra, Pb and Po

When considering removal of uranium, radium (^{226}Ra), lead (^{210}Pb) and polonium (^{210}Po) with activated carbon the type of carbon should be selected based on its adsorptive properties for these radionuclides. Activated carbons exhibit high non-polar capacities for hydrophobic substances such as radon and many organic contaminants. However, their polar properties are usually very limited. Therefore they remove inorganic substances and cations, such as heavy metals, only fairly well. A possible solution for the simultaneous removal of radon and the long-lived radionuclides could be the carbon-mineral adsorbents. The matrices of these adsorbents consist of both active carbon and mineral adsorbents (SiO_2, Al_2O_3, etc.) and show good mechanical properties. Furthermore, these adsorbents usually have better adsorptive properties than each individual component separately.

The mean removal efficiency of uranium, radium, lead and polonium in the field experiments is generally not as good as in the laboratory experiments. In the field tests the removal of uranium and radium decreased gradually with the amount of water treated and the removal of radium was a little higher than that of uranium. The results of polonium and lead from the laboratory and field tests agree much better than for uranium and radium. The reasons to the observed differences have not been fully analysed, but they can be explained partly by the amount of water treated and also by the chemical speciation, which may have the greatest effect.

During the TENAWA project speciation studies were carried out. The differences between the laboratory and field experiments in this study can be explained to some extent by the results from these speciation studies. During these studies filtration experiments were made to find out if uranium, radium, lead or polonium occur in ground waters either as ionic compounds or bound to various sizes of particles.

The results indicated that uranium and radium occur mainly as ions. Because lead and polonium were mainly bound to particles they can be removed from water by utilising adsorption into GAC filters. Correspondingly, uranium and radium should be removed predominately by ion exchangers. These observations are in good agreement with the results obtained by ion exchange experiments carried out during the TENAWA project. It should also be noted that the Finnish ground waters are still softer than any model water used in the lab tests.

However, the variation of the adsorption values obtained in the field experiments indicate that GAC filtration is not very suitable for the adsorption of natural radionuclides, except radon, which is retained as a noble gas very efficiently, even after large volumes of filtered water.

5.8 Removal of Radioactivity by Methods Used for Fe- and Mn-removal from Private Wells

There are still a few questions that remained unanswered. The physico-chemical conditions during the filtration should be examined in greater detail. For example, the aeration-filtration equipment contain various types of masses which have different retention properties. Therefore, the accurate composition of the masses added in the filtration layers need to be known in order to evaluate the results more reliably. At some test locations sampling needs to be continued to discover why the change of masses affected the removal rates.

Also the reduction of lead and polonium varied in a large range. The reason is not know exactly but it may be due to the speciation. Recent studies performed in Finland have indicated that lead and polonium occur in waters mainly adsorbed to various sizes of particles and not so much as soluble compounds. Thus lead and polonium would preferentially be removed by methods used for removing particles rather than by ion exchange.

5.9 Removal of U and Po from Private Ground Water Wells Using Anion Exchange Resins and Removal of Ra and Pb from Private Ground Water Wells Using Cation Exchange Resins

Ion exchange is a proper method for the removal of radium and uranium. Strong basic anion resins for the removal of uranium and strong acidic cation resins for radium removal performed best. The efficiency for lead and polonium varies a great deal, since most of these nuclides are supposed to be particle bound in natural waters and therefore no ion exchange process in the real sense but adsorption to the resins is responsible for their reduction. Therefore the reduction of lead and polonium is a welcome side-effect of uranium and radium removal but ion exchange is not the technology of choice for their removal.

The main disadvantage of cation exchange resins in the sodium form is the more or less total removal of hardness simultaneously with radium. This can be avoided by using resins in the calcium form. For the application of the regenerant $CaCl_2$ in commercially available systems changes in design are necessary. Other influences on water quality which were observed are a decrease in turbidity, phosphate, sulphate and nitrate with anion resins and a reduction in iron mainly with cationic resins. The pH value and the concentration of competing ions had an important influence on the possible run-length of the ion exchangers and must be considered when fixing the period of time between two regeneration procedures. Hygienic deterioration of the water was detected in some cases and cannot be excluded.

No remarkable dose to the residents caused by the treatment systems was observed when the equipment was properly located in the house. But national regulations regarding the handling of waste and the permitted accumulation of radioactivity on the filters may limit the applicability of this technology for private homes.

5.10 Removal of U, Ra, Pb and Po with Adsorptive or Membrane Filters.

By RO and NF systems liquid waste—the retentate—is produced. Due to the fact that no additional chemicals are necessary, the retentate is merely a more concentrated form of the raw water. Concerning radioactivity the mixing of treated water (used in households, low radioactivity) and retentate (high radioactivity) should in sum result in household waste water with the original natural radionuclide concentration.

Because of the increased raw water volume necessary for producing drinking water, membrane technology—if in widespread use—could become a problem in the case of limited water resources and for the capacity of waste water treatment plants if retentate is not alternatively used (e.g. for flushing the toilet).

The experiments showed that part of the removed radionuclides is adsorbed in the treatment units. Depending on national legislation used filter cartridges or membranes have to be handled as ordinary household waste or as low radioactive waste. As a result this can be a key economic question for the use of such treatment devices.

The installation and maintenance of POU systems should be possible without special skills whereas with POE systems this should be done by professionals. The regular use of the units is important because otherwise the membranes would be destroyed.

The reduction of water constituents can be a disadvantage for the consumer of drinking water which is treated by RO, because it is not advisable to drink water which is almost completely de-mineralised. After treatment it would be preferable to have slight water re-hardening.

In natural water the uranyl carbonate complexes $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ and, if phosphate is present, the uranyl phosphate complex $UO_2(HPO_4)_2^{2-}$ are mainly responsible for the mobility of uranium. Below pH 5, the pure uranyl cation UO_2^{2+} is also important. Those five uranium species have been generated in model waters and their rejection at six NF membranes and two open RO membranes was determined in several experiments.

The results show that the uranium removal from water at the six tested NF membranes was mainly between 90% and 98%. Especially the three divalent and multivalent uranyl anion complexes $UO_2\ (HPO_4)_2^{2-}$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ were mostly removed up to 95% or more. Those three complexes are the predominant uranium species in natural water above pH 4. The uncharged uranyl carbonate complex, $UO_2CO_3^0$, that predominates in phosphate-free water between pH 5 and 6.5, was also removed to about 95% in most cases. Besides, the rejection of the pure uranyl cation at pH 3.2 was from 87% to 93%. The high rejection of these five uranium compounds is a first sign that uranium can be removed quite effectively from water by NF membranes. This seems to be valid over a wide range of hydrochemical settings, even in very acidic waters.

The experiments with the extraordinary high uranium concentration of 10 mg/L showed no major difference in the removal efficiencies of the membranes, compared to the 1 mg/L experiments. Therefore, clearly worse removal efficiencies are not to be expected during concentration processes at membranes, which will take place in the case of a higher recovery. Further, there seems to be no clear effect on the uranium removal efficiency due to the presence of a high number of competing ions in the water. This was shown by the experiments with high and low sulphate concentrations.

The rejection results of the three NF membranes (out of 6) studied showed quite similar results: uranium rejection from 95% to 98% and rejection of other water constituents (phosphate, bicarbonate and electrical conductivity) from 75% to 97%. One membrane rejected uranium slightly worse (from 91% to 97%) and other water constituents slightly better (from 80% to 98%). One membrane also removed uranium effectively (from 95% to 98%), but the rejection of other water constituents was only from 45% to 95%. One of the membranes studied had a uranium rejection from 81% to 98% and the rejection of other water constituents from 40% to 80%.

Beside the six NF membranes two RO membranes were tested for comparison. As was expected, these membranes rejected both uranium (from 98% to 99.5% at pH 5 to 8.3) and other water constituents (from 93% to 99.5%) more effectively than the NF membranes.

Finally, the amount of organic uranium species can be estimated, since several authors assume that a certain part of uranium mobilised in water might be due to organic compounds. It can be estimated that the rejection of organic uranium compounds would not be lower than the rejection of the compounds investigated. The reason is that any organic uranyl species, whether anionic, cationic or uncharged, would surely be bigger and heavier than the inorganic uranyl compounds investigated. The molecular weight of the compounds investigated, however, was the main factor for the quite high rejection at all membranes. This is indicated by the similarity of the results of the uranium removal efficiencies in all experiments, without depending on the charge of the compounds. And indeed, even the molecular weight of the lightest uranium compound, the pure uranyl cation, UO_2^{2+} (270 Dalton), is already above the typical molecular weight cut-off (MWC: weight of uncharged organic molecules which are rejected practically completely) of NF membranes. The molecular weight of $UO_2(HPO_4)_2^{2-}$, for example, is 460 Dalton. The typical MWC of NF membranes is about 250 Dalton.

5.11 Speciation of U, Ra, Pb and Po in Water

The removal of uranium, radium, lead and polonium from drinking water depends on their speciation. The speciation of radionuclides in drinking water requires information as to their physico-chemical form in the water phase. For removal of these nuclides knowledge of their speciation in ground water is necessary. It is important to know in which physico-chemical form the radionuclide exists in ground water and how different factors affect its speciation.

Under oxidising conditions uranium exists mainly as its hexavalent state while in reducing condition U(IV) is the predominant oxidation state. U(VI) is present in slightly acid ground waters mainly as UO_2^{2+}. It forms strong complexes with carbonate and hydroxide ions. Uranyl ion is also known to form stable complexes with dissolved organic matter, in the form of humic and fulvic acid. Uranium can also form strong complexes with phosphate, fluoride and sulphate, when these anions are present.

Radium is most frequently found as hydrated Ra^{2+} cation but it can also form complexes with sulphate anions. Radium forms complexes with chloride ions in saline waters. Radium is readily removed from the solution by coprecipitation with insoluble sulphates. Salinity affects the concentration of radium because a solution containing high concentration of cations can exchange radium from a solid phase into the solution.

Lead is particle reactive. It hydrolyses strongly and is adsorbed by minerals. Lead forms many slightly soluble compounds, such as basic lead carbonate and lead silicate. Lead exists in ground water mainly in colloids and coarse particles. In saline ground water Pb forms a soluble lead chloride complex.

Polonium is also particle reactive and it hydrolyses easily. The hydroxy-species can easily be associated with colloids and active surfaces. Organic matter can affect the speciation of polonium. It has been observed that in oceans polonium is adsorbed by organic particles and is enriched in the microlayer of the ocean surfaces. It has also been noticed that bacteria can increase Po concentration in ground water.

The experimental work on the speciation of polonium and lead in ground water indicated that for reliable results it was necessary to use natural ground water as sample material. Using tracers instead of determining naturally occurring polonium and lead can lead to completely false results. The results regarding the proportions of ^{210}Po and ^{210}Pb bound in various particle fractions in ground water have helped other partners to interpret the results obtained by developing different removal methods of natural radionuclides used in the present project.

In the ground waters from drilled wells studied practically all uranium was in highly soluble U (VI) form. Thus, it can be assumed that the oxidation states of uranium has no significant role in removing uranium from drinking water. Instead the pH of ground water affects the removal of uranium and should be studied in more detail in future.

5.12 Disposal of Radioactive Wastes from Water Treatment Methods: Recommendations for the EC

It was pointed out that the radioactive wastes which arise from the treatment of water involve natural radionuclides, but their production, processing, handling, use, holding, etc. cannot be considered practice (as stated in the Basic Safety Standard) and the exemption levels of the Basic Safety Standards are not applicable. That is why there is the possibility of adopting a totally new approach when considering the attitude towards the radioactivity and waste containing natural radioactivity-related problems in connection with different methods for removing radioactivity from drinking water.

It was proposed to recommend that the annual dose to inhabitants from external gamma radiation of GAC filter should not exceed 0.1 mSv. When methods for removing natural radioactivity from drinking water are applied, normally the doses which need to be avoided are of the order of 1 mSv per year. This is why a removal method which simultaneously acts as a gamma radiation source and might irradiate dwellers can not be allowed to cause doses of the same order. The limit should be much smaller—one tenth—otherwise the whole procedure does not make sense. On the other hand, doses much smaller cannot be considered, because the doses from natural radioactivity normally encountered are quite high. In Finland doses from inhalation of radon are about 1–2 mSv per year and from gamma radiation of building materials about 0.1 mSv per year.

It was also proposed to recommend that the dose rate at a distance of 1 m from the GAC filter should not exceed 1 µSv/h. This limit means that one should stay close to the source 100 hours per year, to receive the 0.1 mSv dose presented in the previous chapter. Normally this equipment is located in such parts of the dwellings that longer stays are not needed.

It was also proposed to recommend that possible solid and liquid wastes associated with removal methods could be delivered to communal dumps or discharged into the sewer. The procedures with the radioactive wastes should be as simple as possible to deal with. This encourages private citizens to start using some radioactivity removal method in connection with their own water supplies, if needed. If too complicated procedures are applied the dwellers keep on drinking the water containing high amounts of natural radioactivity.

The private companies selling removal equipment do not want to have responsibility for the possible wastes. Many times the company selling the equipment has nothing to do with the fitting of the equipment at its place of use. The fitters are locally operating private plumbers or small companies.

The fear of radioactivity operates in both directions. People are afraid of radioactivity and want to decrease the amount of natural radioactivity in their drinking water. On the other hand, when this is done there is a special problem with the wastes containing radioactivity. Difficulties in getting rid of them or expensiveness of this process may oppose the idea of lowering concentrations in drinking water.

6. PUBLICATIONS RELATED TO THE PROJECT

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6.3 Abstracts

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The aim of this study was

- to summarise the available information about ion exchange for the removal of natural radionuclides, uranium ($^{238,234}U$), radium (^{226}Ra), lead (^{210}Pb) and polonium (^{210}Po) from drinking water
- to test commercially available equipment for the removal of natural radionuclides from drinking water
- to study the influence of different raw water qualities on the removal process
- to optimise ion exchange technology with respect to resin, and to undesirable influences on the product water quality and on the quantity and quality of waste produced.

These tasks were covered by a literature study, by conducting batch and small column experiments and by testing commercial ion exchange systems in Finnish households as well as in the laboratory.

3.9.1 Literature study

The high efficiency of ion exchange for the removal of radium and uranium was found to be well proven in the US-American laboratory and in bench scale tests as well as in full scale field studies. Concerning the removal of lead and polonium, only single or even no results, respectively, are published. Only sparse literature was found concerning European experiences under European conditions.

Some special questions arose with poor documentation in literature: regenerability of resins, hygienic problems (with domestic treatment devices in particular), the change of water composition by ion exchange treatment (conflicts with drinking water regulations), radioactivity in waste water, the accumulation of radionuclides on the filters (conflicts with radiation protection regulations), and the waste problem (used brine solution).

3.9.2 Batch and column experiments with different resins regarding exchange capacity

Batch and small column experiments using spiked waters and different types of ground-waters were conducted to find ion exchange resins having a high capacity for the removal of uranium, radium, lead and polonium.

The ion exchangers which were selected for testing had earlier been studied for decontamination of metallurgical waste effluents and the removal of radionuclides from nuclear waste solutions. A total of eleven ion exchange materials (six organic resins and five inorganic ion exchangers) were evaluated with respect to their ability to remove U and Ra from three different groundwater simulants.

In batch experiments the highest distribution coefficient (K_D) values were obtained by the strong basic anion resin (SBA) in the case of all water simulants studied. The synthetic mica, Na-4-mica, was the only inorganic ion exchanger which was found to take uranium quite well. The highest K_D values for radium (K_D >10^6 mL/g_{dry}) were obtained by the inorganic ion exchangers, sodium titanate and manganese dioxide.

Using the results of these batch experiments two inorganic and five organic ion exchangers were selected for the column experiments with the real groundwater having high uranium content (200 Bq/L). The breakthrough levels of uranium, radium, lead and polonium were determined to evaluate decontamination factors. The best decontamination factor for uranium was with the strong basic anion resin, being between 20 and 120. The best exchangers for removal of ^{226}Ra from the groundwater were the weak and the strong acidic cation resins (WAC and SAC) and zeolite A. The decontamination factors (*DF*) for WAC, SAC and zeolite A were 2–26, 2–4 and 4–5. The better *DF*s were obtained for the weak acidic cation resin rather than for the strong acidic cation resin with a slow flow rate (15 BV/h).

The best results for removal of ^{210}Po and ^{210}Pb from water were received with the strong and weak basic anion exchangers. However, the mechanism of removing these nuclides is not an ion exchange process. Polonium and lead are probably mainly bound in particles and adsorbed on the surface of the anion resins.

3.9.3 Batch and column experiments with different resins regarding regeneration

Detailed regeneration studies were performed for ^{226}Ra, ^{210}Pb, ^{210}Po (cation exchange) and uranium (anion exchange). Cation exchange studies were performed for comparison of regeneration with NaCl and $CaCl_2$ solutions. In anion exchange studies various resins were compared for their regenerative abilities. In addition, regeneration kinetics, the influence of concentration and stoichiometry of the regenerate were studied.

Under conditions which were typical for the concentration and stoichiometric ratio of a water softening device, the result of ^{226}Ra regeneration was very poor (about 6% and 22% regeneration efficiency for sodium and calcium as regenerate, respectively). Results for ^{210}Pb and ^{210}Po were much higher. The difference between the extent of regeneration using NaCl and $CaCl_2$ solutions as regenerate is greatest for ^{226}Ra, less for ^{210}Pb and very small for ^{210}Po.

The influence of the stoichiometric ratio between regenerate and total resin capacity is linear for ^{226}Ra, whereas ^{210}Po behaves indifferently to variations of stoichiometry between one and three. In contrast to ^{226}Ra, variation of the concentration of the regenerate between 1 and 2.4 had no influence on ^{210}Po regeneration. Repeated regeneration after one uptake or after repeated uptakes showed for ^{226}Ra a constant partition coefficient, whereas the ratio between regenerated ^{210}Po to ^{210}Po on the resin decreased with each regeneration step. This is important for the accumulation of radionuclides on ion exchange units with regular regeneration, because ^{210}Po does not reach the limit of a geometrical series such as ^{226}Ra.

Batch tests for the regeneration of uranium from strong basic anion exchange resins showed a clear influence of regenerate concentration and stoichiometric ratio on the extent of regeneration, when both parameters were relatively low. Regeneration kinetics were similar to ^{226}Ra, the gel-type resins achieving a slightly higher efficiency for regeneration than the macroporous resin, the best result being achieved by a nitrate selective resin.

A small column test was carried out to study the efficiency of uranium regeneration from a strong basic anion resin using a concentrated sea salt solution. Uranium recovery efficiency was 99.4%. Uranium was mostly desorbed in the first few bed volumes of regenerant. At 5.6 bed volume of regenerant the recovery efficiency was 98.5%.

3.9.4 Influence of water composition – small column tests and simulation

The influence of the nuclide activity, competing ions and pH value on the removal of uranium, radium and lead was evaluated by conducting small column tests (mixed bed exchangers containing 80% SAC resin and 20% SBA resin) with six different water types.

Studies conducted earlier show that the feed water composition has an important effect on the possible run-length of an anion exchanger for removing uranium. Especially the strong effect of pH and the sulphate concentration is pointed out. Concerning the influence of water quality on the removal of the other natural radionuclides, no information was found.

Commercially available ion exchangers are usually regenerated at short intervals (e.g. weekly) to suppress bacteria growth and to avoid the accumulation of huge amounts of radioactivity. Usually the capacity for removing radionuclides is only partly exhausted during this interval. With smaller columns, the capacity could be used more effectively and regenerant agent could be saved. Since for reasons of convenience a certain water flow is necessary in a household (10 to 20 litres/minute) this would result—if, as is common practice, no storage tank is used—in higher filter velocities and small contact times between the water to be treated and the resin. It is not clear which minimum contact times are necessary to remove radionuclides effectively.

The aim of the study was

- to check whether high flow rates/small empty bed contact times (EBCT) can be used
- to examine the influence of the feed water quality on the removal of radium, lead and uranium by ion exchange by conducting small column tests
- to check whether the results of the tests can be calculated using a simulation programme
- to extrapolate the results for a wider range of feed water qualities, if possible.

Pre-tests showed that high flow rates result in an initial breakthrough of the ions to be removed and make the breakthrough curve flatter. This reduces the effective run-length of an ion exchanger, when a limit for the effluent concentration must be set. A flow rate of 200 BV/h (related to the SAC resin volume) is an acceptable value for the removal of radium and lead, as the tests demonstrated. The resulting 800 BV/h in the mixed bed exchanger for the SBA portion were too high to remove uranium effectively, the effluent concentration being about 20% of the feed value at the very beginning. For practical application this means that either the maximum flow rate for the simultaneous removal of radium, lead and uranium by mixed bed exchangers must be far lower than the tested 160 BV/h (related to the total bed volume) or the portion of SBA resin must be increased (resulting in a minimum use of the capacity for uranium removal till regeneration induced by lead or radium breakthrough starts). Small bed volumes and the optimal use of the resin capacity for radionuclide removal resulting in minimum regeneration agent consumption on the one hand and short regeneration intervals for hygienic reasons on the other hand are only possible with low flow rates. As a consequence ion-exchangers with constant flow rate followed by a storage tank should be preferred to an in-line installation.

Filter geometry had only a small impact on the form of the effluent curve, a slightly later breakthrough being observed with the more compressed filter form (lower ratio of height to diameter). This could be explained by the lower real velocity of the water in the filter bed.

Two ion exchange simulation programs were tested as to their applicability for calculating radionuclide removal. A comparison with experiments reported in the literature on radium removal showed a good correspondence of calculated and measured data. This was also true for our own radium experiments, but not for lead and uranium. The reasons for this are supposed to be the partly particle-bound portion of lead in natural waters (which was proved), the change of lead speciation with pH and other water quality parameters resulting in the variation of the affinity value, and the initial breakthrough of uranium caused by the high flow rate which was not reproducible by the simulation programme.

Radium broke through to 10% of the feed concentration after 1 000 to 2 000 BV had been treated. The largest reduction of radium removal capacity was observed with high total hardness followed by elevated sodium values; this was also confirmed by the extrapolation using a simulation programme. pH or radium concentration in feed water had no significant influence.

Lead broke through from the beginning to about 20% of feed concentration, except the low pH water type, which reached the 10% breakthrough only when about 1 000 BV had been treated. For the other water types the 100% breakthrough occurred already after 200 to 500 BV. As previously mentioned, a pH of 7 improved the removal efficiency enormously compared to the pH 8 water types. Little impact was also observed from hardness (earlier breakthrough with high hardness), the sodium and the lead concentration having no significant influence.

The measured uranium effluent curves look very flat; an initial breakthrough of more than 20% occurred because of the high flow rate. Even after more than 40 000 BV was treated, when the experiments were stopped, there was still about 60% of the uranium in the feed water removed. Contrary to the results reported in the literature, the greatest impact on the effluent concentration was observed from chloride and not from sulphate concentration. For final conclusions experiments with lower flow rates and a longer investigation time are necessary.

For practical application this means that feed water quality has an important influence on the capacity of ion exchangers for radionuclide removal. Water quality must be considered when fixing the regeneration intervals; capacities should be given by the manufacturers dependent on the content of competing ions and the pH of the feed water.

3.9.5 Tests of commercially available equipment

Several water treatment systems for domestic or laboratory use based on ion exchange technique are commercially available. Most of them are primarily developed to reduce hardness or iron and manganese (cation exchangers), to reject nitrate (anion exchangers) or to de-mineralise water (mixed bed exchangers).

Field and laboratory tests with several types of equipment were conducted to evaluate the efficiency of such commercially available ion exchange systems for removing radionuclides. The effect of the treatment process on other water quality parameters was studied and the quantity and quality of waste produced was determined.

Regeneration tests with the commercial systems and batch and column experiments simulating field conditions were conducted.

3.9.6 Field tests

Ion exchange units were installed in six private homes to treat either all the household water or the water for human consumption only. Because of the excellent results of earlier studies ORWA strong basic anion (SBA) or strong acidic cation (SAC) resins were used in all ion exchange units.

ORWA strong basic anion resin removed uranium very effectively from drinking water. The removal was over 95% at all the test places and independent of the filter type, water quality and bed volume. The removal of radium by the ORWA cation resin was over 94%. The anion resin also retained from 35% to 65% of radium (possibly by anionic radium compounds). Removal of lead and polonium was uneven mainly due to their speciation.

The main water quality improvement caused by the ion exchange was attained by removing organic matter simultaneously with radionuclides. The hygienic quality did not seem to deteriorate. No coliform bacteria were found in any of the test places. The number of heterotrophic colony forming bacteria either slightly increased or decreased during the treatment. The other improvements were achieved by the decrease of turbidity, phosphate, sulphate and nitrate (with anion resins).

The external gamma dose equivalent rate varied from 0.13 to 11.3 μSv/h in various test places. Mixed bed resins had the highest values because cation resin retained radium, which generated radon and its daughters in the unit. The dose rates on the surface of the anion exchangers were low, near the background value. Dose rate measurements on the surface of the unit and also at various distances from the unit indicated that the ion exchangers do not expose residents to any dose if the filters are properly located.

The regeneration studies in the laboratory indicated that about 70% of uranium could be regenerated, when water contained a lot of organic matter. When water quality was more innocuous (no organic matter) better regeneration efficiency could be achieved (near 100%). Both sea salt and NaCl removed uranium equally efficiently. The empty bed contact time (EBCT) did not have significant influence on regeneration efficiency. The regeneration of a tap filter was carried out in the laboratory after six month’s use in the private house. The results obviously indicated near 100% reduction efficiency for uranium. For a system with automatic regeneration which had been in domestic use before regeneration efficiency by using saturated sea-salt solution was over 96%. It can be assumed that the uranium is regenerated almost completely by the normal regeneration procedures applied for these types of commercial units.

4.7 Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of U, Ra, Pb and Po

The laboratory experiments showed that lead and polonium ions were removed quantitatively by all activated carbon types investigated and that no dependence on pH value, water hardness or DOC content of the water on adsorption was noticeable. The adsorption of radium and uranium was, though, dependent on the coal type. Low water hardness increased the adsorption rates and higher DOC contents decreased the adsorption rates. The laboratory tests were carried out to define a granulated activated carbon for the field experiments, with best adsorption behaviour for natural radionuclides. Two coal types (F-100 and Aqua sorb) showed the best results.

The results of the field tests showed that GAC filtration (when carbon is selected based on the adsorption rate of radon) does not offer a viable technique for removing the long-lived radionuclides of the uranium series along with radon. No clear tendency regarding the removal of uranium, radium, polonium, and lead could be discerned. It is obvious that the chemical forms (speciations) of these radionuclides vary greatly in the waters that were studied. The best reduction was obtained for polonium and the poorest for uranium. The results for the same radionuclide varied between different test locations.

A consumer guide was prepared. The guide is intended to be used by the water utility owner to enable one to define the problem and to evaluate the possible solutions in case the water contains excessive levels of natural radioactivity.

4.8 Removal of Radioactivity by Methods Used for Fe- and Mn-removal from Private Wells

Iron and manganese removal equipment based on various removal principles are not a viable treatment alternative for removing natural radionuclides. For example in aeration and filtration equipment the amount of air applied to oxidise iron is not sufficient to remove radon. The air-to-water ratio is mostly 1:10 while it should be 10:1 in order to remove radon sufficiently.

The removal of the long-lived radionuclides ($^{238,234}U$, ^{226}Ra, ^{210}Pb and ^{210}Po) varied a great deal depending on the type of equipment and the radionuclide composition of the water. Uranium was best removed by ion exchange as long as anion exchange resin had been added in the filter. Radium was removed by cation exchangers and greensand filters regenerated with $KMnO_4$. The reduction of lead and polonium varied within a large range mainly due to their varied speciation in natural waters.

External gamma dose rate measurements on the surface of the equipment and at various distances indicated that this equipment does not significantly increase the dose for residents. The dose rates on the surface of the equipment varied from 0.09 to 1.90 µSv/h at the different test places. The highest values occurred with the highest radon concentration in the raw water.

The range of the removal efficiencies attained by the various types of iron and manganese removal equipment based on different principles are set out in Table XIV.

Table XIV. *The range of reduction percentages for Rn, Ra, U, Pb and Po by various Fe and Mn removal equipment based on different principles.*

Equipment type	**Reduction (%)**				
	^{222}Rn	**^{226}Ra**	**$^{238,234}U$**	**^{210}Pb**	**^{210}Po**
Aeration-filtration	12–89	3–93	0–92	21–70	33–82
Regenerated by $KMnO_4$	0–44	56–97	6–60	12–59	40–87
Ion exchangers					
- cation resin	–	50–92	5–84	13–93	79–97
- anion and cation resins	–	69–99	50–99	0–73	0–97

The results of the water quality analyses indicated that water quality improved rather than deteriorated during the treatment due to the removal of Fe, Mn and humus compounds (in some test places).

4.9 Removal of U and Po from Private Ground Water Wells Using Anion Exchange Resins and Removal

of Ra and Pb from Private Ground Water Wells Using Cation Exchange Resins

Batch and small column experiments using spiked waters as well as different types of real groundwater were conducted to find ion exchange resins that have a high capacity for the removal of uranium, radium, lead and polonium.

The strong basic anion resin gave the best results for uranium in both the batch experiments for determining the K_D value and the column tests for the evaluation of the decontamination factor.

The highest K_D values for radium were obtained by the inorganic ion exchangers, sodium titanate and manganese dioxide, while the best performance in the column tests was achieved with weak and strong acidic cation resins and the inorganic exchanger zeolite A.

The best results for the removal of polonium and lead from water were obtained by the strong and weak basic anion resins. However, the mechanism of removing these nuclides is only partly an ion exchange process. Polonium and lead are possibly mainly bound to particles in natural waters and adsorb to the surface of the anion resins.

The influence of nuclide activity, competing ions and pH value on the removal of uranium, radium and lead was evaluated by conducting small column tests (mixed bed exchangers containing strong acidic cation and strong basic anion resins) with six different water types. Because of the good correspondence with the measured data it was possible to extrapolate the results for radium to a wider range of water qualities by using simulation programmes.

The greatest reduction of radium removal capacity was observed in conjunction with high total hardness followed by elevated sodium values. No significant influence was observed from pH or radium concentration in feed water.

The removal efficiency for lead was much better at pH 7 than at pH 8, and little influence was observed from hardness. The feed concentration of sodium and lead was of no significant influence.

Flat effluent concentration curves were measured for uranium because of the high flow rate used in the experiments. Contrary to the results reported in the literature, the greatest impact on the effluent concentration was observed in the case of chloride and not in the case of sulphate concentration. For final conclusions experiments using lower flow rates and longer investigation time would be necessary.

For practical applications this means that water quality has an important influence on the capacity of ion exchangers for radionuclide removal. Water quality must be considered when fixing the regeneration intervals; capacities should be given by the manufacturers dependent on the concentrations of competing ions and pH of the feed water.

Although the maximum flow rate which can be used for achieving an acceptable breakthrough curve depends greatly on the properties of the individual resin, a range of 80 to 200 BV/h was determined as reasonable throughout the column tests. Filter geometry had only minor influence on the form of the effluent curve; an insignificant later breakthrough was observed with a more compressed filter form (lower ratio of height to diameter).

Regeneration tests both in the laboratory and in the field showed that uranium can be almost completely (up to 100%) removed from strong basic anion resins by sodium chloride or sea salt solutions. Empty bed contact time (EBCT) had no significant influence on regeneration efficiency. The clear influence of the concentration of regenerant and the total mass of salt applied on the extent of regeneration was observed. The efficiency was reduced to only about 70%, when water rich in organic matter was treated.

When simulating the conditions in a commercially available ion exchanger containing strong acidic cation resin (domestic water softener) the efficiency of radium regeneration was poor, only from 6% to 22%; this was proved in practical experiments with such a system. Slightly higher results were achieved with gel type resins than with macro-porous resins. With $CaCl_2$ as an alternative to NaCl higher efficiencies were reached but the application in the water softener failed because of a blockage in the system. The constant separation factors for radium resulted in an upper limit of activity accumulated on the ion exchanger after repeated operation and regeneration cycles; the accumulation followed a geometrical series.

Higher efficiencies but the same behaviour were observed for lead on the strong acidic cation exchanger.

The mass of salt applied and the concentration of the regenerate exercised practically no influence on the regeneration efficiency of polonium. In addition, the kinetic behaviour of the regeneration process for polonium is totally different from that for uranium, radium and lead. This clearly indicates that polonium is only adsorbed to the resin and no ion exchange in the real sense happens.

Field tests (in Finnish households) and laboratory tests with several different commercially available ion exchange systems were conducted to evaluate their efficiency in removing radionuclides, their impact on other water quality parameters and to determine the quantity and quality of waste produced.

Ion exchangers containing strong basic anion resin in the chloride form removed over 95% of uranium at all test places, independent of water quality. Many thousand bed volumes of natural water can be treated without regeneration—uranium breakthrough does not primarily limit the use of the filter. More likely it is restricted by the clogging of the filter, by national regulations concerning the maximum allowable amount of uranium to be accumulated on the filter or for hygienic reasons.

The anion resin also partly removed radium (from 35% to 60%), possibly because of anionic Ra compounds. Systems containing strong acidic cation resins in the sodium form removed radium in the range of 90% to 95%. Radium reduction nearly always exceeded hardness removal, while total hardness—an easy to measure parameter—might be used as a surrogate for regular qualitative checks of the operation of small cation exchange systems by the owner. The removal of lead and polonium varied a great deal due to their varied speciation in natural waters.

Simultaneously with radionuclides a decrease of turbidity, phosphate, sulphate and nitrate (with anion resins) was observed. The decrease of iron occurred mainly with cation resins but also with anion resins if organically bound iron was present. The more or less total removal of hardness (calcium and magnesium) by cation exchange resins in the sodium form must be judged negatively from the point of view of health and conflicts with many national drinking water regulations, which demand a minimum hardness. Furthermore, the water tends to be corrosive, which makes the addition of corrosion inhibitors necessary to protect metal pipes. To avoid this effect strong acidic cation resins in the calcium form were successfully tested in point-of-use ion exchangers (countertop pour-through filters). For the use of $CaCl_2$ in point-of-entry devices with automatic regeneration changes of the design are necessary.

Hygienic studies showed that the heterotrophic plate count may increase when using ion exchangers, but no negative health effects on the people were observed at the test places.

Dose rate measurements on the surface of the ion exchangers and also at various distances from the filters indicated that no remarkable dose for the residents is caused by the treatment systems, if they are properly located in the house.

Ion exchange systems cause either solid waste, exhausted filter cartridges from point-of-use systems, or liquid waste, the regeneration agent used. Since the activity found in the waste depends on the quality of raw water, the period between two regeneration cycles or the frequency of change of cartridges and the individual type of system, only rough estimations can be given. The exhausted filter cartridges may contain an activity of up to several 100 Bq/g. The regeneration agent used, high in salinity, has a radionuclide concentration from 10 to 30 times the feed value; the quantity is in the range from 3% to 10% of the volume of water treated.

A consumer guide was prepared. The guide is intended to be used by the water utility owner to enable one to define the problem and to evaluate the possible solutions in case the water contains excessive levels of natural radioactivity.

4.10 Removal of U, Ra, Pb and Po with Adsorptive or Membrane Filters

Hydroxyapatite has a good capability for adsorbing uranium and radium as shown in laboratory experiments and also in field experiments with very small flow rates. The high adsorption at slow flow indicate that a strong interaction between the feed water and the surface of the hydroxyapatite is necessary to gain good results. Therefore a new granular form has to be discussed to obtain smaller and perhaps more porous particles to increase the surface and contact time.

The RO and NF systems (laboratory experiments) tested, typical of the great number of commercially available ones, removed on average from 95.6% to 99.8% of the radioactive compounds radium (^{226}Ra), uranium and lead (^{210}Pb) from the feed water. The measured gross alpha reduction showed that the same is true for polonium (^{210}Po). Concerning the removal of radioactivity, no significant differences were observed between the RO units and the NF system.

In several cases no radioactivity was found in the retentate but it was adsorbed onto the treatment systems. High adsorption rates were observed for ^{210}Pb in particular. GAC pre-filters seemed to favour this effect.

A comparison of radioactivity with electrical conductivity (EC) and total hardness (TH) rejection showed that EC and TH always exceed radioactivity in the permeate and therefore might be used as surrogates for checking the proper operation of RO and NF systems regarding radioactivity removal.

Additionally to radioactive isotopes, RO and NF systems also reduce all other dissolved compounds to a high degree (average 95%) and decrease the pH value, resulting in water which favours corrosion and is poor in essential minerals for human health. To reduce these unfavourable effects, filtration over granular calcium-carbonate ($CaCO_3$) was tested as a post-treatment step (re-hardening). About 15% to 35% of the original hardness was reached by this method and the water can be brought again into lime-carbonate equilibrium so that it does not behave corrosively anymore. No significant difference was observed between waters from RO and NF systems.

A microbiological analysis of feed water and permeate showed that the hygienic quality of the water can deteriorate when using such kinds of treatment systems where the treated water is stored in the storage tank for daily supply for drinking and cooking.

The NF pilot plant study enabled one to estimate the suitability of NF membranes for removing uranium from water. It showed that the most important species of uranium in natural water, which represent anion, cation and uncharged compounds, can be removed to about 95% over a wide range of pH and hydrochemical settings. It showed further that the heavy molecular weight of uranium compounds is mainly responsible for the high rejection. Since even the molecular weight of the uranyl cation, which is the lightest uranium compound in water, is above the typical molecular weight cut-off of NF membranes, it can be expected that the rejection of other uranium compounds, not investigated in this study, would also be more than 90%.

The uranium rejection at the NF membranes at various hydrochemical settings was from 95% to 98% in most cases. The rejection of other constituents of water (phosphate, bicarbonate and electrical conductivity) differed from 40% to 97%. The two RO membranes rejected from 98% to 99.5% of uranium and from 93% to 99.5% of other water constituents.

The suitability of two commercially available POE-RO devices for removing $^{238,234}U$, ^{226}Ra, ^{210}Po and ^{210}Pb from drinking water was determined in field tests. While the radionuclides were removed by more than 90%, the rejection of other water constituents was mainly above 94%.

The membrane devices used in the field tests were suitable for treating drinking water. The main feature of RO equipment was its ability to remove most water constituents effectively. The best reduction of water constituents achieved was over 94%. The reductions of uranium, radium and polonium were over 90%.

4.11 Speciation of U, Ra, Pb and Po in Water

The literature study indicated that despite a very large number of investigations on the speciation of uranium, our knowledge regarding ground water is still limited. The composition, abundance and properties of many components of ground water systems are poorly known. This applies particularly to natural organic matter and colloidal components. The speciation of radium has been studied moderately but especially the knowledge of the speciation of radioactive lead and polonium in ground water is poor and only a few articles are available.

The principal objective of this study was to find out the division of ground water ^{210}Po and ^{210}Pb into soluble and particle-bound fractions. For this purpose real ground water samples were filtered using filters of varying pore sizes. It was found that these radionuclides exist mainly as particles in ground waters. Only in one water were considerable fractions of them seen to be in soluble form. It was also found that the sizes of the particles carrying the radionuclides vary markedly from water to water.

The secondary objective was to identify the chemical factors affecting the presence of polonium and lead in particles. The chemical composition of the waters prior to and subsequent to the filtrations were determined but only a few indicative results could be obtained suggesting that iron and aluminium containing colloidal particles may be responsible for carrying the radionuclides.

One main conclusion from the results of this study is that correct results can be obtained only by using real ground water samples. Tracers to mimic the behaviour of naturally occurring radionuclides cannot be used.

The initial phase of this study was to study whether these radionuclides are present in groundwaters in ionic forms which could be removed by ion exchange materials. It was observed that polonium and lead are mainly present as particles and thus ion exchange would not be the primary method for these nuclides. However, it is probable that they, though not exchanged into ion exchangers, may be adsorbed on surfaces of the exchanger material and equipment.

In the ground waters studied representing, on the one hand, ground water with good water quality but rich in soluble uranium and, on the other hand, groundwater with relatively high NaCl concentration and high content of humus material, practically all uranium (>95%) was in the highly soluble U(VI) form.

4.12 Disposal of Radioactive Wastes from Water Treatment Methods: Recommendations for the EC

The radioactive wastes arising from the treatment of water involve natural radionuclides, but their production, processing, handling, use, holding, etc. cannot be considered practice (as stated in the Basic Safety Standards) and the exemption levels of the Basic Safety Standards are not applicable. However, wastes from water treatment methods involving natural radionuclides may lead to a significant increase in the exposure of the members of the public (or workers who are handling the waste) to radioactivity.

The following recommendations were made. The Member Countries of the European Union can use the recommendations made in this report as a basis for their own regulations or the European Union may recommend a common approach for all the Member Countries.

- The radon-laden air from the aerator should be directly funnelled into the open air. The aerator itself does not accumulate any radionuclides.
- It is recommended that the annual dose to residents from the external gamma radiation of a GAC filter should not exceed 0.1 mSv. GAC filters emit gamma radiation when they are in service. The higher the radon concentration and the larger the water usage, the more intense the external gamma dose rate around the filter.
- It is also recommended that the dose rate at a distance of 1 m from the GAC filter should not exceed 1 µSv/h. As a rule of thumb, if the radon concentration of water exceeds 2000 Bq/L, special shielding is needed. Instead of constructing special shielding, the location of a GAC filter can be chosen in such a way that the distance from the filter to occupied rooms is long enough to attenuate the gamma radiation.
- The use of GAC filter is not recommended if the radon concentration of water exceeds 5 000 Bq/L.
- It is recommended that used GAC filter material could be discharged into communal dumps after it has been “aged” about four weeks after use. The GAC filters also accumulate ^{210}Pb. Depending on the water consumption and radon concentration in influent, high activities of ^{210}Pb may be found in spent GAC beds. When the GAC filter is no longer used, the amount of radon in the filter decreases rapidly and is close to zero after four weeks. Simultaneously the external dose rate around the filter decreases. Normally the spent carbon contains high amounts of ^{210}Po and ^{210}Pb and low amounts U and ^{226}Ra.
- It is recommended that if Fe- and Mn-removal methods are used and backwashing or regeneration is carried out about once a week, the liquid could be discharged into the sewer and after use the spent matrix could be discharged into municipal dumps. Depending on the Fe- or Mn-removal system, large amounts of radionuclides may be accumulated by the equipment. Backwashing or regeneration at regular intervals, however, enables a safe daily use of these units because radionuclides are rinsed out of the fixed bed and drained into the sewer. The higher the concentration of radionuclides and the higher the daily water usage, the more often backwashing or regeneration should be carried out. The

regeneration interval is in most cases frequent enough to prevent this technique from causing a problem of waste disposal.

- It is recommended that if anion or cation exchange resins are used and regeneration is done about once a week, the regeneration liquid could be discharged into the sewer. It is also recommended that the resins of the exchange units without automatic regeneration could be discharged into municipal dumps. In connection with ion exchangers different operation principles and exchange materials can be utilised. Organic ion exchangers (resins) can usually be regenerated. The properties of many inorganic exchangers (mineral based) cannot be restored by regeneration and therefore they must be discarded after exhaustion.
- It is recommended that the solid wastes produced by membrane techniques (i.e. spent membranes and pre-filters) could be discharged into communal dumps. The other wastes produced by membrane techniques are not accumulated in fixed matrices. The concentrate containing radionuclides, is constantly drained into the sewer as the unit operates. The concentrations of radionuclides in concentrate are, however, low and do not create a waste problem.

5. DISCUSSION

5.1 Survey of Literature on Natural Radioactivity in Drinking Water and Treatment Methods in European Countries

The data on levels of natural radionuclides in ground, drinking and mineral water in 17 European countries and the distribution of uraniferous deposits in Europe enabled the drawing of a European map. This map shows regions which are geologically dominated by basement rocks (especially granite plutons and metamorphic rocks), to be the most important areas with potentially elevated levels of natural radionuclides in ground water. Typical geological settings for such basement rocks are orogen cores and roots of eroded orogens. In Europe, this applies to the following regions:

- the Proterozoic part of the Fenno-Scandinavian (Baltic) Shield which is almost entirely formed of high grade metamorphic rocks and granite plutons,
- the Pre-cambrian of the Ukrainian Shield and the Scottish Grampians and Highlands,
- the Moldanubian zone, which is the inner zone of the Hercynian orogen, corresponding to the area of maximum orogenic, metamorphic and plutonic activity. It includes (1) the Vendée of the Armorican Massif, (2) the French Central Massif, (3) Vosges and the Black Forest, and finally (4) the Bohemian Massif with adjacent areas in south-eastern Germany and northern Austria,
- the Central Iberian zone, which is the south-western foothill of the Herzynian orogen on the Iberian peninsula, and
- to a lesser extent on Corsica and Sardinia, in the Rhodope massif and in the central Alps.

Beside these granite-related regions other small-scale areas surely exist with high contents of natural radionuclides in ground water. For example, areas with small uraniferous accumulations of local importance which typically occur in felsic volcanics or in surrounding sedimentary rocks.

5.2 Intercomparison of Analysis Methods

The intercomparison runs accompanying the analytical work of the project were highly justified by the quality of the data, improving from exercise to exercise.

5.3 Definition and Classification of Different Water Types and Experimental Conditions

With the definition of the experimental conditions and the definition of water types to be selected for the tests an important project basis was laid. Although the partners were not able to cover all the water types for organisational reasons and due to the restricted budget, sufficient and comparable results have been achieved throughout the project.

The ftp-server, communication platform and database of the TENAWA project allowed an efficient and quick information transfer between the research groups independent of the document size. The TENAWA homepage will also be used after the end of the project for the dissemination of the results and reports to the scientific community.

5.4 Removal of Radon by Aeration: Testing of Commercially Available Equipment for Domestic Use

Radon removal systems based on aeration can be designed and installed in different ways. The following aspects should be considered when the installation is designed:

- average water consumption
- maximal momentary consumption
- radon concentration in raw water

- the need for untreated water
- previously installed components
- additional treatment units
- requirements for the room where water treatment is carried out
- maintenance of the system.

One result of this study was the development of a standard sampling protocol. The previously used conventional tests did not provide enough information either about the effective capacity of the aerators or about the real removal efficiency. New manufacturers of aerators have come into the market since this study started. It is important to be able to compare these equipment even-handedly and also to monitor the operation of the ones already installed. The manufacturers can benefit from the newly introduced parameter, the effective flow rate, when designing the aerators. The sampling protocol, including the plot of radon concentration against the volume of water flowed, indicates unfavourable and otherwise undetectable phenomena such as leaking solenoid valves or malfunction of the control unit.

The proposed sampling protocol includes constant measuring of the flow rate applied and frequent sampling of the continuous water flow in order to cover all situations of water consumption. Information on the removal efficiency and whether the installation has been carried out appropriately can be gained from the results. The sampling enables calculating the removal efficiency that is most applicable to assessing exposure through ingestion but it also makes it possible to measure the removal efficiency related to water volume, which is more indicative for assessing exposure through inhalation.

Some effects of the aeration process on certain water quality parameters could be demonstrated. As might be expected, the iron (Fe) and manganese (Mn) concentrations were generally lower in the treated water than in the raw water. Iron precipitates as ferric hydroxide during aeration and manganese may be co-precipitated at the same time. These iron and manganese precipitates can cause fouling of the treatment system if they are not removed. The precipitates can settle down on the bottom of the aeration tank, be removed by a sediment filter installed after the aerator, or be released into the water line.

The water becomes virtually saturated with oxygen during aeration. This improves the taste of the water and reduces the corrosiveness. Carbon dioxide is also removed, which causes a rise in the pH value. Water with a higher pH value is less corrosive for the plumbing. Other water quality parameters change only slightly. No clear trends in their results could be observed.

The results gained from this project indicate that radon removal by aeration did not increase the bacterial densities of the water. However, factors affecting bacterial growth, i.e. microbiological quality, organic carbon and the nutrient concentrations of raw water should always be examined before installing an aeration unit. Heterotrophic plate counts should be included in routine water quality surveillance in order to obtain information on the fluctuation of the microbiological quality of raw water and the need of maintenance, cleaning and disinfection of the water treatment equipment.

The type and model of aerator should be selected according to water consumption and the radon concentration in the raw water. The manufacturer should guarantee a certain water output for each available system. The first factor affecting the water output of the system is the aeration time. Longer aeration times are needed to reduce higher concentrations of radon. The water output of the system diminishes, however, when the aeration time is prolonged. Therefore, the aeration time should be adjusted so that a sufficient reduction is achieved and no unnecessary aeration takes place. However, during this study it was noticed that the radon concentration of the raw water can vary significantly. The aeration time should always be set longer than needed at the time of sampling.

The second factor contributing to the water production capacity is the size and the pre-pressure of the pressure tanks (when installed after the aerator). The effective volume of the pressure tank should be large enough to enable sufficient water feed into the plumbing during aeration.

Instead of installing pressure tanks, another way of guaranteeing sufficient water supply is to direct aerated water into a storage tank. These tanks can be very large and they require a lot of cool space. A practical application is to build a “dummy well” which is filled up with aerated water.

The third factor affecting the water production capacity is the well pump. A pressure tank must always be installed after an ejector pump. An ejector pump is usually not as efficient as a submersible pump but the pressure tank adds its capacity to fill up the aerator. If the well is situated far from the aerator and a submersible pump is used (without a pressure tank), the time that the pump needs to fill up the aerator can be quite long. Most aerators have a spray mouth-piece or an ejector mounted at the inlet of the aerator in order to intensify the radon removal. The spray mouth-piece and the ejector function more efficiently with high water pressure. Consequently, the radon removal efficiency can decrease if the incoming water pressure is low.

When the radon concentration in the raw water is extremely high the short-lived radon daughters can also cause a significant effective dose even though the radon has been expelled from the water. The most significant daughter products are lead (^{214}Pb) and bismuth (^{214}Bi). According to one estimate the dose caused by the radon daughters is 10% of the corresponding radon concentration. The freshly aerated water should, therefore, stand for a while before consumption. The pressure tanks or the storage tank must be large enough to enable the delay that is needed to reduce the activity of the radon progeny. When large tanks are installed the water production capacity of the system improves. Long storing times, however, can cause the growth of bacteria.

The nature of this study was more of a practical testing programme than research. For the consumer it is very important that this kind of relatively new equipment undergoes long-term testing under the surveillance of qualified independent scientists and technicians to find out if they are capable of doing what the manufacturers claim that they can do. And further, that they can perform reliably for a long time without needing too much maintenance. This kind of equipment is often “forgotten” by the residents once it has been installed. Therefore it is important that the residents have written directions as to how the equipment should be used.

From the radiation protection point of view the general conclusion that can be drawn is that aerators are very capable of also reducing very high radon concentrations in drinking water to acceptable levels. This confirms experiences from the United States and Sweden, where this kind of equipment has been in use for a number of years.

Most of the problems that have been encountered have been of a technical nature and can easily be solved. There is, however, one area of problems that needs further investigation. This is the risk of hygienic problems in the long-term use of aerators when the equipment is used in different environments, for instance in areas with warm climates. The quality of the raw water is very important in this context. The combined effects of the environment of the installation, for instance indoors in a warm cellar, the material of the equipment, for instance transparent or semi-transparent plastic, the technical design of the system, the quality of the air that is mixed with the water and the quality of the raw water. All these are factors that affect the hygienic quality of the water treated. More research is needed to investigate the risks involved.

5.5 Removal of Radon by Aeration: Testing of Various Aeration Techniques for Small Water Works

The investigations showed that aeration is a highly effective method for removing radon from water. Removal efficiencies of more than 98% can be achieved, for example, with a fine bubble shallow bed aerator. Various types of aeration equipment are manufactured. All of them benefit from the same physical principle: gas exchange takes place at the interface of the phases of air and water. Therefore, each aeration method intends to create as large an interface as possible. The usability of a certain type of aeration equipment for removing radon, as well as CO_2, is very much dependent on several operation parameters, especially the amount of water to be treated, the available space and the degassing target. Most aeration facilities can be constructed to achieve radon removal efficiencies of more than 95% or even more than 99%. In most modern aeration facilities, where an active use of air takes place, high gas exchange rates are mainly a question of the throughput of air, which means a question of operation costs.

It was further recognised that radon and carbon dioxide show a very similar removing behaviour during aeration, which can be explained by the similar Henry's law constants for both gases (radon: $2.26 \cdot 10^3$ bar and CO_2: $1.51 \cdot 10^3$ bar; at 20°C water temperature and atmospheric pressure). Therefore, it is possible to estimate the radon removal efficiency of aeration equipment from its carbon dioxide removal efficiency. The latter has to be known by the manufacturer, since water aeration is a widespread treatment method for the de-acidification of water.

Finally, the study showed that water aeration is a very effective tool for radiation protection in waterworks. By operating water aeration equipment it is possible to reduce the radon degassing potential (from the treated water into the air) to a minimum and to reach moderate indoor air radon levels. To achieve this, it is necessary though that the process-air is led out of the aeration equipment and out of the waterworks completely.

5.6 Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of Radon

GAC filtration can be considered an inexpensive and easy way of mitigating high concentrations of radon in household water.

The longevity of a GAC batch was not discovered, because most filters exhibited constant removal efficiency for radon throughout the study. Therefore, no recommendations regarding the effective lifetime of a GAC batch can be given.

It was obvious that some anionic species reduced the adsorption rate of radon on GAC. According to the results, this could be either humus or uranium. The data, however, were too limited. At present there are some 50 GAC filters installed for radon removal in Finland. In order to give recommendations concerning the maximum levels of the interfering substances more water quality data are needed from these filters.

One of the main concerns in applying GAC filtration in domestic use is the external gamma radiation that can cause radiation exposure for the residents. An external dose rate as measured on the surface of a GAC unit installed in permanent use could exceed the normal background level even by a factor of one thousand. With proper shielding, instructions and placement of the unit in a non-residential area, elevated doses to the residents, however, can be avoided.

In order to minimise exposures different types of radiation shields have been studied. Lead attenuates gamma radiation most efficiently. A lead shield, however, may be expensive and it is made of toxic metal, which must be considered a potential health risk. Bricks and concrete can be applied, but the thickness of the shield must be considerably greater than for lead. A water jacket can be built. Water attenuates gamma rays, and is cheap. However, residential radiation exposure cannot always be eliminated sufficiently, especially when the influent radon activity is high. Therefore radon removal applying GAC filtration often remains a viable treatment method only when the radon concentration is low.

5.7 Removal of Radionuclides from Private Well Water with Granular Activated Carbon (GAC): Removal of U, Ra, Pb and Po

When considering removal of uranium, radium (^{226}Ra), lead (^{210}Pb) and polonium (^{210}Po) with activated carbon the type of carbon should be selected based on its adsorptive properties for these radionuclides. Activated carbons exhibit high non-polar capacities for hydrophobic substances such as radon and many organic contaminants. However, their polar properties are usually very limited. Therefore they remove inorganic substances and cations, such as heavy metals, only fairly well. A possible solution for the simultaneous removal of radon and the long-lived radionuclides could be the carbon-mineral adsorbents. The matrices of these adsorbents consist of both active carbon and mineral adsorbents (SiO_2, Al_2O_3, etc.) and show good mechanical properties. Furthermore, these adsorbents usually have better adsorptive properties than each individual component separately.

The mean removal efficiency of uranium, radium, lead and polonium in the field experiments is generally not as good as in the laboratory experiments. In the field tests the removal of uranium and radium decreased gradually with the amount of water treated and the removal of radium was a little higher than that of uranium. The results of polonium and lead from the laboratory and field tests agree much better than for uranium and radium. The reasons to the observed differences have not been fully analysed, but they can be explained partly by the amount of water treated and also by the chemical speciation, which may have the greatest effect.

During the TENAWA project speciation studies were carried out. The differences between the laboratory and field experiments in this study can be explained to some extent by the results from these speciation studies. During these studies filtration experiments were made to find out if uranium, radium, lead or polonium occur in ground waters either as ionic compounds or bound to various sizes of particles.

The results indicated that uranium and radium occur mainly as ions. Because lead and polonium were mainly bound to particles they can be removed from water by utilising adsorption into GAC filters. Correspondingly, uranium and radium should be removed predominately by ion exchangers. These observations are in good agreement with the results obtained by ion exchange experiments carried out during the TENAWA project. It should also be noted that the Finnish ground waters are still softer than any model water used in the lab tests.

However, the variation of the adsorption values obtained in the field experiments indicate that GAC filtration is not very suitable for the adsorption of natural radionuclides, except radon, which is retained as a noble gas very efficiently, even after large volumes of filtered water.

5.8 Removal of Radioactivity by Methods Used for Fe- and Mn-removal from Private Wells

There are still a few questions that remained unanswered. The physico-chemical conditions during the filtration should be examined in greater detail. For example, the aeration-filtration equipment contain various types of masses which have different retention properties. Therefore, the accurate composition of the masses added in the filtration layers need to be known in order to evaluate the results more reliably. At some test locations sampling needs to be continued to discover why the change of masses affected the removal rates.

Also the reduction of lead and polonium varied in a large range. The reason is not know exactly but it may be due to the speciation. Recent studies performed in Finland have indicated that lead and polonium occur in waters mainly adsorbed to various sizes of particles and not so much as soluble compounds. Thus lead and polonium would preferentially be removed by methods used for removing particles rather than by ion exchange.

5.9 Removal of U and Po from Private Ground Water Wells Using Anion Exchange Resins and Removal of Ra and Pb from Private Ground Water Wells Using Cation Exchange Resins

Ion exchange is a proper method for the removal of radium and uranium. Strong basic anion resins for the removal of uranium and strong acidic cation resins for radium removal performed best. The efficiency for lead and polonium varies a great deal, since most of these nuclides are supposed to be particle bound in natural waters and therefore no ion exchange process in the real sense but adsorption to the resins is responsible for their reduction. Therefore the reduction of lead and polonium is a welcome side-effect of uranium and radium removal but ion exchange is not the technology of choice for their removal.

The main disadvantage of cation exchange resins in the sodium form is the more or less total removal of hardness simultaneously with radium. This can be avoided by using resins in the calcium form. For the application of the regenerant $CaCl_2$ in commercially available systems changes in design are necessary. Other influences on water quality which were observed are a decrease in turbidity, phosphate, sulphate and nitrate with anion resins and a reduction in iron mainly with cationic resins. The pH value and the concentration of competing ions had an important influence on the possible run-length of the ion exchangers and must be considered when fixing the period of time between two regeneration procedures. Hygienic deterioration of the water was detected in some cases and cannot be excluded.

No remarkable dose to the residents caused by the treatment systems was observed when the equipment was properly located in the house. But national regulations regarding the handling of waste and the permitted accumulation of radioactivity on the filters may limit the applicability of this technology for private homes.

5.10 Removal of U, Ra, Pb and Po with Adsorptive or Membrane Filters.

By RO and NF systems liquid waste—the retentate—is produced. Due to the fact that no additional chemicals are necessary, the retentate is merely a more concentrated form of the raw water. Concerning radioactivity the mixing of treated water (used in households, low radioactivity) and retentate (high radioactivity) should in sum result in household waste water with the original natural radionuclide concentration.

Because of the increased raw water volume necessary for producing drinking water, membrane technology—if in widespread use—could become a problem in the case of limited water resources and for the capacity of waste water treatment plants if retentate is not alternatively used (e.g. for flushing the toilet).

The experiments showed that part of the removed radionuclides is adsorbed in the treatment units. Depending on national legislation used filter cartridges or membranes have to be handled as ordinary household waste or as low radioactive waste. As a result this can be a key economic question for the use of such treatment devices.

The installation and maintenance of POU systems should be possible without special skills whereas with POE systems this should be done by professionals. The regular use of the units is important because otherwise the membranes would be destroyed.

The reduction of water constituents can be a disadvantage for the consumer of drinking water which is treated by RO, because it is not advisable to drink water which is almost completely de-mineralised. After treatment it would be preferable to have slight water re-hardening.

In natural water the uranyl carbonate complexes $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ and, if phosphate is present, the uranyl phosphate complex $UO_2(HPO_4)_2^{2-}$ are mainly responsible for the mobility of uranium. Below pH 5, the pure uranyl cation UO_2^{2+} is also important. Those five uranium species have been generated in model waters and their rejection at six NF membranes and two open RO membranes was determined in several experiments.

The results show that the uranium removal from water at the six tested NF membranes was mainly between 90% and 98%. Especially the three divalent and multivalent uranyl anion complexes $UO_2\ (HPO_4)_2^{2-}$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ were mostly removed up to 95% or more. Those three complexes are the predominant uranium species in natural water above pH 4. The uncharged uranyl carbonate complex, $UO_2CO_3^0$, that predominates in phosphate-free water between pH 5 and 6.5, was also removed to about 95% in most cases. Besides, the rejection of the pure uranyl cation at pH 3.2 was from 87% to 93%. The high rejection of these five uranium compounds is a first sign that uranium can be removed quite effectively from water by NF membranes. This seems to be valid over a wide range of hydrochemical settings, even in very acidic waters.

The experiments with the extraordinary high uranium concentration of 10 mg/L showed no major difference in the removal efficiencies of the membranes, compared to the 1 mg/L experiments. Therefore, clearly worse removal efficiencies are not to be expected during concentration processes at membranes, which will take place in the case of a higher recovery. Further, there seems to be no clear effect on the uranium removal efficiency due to the presence of a high number of competing ions in the water. This was shown by the experiments with high and low sulphate concentrations.

The rejection results of the three NF membranes (out of 6) studied showed quite similar results: uranium rejection from 95% to 98% and rejection of other water constituents (phosphate, bicarbonate and electrical conductivity) from 75% to 97%. One membrane rejected uranium slightly worse (from 91% to 97%) and other water constituents slightly better (from 80% to 98%). One membrane also removed uranium effectively (from 95% to 98%), but the rejection of other water constituents was only from 45% to 95%. One of the membranes studied had a uranium rejection from 81% to 98% and the rejection of other water constituents from 40% to 80%.

Beside the six NF membranes two RO membranes were tested for comparison. As was expected, these membranes rejected both uranium (from 98% to 99.5% at pH 5 to 8.3) and other water constituents (from 93% to 99.5%) more effectively than the NF membranes.

Finally, the amount of organic uranium species can be estimated, since several authors assume that a certain part of uranium mobilised in water might be due to organic compounds. It can be estimated that the rejection of organic uranium compounds would not be lower than the rejection of the compounds investigated. The reason is that any organic uranyl species, whether anionic, cationic or uncharged, would surely be bigger and heavier than the inorganic uranyl compounds investigated. The molecular weight of the compounds investigated, however, was the main factor for the quite high rejection at all membranes. This is indicated by the similarity of the results of the uranium removal efficiencies in all experiments, without depending on the charge of the compounds. And indeed, even the molecular weight of the lightest uranium compound, the pure uranyl cation, UO_2^{2+} (270 Dalton), is already above the typical molecular weight cut-off (MWC: weight of uncharged organic molecules which are rejected practically completely) of NF membranes. The molecular weight of $UO_2\,(HPO_4)_2^{2-}$, for example, is 460 Dalton. The typical MWC of NF membranes is about 250 Dalton.

5.11 Speciation of U, Ra, Pb and Po in Water

The removal of uranium, radium, lead and polonium from drinking water depends on their speciation. The speciation of radionuclides in drinking water requires information as to their physico-chemical form in the water phase. For removal of these nuclides knowledge of their speciation in ground water is necessary. It is important to know in which physico-chemical form the radionuclide exists in ground water and how different factors affect its speciation.

Under oxidising conditions uranium exists mainly as its hexavalent state while in reducing condition U(IV) is the predominant oxidation state. U(VI) is present in slightly acid ground waters mainly as UO_2^{2+}. It forms strong complexes with carbonate and hydroxide ions. Uranyl ion is also known to form stable complexes with dissolved organic matter, in the form of humic and fulvic acid. Uranium can also form strong complexes with phosphate, fluoride and sulphate, when these anions are present.

Radium is most frequently found as hydrated Ra^{2+} cation but it can also form complexes with sulphate anions. Radium forms complexes with chloride ions in saline waters. Radium is readily removed from the solution by coprecipitation with insoluble sulphates. Salinity affects the concentration of radium because a solution containing high concentration of cations can exchange radium from a solid phase into the solution.

Lead is particle reactive. It hydrolyses strongly and is adsorbed by minerals. Lead forms many slightly soluble compounds, such as basic lead carbonate and lead silicate. Lead exists in ground water mainly in colloids and coarse particles. In saline ground water Pb forms a soluble lead chloride complex.

Polonium is also particle reactive and it hydrolyses easily. The hydroxy-species can easily be associated with colloids and active surfaces. Organic matter can affect the speciation of polonium. It has been observed that in oceans polonium is adsorbed by organic particles and is enriched in the microlayer of the ocean surfaces. It has also been noticed that bacteria can increase Po concentration in ground water.

The experimental work on the speciation of polonium and lead in ground water indicated that for reliable results it was necessary to use natural ground water as sample material. Using tracers instead of determining naturally occurring polonium and lead can lead to completely false results. The results regarding the proportions of ^{210}Po and ^{210}Pb bound in various particle fractions in ground water have helped other partners to interpret the results obtained by developing different removal methods of natural radionuclides used in the present project.

In the ground waters from drilled wells studied practically all uranium was in highly soluble U (VI) form. Thus, it can be assumed that the oxidation states of uranium has no significant role in removing uranium from drinking water. Instead the pH of ground water affects the removal of uranium and should be studied in more detail in future.

5.12 Disposal of Radioactive Wastes from Water Treatment Methods: Recommendations for the EC

It was pointed out that the radioactive wastes which arise from the treatment of water involve natural radionuclides, but their production, processing, handling, use, holding, etc. cannot be considered practice (as stated in the Basic Safety Standard) and the exemption levels of the Basic Safety Standards are not applicable. That is why there is the possibility of adopting a totally new approach when considering the attitude towards the radioactivity and waste containing natural radioactivity-related problems in connection with different methods for removing radioactivity from drinking water.

It was proposed to recommend that the annual dose to inhabitants from external gamma radiation of GAC filter should not exceed 0.1 mSv. When methods for removing natural radioactivity from drinking water are applied, normally the doses which need to be avoided are of the order of 1 mSv per year. This is why a removal method which simultaneously acts as a gamma radiation source and might irradiate dwellers can not be allowed to cause doses of the same order. The limit should be much smaller—one tenth—otherwise the whole procedure does not make sense. On the other hand, doses much smaller cannot be considered, because the doses from natural radioactivity normally encountered are quite high. In Finland doses from inhalation of radon are about 1–2 mSv per year and from gamma radiation of building materials about 0.1 mSv per year.

It was also proposed to recommend that the dose rate at a distance of 1 m from the GAC filter should not exceed 1 µSv/h. This limit means that one should stay close to the source 100 hours per year, to receive the 0.1 mSv dose presented in the previous chapter. Normally this equipment is located in such parts of the dwellings that longer stays are not needed.

It was also proposed to recommend that possible solid and liquid wastes associated with removal methods could be delivered to communal dumps or discharged into the sewer. The procedures with the radioactive wastes should be as simple as possible to deal with. This encourages private citizens to start using some radioactivity removal method in connection with their own water supplies, if needed. If too complicated procedures are applied the dwellers keep on drinking the water containing high amounts of natural radioactivity.

The private companies selling removal equipment do not want to have responsibility for the possible wastes. Many times the company selling the equipment has nothing to do with the fitting of the equipment at its place of use. The fitters are locally operating private plumbers or small companies.

The fear of radioactivity operates in both directions. People are afraid of radioactivity and want to decrease the amount of natural radioactivity in their drinking water. On the other hand, when this is done there is a special problem with the wastes containing radioactivity. Difficulties in getting rid of them or expensiveness of this process may oppose the idea of lowering concentrations in drinking water.

6. PUBLICATIONS RELATED TO THE PROJECT

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