

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. ²²²Rn, U, ²²⁶Ra, ²¹⁰Pb, ²¹⁰Po, gross-alpha, Fe, Mn, TOC, pH, temperature and heterotrophic plate count were monitored regularly. SiO₂, redox potential, O₂, CO₂, colour, KMnO₄, acidity, PO₄³⁻, NO₃⁻ and NH₄⁺ 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:

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

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

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

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		Time in service (months)	Water treated (BV)	Radon reduction(%)
	Influent (Bq/L)	Effluent (Bq/L)			
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.

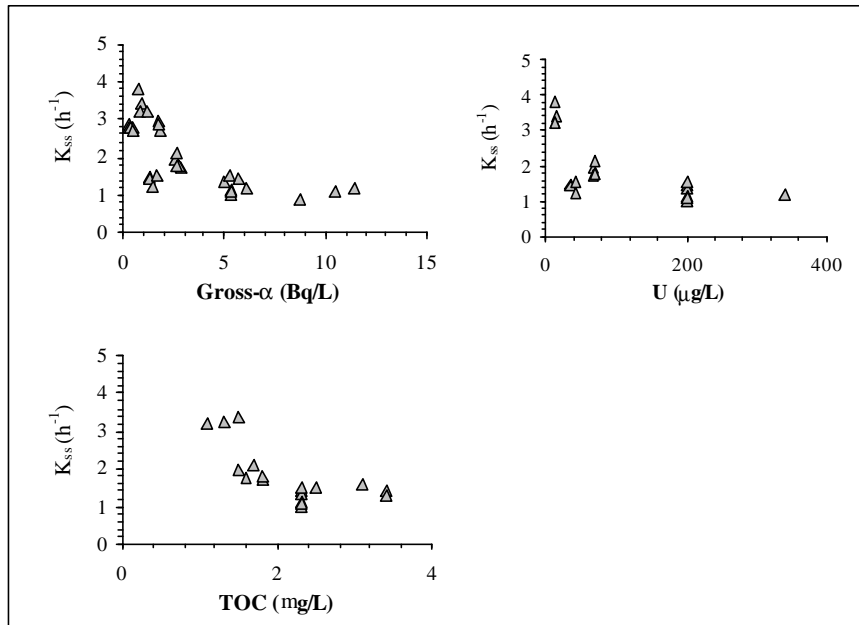


Figure 5. The rate of adsorption (K_{ss} constant) as a function of gross-alpha, uranium and total organic carbon (TOC) concentration of the influent. A negative correlation was obtained.

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.

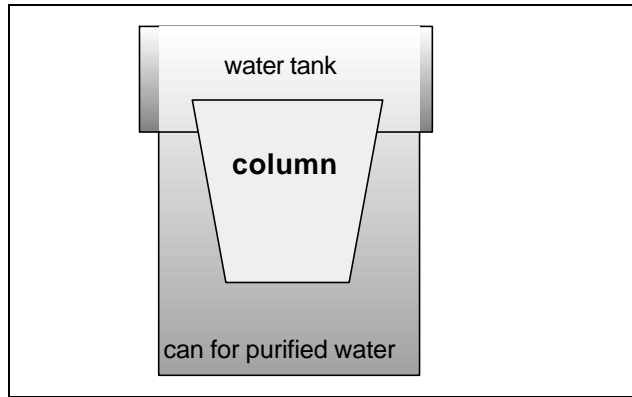


Figure 6. Filter system for the removal of radionuclides from drinking water.

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 (mg/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	0.109	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.

The aim of this study was

- to summarise the available information about ion exchange for the removal of natural radionuclides, uranium ($^{238,234}\text{U}$), 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 CaCl₂ 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 $\mu\text{Sv/h}$ 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.