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A CASE STUDY ON REMOVAL OF NATURAL RADIONUCLIDES FROM DRINKING WATER USING CONVENTIONAL IRON AND MANGANESE REMOVAL EQUIPMENT

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Abstract

The ability of conventional equipment intended for removing Fe and Mn to also remove ^{222}Rn, ^{226}Ra, ^{234,238}U, ^{210}Pb and ^{210}Po from private well water was examined at 12 houses in Finland. The operational principles of the equipment were based on aeration and filtration, ion exchange or manganese greensand filtration. The results indicated that ^{222}Rn removal efficiencies using aeration and filtration varied greatly, from 10 to 90 %. The best removal efficiencies for ^{234,238}U and ^{226}Ra of 80 to 99 % were attained by ion exchangers when anion and cation resins were used in the same filter. Manganese greensand filtration removed over 95 % of ^{226}Ra but less than 60 % of ^{234,238}U. Highly variable efficiencies of the equipment in removing ^{210}Pb and ^{210}Po (0 to 97 %) were observed. However, at most of the test sites studied the activity concentrations of various radionuclides in the treated water were under the guideline values set in Finland.

Key words – natural radionuclides, drinking water treatment, Fe and Mn removal

Introduction

Private wells are commonly used in Finland as a drinking water source in the sparsely populated countryside. The number of private wells in permanent use is estimated to be about 500 000 (Mäkeläinen et al, 2001). However, the guideline values of 0.2 mg/l for Fe and 0.05 mg/l for Mn are exceeded in 20–25 % of these private wells (Korkka-Niemi et al, 1993). A proportion of them have been drilled into the bedrock where the groundwater can be highly radioactive, especially in granite rock areas, whereas the activity levels of natural radionuclides in dug wells are typically low (Salonen, 1994; Salonen et al, 2002; Vesterbacka et al, 2005a). A recent study revealed that the ^{222}Rn concentration in about 10 % of the drilled wells exceeds 1 000 Bq/l and 18 % have a uranium (^{238}U) concentration higher than 15 µg/l (Vesterbacka et al, 2005a). Thus, the simultaneous removal of radionuclides and Fe or Mn is needed and a considerable economic saving would be made if all these elements could be removed with the same equipment. ^{222}Rn and ^{234,238}U are the typical radionuclides that need to be removed from Finnish bedrock waters, whereas the removal of ^{226}Ra, ^{210}Pb or ^{210}Po is required less frequently.

Three principally different types of Fe and Mn removal equipment are available on the Finnish markets which are based on aeration and filtration, manganese greensand filtration or ion exchange. All three processes efficiently remove Fe and Mn, but their ability to remove natural radionuclides has not been thoroughly studied in Finland. They could, however, potentially be used for that purpose because: 1) ^{222}Rn is removed by aeration (Vesterbacka et al, 2003), 2) ^{234,238}U and ^{226}Ra are removed by ion exchangers (Huikuri et al, 2000; Vesterbacka et al, 2003), and 3) the removal of ^{234,238}U and ^{226}Ra should be possible with equipment that precipitates Fe and Mn as hydroxides whose adsorptive capability is utilized in radiochemical analyses of ^{234,238}U and ^{226}Ra (Sill, 1987; Nour et al, 2004). Several measurements on water samples sent to the Radiation and Nuclear Safety Authority (STUK) for radionuclide analysis have indicated that a considerable proportion of ^{234,238}U and ^{226}Ra had been removed by some types of

Table 1. *Basic information on the cation and anion resin used in exchangers to remove Fe and Mn from drinking water.*

Parameter	Anion resin	Cation resin
Matrix	Makroporous polystyrene or cross link poly vinyl benzene	Spherical beads or polystyrene cross linked with divinylbenzene
Functional group	$-N^+(CH_3)_3$	$R-SO_3^-$
Physical form	Cl-	Na+ or H+
Particle size range	0.3 –1.2 mm	0.3 –1.2 mm
Total exchange capacity	>1.0 eq/l (Cl^- form, wet)	min. 1.8 eql/l (H+ form, wet)
Moisture content	50 to 70 % (Cl^-form)	45 to 55 % (H+ form)
pH range operating	0 – 14	0 – 14
Service flow rate	up to 50 BV/h, normally 10 to 30 BV/h	8 – 40 BV/h
Regeneration	NaCl, or NaCl 10 % + NaOH 2 %	NaCl, HCl or H_2SO_4

equipment. Nevertheless, no definite conclusions can be made on the basis of separate measurements before the removal efficiencies have been monitored over time.

The main aim of this study was to examine how efficiently natural radionuclides can be removed by various types of Fe- and Mn-removal equipment used in private households and how these results can be utilized for other sites or waters. The study was continued in 12 homes over one year. The removal efficiencies of Fe, Mn and organic matter and changes in pH value were also examined.

The commercial equipment in private households assessed here removed Fe and Mn according to three principles: aeration and filtration, manganese greensand filtration and ion exchange.

Regulations and recommendations

The Finnish regulations, which cover public water sources (Guide ST-12.3, 1993), state that the effective dose from ingested radionuclides should not exceed the value of 0.5 mSv per year. Radon and the long-lived radionuclides of $^{234,238}U$, ^{226}Ra, ^{228}Ra ^{210}Pb and ^{210}Po are included in this dose, but not radon released from water to air. The European Union (EU) drinking water directive (DWD) lays down a reference dose of 0.1 mSv per year for public waterworks (Council Directive 98/83/EY, 1998). In practice, only isotopes of U and Ra are included in this dose. The Commission of the European Communities issued a recommendation on the protection of the public against exposure to ^{222}Rn in drinking water supplies (Commission Recommendation 2001). This issue was taken into account in decree 401/2001 of the Finnish Ministry of Social Affairs and Health, where an activity level of 300 Bq/L for ^{222}Rn was set for units with less than 50 consumers and a guideline value of 1000 Bq/L for private wells. However, no recommendations for long-lived radionuclides ($^{234,238}U$, ^{226}Ra, ^{228}Ra ^{210}Pb, ^{210}Po) were issued. The EU recommendation gives a reference concentration of 0.1 Bq/L for ^{210}Po and 0.2 Bq/L for ^{210}Pb (Commission Recommendation 2001).According the DWD the guideline for ^{238}U is approximately 100 µg/L, a value that is used for private wells in Finland. In 2003 the WHO proposed a provisional guideline of 15 µg/L for ^{238}U based on its chemical toxicity (WHO 2004). In the near future, the DWD will be revised and national regulations will also be modified.

Aeration and filtration equipment

Fe removal is based on the oxidation of Fe^{2+} to Fe^{3+} by applying air or oxygen to water. This can be performed either by spraying water into a chamber that is impregnated with air or oxygen or by applying air to water as small bubbles. In the studied equipment, aeration is achieved by various methods; in Eurowater equipment a compressor blows air into the aeration chamber, in OVO equipment water is continuously circulated between the filter and pressure chamber, in Göinge Kombi equipment water is sprayed into and continuously circulated in the chamber, and in AF Series equipment water is sprayed into the chamber using air.

Manganese greensand filtration equipment

Manganese-treated greensand is a special silica-based glauconitic greensand that is capable of removing soluble Fe, Mn and also H_2S from drinking water systems by oxidizing with MnO_2 and by acting as a filter. The ferriprecipitates formed in the filter are very important catalysers in continuing the oxidation reaction of Fe and Mn. An optimal pH range in water is between 7.5 and 8.0. (Frek, 1996; Ala-Peijari 1994.)

Ion exchange units

Fe and Mn removal is maintained using a cation exchange resin in the filter (Table 1). During normal operation, raw water enters the filter through an inlet at the top of the filter. As the water passes through the ion exchange bed, positively charged ions are retained in the exchange sites of the resin and a corresponding number of Na cations are released into the water.

Experimental

Test sites

The efficiency of Fe- and Mn-removal equipment was examined at 12 private homes whose water supply was known to contain some amounts of natural radionuclides. The equipment had been installed at these homes before the radionuclide removal studies began to remove only Fe or Mn from all household water (Tables 2 and 3). No changes to their normal operation were performed. The equipment at six homes was based on aeration and filtration, at one home on manganese greensand filtration and at the remaining five homes on ion exchangers. At all these test sites drilled well water was permanently used throughout the year.

Sample collection

Water samples were collected by an employee of STUK or the owners of the private wells during the years 1998 and 1999. Raw water was collected from sampling taps before it entered the Fe and Mn removal equipment and the treated water was usually sampled from the kitchen taps in the houses.

Before collecting the samples, the water was allowed to run for 15 to 30 minutes in order to ensure that it came directly from the well and had not been stored in the pipe system or pressure tank. Samples for the determination of long-lived radionuclides (^{234}U, ^{238}U, ^{226}Ra, ^{210}Po and ^{210}Pb) were directly collected into one-litre polyethylene plastic bottles from the taps. In the laboratory, water samples were concentrated with hydrochloric acid and aerated in order to remove ^{222}Rn. Samples for ^{222}Rn analysis were taken directly into liquid scintillation glass vials that had been pre-filled with a scintillation cocktail.

Water samples were collected three times in separate seasons from each test site to observe the possible effect of the seasonal variations in radionuclide contents of raw water on the removal efficiencies. The first samples were collected during the winter (between October and February), the second samples during the spring (between

Table 2. *The equipment type at various test sites and Fe, Mn, organic matter and radionuclide contents in the raw water. Mean values ± standard deviation for ^{222}Rn, ^{226}Ra, ^{238}U, ^{210}Po and ^{210}Pb from different samplings are presented. Standard deviation is not reported in test sites where radiochemical analyses of ^{238}U, ^{210}Pb and ^{210}Po were performed only once.*

Test site	Equipment type and model	pH	Fe (mg/l)	Mn (mg/l)	Organic mater* (mg/l)	^{222}Rn (Bq/l)	^{226}Ra (Bq/l)	^{238}U (µg/l)	^{210}Pb (Bq/l)	^{210}Po (Bq/l)
Aeration and filtration equipment										
1-A	Eurowater NSB 40/60	7.0	1.4	0.22	4.5	190±40	<0.01	3.6**	0.03	0.006
1-B	OVO 55P	6.0	2.9	0.07	24.9	850±20	0.23±0.10	120±7	0.15±0.06	0.12±0.02
1-C	OVO 55R	7.0	5.8	0.29	10.9	2700±360	0.22±0.06	4±0	0.11±0.03	0.14±0.03
1-D	Göinge Kombi 50	6.9	1.5	1.3	5.4	5600±1400	0.36±0.08	3.1	0.41	0.47
1-E	AF500	7.1	4.5	0.14	2.7	520±40	0.04±0.01	13.6	0.051	0.289
1-F	AF400	7.5	1.2	0.12	1.7	590±30	0.09±0.02	3.6**	0.06	0.05
Manganese Greensand filtration equipment										
2-A	FeMn 20-R	7.3	2.70	0.27	2.3	7700±3000	0.30±0.03	22±17	0.29±0.004	0.19±0.05
Ion exchangers										
3-A	PS 36 (cation resin)	7.1	6.0	1.1	11.5	580±70	0.09±0.04	1.6	0.08	0.05
3-B	Mark-1000 (cation resin)	8.4	0.02	0.004	4.6	1500±200	0.16±0.03	112±13	0.09	0.13
3-C	Cul-Brook, limestone 6.1 (cation and anion resin)	15.0	0.25	24.3	580±70	0.11±0.02	14.5	0.78	1.24	
3-D	AHSL-300 8.0 (cation and anion resin)	0.52	0.22	26.1	590±140	0.36±0.02	12±1	–	–	
3-E	DD-30HDH 6.8 (cation and anion resin)	4.1	0.16	8.6***	1700±80	0.50±0.11	118±1	0.19±0.08	1.58±0.25	

Table 3. *The equipment type at various test sites and Fe, Mn, organic matter and radionuclide contents in the treated water. Mean values ± standard deviation for ^{222}Rn, ^{226}Ra, ^{238}U, ^{210}Po and ^{210}Pb from different samplings are presented. Standard deviation is not reported in test sites where radiochemical analyses of ^{238}U, ^{210}Pb and ^{210}Po were performed only once.*

Test site	Equipment type and model	pH	Fe (mg/l)	Mn (mg/l)	Organic mater* (mg/l)	^{222}Rn (Bq/l)	^{226}Ra (Bq/l)	^{238}U (µg/l)	^{210}Pb (Bq/l)	^{210}Po (Bq/l)
Aeration and filtration equipment										
1-A	Eurowater NSB 40/60	7.7	0.03	0.025	3.7	140±50	<0.01	0.9**	0.016	0.003
1-B	OVO 55P	9.1	0.13	0.004	13.8	490±350	0.07±0.06	58±21	0.05±0.02	0.07±0.02
1-C	OVO 55R	8.2	0.35	0.08	6.7	1800±330	0.17±0.08	4±0	0.07±0.04	0.04±0.01
1-D	Göinge Kombi 50	7.6	0.012	0.096	4.5	3000±220	0.16±0.11	2.7	0.25	0.08
1-E	AF500	9.2	1.4	0.041	2.1	330±60	0.02±0.01	12.0	0.021	0.076
1-F	AF400	9.5	0.21	0.001	1.6	410±10	0.05±0.02	1.3**	0.05	0.03
Manganese Greensand filtration equipment										
2-A	FeMn 20-R	7.6	0.006	0.001	2.4	7200±3500	<0.01	17±19	0.13±0.01	0.09±0.02
Ion exchangers										
3-A	PS 36 (cation resin)	7.3	0.059	0.001	10.2	550±30	<0.01	1.3	0.011	0.010
3-B	Mark-1000 (cation resin)	8.4	0.026	0.001	5.2	1400±200	0.05±0.04	108±14	0.08	0.004
3-C	Cul-Brook, limestone 7.3 (cation and anion resin)	0.80	0.023	8.9	510±80	<0.01	2.4	0.06	0.11	
3-D	AHSL-300 (cation and anion resin)	8.1	0.045	0.009	12.6	570±180	0.16±0.24	1.4±1.9	–	–
3-E	DD-30HDH (cation and anion resin)	6.3	0.42	0.004	2.4	1400±140	0.02±0.01	1.6±1.7	0.08±0.10	0.10±0.06

* determined as number of KMnO$_4$, ** Uranium concentration (µg/l) estimated from gross alpha results

April and May) and the third samples during the summer and autumn (between June and October). The concentration of Fe, Mn, pH and organic matter was determined once at each test site.

The removal efficiency (%) of each radionuclide was calculated from the difference in its activity concentration between raw and treated water as shown in Equation 1.

$$\text{Removal efficiency (\%)} = \frac{A_o - A}{A_o} 100 \qquad (1)$$

where A$_o$ is the activity concentration of a radionuclide in the raw water (Bq/l) and A is its activity concentration in the treated water (Bq/l).

Analytical methods for determining radionuclide and Fe, Mn and organic matter contents

The number of radionuclides analyses carried out from each sample varied according to the activity levels observed after the sample had been screened by measuring its ^{222}Rn concentration, and gross alpha and gross beta activity.

The radionuclide analysis methods used at STUK for ^{222}Rn, ^{238}U, ^{234}U, ^{210}Pb and ^{210}Po have been accredited according to the European Standard EN ISO/IEC 17025:2000 (European standard EN ISO/IEC 17025). The methods used have been validated and their analytical quality assurance includes calibration, internal quality control measurements, measurement of reference material and participation in proficiency testing or inter-laboratory testing. ^{226}Ra determination is not included in the accreditation, but analytical quality control has been ensured by the same methods used in the other determinations. The lower limit of detection (LLD) and the minimum detection limit (MDL) for each method were calculated using the Currie definition and the formula presented by the EPA, respectively (Currie L.A, 1968; Johns et al, 1979). Brief descriptions of the determination methods are given below.

The ^{222}Rn concentration was determined with a 1414 Guardian liquid scintillation spectrometer (Salonen, 1993a; Salonen et al, 1997). The concentration of ^{222}Rn was calculated from the alpha spectrum using a counting efficiency of 290 ± 5 %. The lower limit of detection at the 95 % confidence level with the Guardian is 0.17 Bq/l for 0.010 litres of water and 60 minutes of counting. The repeatability of the method is 4 %.

Determination of the gross alpha activity is based on concentrating water directly in a liquid scintillation vial and measuring the sample activity with a low background liquid scintillation spectrometer (Salonen, 1993b). The sample is prepared by evaporating water (usually 2 times the vial volume, 38 ml) to dryness with a freeze-dryer in a teflon-coated polyethylene vial (Zinsser). The residue is dissolved in 1 ml of 0.5 M hydrochloric acid and then 21 ml of scintillation cocktail (Optiphase Hisafe 2^{TM}, PerkinElmer) is added. The sample was counted one month after sample preparation, during which time ^{226}Ra attains equilibrium with ^{222}Rn and its short-lived daughters. Counting was performed with a 1220 Quantulus^{TM} (PerkinElmer), which is equipped with an anticoincidence guard counter and a pulse shape analyser (PSA). The PSA separates alpha and beta particles into their own spectra, which enables the calculation of the gross alpha and beta activities of the sample. The lower limit of detection was 0.02 Bq/l for gross alpha and 0.2 Bq/l for gross beta at a 95 % confidence level for 0.038 litres of water and 180 minutes of counting.

The ^{226}Ra concentration was also determined in each sample because it could be directly calculated from the gross alpha spectrum of the liquid scintillation spectrometer. ^{226}Ra activity is calculated from the gross alpha spectrum on the basis of the counts measured in a window set in the area of the ^{214}Po peak (Salonen, 1993b). This gives quite accurate results for ^{226}Ra because no other natural or artificial radionuclides have alpha emissions in the same energy range. The counting efficiency of ^{214}Po (and thus of ^{226}Ra) in the selected window is 86 ± 3 %. The lower limit of detection for ^{226}Ra is 0.01 Bq/l at a 95 % confidence level for 0.038 litres of water and 180 minutes of counting.

The radiochemical analyses of ^{238}U, ^{210}Pb and ^{210}Po were performed on water samples at least once. ^{234}U and ^{238}U concentrations were determined by using radiochemical separation and alpha spectrometry (AlphaAnalyst from Canberra). The water sample was concentrated by applying iron scavenging. The precipitate was dissolved in concentrated HCl, and ^{234}U and ^{238}U were then separated from other radionuclides by the ion exchange method (by using Dowex 1x8, 50/100 mesh). ^{234}U and ^{238}U were co-precipitated with CeF_3 for alpha measurement (Liberman et al, 1968; Sill, 1981; Sill, 1987) and the sample was counted with an alpha spectrometer. The minimum detectable activity (MDL) was 0.5 mBq/L for one litre of water and 1000 minutes of counting. ^{232}U was used as a chemical yield tracer. The repeatability of the method is 8 %. The tracer yield varied between 70–100 % depending on the original quality of water in the analysis.

^{210}Pb and ^{210}Po concentrations were determined by the spontaneous deposition of ^{210}Po on a silver disk and alpha spectrometric measurement (AlphaAnalyst) of ^{210}Po activity (Häsänen, 1977; Vesterbacka et al, 2005c). Before deposition the water sample was concentrated by evaporation in a water pool. The ^{210}Po is deposited from 0.5M HCl solution at a temperature of 80 °C with a four-hour deposition time and counted with the alpha spectrometer. The solution remaining from the ^{210}Po deposition is stored for at least 200 days to allow the in-growth of ^{210}Po, which is a daughter product of ^{210}Pb. The second ^{210}Po deposition was then carried out and its ^{210}Po activity was counted. The final ^{210}Po result is calculated using the results from these two depositions. The ^{210}Pb result was calculated from the second ^{210}Po deposition. The in-growth ^{210}Pb from ^{222}Rn between sampling and ^{222}Rn aeration in the laboratory was subtracted to obtain the final ^{210}Pb concentration in the water sample (Vesterbacka et al, 2002). The minimum detectable activity (MDL) was 0.5mBq/L for one litre of water and 1000 minutes of counting. ^{209}Po was used as a chemical yield tracer. The repeatability of the ^{210}Po method is 6 % and that of the ^{210}Pb method 15 %. Tracer yield varied between 30 to 100 % depending on the original quality of water in the analysis.

Fe, Mn and organic matter contents were assessed by an accredited water laboratory at the City of Helsinki, Environment Centre.

Results and discussion

The removal efficiencies of ^{238}U-series radionuclides are reported separately for each type of equipment (Table 4), since the efficiencies varied greatly depending on the operational principle of the equipment used.

Aeration and filtration

This equipment type was assessed at six test sites. ^{222}Rn removal from water is most often based on various aeration methods (Lowry et al, 1987; Dixon et al, 1991). Radon removal efficiencies are generally quite good, ranging from 67–99 % for various aeration techniques applied at waterworks and 90–100 % for aerators used in private households (Annanmäki et al, 2000; Salonen et al, 2002; Vesterbacka et al, 2003). In this study the best ^{222}Rn removal of about 90 % recorded in occasional sampling was attained with the OVO 55P. Quite reason-

Table 4. *The radionuclide removal efficiencies with various equipment installed for removing Fe and Mn at various test sites.*

Test site	Fe-Mn removal method	Manufacturer name	Equipment type and model	Ranges for radionuclides removal efficiencies (%)				
				^{222}Rn	^{226}Ra	^{238}U	^{210}Pb	^{210}Po
1-A	Aeration + filtration	Hyxo Oy	Eurowater NSB 40/60	19–43	–	67–82	48	50
1-B	Aeration + filtration	Omavesi Oy	OVO 55P	12–89	48–93	36–65	67–70	33–40
1-C	Aeration + filtration	Omavesi Oy	OVO 55R	21–44	8–44	0	21–52	69–70
1-D	Aeration + filtration	Aqua Expert Oy	Göinge Kombi 50	27–52	3–78	11	40	82
1-E	Aeration + filtration	Akva Filter Oy	AF500	24–47	67–50	33–36	59	74
1-F	Aeration + filtration	Akva Filter Oy	AF400	26–34	40–57	54–92	29	47
2-A	Manganese Greensand	Aqua Expert Oy	FeMn 20-R	0–23	98	11–60	52–59	53–57
3-A	Ion exchanger	HOH Separtec Oy	PS 36 cation resin	0–11	96–98	9–47	86	79
3-B	Ion exchanger	Kaiko Oy	Mark-1000 cation resin	3–9	50–88	0–5	13	97
3-C	Ion exchanger	Kaiko Oy	Cul-Brook. limestone cation+anion	8–11	80–98	100	93	91
3-D	Ion exchanger	HOH Separtec Oy	AHSL-300 cation+anion	0–16	89–97	77–99	–	–
3-E	Ion exchanger	Callidus Oy	DD-30HDH cation+anion	12–33	94–100	98–100	29–73	90–97

able removals of 50 % or higher were also achieved with the models Kombi50, AF500 and AF400 in occasional samplings, while for other equipment the highest removals were 40 %. Inefficient removal of ^{222}Rn is mainly due to the insufficient amount of air applied in most equipment. For Fe or Mn removal only 2 litres of air is needed for 20 litres of water to be treated or 0.6 ml of air for 1 mg of Fe. This amount of air is insufficient for ^{222}Rn removal. In most aerators designed for ^{222}Rn removal the air to water ratio is higher than 10:1 (Lowry et al, 1987; Dixon et al, 1991). In Fe- and Mn-removal equipment this ratio is only about 1:10, and such equipment was quite evidently only partly able to remove ^{222}Rn. The only means to enhance the ^{222}Rn efficiency is to increase the air-to-water ratio, to add droplet spraying in the equipment or to increase the amount of activated carbon among the other filtration masses. Further studies are necessary in order to determine whether such changes are possible in the equipment studied here. Another possible reason for the insufficient ^{222}Rn removal is that the tested equipment had closed tanks and thus operated under higher pressures when ^{222}Rn removal is not efficient.

Prior to our study the efficiency of this type of equipment in removing ^{238}U, ^{226}Ra, ^{210}Pb and ^{210}Po had not, as far as we know, been studied elsewhere. Their removal could take place by a few mechanisms: by adsorption on particles and colloids, as precipitates and by co-precipitation with Fe and Mn hydroxides. Water quality has the primary effect on the formation of particles, precipitates and colloids in water. Depending on the amount and composition of colloids, quite variable amounts of ^{234,238}U, ^{226}Ra, ^{210}Pb and ^{210}Po can be expected to be removed during the filtration of colloids and particulate matter. In this study, the removal efficiencies for ^{238}U and ^{226}Ra varied from 0 to 93 % (Table 4). The best efficiency of 92 % for ^{238}U was achieved with the AF400 (test site 1-E), and that of 93 % for ^{226}Ra with the OVO 55P (test site 1-B). ^{210}Pb removal varied from 20 to 70 % irrespective of the ^{210}Pb concentration and that of ^{210}Po between 30 and 80 %. The removal of ^{210}Pb and ^{210}Po by conventional removal methods such as ion exchange has been found to be difficult, as these nuclides are mostly bound to particles of various sizes (Lehto et al, 1999; Vaaramaa et al, 2003; Vesterbacka et al, 2005b). Since only a few water quality parameters were analyzed in this study, no further analysis of their effect on the radionuclide removal could be made.

Manganese greensand filtration

Manganese greensand filtration was assessed at only one test site. In this study, the removal efficiency for ^{222}Rn was very low (0 to 20 %), which was evidently due to the operational principle of the manganese greensand filtration equipment. No aeration is used in this method and ^{222}Rn is not significantly adsorbed in the greensand bed.

The results indicated that ^{226}Ra removal was very good, over 95 %, which is consistent with the efficiencies of up to 88 % attained elsewhere (Valentine et al, 1990; Qureshi et al, 2003). The good removal is based to the use of potassium permanganate, which forms a fresh coating of manganese dioxide (MnO_2) on the greensand granulate surfaces. This coating acts as an efficient adsorbent, especially for ^{226}Ra but also for ^{238}U.

At our test sites the removal efficiency for ^{238}U varied from 10 to 60 % at various samplings. ^{238}U was probably removed by co-precipitation with Fe and Mn hydroxides. The removal of ^{210}Po and ^{210}Pb varied from 50 to 60 %, probably depending on the ^{210}Po and ^{210}Pb speciation in the raw water. The removal of ^{210}Pb and ^{210}Po from drinking water is dependent on their occurrence forms (ions or particles) in groundwater and the removal methods used, as mentioned earlier.

Ion exchange units

This type of equipment was assessed at five test sites. In groundwater, ^{222}Rn occurs in a gaseous form and is uncharged, and is thus obviously not removed from water by ion exchange. Therefore, the removal efficiencies are not reported here.

The ion exchange units removed variable amounts of ^{238}U from water. The removal efficiencies varied from close to zero to 99 %, evidently depending on the type of resin used and the charge of uranium complexes that occurred in the water. In the pH range of 6.5 to 9, which is typical of most of our test sites, ^{238}U mainly exists as a negatively-charged carbonate complex of $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ (Ivanovich et al, 1982). In the pH range of 7 to 9, ^{238}U also forms a positive carbonate complex of $(UO_2)_3(OH)_5^+$, although its contribution is only 10 % of the total ^{238}U dissolved in water. The negatively-charged complexes are efficiently removed with anion resins. The uncharged ^{238}U complex of $UO_2CO_3^0$ can also be efficiently removed at a pH of less than 6.5 where this complex occurs. This is due to the formation of $UO_2(CO_3)_3^{4-}$ on the resin sites (Zhang et al, 1994). The use of strong base anion (SBA) resins for ^{238}U removal has been reported by several authors (Sorg, 1990; Zhang et al, 1994; Huikuri et al, 2000). In these studies the removal efficiency of ^{238}U has typically been over 98 %, which is in agreement with the present study at the test sites where anion exchange resin was used (test sites 3-C, 3-D and 3-E). At two sites (3-A and 3-B), ^{238}U removal was less than 25 % because there was only a cation resin, and U cannot be efficiently removed without using an anion resin. The minor removal that was achieved was possibly due to the retention on the filter of uncharged or positively-charged ^{238}U complexes or ^{238}U bound to particles.

In this study, the removal efficiency for ^{226}Ra varied from 50 to 100 %. ^{226}Ra is known to be efficiently removed by strong acid cation (SAC) resins, which are normally used for removing Fe, Mn and hardness from water, and ^{226}Ra removal efficiencies of 80 and 98 % have been reported (Clifford, 1990; Vesterbacka et al, 2003). The decreased removal attained especially at test site 3-B in this study can be explained by the fact that other ions possibly occurring in the groundwater, such as Ca, Mg, Fe and Mn, significantly compete with ^{226}Ra at the ion exchange sites. Clifford 1990 reported that increased concentrations of these cations reduced the efficiency of ^{226}Ra removal. The removal efficiency of ^{210}Po and ^{210}Pb varied over a large range from 13 % to 97 %, similarly to the other Fe and Mn removal equipment in this study.

Advantages and disadvantages

One advantage of the aeration and filtration equipment is that it is easy to service. As the equipment also acts as a pressure chamber, separate chambers are not needed. This is a very important advantage since many house owners have not reserved any space for water treatment units in their house. Aeration also removes pad odour and thus improves the taste of the drinking water. The disadvantages are occasionally low ^{222}Rn and Mn removal efficiency, valves in the aeration chamber can clog up, the compressor needs servicing and is noisy. If activated carbon or anion exchange resin could be added to the equipment it would be capable of removing Rn, U and Ra efficiently and its usefulness for the simultaneous removal of radionuclides, Fe and Mn would become better.

Manganese greensand filtration equipment is rarely used in private households in Finland, possibly due to the need for regeneration with chemicals like $KMnO_4$, which must be handled very carefully. However, only a minor quantity of chemicals is needed in the regeneration and they have the capability to disinfect water. Additionally, water quality remains good in this treatment. Comparing radionuclide removal, the best results were achieved for ^{226}Ra.

Ion exchangers are less technical than the other equipment tested. They need less space compared to aeration and filtration equipment and the same unit can be equipped with anion and cation resins, which saves space. Additionally, ion exchangers remove water contaminants such as NO_3, NH_4 and NO_2. The main disadvantages are the very soft treated water achieved using cation resins, the regeneration mechanism that can clog up and the organic resins that can decompose and thus spoil the water quality.

Wastes

The amount of radionuclides in liquid or solid wastes produced by the tested equipment depends on the radionuclide levels in raw waters, the regeneration and backwash intervals and on changing the masses in the equipment. Ion exchangers and manganese greensand filtration equipment are regenerated or backwashed after short intervals of between 2 and 7 days to ensure their safe usage. This usually requires that the radioactivity levels are low enough in brines or rinsing water to be drained into the sewer. Solid wastes are created in cases when the radioactivity accumulated in the masses or materials in equipment is removed from usage. In Finland, solid wastes can be disposed at municipal dumps.

Conclusion

This study demonstrated that it is possible to apply conventional Fe and Mn removal equipment for the simultaneous removal of Fe, Mn and natural radionuclides, although the removal is not always efficient. At most test sites the activity concentrations of ^{234,238}U, ^{226}Ra, ^{210}Pb and ^{210}Po in the treated water were under the guideline values set in Finland for private houses, whereas initially high ^{222}Rn concentrations could not be sufficiently reduced. The removal efficiencies for various nuclides were highly dependent on the equipment type, on the radionuclide to be removed and on its concentration in the raw water. ^{222}Rn removal was the most insufficient, even though aeration and filtration equipment was used due to the deficient amount of air applied in the equipment. ^{226}Ra and ^{234,238}U removals were efficient using manganese greensand filtration and a cation exchanger for Ra, and an anion exchanger for U. Quite variable amounts of ^{210}Pb and ^{210}Po were removed at different samplings and by the various equipment. This is assumed to depend a great deal on their tendency to be bound to various sizes of particles, which varies considerably from one sampling to another.

No definite conclusions can be drawn on the basis of this preliminary study in which only the removal of Fe, Mn and organics was examined in addition to radionuclides. No modifications or adjustments were made to the conventional Fe and Mn removal equipment in order to observe whether the removal capabilities for ^{222}Rn, and possibly other radionuclides, would be sufficiently improved to attain compliance with the requirements.

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