Water Supply

Water Supply Vol 23 No 1, 288 doi: 10.2166/ws.2022.425

Can activated carbon filtration of groundwater cause radiation safety problems?

Jukka T. Tyrväinen [a,b,*], Jonne Naarala [a] and Tuukka Turtiainen [c]

[a] Department of Environmental and Biological Sciences, University of Eastern Finland, P. O. Box 1627, 70211 Kuopio, Finland
[b] Alva-yhtiöt Ltd, P. O. Box 4, 40101 Jyväskylä, Finland
[c] Radiation and Nuclear Safety Authority (STUK), Jokiniemenkuja 1, 01370 Vantaa, Finland
*Corresponding author. E-mail: jukka.tyrvainen@uef.fi

JTT, 0000-0002-9022-7334; JN, 0000-0002-5240-968X; TT, 0000-0001-8695-1461

ABSTRACT

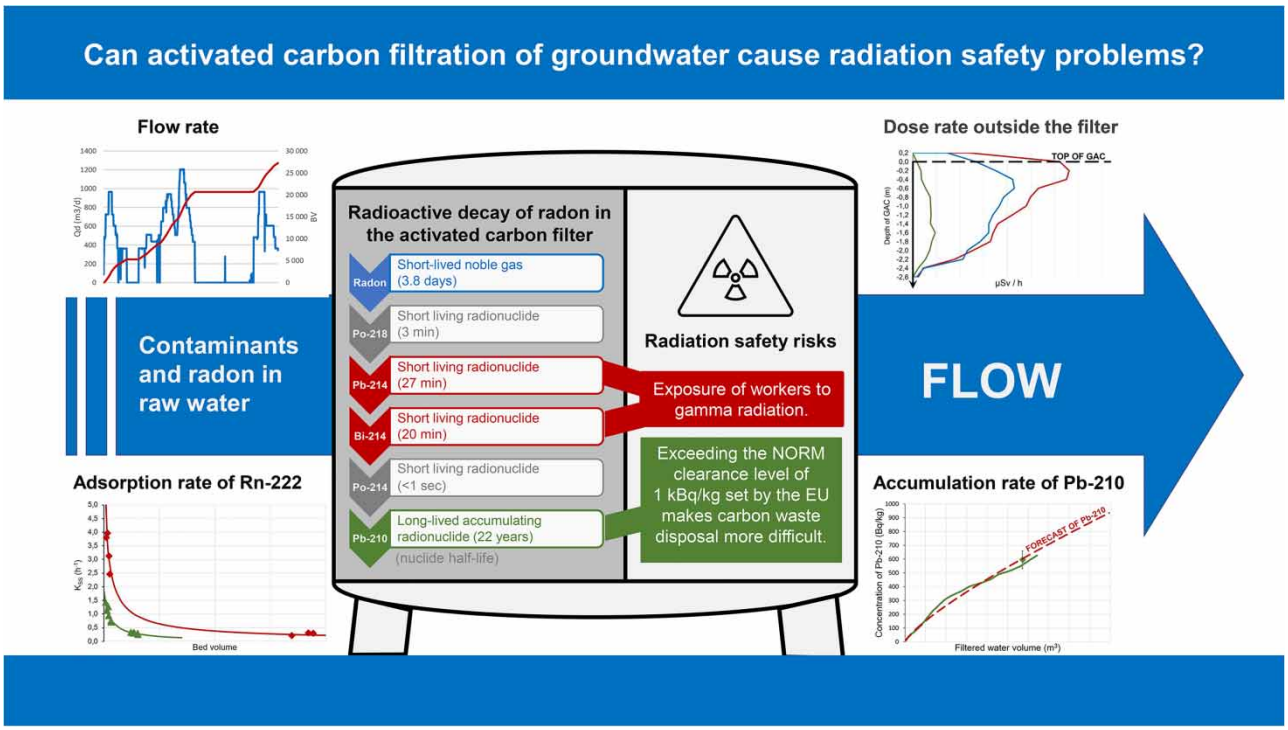
Activated carbon filtration is commonly used to remove groundwater contaminants in water utilities. During its use, also groundwater radon is adsorbed on activated carbon where it radioactively decays to Pb-210 within a few days. The intermediate stages of radioactive decay produce gamma radiation outside the filter, which can be harmful to health. In addition, EU legislation sets a clearance level of 1 kBq/kg for the Pb-210 concentration of waste, above which disposal of carbon waste can be complicated, depending on national legislation. This study focused on activated carbon filters from two groundwater plants. Measurements were made over the service lifetime of the activated carbon and included measurements of adsorption of radon from water to carbon, radiation dose rates outside the filters and Pb-210 concentrations in the carbon. The study observed a rapid decrease in the radon adsorption rate of activated carbon during the first year of use. This phenomenon has a significant effect on the concentration of Pb-210 in the activated carbon waste at the end of service life. The calculated forecast model clearly showed that the risk of exceeding the clearance level of Pb-210 increases if the radon concentration in the raw water exceeds 100 Bq/L.

Key words: ^{210}Pb, drinking water, GAC, gamma radiation, NORM, radon

HIGHLIGHTS

- Retention of groundwater radon in the GAC filter causes radiation problems.
- The adsorption rate of Rn-222 on carbon decreases over service time.
- Radioactive decay produces gamma radiation that is harmful to health.
- The radon decay product Pb-210 accumulates in activated carbon.
- The NORM clearance level may make it difficult to dispose of GAC waste.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Granular activated carbon (GAC) filtration is commonly used to remove trace contaminants, organic micropollutants such as pesticides, and their degradation products from groundwater. At the same time, the filter adsorbs radon (Rn-222), which is present in all groundwater. Radioactive radon and its decay products can pose a radiation safety risk to the operating personnel and a waste management problem for spent activated carbon (Lowry *et al.* 1988; Annanmäki *et al.* 2000).

Radon is a radioactive noble gas that does not react chemically in the environment. It is continuously generated from ubiquitous crustal uranium (U-238) with a half-life of 4.5 billion years. Gaseous radon dissolves easily in groundwater and moves well with groundwater flows and soil air currents. Its mobility is limited by its short half-life, 3.8 days. The radon concentration in groundwater depends on the uranium concentration in the soil and bedrock and the quality of groundwater. The groundwaters are often soft in Finland, and high bicarbonate concentrations in groundwater correlate with higher uranium concentrations (Lopes *et al.* 2017). The typical radon concentration in dug wells in Sweden is 10–300 Bq/L (in granite areas 40–400 Bq/L), average 43 Bq/L (Åkerblom *et al.* 2005). The average concentration in Finland is 50 Bq/L (Vesterbacka *et al.* 2005), and in 3% of the wells the concentration is over 300 Bq/L (Lopes *et al.* 2017).

When water is used, radon is released into the air where it forms solid decay products, which are also radioactive. The inhaled decay products attach to the lungs and bronchi and cause radiation exposure. Radon is also absorbed by the body through ingestion (ICRP 2017; Zagà *et al.* 2021). Due to the carcinogenic risk, the EU Commission has set a parametric value 100 Bq/L for the radon content of tap water, but a Member State may set a maximum level of 100–1,000 Bq/L in national legislation (EURATOM 2013a).

Radon adsorbed on the GAC filter decays through four short-lived radionuclides (Po-218, Pb-214, Bi-214 and Po-214) into the long-lived isotope of lead, Pb-210. This generates gamma radiation that can be detected outside the GAC filter. Gamma radiation is suspected to pose a radiation safety risk near GAC filters installed in homes when the radon content of raw water is very high (Lowry *et al.* 1988). In contrast, gamma radiation from GAC filters used in the removal of environmental pollutants in groundwater plants, has been less studied.

Another potential problem is the long-lived lead isotope Pb-210 formed in GAC filters. If the concentration of Pb-210 in activated carbon exceeds the clearance level of 1 kBq/kg of Naturally Occurring Radioactive Materials (NORM) laid

down in the EU directive, or the national clearance level which may be even stricter, the owner of the waste must notify the competent authority (EURATOM 2013b). In these cases, the competent authority will usually require a more detailed assessment of the radiation exposure. The investigation should cover occupational and public exposure caused by the storage, handling, transport, and disposal of the used GAC. If the clearance level for the occupational or public exposure is exceeded, the handling and disposal of GAC may require licensing. Preparing the investigation and the application for a license is time consuming and requires the consulting of a radiation protection expert. If NORM waste is treated in an incinerator, Pb-210 will be transferred to the fly ash and equipment of the incinerator (IAEA 2003), so incineration is not recommended. Most European states allow NORM waste to be landfilled, provided the procedure is approved by the competent authority. For example, in France, U-238 series NORM waste can be landfilled at a maximum concentration of 20 kBq/kg and in Sweden 10 kBq/kg of dry matter (Garcia-Talavera *et al.* 2021).

Similarly, waste legislation includes a ban on landfilling of organic carbon, which in some cases has been interpreted as also applying to activated carbon waste (EC 2002). Recycling and other uses are the primary methods of waste treatment compared to landfilling. However, landfill restrictions do not apply if it can be justified that the waste is not suitable for recycling or energy production and if the landfill would be the best solution environmentally. The interpretation of the waste legislation on the landfilling of activated carbon exceeding the NORM clearance level concentration is unclear and vary from country to country (Garcia-Talavera *et al.* 2021). Exceeding the NORM limit value can cause significant additional costs for the design, approval, and implementation of carbon waste disposal.

In this study, long-term adsorption of radon on activated carbon was measured at two groundwater plants. The aim of the study was to assess the magnitude of the radiation safety risk associated with GAC filtration. The aim was also to draw up recommendations to ensure the radiation safety of workers during the use of the activated carbon and to avoid exceeding the clearance level of Pb-210 and thus waste treatment problems.

2. MATERIALS AND METHODS

2.1. Study sites

The Pekonniemi groundwater plant is located in the city of Jyväskylä, in Central Finland. The groundwater is pumped from Keljonkangas alluvial aquifer that is part of the Central Finland end moraine. The aquifer has formed at the end of the ice age in the ice-marginal process. As the glacier melted, various water-permeable gravel and sand layers formed in the valleys and slopes of the bedrock (SYKE 2020b). The Pekonniemi intake has one dug well. GAC filters have been installed to remove tri- and tetrachloroethylene in 2010. The daily use of Pekonniemi varied during the study period from 300 to 1,200 m^3/d and the plant had production shutdowns lasting several months.

The second research site was the Alalampi groundwater plant in the municipality of Keuruu. The alluvial aquifer is located on a northwest-southeast esker. The core part of the esker is sand and sandy gravel, and the soil at the edges of the esker is silty (SYKE 2020a). The groundwater intake has two screen wells that are used alternately. The distance between the wells is only 10 meters. Pesticides and their decomposition products were detected in the groundwater in 2009 and the following year GAC filters were installed at the plant. The major compounds removed by the GAC filter are atrazine, BAM (2,6-dichlorobenzamide), hexazinone, lenacil, and terbuthylazine. Unlike Pekonniemi, the Alalampi intake stops for a few hours every day.

Pumping histories, water qualities, design values and utilization rates of groundwater plants during the service life of activated carbon (GAC) are presented in Appendixes A-C. The quality of raw water in both intakes is otherwise good, but slightly acidic.

The activated carbon grade used at the Pekonniemi water plant is Silcarbon S835 (Silcarbon Aktivkohle GmbH, Kirchhundem, Germany) and Alalampi AquaSorb® AS2000 12 × 40 US MESH (Jacobi Carbons AB, Kalmar, Sweden). Both activated carbons are manufactured by a steam activation process from coal. In the spring of 2021, Filtrasorb® F300 8 × 30 US MESH (Calgon Carbon Corporation, Pittsburgh, USA) carbon was installed as a reference carbon in one of the three filters at Pekonniemi. F300 is made of bituminous coal by a process known as reagglomeration (Kaya *et al.* 1997). The specific weights and weighing results for activated carbon are presented in Appendix D.

2.2. Sampling and measurements

Initially, the radon adsorption efficiency of old activated carbons was studied by analysing the radon concentration in the influent and the effluent and by measuring the ambient dose rate of gamma radiation outside the filters. In addition, material samples were taken from the old carbons for the determination of the activity concentration of naturally occurring radionuclides. After the initial test period, the carbons in both waterworks were replaced with new ones of similar quality and

the radon adsorption efficiency and dose rate of the new carbons were also determined. In Pekonniemi, different flow rates were set for parallel filters to obtain samples at different contact times.

Water samples for the determination of radon concentration were taken by passing water from the sample tap with a hose to the bottom of a 500 ml beaker. The water was allowed to drain over the edge until the water in the beaker changed several times and all air bubbles were removed. A 10 ml water sample was taken from the beaker with a pipette and injected into a scintillation vial pre-filled with scintillation cocktail (12 ml of Ultima Gold XR; PerkinElmer Inc, Boston, USA). The water sample and liquid scintillation cocktail were immediately mixed after closing the vial (Kitto 1994).

Ambient dose equivalent rates due to gamma radiation from GAC filters were measured using a calibrated DGM-Turva (Kata Safety Oy, Joensuu, Finland) dose rate meter. Measurements were made on the outer surface of the filter jacket and in series of measurements at 0.1–0.8 m from the filter. Each measurement was made as the arithmetic mean of at least 10 consecutive readings so that the interval between individual measurements was at least 10 s. The background dose rate inside the service building was measured at a distance of at least 4 meters from the GAC filters. The background dose rate was subtracted from the measured mean value and the result was corrected using the calibration coefficient provided by Finnish Radiation and Nuclear Safety Authority (STUK), which is the national standard laboratory for radiation quantities.

Activated carbon samples were taken from the surface layer of each GAC filter through the service hatch to determine the Pb-210 concentration. In addition, GAC filters from Pekonniemi were sampled from the bottom layer through the filter drain valve.

The flow data for Pekonniemi were process data retrieved from the automation system's historical database, and for Alalampi, data from operating logs and reports were used. The process flow meters were magnetic flow meters connected to the automation systems, whose models were Proline Promag 10W (Endress + Hauser AG, Reinach, Swizerland) in Pekonniemi and Sitrans FM MAG3100/5000 (Siemens, Munich, Germany) in Alalampi. The accuracy of the flow measurements in the calculations was 1%, which was estimated to include both the internal error of the flow meter and the error caused by the process installation.

The amount of carbon installed, and the technical drawings of the filters were used to calculate the volume of the carbon bed and contact time. The sorting of the granules during rinsing can cause changes in the volume of activated carbon.

2.3. Analyses

The concentration of radon in water and Pb-210 in activated carbon samples were analysed in the laboratory of the Finnish Radiation and Nuclear Safety Authority (STUK) in Helsinki. The laboratory is accredited according to the international standard EN ISO/IEC 17025:2017 (FINAS 2021).

Radon concentrations were analysed using the Guardian 1414 Liquid Scintillation Counter (EG&G Wallac, Turku, Finland) (Salonen & Hukkanen 1997). The uncertainties in the pulse rate of the sample and the calibration of the device have been taken into account in the results.

The activity concentration of Pb-210 in activated carbon was determined from the gamma energy of 46.5 keV measured by broad energy germanium detectors (Canberra Industies, Meridien, USA) and analysed by UniSAMPO Gamma Spectrum Analysis Software (Aarnio *et al.* 2001). The uncertainties include both statistical uncertainty and uncertainty due to the efficiency calibration. The method, which is modified from IEC 1452 (IEC 1995) standard, is documented in the quality manual of the laboratory.

2.4. Calculations

At the beginning of its service life, radon concentration of the new activated carbon increases until it reaches a steady state at which the rate of radon adsorption is equal to the rate of radioactive decay. The adsorption-decay steady state is shown in the equation (Lowry & Lowry 1987):

$$C_t = C_0\, e^{-K_{SS}\, t} \tag{1}$$

$$K_{SS} = \frac{-ln\dfrac{C_t}{C_0}}{t} \tag{2}$$

where: C_t Rn-222 concentration in effluent water (Bq/L)

C_0 Rn-222 concentration influent water (Bq/L)

K_{SS} Steady state adsorption-decay constant (h^{-1})
t Empty-bed contact time, EBCT (h)

Based on Equation (1), the change in radon concentration (ΔC) can be presented by equation:

$$\Delta C = C_0 - C_t = C_0 - (C_0\, e^{-K_{SS}\, t}) \tag{3}$$

The daily adsorbed activity of radon was determined from the flow and the difference between the influent and effluent concentrations. The concentration of Pb-210 formed as a result of radioactive decay of radon was calculated according to the law of radioactive decay:

$$C_{Pb210} = \frac{\tau_{Rn222}}{\tau_{Pb210}} \times C_{Rn222} = 0.0004693\, C_{Rn222} \tag{4}$$

where: C_{Pb210} Pb-210 concentration in the GAC (Bq/GAC kg)

C_{Rn222} Rn-222 concentration in the GAC (Bq/GAC kg)
τ_{Pb210} Pb-210 radioactive half-life (22.3 year)
τ_{Rn222} Rn-222 radioactive half-life (3.82 day)

The activities of radon and Pb-210 at the end of the reference periods were determined by summing the daily activities which were corrected to represent each calculating date:

$$A = A_0 \times e^{-\left[\frac{\ln(2)}{\tau_{1/2}} \times (t - t_0)\right]} \tag{5}$$

where: A Residual activity at the end of the reference period (Bq)

A_0 Initial activity (Bq)
$\tau_{1/2}$ Radioactive half-life (d)
$(t - t_0)$ Time between A and A_0 (d)

3. RESULTS

3.1. The ability of GAC to adsorb radon with short EBCTs

In the Pekonniemi groundwater plant, the average radon concentration in raw water was 62.8 Bq/L ($n = 14$) and the range of individual measurements was 60.2–67.0 Bq/L. The adsorption efficiency of the new S835 activated carbon was 29–60% of radon and 54–75% with the new F300 carbon, but only 10–28% with the old S835 carbon (EBCT 20–60 min). In Alalampi, the radon concentration in raw water was slightly lower, 55.7 Bq/L ($n = 9$). Radon concentration in well #1 ranged 58.3–61.0 Bq/L and in well #2 49.2–53.4 Bq/L. The radon adsorption efficiency of the new AS2000 carbon was 37–52% and that of the old AS2000 only 4–12% (EBCT 11–12 min). The analyses of carbon grades S835 and AS2000 covered the entire service life of the activated carbon, but the analyses of the F300 only the beginning. The adsorption efficiencies measured on different days are shown in Appendix E.

Figure 1 shows radon remaining as a function of EBCT fitted to the logarithmic plot similar to Lowry & Lowry (1987). With the new S835 carbon, 90% radon reduction can be achieved in about 90 minutes and 99% in about 180 min. Deterioration of the adsorption efficiency started immediately after the introduction of the new carbon, and the adsorption efficiency of the carbon at the end of its service life is very poor.

The adsorption-decay constant (K_{SS}) of the steady state GAC filter depends on the properties of the activated carbon and describes the first-order adsorption rate of radon in the carbon. The temporal deterioration of the K_{ss} was modelled

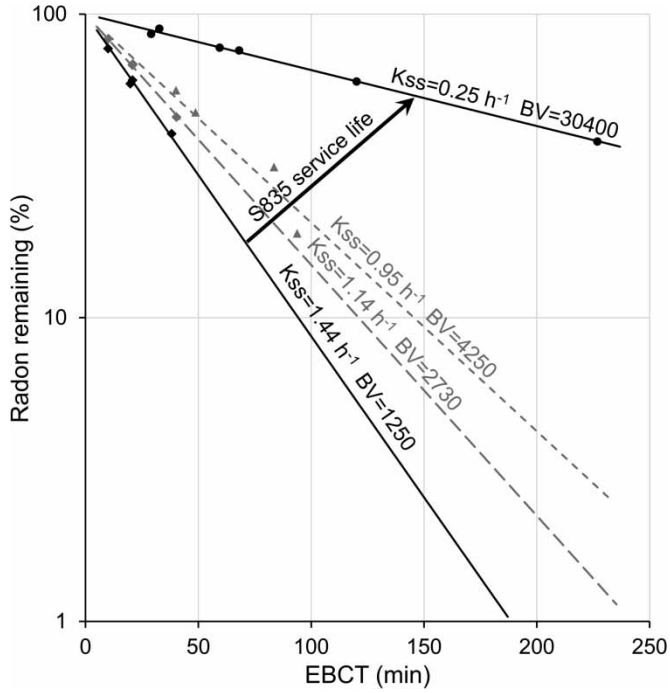


Figure 1 | Percent radon remaining as a function of empty-bed contact time (EBCT). From the graphs can be observed deterioration of the adsorption over the service life of S835 carbon. The steady state adsorption-decay constants (K_{SS}) and Bed Volumes (BV) are measured results.

with log-logistic equation:

$$K_{SS} = A - \frac{A}{1 + \left(\frac{BV}{B}\right)^{-C}} \tag{6}$$

where: K_{SS} Steady state adsorption-decay constant (h^{-1})

BV Bed volumes

A The maximum value of K_{SS}

B, C The parameters specifying the shape

Figure 2 shows the change in the value of K_{SS} over the service life of the activated carbon. In Pekonniemi, the K_{SS} value of the S835 carbon decreased from 1.44 to 0.25 h^{-1} during the service life of activated carbon. In Alalampi, over the very long service life reduced the K_{SS} value of the AS2000 from 3.8 to 0.30 h^{-1}. The K_{SS} equations shown in the Figure 2, have been used to calculate accumulated Pb-210. The S835 carbon data extends to the inflection point of change, and the equation used fits well with the measured data. The AS2000 measurement results are only from the beginning and end of the service life, which makes the fit less accurate.

The observed temporal deterioration of radon adsorption efficiency (Figure 1) was compared to the temporal trends observed in the adsorption efficiencies of other substances. The mean adsorption of trichloroethylene calculated from co-sampled pairs was 3.0 µg/L (reduction 58%) and non purgeable organic carbon (NPOC) 0.2 mg/L (18%). At the beginning of the carbon life 0.6–0.9 mg NPOC/L of organic matter was adsorbed, but after 1.5 years only <0.1 mg NPOC/L. Adsorption of other substances such as iron and manganese could not be shown statistically in water samples.

Trichloroethylene, iron, and manganese concentrations were analysed from samples of S835 carbon material taken during carbon exchange. Trichloroethylene was found only at the top of the filters 1.0 mg/kg, iron at the top 1,700 mg/kg and bottom 3,800 mg/kg, manganese at the top 14 mg/kg and bottom 91 mg/kg (Appendix B).

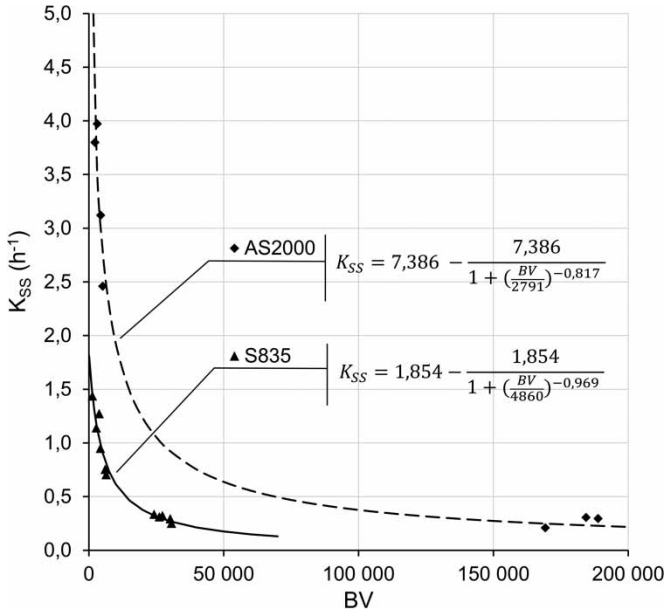


Figure 2 | The steady state adsorption-decay constants (K_{SS}) as a function of bed volume (BV). Equations have been used in Pb-210 activity accumulation calculations in activated carbons S835 and AS2000.

3.2. Radon accumulation in the GAC

As the flow of raw water changes, the combined effect of radon inflow and EBCT change determines the accumulation rate and steady-state concentration of radon on activated carbon. The calculated curve in Figure 3 shows that the highest accumulation rate of radon in the carbon takes place at short EBCTs, although adsorption is known to improve with long EBCTs.

Figure 4 shows the steady-state concentration of radon in the activated carbon as a function of EBCT. The results are calculated from water samples using different carbon grades and the filter was in the steady state. The results for the new carbons

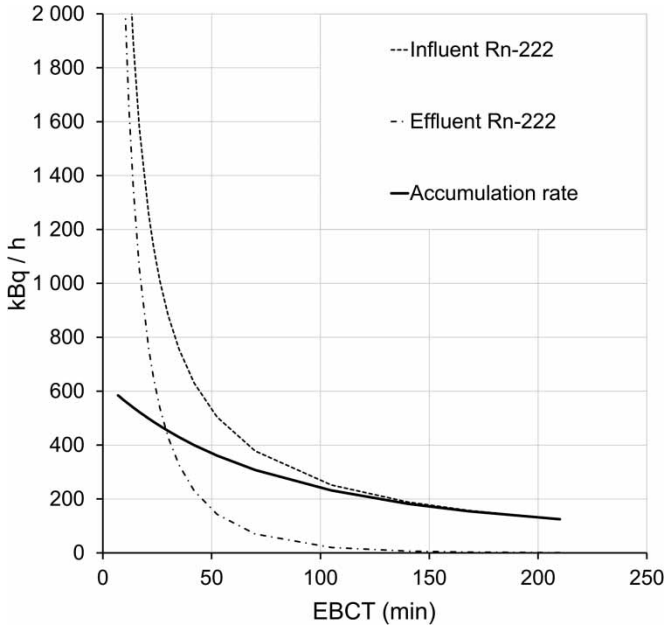


Figure 3 | The calculated accumulation rate of radon as a function of empty-bed contact time (EBCT). New S835 carbon, adsorption-decay constant (K_{SS}) 1.44 h^{-1} and radon concentration influent water 63 Bq/L.

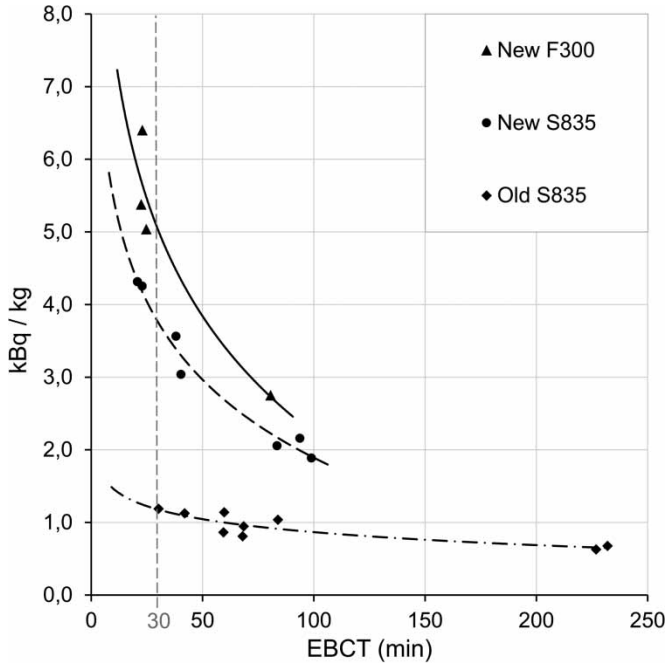


Figure 4 | Concentration of radon at steady state in various activated carbons as a function of empty bed contact time (EBCT). Radon concentration influent water 63 Bq/L.

are for the first 3 months and the old ones for the last year of use. Special attention should be paid to the results of short contact times, as in water plants, GAC filters are usually designed for 10–30 minutes EBCT. With a short 30 minutes EBCT, the radon concentration of the new F300 carbon was about 35% higher than that of the new S835. Correspondingly, at the end of the service life, the radon concentration of the old S835 was only 30% of the concentration of the new carbon.

3.3. Dose rate from radon decay products outside the GAC filter

Dose rates caused by the short-lived decay products were measured from outside the GAC filters. Figure 5 shows the radiation profiles measured from the outer surface of the filter for the three new and the one old carbon in steady state. The maximum dose rate in Pekonniemi measured from the surface of the new F300 carbon filter was 3.31 $\pm$ 0.20 μSv/h at the top of the filter, to which the influent is directed. The mean dose rate over the entire length of the sheath was 2.22 $\pm$ 0.05 μSv/h. The radiation profile of the new S835 carbon was significantly lower and the dose rate was a maximum of 2.15 $\pm$ 0.15 μSv/h and an average 1.64 $\pm$ 0.03 μSv/h. The measured dose rates of the old S835 carbon were very low, $<$0.5 μSv/h at the outer surface of the filter. The AS2000 carbon dose rate in Alalampi was lower than in Pekonniemi carbons, the maximum was 1.72 $\pm$ 0.08 μSv/h and the average 1.43 $\pm$ 0.03 μSv/h. The depth of AS2000 carbon was smaller than carbons in the Pekonniemi filters, as can be clearly seen from the figure.

Figure 6 illustrates dose rates measured at a working distance with equal curves from filter jacket. The measurement was made about a month after the introduction of the new F300 activated carbon, when the radiation values were at their highest. The dose rate measured directly from the outer surface of the filter (3.31 μSv/h, Figure 5) decreases rapidly with increasing distance, at the distance of 1.0 m the dose rate is less than 0.75 μSv/h.

3.4. Accumulation of Pb-210

The activity of Pb-210 accumulated in activated carbon at the end of service life was calculated based on the results of radon concentrations in water samples. The decrease in the adsorption rate of activated carbon was taken into account by separately calculating the change in the K_{SS} constant for each day of use using the equations in Figure 2. The Pb-210 concentrations calculated using Equations (4) and (5) and the concentrations analysed from the material samples are presented in Figure 7 and Appendix F. The calculated average Pb-210 concentration differs by only 6% from the average of material samples on the day of sampling.

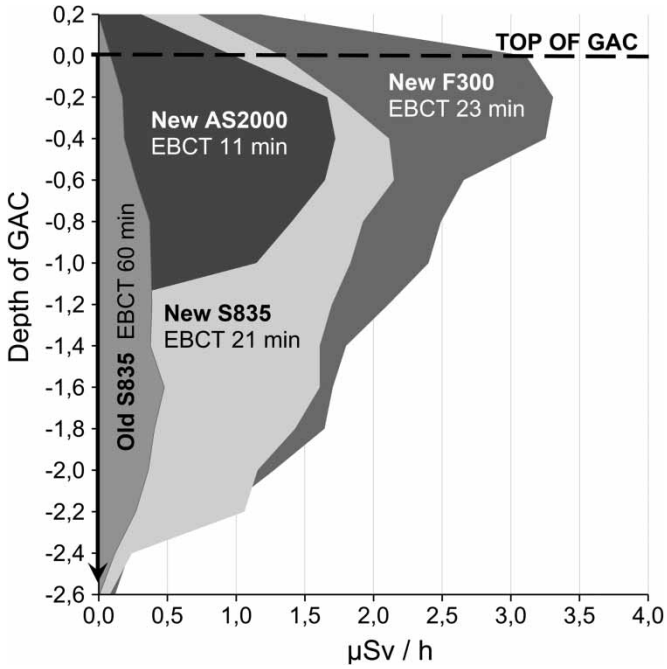


Figure 5 | Radiation dose rates measured from the outer surface of the activated carbon (GAC) filter. Pekonniemi F300 and S835 carbon filters had a jacket material of 4 mm steel and Alalampi AS2000 filter fiberglass. Empty-bed contact times (EBCT) are shown on the figure.

When modelling the accumulation of Pb-210, the specific weight of the carbon is an important variable which varies according to the water content of sample. Based on the weighing of the material samples in Pekonniemi, the activated carbon had sorted in the filters so that the specific weight of the surface samples is clearly lower than the weight of the samples taken from the bottom. Activated carbon is washed efficiently, and pumping is very rarely stopped, which explains the sorting of the material in the washing direction. In Alalampi the material samples were taken only from the surface of the carbon and their specific weight was clearly higher than specified by the manufacturer. The results show the sorting of the filter material in the flow direction. In Alalampi, the pumps are started and stopped daily. From this, pressure shocks are applied to the filter, which could explain the sorting of the filter material according to the flow direction. The sorted specific weights of the surface and bottom samples are taken into account in Figure 7.

Figure 8 shows two forecast models for Pb-210 concentration based on the amount of water treated and the concentration of radon in the raw water. The specific weight of activated carbon is used weight of drained dried carbon. The models are based on the measurement results of Pekonniemi and Alalampi and are clearly different.

4. DISCUSSION

4.1. Radon adsorption

The typical EBCT of activated carbon filters designed to remove solvents and pesticides is short, typically 10–30 minutes (Lykins *et al.* 1990; Crittenden *et al.* 2012), and the reduction of radon is only 40–60% (Lowry & Brandow 1985; Dixon & Lee 1988; Hiltebrand *et al.* 1988). Instead, several previous radon studies have focused on the elimination of very high radon concentrations from raw water with activated carbon. The reductions are usually required to be 90–99%, in which case the EBCT must be significantly longer than in this study, 70–120 min (Lowry *et al.* 1987).

The concentration of radon adsorbed from water to carbon is determined by Equation (3) (Section 2.4), where the EBCT is inversely proportional to flow rate. The influent flow of radon to the filter increases linearly with increasing flow rate or radon concentration. In this study, we found that the increase in flow rate produces more radon to the filter, than a decrease in adsorption rate reduces the rate of accumulation. Correspondingly, as EBCT increases, incoming radon flow decreases faster than the adsorption rate increases. Although the kinetics of the adsorption rate shown in

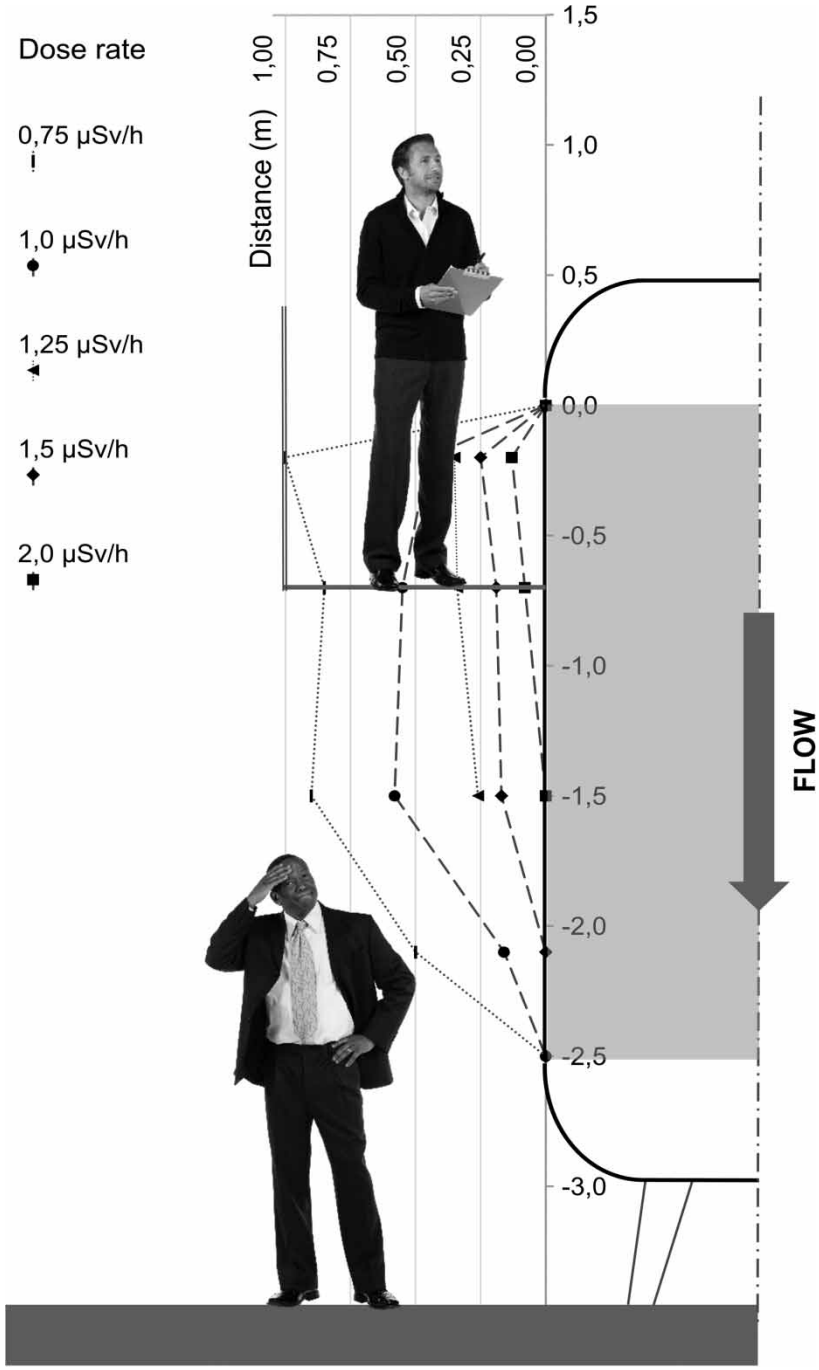


Figure 6 | Equivalent dose rate curves from the filter based on maximum dose rate of radon with new F300 carbon in Pekonniemi (Figure 5). The calculated concentration of radon in the carbon 13.6 $\pm$ 0.57 MBq/GAC m^3.

Equations (1)–(2) (Section 2.4) have long been known (Lowry & Lowry 1987), the importance of this phenomenon is emphasized when calculating the accumulation of radon in activated carbon at short EBCT <60 min, which is especially evident in the radon accumulation rate in Figure 3.

In the case of new carbon (Figure 5), the adsorption takes place mainly at the point where the water enters the filter, which is also reflected in the measurements of the vertical gamma activity profiles of several other studies (Lowry & Brandow 1985; Turtiainen *et al.* 2000). The uneven distribution of radon in the activated carbon filter can be explained by the Half Lengths effect. If the first period of the filter binds 50% of the impurity (radon), the second period of equal length binds 25% and the

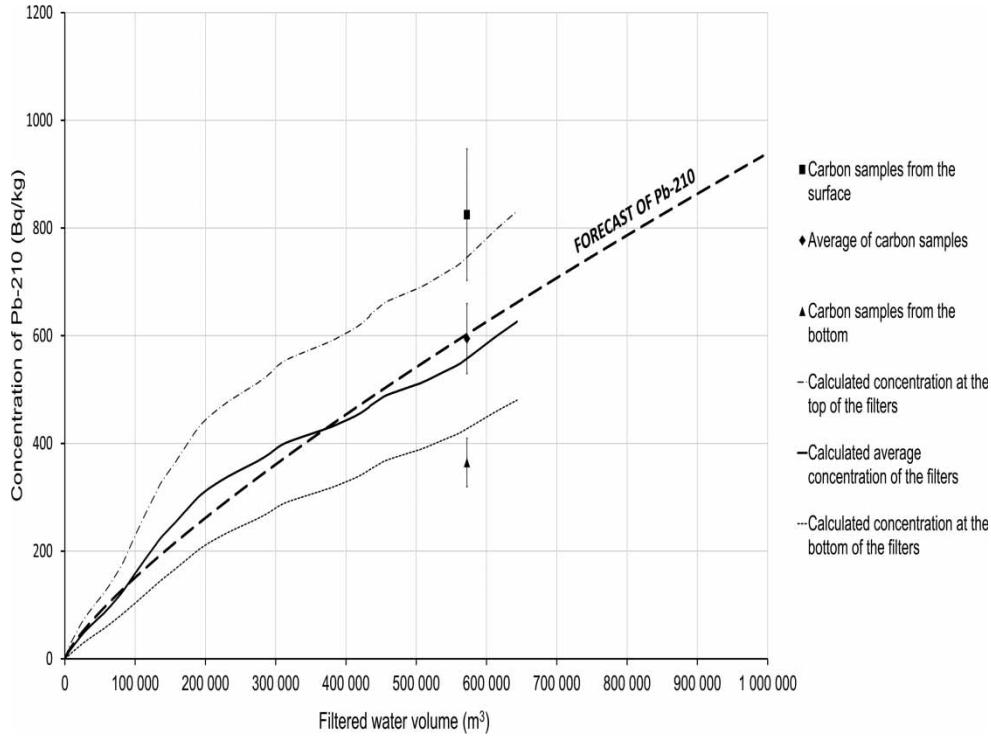


Figure 7 | Pb-210 concentrations and forecast model in activated carbon, calculated from the basis of radon accumulation, and Pb-210 concentrations measured from the S835 carbon samples. Dried carbon 480 kg/m^3. The radon concentration influent water 63 Bq/L and the uncertainty coverage factor k = 2.

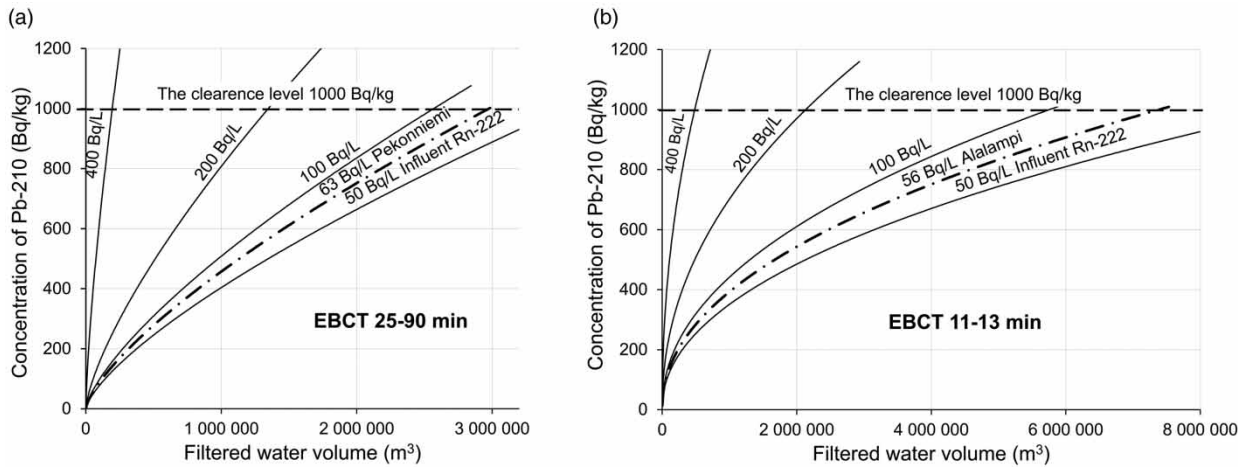


Figure 8 | Forecast models for Pekonniemi (a) and Alalampi (b) of activated carbon Pb-210 concentration at different influent radon concentrations. Drained dried carbon 880 kg/m^3.

third 12.5% of the initial concentration (WQA 2013). When the adsorption capacity of the carbon is impaired, detachment and re-attachment of nuclides smooth out the vertical distribution.

The K_{SS} constant describes the rate of radon adsorption on carbon. The K_{SS} of each measured carbon type began to decline immediately after the deployment, and the K_{SS} was halved at about 8000 BV (4–10 months, Figure 2). This has a significant effect on the magnitude of total Pb-210 accumulation. Adsorption of organic compounds, iron, manganese or other particles in activated carbon or the growth of biofilms have been suspected of causing to impair adsorption of the activated carbon

(Kinner *et al.* 1990). Differences in hydraulic properties of the filter or influent water quality have been estimated in the literature to cause variations in K_{SS} values (Alabdula'aly & Maghrawy 2011). The temperatures of the investigated groundwater were +5– + 7 °C. Guo *et al.* (2017), in cold conditions the adsorption capacity of activated carbon is better than in warm conditions. In studies with long contact times a decrease in K_{SS} is more difficult to detect than with short (EBCT <60 min) contact times of this study.

With the exception for compounds to be removed, at both water plants, the raw water was of good physico-chemical quality and the amount of organic matter was low (Appendix B). The microbiological quality of activated carbon was not studied separately, but some estimates can be made based on the change in organic matter concentration. Velten *et al.* (2011) has shown that the growth of biofilm consumes a lot of dissolved organic carbon (DOC) at the beginning of the activated carbon use, but after the inflection point, DOC is consumed only for the maintenance and vital functions of the biofilm. NPOC results are available for the organic matter content at Pekonniemi. In the months after the changing of activated carbon, 0.6–0.9 mg NPOC/L of organic matter was retained in the filter, but <0.1 mg NPOC/L after the inflection point (1.5 years). This was much less than the 0.3–0.5 mg DOC/L reported by Velten *et al.* (2011). In Finland, phosphorus has been shown in many cases to be the limiting nutrient for biofilms of the water supply network (Miettinen *et al.* 1997), so phosphorus scarcity may explain the difference in results. In Middle-Finland, groundwater is usually low in phosphorus (Lahermo *et al.* 2002), at Pekonniemi 9.0 μg/L.

4.2. Significance of gamma radiation outside the filter

Radon adsorbed on the GAC filter decays into long-lived Pb-210 through four short-lived decay products. Two of these, Pb-214 and Bi-214 emit relatively intense gamma radiation outside the filter. The magnitude of the dose rate is determined by the concentration of radon in carbon, the measuring distance, and the properties of the media.

As a result of the self-attenuation of gamma radiation by the water-carbon mixture, about 90% of the radiation measured from outside the filter is generated at distance of less than 30 cm from the filter jacket. If the flow rate slows down near the jacket compared to the middle area of the filter, the concentration of radon in carbon near the jacket is also lower than in the middle of the filter. In case of uneven distribution, the radon concentration of the filter cannot be assessed by external dose measurement.

Outside the filter, the dose rate decreases rapidly, at working distance, the dose rate is only half of its maximum value (Figure 6). In Pekonniemi, the maximum dose rate of 0.75–1.25 μSv/h with F300 carbon was measured from the working distance ($C_0 = 62.5$ Bq/L, EBCT 23 min). If the radon concentration in the raw water is high (400 Bq/L) and the contact time is short (EBCT 10 min), the dose rate could increase to 30 μSv/h on the outer surface of the filter jacket and at a working distance of 0.5 m 5–10 μSv/h. As the adsorption rate of radon decreases during the use of activated carbon, the external dose rates also decrease. In Pekonniemi, both the measured radon accumulation rate and the measured dose rate both decreased to approximately one-fifth of the original after three years of use.

Water plant maintenance personnel do not work long periods of time near the GAC filter. Typical tasks are carbon change, backwash (an automated process), possible repairs, and water sampling. The dose received by the worker can be estimated based on the dose rate, working distance, and time. If the working distance is 0.5 m and the working time is 8 h/a, the occupational dose from gamma radiation in Pekonniemi would be about 8 μSv/a. At the maximum dose rate of 5–10 μSv/h, the annual dose would be 40–80 μSv/a. This dose does not exceed the usual reference value for occupational exposure to natural radioactivity (1 mSv/a excluding radon in indoor air) and can be compared, for example, to the annual dose of 50 μSv/a received from air travel (STUK 2020). Based on the results, working of several days near GAC filters should be avoided if the radon concentration in the raw water exceeds 200 Bq/L and the activated carbon is less than one year old. When designing new water plants, the radiation risk must be taken into account in the design of work areas and maintenance bridges.

4.3. Accumulation of Pb-210 in carbon waste

Activated carbon accumulates Pb-210, which is produced by the radioactive decay of radon adsorbed on carbon. In activated carbon samples taken from Pekonniemi, the concentrations of Pb-210 in the surface samples were more than twice as high as in the samples taken from the bottom (Appendix F). A similar uneven accumulation of radon can be observed in the water samples taken from different parts of the filter, and in the radiation dose rate profiles in Figure 5.

During the long period of use, the accumulated radon in the activated carbon is practically completely decayed into Pb-210, and some of the formed Pb-210 has had enough time to decay further into the stable isotope Pb-206. In Pekonniemi, the

average accumulation of Pb-210 calculated based on water samples was practically equal as the average of the material samples. Although the log-logistic model used for the K_{SS} deterioration had to interpolate a large BV range, the result was in good agreement with the measured one.

In the GAC filter, detachment and reattachment of both radon and Pb-210 atoms occur, which increase as the filter material ages. The phenomenon is described by the K_{SS} constant. For radon, this can be seen in Figure 5 as a maximum point shift and smoothing as the K_{SS} decreases. Unlike radon, Pb-210 is chemically highly reactive in the aquatic environment. The main explanation for the solubility of lead is pH, and the most significant change in solubility occurs between pH 6.0 and 7.0 (Sigworth & Smith 1972). Lead precipitates at pH 8–11 into lead oxides and carbonates. At pH <8, part of the lead dissolves into lead ions, but in the pH range 5–8.5 lead can also be present as carbonates if there is enough carbon dioxide in the water (Naylor & Dague 1975). In Finland, groundwater is typically slightly acidic. The pH values of the raw water in Pekonniemi and Alalampi are 6.4 and 6.2, so the state of lead depends on the pH-carbon dioxide balance. The small difference between the calculated and measured Pb-210 in the samples (Figure 7) shows that, at least in Pekonniemi, there is no significant release due to the dissolution of lead. Some studies have reported that activated carbon removes more than 90% of Pb-210. The result suggests very good retention of Pb-210, but measurements have been reported in the higher pH range of 7.1–8.1 (Turtiainen *et al.* 2000) than in this study (pH 6.2–6.4).

When activated carbon is used for several years, the concentration of Pb-210 in the filter may exceed the NORM clearance level of 1 kBq/kg. As stated at the outset, the limit values for the disposal of Pb-210 in landfills differ from one country to another (Garcia-Talavera *et al.* 2021). Similarly, in some countries the dry weight of the sample is used in the clearing level comparison (SSMFS 2018) and in others, such as Finland, the weight of the sample in the moisture content of the treatment. Predictive models of Pb-210 reported in the literature have generally been calculated for dried activated carbon (Martins 1992; Lewis & Houle 2008) which should be considered when comparing the models.

Figure 8 shows two forecasts of Pb-210 accumulation. The specific weight of the drained dried carbon (880 kg/m^3) has been used as the weight of the material in the forecasts, and the forecasts can be scaled to different water contents. With the normal 4–5-year service life of activated carbon, the risk of exceeding the clearance level increases if the radon concentration in the raw water exceeds 100 Bq/L. The accumulation of Pb-210 in the Pekonniemi GAC was faster than in the Alalampi GAC, based on both water and material samples, so the difference in accumulation rates is real. The differences are explained by the quality of raw water, the quality of the carbon (K_{SS}), the contact time (EBCT) and the possible release of Pb-210 over the long period of use. Attention should be paid to the radon concentration and pH of raw water and the changes in the K_{SS} value of activated carbon (Figure 2). The data of the Pekonniemi covered the entire life cycle of carbon better than the data of Alalampi, which may also explain the difference in forecasts.

4.4. Uncertainties of the study

The main challenge in preparing a Pb-210 accumulation forecast is related to the uncertainty of the radon measurement results. Analyses of water samples were performed in STUK's laboratory, which is the standard laboratory for radiation measurements in Finland. The results take into account statistical uncertainties in the count rate of ionizing radiation and the calibration of the measuring instrument. Uncertainties were increased by the delivery time of the samples to the laboratory, which ranged from 2 to 5 days. Especially with older activated carbons for which a low (<5%) radon adsorption efficiency is calculated, the uncertainty of the result may be significant (Appendix E).

Another noteworthy source of uncertainty is the accuracy of flow measurements in water utilities. The measuring equipment is factory calibrated, but the best measuring accuracy is only achieved within a certain flow rate range specified by the manufacturer. As the groundwater pumps in both plants are operated on/off, it can be estimated that there are no slow flows that impair the measurement accuracy. The measurement accuracy can also be impaired by the flow conditions at the installation site and the processing of the measurement signal in the data transmission and reporting system.

The technical dimensional accuracy of the filter equipment, and in particular the actual amount of carbon in the filter and any channelling of the flow, may impair the accuracy of the derived results. The volume of carbon is not an exact measurand and may vary during use, for example due to carbon sorting.

The accumulation model for radon and Pb-210 is particularly affected by the adsorption rate of carbon and its deterioration during use. K_{SS} is a variable that depends on the quality of carbon and water at a particular point in time. Several measurements of radon concentration (and thereby K_{SS} value) in water are needed for the accumulation estimates for the entire service life.

The concentration of radon or Pb-210 in the carbon is expressed in relation to the specific weight, which depends on the water content of the sample. It is important to note whether the results are reported in completely dry, drained, or wet weight of the carbon.

Modelling of Pb-210 accumulation leaves uncertainty about the long-term dissolution of Pb-210, which may affect the final Pb-210 concentration.

5. CONCLUSIONS

In waterworks using groundwater from alluvial aquifer, gamma radiation outside activated carbon filters is unlikely to pose a significant radiation protection problem. However, if the raw water contains more than 200 Bq/L of radon, it is recommended to measure the dose rate approximately 3 weeks after the addition of activated carbon and to assess the occupational radiation safety risk and to avoid prolonged work near filter. After about a year of use, the dose rate decreases significantly.

The concentration of Pb-210 retained in activated carbon may exceed the clearance level of 1 kBq/kg for NORM materials. Pb-210 was found to be unevenly distributed in the filter material. When typical usage times of carbon batches are considered, we can conclude that the risk of exceeding the NORM clearance level increases significantly when the concentration of Pb-210 in raw water exceeds 100 Bq/L. If the clearance level is exceeded, the owner of the waste is responsible for notifying the competent authority, and for correct treatment and disposal of the carbon waste.

The national radiation authority and the waste management authority should jointly provide guidance on the final disposal of carbon waste used for groundwater treatment, so that proper treatment of the waste is possible, and the procedure is known to the waste owners.

ACKNOWLEDGEMENTS

The authors wish to thank Dr Niina Leikoski for her help in sampling the activated carbons and Dr Antti Kallio for analyzing the gamma-ray spectra of these samples. The authors also want to acknowledge Mrs Tarja Heikkinen's great work on radon measurements in water samples, and Keuruu waterworks and water treatment team at Alva-yhtiöt Ltd for making this study possible.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

Aarnio, P. A., Nikkinen, M. T. & Routti, J. T. 2001 UNISAMPO, comprehensive software for gamma-spectrum processing. *Journal of Radioanalytical and Nuclear Chemistry* **248** (2), 371–375.

Åkerblom, G., Falk, R., Lindgren, J., Mjönes, L., Östergren, I., Söderman, A.-, Nyblom, L., Möre, H., Hagberg, N., Andersson, P. & Ek, B. 2005 Natural radioactivity in Sweden, exposure to external and internal radiation. In *Paper Presented at the Proceedings of the XIV Regular Meeting of the Nordic Society for Radiation Protection, NSFS*, Rättvik, Sweden, pp. 207–214.

Alabdula'aly, A. I. & Maghrawy, H. B. 2011 Comparative study of different types of granular activated carbon in removing medium level radon from water. *Journal of Radioanalytical and Nuclear Chemistry* **287** (1), 77–85.

Annanmäki, M., Turtiainen, T., Jungclas, H. & Rausse, C. 2000 Disposal of Radioactive Waste Arising from Water Treatment: Recommendations for the EC. In *Final Report of the WP 8 of the TENAWA Project*, Helsinki, Finland.

Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J. & Tchobanoglous, G. 2012 *MWH's Water Treatment: Principles and Design*, 3rd edn. John Wiley & Sons, Inc, New Jersey, USA.

Dixon, K. L. & Lee, R. G. 1988 Radon Survey of The American Water Works System. In *Paper Presented at the The NWWA Conference: Radon, Radium, and Other Radioactivity in Ground Water*, pp. 311–345.

EC 2002 Establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. *Council Decision 2003/33/EC of The European Union*. Available from: https://eur-lex.europa.eu/eli/dec/2003/33(1)/oj.

EURATOM 2013a Laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption. *Council Directive 2013/51/EURATOM of The European Union*. Available from: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32013L0051.

EURATOM 2013b Laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation. *Council Directive 2013/59/EURATOM of the European Union*. Available from: https://eur-lex.europa.eu/eli/dir/2013/59/oj.

FINAS 2021 ppendix 1 of Decision T167/M23/2021, Accredited Testing Laboratory. *FINAS, Accreditation unit of the Finnish Safety and Chemicals Agency*.

Garcia-Talavera, M., Mrdakovic Popic, J., Görts, P., Pepin, S. & Jones, K. 2021 *Application of the Concepts of Exemption and Clearance to the Regulation of Naturally Occurring Radioactive Material (NORM) Across HERCA Countries*. HERCA Report 2021, HERGA WG NAT.

Guo, L., Wang, Y., Zhang, L., Zeng, Z., Dong, W. & Guo, Q. 2017 The temperature dependence of adsorption coefficients of ^{222}Rn on activated charcoal: an experimental study. *Applied Radiation and Isotopes* **125**, 185–187.

Hiltebrand, D. J., Dyksen, J. E. & Raman, K. 1988 Radon in Water Supply Wells: Treatment Facility Requirements and Costs. In *Paper Presented at the NWWA Conference: Radon, Radium, and Other Radioactivity in Ground Water*, pp. 521–534.

IAEA 2003 *Extent on Environmental Contamination by Naturally Occurring Radioactive Material (NORM) and Technological Options for Mitigation*. IAEA; International Atomic Energy Agency.

ICRP 2017 Occupational Intakes of Radionuclides. *ICRP Publication 137, Part 3. (No. 46)*.

IEC 1995 *International Standard IEC 1452, Nuclear Instrumentation – Measurement of Gamma-ray Emission Rates of Radionuclides – Calibration and use of Germanium Spectrometers*. International Electrotechnical Comission, Geneva, Switzerland.

Kaya, E., Cho, H. & Hogg, R. 1997 Reagglomeration phenomena in fine dry grinding of coal. *Minerals and Metallurgical Processing* **14** (2), 37–42.

Kitto, M. E. 1994 Characteristics if liquid scintillation analysis of radon in water. *Journal of Radioanalytical and Nuclear Chemistry* **185** (1), 91–99.

Kinner, N. E., Malley Jr., J. P. & Clement, J. A. 1990 *Radon Removal Using Point-of-Entry Water Treatment Techniques*. Report no. EPA/600/2-90/047.

Lahermo, P., Tarvainen, T., Hatakka, T., Backman, B., Juntunen, R., Kortelainen, N., Lakomaa, T., Nikkarinen, M., Vesterbacka, P., Väisänen, U. & Suomela, P. 2002 *One Thousand Wells – the Physical-Chemical Quality of Finnish Well Waters in 1999*. Report of Investigation 155. Geological Survey of Finland, Espoo, Finland.

Lewis, R. K. & Houle, P. 2008 Disposal of Granular Activated Charcoal used for the Treatment of Radon-222 in Well Water. In *Paper Presented at The American Association of Radon Scientists and Technologists 2008 International Symposium Las Vegas NV*.

Lopes, I., Vesterbacka, P. & Kelleher, K. 2017 Comparison of radon (Rn-222) concentration in Portugal and Finland underground waters. *Journal of Radioanalytical and Nuclear Chemistry* **311**, 1867–1873.

Lowry, J. D. & Brandow, J. E. 1985 Removal of radon from water supplies. *Journal of Environmental Engineering (United States)* **111** (4), 511–527.

Lowry, J. D. & Lowry, S. B. 1987 Modelling point-of-entry radon removal by GAC. In *Paper Presented at the Proceedings of AWWA Seminar on Radionuclides in Drinking Water, Annual Conference, Kansas City*, pp. 129–140.

Lowry, J. D., Brutsaert, W. F., McEnerney, T. & Molk, C. 1987 Point-of-entry removal of radon from drinking water. *Journal/American Water Works Association* **79** (4), 162–169.

Lowry, J. D., Lowry, S. B. & Toppan, W. C. 1988 New Developments and Considerations for Radon Removal from Water Supplies. In *Paper Presented at The 1988U.S. EPA Symposium on Radon and Radon Reduction Technology*, Denver, CO.

Lykins, B. W., Clark, R. M. & Westrick, J. J. 1990 Treatment Technologies for Meeting U.S. Drinking Water Regulations. In *Paper Presented at the Joint Annual Conference Ontario Section AWWA/Ontario Muncipal Water Association Toronto*, Ontario, Canada.

Martins, K. L. 1992 Practical guide to determine the impact of radon and other radionuclides on water treatment processes. *Water Science and Technology* **26** (5–6), 1255–1264.

Miettinen, I. T., Vartiainen, T. & Martikainen, P. J. 1997 Phosphorus and bacterial growth in drinking water. *Applied and Environmental Microbiology* **63** (8), 3242–3245.

Naylor, L. M. & Dague, R. R. 1975 Simulation of lead removal by chemical treatment. *Journal American Water Works Association* **67**, 560–565.

Salonen, L. & Hukkanen, H. 1997 Advantages of low-background liquid scintillation alpha-spectrometry and pulse shape analysis in measuring 222rn, uranium and 226ra in groundwater samples. *Journal of Radioanalytical and Nuclear Chemistry* **226** (1–2), 67–74.

Sigworth, E. A. & Smith, S. B. 1972 Adsorption of inorganic compounds by activated carbon. *Journal American Water Works Association* **64** (6), 386–391.

SSMFS 2018:4 2018 The Swedish Radiation Safety Authority's regulations on naturally occurring radioactive material and building materials (Strålsäkerhetsmyndighetens föreskrifter om naturligt förekommande radioaktivt material och byggnadsmaterial). *The Swedish Radiation Safety Authority's constitution*. Available from: https://www.stralsakerhetsmyndigheten.se/publikationer/foreskrifter/ssmfs-2018/ssmfs-20184/.

STUK 2020 In: *The Average Effective Dose for Finns in 2018 (Suomalaisten Keskimääräinen Efektiivinen Annos Vuonna 2018)* (Siiskonen, T. ed.). STUK, Radiation and Nuclear Safety Authority, Helsinki, Finland.

SYKE 2020a *Groundwater Area Information (Pohjavesialueen Tiedot), Alalampi*. Search 14.10.2021. Available from: https://wwwp2.ymparisto.fi/scripts/povetarea/povetarea.asp.

SYKE 2020b *Groundwater Area Information (Pohjavesialueen Tiedot), Keljonkangas*. Search 14.10.2021. Available from: https://wwwp2.ymparisto.fi/scripts/povetarea/povetarea.asp.

Turtiainen, T., Salonen, L. & Myllymäki, P. 2000 Radon removal from different types of groundwater applying granular activated carbon filtration. *Journal of Radioanalytical and Nuclear Chemistry* **243** (2), 423–432.

Vesterbacka, P., Mäkeläinen, I. & Arvela, H. 2005 Natural radioactivity in drinking water in private wells in Finland. *Radiation Protection Dosimetry* **113** (2), 223–232.

Velten, S., Boller, M.,Köster, O.,Helbing, J., Weilenmann, H.-U. & Hammes, F. 2011 Development of biomass in a drinking water granular active carbon (GAC) filter. *Water Research* **45**, 6347–6354.

WQA 2013 *Granular Activated Carbon (GAC) Fact Sheet*. Water Quality Association, National Headquarters & Laboratory, Illinois, USA.

Zagà, V., Cattaruzza, M. S., Martucci, P., Pacifici, R., Trisolini, R., Bartolomei, P., Giacobbe, R., Patelli, M., Paioli, D., Esposito, M., Fabbri, V., Gallus, S. & Gorini, G. 2021 The 'polonium in vivo' study: polonium-210 in bronchial lavages of patients with suspected lung cancer. *Biomedicines* **9** (1), 1–11.

First received 18 September 2022; accepted in revised form 5 December 2022. Available online 15 December 2022