Original Scientific Paper

^{226}Ra REMOVAL PROCESSES IN CROATIAN WATER FACILITIES

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Received in July 2005
Accepted in March 2006

Today, bottled and tap drinking water mainly originates from underground waters which might contain considerable amounts of naturally occurring radionuclides. One of the most toxic radionuclide in drinking water is ^{226}Ra. Following the metabolism of calcium, it could be deposited into the bone where, in sufficient amount, it could cause bone sarcoma. Although current drinking water preparation techniques are not specifically designed for ^{226}Ra removal they can reduce certain amounts of ^{226}Ra.
This paper presents the efficacy of standard water preparation processes (granular activated carbon, green sand and fixed-leaf filtrations) currently used by Zagreb water supply and two Croatian water bottlers in removing ^{226}Ra. Compared with other studies, the results of our study show low to moderate efficacy in lowering the ^{226}Ra concentration in drinking water. Even so, ^{226}Ra concentrations still comply with the recommendation of the Word Health Organisation (WHO) and with Croatian legislation.

KEY WORDS: *fixed-leaf filtration, GAC filtration, green sand filtration, water treatment*

Water treatment plants were originally designed to remove or inactivate infectious organisms from drinking water (1). With a rising pollution of land and surface waters, it has become obvious that drinking water requires more complex treatment before consumption. Bottled and tap drinking water is now mostly exploited from underground water reservoirs. Although they are quite clean, they could contain higher amounts of naturally occurring radionuclides. Elevated levels of naturally occurring radionuclides in underground waters are mainly associated with uranium- and thorium-rich soil and rock minerals, or with uranium or radium deposits in soil or bedrock (2-4).

Some standard water preparation processes can decrease ^{226}Ra concentration in water (5). Aeration is principally used to add oxygen, ozone and chlorine to water and removing other gasses such as volatile organic chemicals, radon, ammonia, hydrogen sulphide, methane, and carbon dioxide (6). This process has also been proved to reduce ^{226}Ra in the range of 14 % to 58 % and is based on radium adsorption on precipitated ferric hydroxide (5, 7-9). The removal of radium by granular activated carbon (GAC) varies considerably, from 53 % to nearly 100 %, depending on coal type and granular size (3, 8, 10). Between 50 % and 99 % of ^{226}Ra could be removed by green sand filtration, primarily used to remove iron and manganese, while efficacy of sand filtration could vary depending on the amount of suspended solids (3, 8, 17). Very good results in removing ^{226}Ra from water were obtained with ion exchangers (cation resin), ranging from 50 % to 95 % (3, 8). Coagulation and co-precipitation processes are less efficient in ^{226}Ra removal, up to 32 % and 70 % using $Al_2(SO_4)_3$ and $FeCl_3$ as coagulants, respectively (4, 5).

The most efficient are membrane techniques, reverse osmosis and nanofiltration, which remove on average from 96 % to more than 99 % of radium compounds. Apart from radionuclides, these techniques also remarkably reduce the concentrations of other water constituents. The result is a water deficient in useful minerals (2, 3).

Although tap water is still the major source of drinking water, there are many new bottled water brands on the Croatian market (11). According to the Vodoopskrba i odvodnja, the national tap water supplier Zagreb has reserves of drinking water that can meet twice the present demand (12). Furthermore, the Croatian bottlers claim that raw waters they use are of very good quality and require only minor treatment before bottling. Conventional treatments can eliminate suspended materials, colours, odours and flavours, and considerably decrease organic matter, nitrates, ammonia and iron (13). With the increased use of underground water for drinking, elimination of radionuclides has become more topical. Underground waters often contain elevated concentrations of naturally occurring ^{226}Ra. Since ^{226}Ra is carcinogenic to humans, it is important to reduce its concentration to an acceptable level. The aim of this paper was to present current ^{226}Ra concentrations in raw waters and waters treated by some Croatian water suppliers and bottlers using common treatment methods.

MATERIALS AND METHODS

Samples

Water was sampled from four water supply wells in Zagreb, (Wells 1-4, one sample from each well) in 2004. Water from underground reservoirs is directly distributed to Zagreb households without preparation, save for Well 2, where water is filtered using GAC.

Samples were also taken from raw (inflow) and treated waters, at specific stages of the treatment process, from two Croatian drinking water bottling plants, P1 (Figure 1) and P2 (Figure 2). Water bottling plant P1 treats and bottles mineral water while water bottling plant P2 prepares and bottles spring water. Water treatment included GAC filtration, green sand filtration and fixed-leaf filtration, as presented in Figures 1 and 2. Arrows show the treatment stages at which water was sampled. These are the most common processes used to purify water from inorganic and organic matter (14).

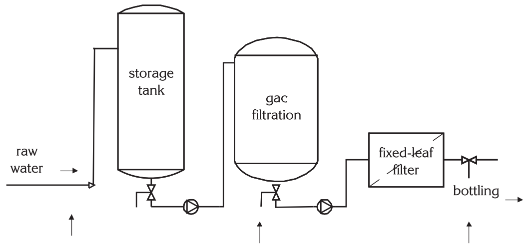

Figure 1 *Mineral water processing in water bottling plant P1; arrows indicate sampling sites*

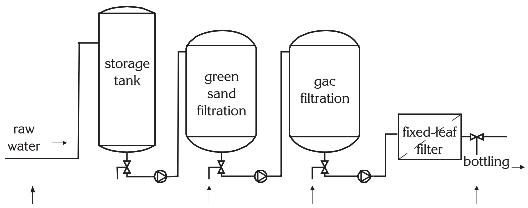

Figure 2 *Spring water processing in water bottling plant P2; arrows indicate sampling sites*

^{226}Ra determination

Barium carrier was added to the water samples (250 mL) and radium was co-precipitated with barium sulphate from a solution containing ethylenediaminetetraacetate. The precipitate was converted to carbonate, which was then dissolved in nitric acid. Radium daughter products were excreted from this solution into thenoyltrifluoroacetone. Barium sulphate was then re-precipitated and weighed to determine carrier recovery (15). In all samples ^{226}Ra was determined using alpha Si partially depleted PIPS detector (active area 450 mm^2, alpha resolution for ^{241}Am 19 keV) for at least 80000 s. Low-limit detection and measured background were $2.5 \cdot 10^{-4}$ cps and $1.7 \cdot 10^{-4}$ cps respectively.

RESULTS

Table 1 shows ^{226}Ra concentrations in raw and treated waters from the Zagreb water supplier and from the two water bottlers at different processing stages. While ^{226}Ra concentrations ranged from <1 mBq L^{-1} to 348 mBq L^{-1} in raw water, this range in the final stage of treatment was from <1 mBq L^{-1} to 292 mBq L^{-1}.

Table 1 ^{226}Ra concentration (± counting error) in raw and treated waters from Zagreb water supply and water plants P1 and P2. Each number is the result of one measurement from each sample

Sample	^{226}Ra concentration / mBq L^{-1}
Raw water	
Well 1	1.3 ± 0.8
Well 2	20 ± 3
Well 3	1.4 ± 0.9
Well 4	5 ± 3
Water bottling plant P1	348 ± 11
Water bottling plant P2	37 ± 7
Water after treatment	
Green sand filtration	
Water bottling plant P2	23 ± 4
GAC filtration	
Water bottling plant P1	342 ± 12
Water bottling plant P2	14 ± 7
Well 2	6 ± 3
Fixed-leaf filtration	
Water bottling plant P1	292 ± 11
Water bottling plant P2	1.2 ± 0.8

The ^{226}Ra concentration limit in drinking water recommended by the World Health Organization (WHO) is <1000 mBq L^{-1} (16). Even though Croatian legislation does not define the limit concentration for ^{226}Ra, it has set its maximal annual total body dose to 0.1 mSv (17). According to Equation 1 (16) the calculated maximal allowed ^{226}Ra concentration in drinking water is 489 mBq L^{-1}.

$$GL = \frac{IDC}{h_{ing} \cdot q} \quad (1)$$

where

GL concentration of ^{226}Ra in drinking water [Bq L^{-1}]
IDC individual dose criterion equalling 0.1 mSv $year^{-1}$ [mSv y^{-1}]
h_{ing} dose coefficient for ingestion by adults equalling $2.8 \cdot 10^{-4}$ mSv Bq^{-1} [mSv Bq^{-1}]
q annual ingested volume of drinking water, assumed to be 730 L $year^{-1}$ [L y^{-1}]

From Table 1 it follows that all ^{226}Ra concentrations in water samples are below the calculated Croatian limit and the WHO recommendation.

DISCUSSION

Underground water reservoirs in Zagreb show low concentrations of ^{226}Ra. It is surprising that nearly all water comes to the households untreated. Only at one location (Well 2) is the water filtered through GAC filters before use. This procedure removes about 70 % of ^{226}Ra content.

In the water bottling plant P1, raw water is first placed into a storage tank which serves as a heat exchanger, decreasing the temperature of raw water from about 60 °C to (9-12) °C. From the storage tank water passes through the GAC filter, which decreases ^{226}Ra concentration from 348 mBq L^{-1} to 342 mBq L^{-1}, i.e. by 2 %. Very often additional filtration is necessary to remove tiny particles. For this purpose fixed-leaf filter was used in the water bottling plant P1, which reduced ^{226}Ra concentration by another 15 %.

The ^{226}Ra concentration of raw spring water in the water bottling plant P2 is only 37 mBq L^{-1}. Green sand filtration reduces it further by 38 %. GAC filtration shows a similar efficacy, reducing the ^{226}Ra concentration by another 39 %. In the last step, fixed-leaf filtration reduces ^{226}Ra concentration by another 93 %.

Compared with the published data on ^{226}Ra removal efficacy, which range from 34 % to 94 % (3, 8-10), our results show low to moderate efficacy in reducing ^{226}Ra concentration by GAC filtration. Even though green sand filtration can reduce ^{226}Ra content by as much as 99 % (3, 17) our result (38 %) shows Ra removal that is even lower than the minimal recorded value (50 %) (8).

It is believed that ^{226}Ra removal efficacy depends on the variation in water composition, ^{226}Ra form in the water, and the quality of filter. When it comes to the GAC filtration, it was found that a decrease in water hardness and in the particle size of activated carbon is followed by an increase in ^{226}Ra removal efficacy (3). Additionally, the amount of processed water also affects ^{226}Ra removal. It is also assumed that its retention is mainly connected with the formation of complexes with humus and fulvic acids and with precipitation onto ferric hydroxide, or in other words, onto particles which are big enough to be retained by GAC, greensand or fixed-leaf filters (3).

As the concentration of ^{226}Ra decreased negligibly in the water filtered by GAC in the water bottling plant P1, it is possible that this water contains ^{226}Ra mainly in ionic form (not on suspended particles which could be retained by filtration). In contrast, the GAC filtration of Zagreb water supply considerably decreased the ^{226}Ra concentration (70 %) in tap water. It could not be firmly concluded that the efficacy this high is only due to ^{226}Ra adsorption onto bigger particles and further tests are necessary.

Although water purification processes used in Croatia are not specifically designed for radionuclide removal, they show a certain efficacy in removing ^{226}Ra. Some studies indicate that, with slight adjustments, conventional techniques of water purification can significantly decrease the content of dissolved radionuclides (controlling pH value, adding conventional chemical reagents) (13).

However, methods to remove radioactivity from drinking water could create waste which contains higher amounts of natural radionuclides. Some studies claim that this wastes requires special treatment and should not be discharged into communal dumps or city sewer systems (3, 5, 10).

CONCLUSION

The analysed Zagreb water supplier line and two water bottling plants were taken as representative of the current trends in drinking water preparation in Croatia. In all analysed samples ^{226}Ra concentration was acceptable for drinking. Water from Zagreb water supply is mainly used without pretreatment while water bottlers use more complex treatment methods. Generally, this study has confirmed that it is possible to reduce ^{226}Ra concentration using conventional methods such as GAC, green sand and fixed-leaf filtration, even though it is not their primary purpose.

Future preparation of drinking water will have to be adjusted for reducing radioactivity, as waters from wells and springs could contain high amounts of naturally occurring radionuclides.

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Sažetak

PROCESI UKLANJANJA ^{226}Ra U POSTROJENJIMA ZA PRIPREMU PITKE VODE U HRVATSKOJ

Danas se kao pitke vode uglavnom rabe podzemne vode koje prirodno mogu sadržavati povišene koncentracije radionuklida. Jedan od radionuklida koji se u podzemnim vodama može naći u vrlo visokoj koncentraciji jest visokotoksičan ^{226}Ra. Njegov metabolički put u organizmu sličan je metaboličkomu putu kalcija, što znači da se može deponirati u kostima i time povećati rizik od nastanka raka kostiju. Iako standardne metode za pripremu pitke vode nisu specijalno oblikovane za uklanjanje radija, pokazalo se da se koncentracija ^{226}Ra tijekom tih procesa smanjuje.
U ovom radu željela se ispitati efikasnost izdvajanja ^{226}Ra prilikom standardnih procesa pripreme vode (filtracija na aktivnom ugljenu, filtracija na zelenom pijesku, pločasti filtar) koji se primjenjuju u Zagrebačkom vodovodu i dvjema punionicama vode u Hrvatskoj.
U usporedbi s podacima koje navode drugi autori, opisani procesi filtracije pokazuju slabiju efikasnost izdvajanja ^{226}Ra. Međutim, pitka voda dobivena tim procesima sadržava ^{226}Ra u koncentraciji koja zadovoljava hrvatske propise te preporuke Svjetske zdravstvene organizacije.

KLJUČNE RIJEČI: *filtracija na aktivnom ugljenu, filtracija na pločastom filtru, filtracija na zelenom pijesku, procesi pripreme vode*

REQUESTS FOR REPRINTS:

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