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Accumulation of naturally occurring radioactive materials on the filters utilized in bottled mineral-water facilities

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ABSTRACT

Bottled mineral-water is typically produced through filtering processes of groundwater in many countries. Although naturally occurring radioactive materials (NORMs) are present in ambient groundwater, the accumulation of NORMs to filters used by bottled mineral-water plants and their total radioactivity was never studied. The radioactivity of NORMs in water and filter samples were determined for a total of thirteen bottled mineral-water facilities in Korea. The NORM levels were quite low in raw water (i.e., groundwater before filtered), and uranium and radon contents were lowered after filtering. However, minor increases of uranium concentration were observed after the treatment processes in two mineral-water plants used only membrane filters. The measured surface radiations sharply increased at the filters installed at the front of water treatment processes regardless of filter types. Diverse radionuclides including lead and polonium were found inside these filters with comparatively high radioactivity. In particular, the estimated total radioactivity of one of the used filters exceeded 1 Bq g^{-1} and 1000 kBq yr^{-1} that are the guideline values regulated by the Nuclear Safety and Security Commission in Korea for by-products occurring after any treatment processes. The elevated radiation may result in potential risk during bottling, transport, and disposal processes, therefore, proper management and disposal of the filters should be considered in bottled mineral-water treatment facilities.

1. Introduction

Groundwater has been primarily used to produce bottled natural-water for drinking in numerous countries because groundwater is a comparatively safe, clean, and economical water, and contains essential mineral-ingredients for human health. However, in ambient groundwater, naturally occurring radioactive materials (NORMs) such as uranium, thorium, and radium are also present through water-rock interaction during geological time-periods. Although dissolved concentrations of NORMs in groundwater are dependent on local geologic settings in a given region (e.g., high concentrations of uranium are typically observed in the groundwater of granitic bedrock regions), the NORMs are ubiquitous materials in groundwater environments (Shin et al., 2016; Smedley et al., 2006; Stalder et al., 2012; Vinson et al., 2009).

The groundwater for production of the bottled mineral-water should be treated by minimized physical water treatment processes to prevent any alteration of clean groundwater quality in many countries (IBWA, 2012). Regulations of the Ministry of Environment in Korea or equivalent institutes in other countries, for example, allow physical filtering and disinfection processes only without any chemically related treatments (ME, 2016; US FDA, 2016). Membrane filters (MF) and activated carbon (AC) were usually utilized for the filtering, and ozonation and ultraviolet irradiation for the disinfection processes. The AC filter is capable of removing radionuclides such as uranium and radium from aqueous solution with approximate 10–40% efficiency (WHO, 2011), because activated carbon has a strong sorption affinity for metals using numerous functional groups on the surface (Abbasi and Streat, 1994).

Although there are no direct regulations regarding radioactivity of the filters used by the bottled natural-water facilities, some countries regulated radioactive level for residual materials after any

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treatment processes in plants. In the case of US, the Environmental Protection Agency (EPA) declared that the residual materials containing >0.05 wt% of uranium or thorium (or >~12.4 Bq g^{-1} for natural uranium) must be treated by a general licenser permitted by the Nuclear Regulatory Commission (NRC). In addition, a disposal of the residual materials exceeding ~6.80 kg at a time or ~68.0 kg at one calendar year requires specific license from NRC (US EPA, 2006). The Nuclear Safety and Security Commission (NSSC) of Korea also regulated the radioactivity level of by-products below 1 Bq g^{-1}, and total radioactivity of <1000 kBq yr^{-1} for proper disposal (NSSC, 2012).

Although radioactivity of NORMs in filters may result in adverse effects on management and disposal processes at the water treatment facilities, only few studies investigated the radioactivity of NORMs in the residual materials produced by a water treatment system. For instance, the radioactivity levels of radon gas and radium isotopes were evaluated from the solid residuals in both pipe-scale deposits and accumulated sediments after water treatment (Fisher et al., 2000; Friedman et al., 2010; Valentine and Stearns, 1994). Likewise, the accumulation of uranium, thorium, and radium radionuclides has been reported in the sludge generated at the drinking water system in Spain (Fonollosa et al., 2015; Palomo et al., 2010) and US (Lytle et al., 2014). These studies reported the accumulation of inorganic contaminants including radium in the solid residuals from the water distribution systems, and potential problem on water quality through releasing of the accumulated contaminants back to drinking water. However, there are no studies on radioactivity of the filters used in the mineral-water treatment facilities so far.

Therefore, the goal of this study is to evaluate potential accumulation of radionuclides in the MFs and AC filters, and estimate the annual total radioactivity of the filters in bottled mineral-water plants. Following specific objectives are to determine the radioactivity of radionuclides in the filters, and compare with the regulatory radioactivity level for improving proper management and disposal of the filters.

2. Materials and methods

2.1. Study sites

A total of thirteen bottled mineral-water facilities (termed by A to M) in Korea were investigated to determine the potential accumulation of NORMs at both MFs and AC filters during mineral-water treatment processes. The bottled water facilities were predominantly located at rural areas to prevent anthropogenic contamination. No detailed information on the investigated plants including geographical locations provided in this study due to request of the plants. The bedrock geology around the investigated facilities is typically divided into two rock types—i.e., the Precambrian and Jurassic granitic rocks, and the Cretaceous sedimentary rocks. Approximately half of the plants were placed on the granitic bedrock, and the others on the sedimentary bedrock (Table 1). The individual facilities have 1 to 6 wells to pump groundwater, and the well depth ranged from approximately 70 to 390 m below surface.

The produced groundwater are initially stored at raw-water storage tank in each facility, and used as incoming-water for water filtering processes (Fig. 1). The water treatment processes mainly included 3–6 steps of water filtering processes. Various micro-sized MFs were utilized during physical filtration of colloidal materials in all facilities while pre-filter and AC filter were optionally positioned in early stages of water treatment processes depending on the groundwater quality. Seven facilities of A, C, E, F, H-1, I, and M used the pre-filter (bag filter or 5–75 μm MF) to remove fine particles such as sediments, soils, and rock fragments.

Table 1
Summary information for groundwater wells in individual bottled mineral water facilities.

Plant	*n* of wells	Well depth	Bedrock Type
A	2	180–181	Sedimentary
B	6	73–389	Granitic gneiss
C	4	153–218	Biotite gneiss
D	4	153–300	Granite
E	2	122–124	Sedimentary
F	5	162–239	Granite
G	3	140–340	Granitic gneiss
H	3	205–254	Meta-sedimentary
I	3	148–300	Granite
J	2	127–170	Sedimentary
K	3	142–188	Sedimentary
L	1	325	Volcanic
M	6	189–243	Granitic gneiss

The AC filter was installed in only six facilities (A, C, G, H-1, I, and M) to uptake dissolved ions and volatile organic chemicals. These AC filters were usually exchanged every year, but the M plant replaced the AC filters every 3 months due to their cartridge type. The MFs were typically replaced every 3–10 months dependent on filter conditions. After the last step in filtering processes, the treated water (i.e., equivalent to outgoing water) is packed for production of bottled mineral-water at individual facilities.

2.2. Sample collection

To evaluate the changes in water chemistry and radioactivity through water filtering processes, incoming- and outgoing-water samples were directly collected at six facilities (A, C, G, I, K, M), while the remaining facilities (B, D, E, F, H, J, L) provided all water samples because of difficult accessibility. In addition to both incoming and outgoing water samples, a series of water samples at the end of each filtering steps were collected in four facilities of B, D, K and M. The three water plants of C, G, and M provided some of the used MFs or AC filters for analyses of remaining radionuclides in a filter.

Approximately 2 and 4-L of water were sampled in polyethylene containers for the analyses of gross alpha (α) and gross beta (β), and radium isotopes (i.e., *Ra*-226 and 228), respectively. For measurement of radioactivity in radon, a narrow-neck glass bottle inside a large container was prepared, and the water was slowly filled into the glass using a tube. After the glass bottle was completely submerged, and subsequently, the water spilled over the large container, the Teflon-lined cap was submerged under the water and capped the glass bottle to prevent inflow of air bubbles. Additionally, water sample with ~100 mL was separately filtered using a 0.45 μm acetate membrane filter (Whatman, Hercules, USA) to analyze anion and cation concentrations in water. The filtered water of 50 mL was acidified below pH 2 by adding concentrated nitric acid to avoid mass losses through precipitation and adsorption processes of uranium, thorium, and other cations. Finally, all water samples were delivered to the laboratory within 12 h, and stored at 4 °C in a dark.

2.3. Analyses for water and filter samples

As *in situ* field parameters of water quality, temperature, pH, electric conductivity (EC), oxidation reduction potential (ORP) and dissolved oxygen (DO) were measured by portable multiple meter (Orion A325/A326, Thermo Scientific, USA). Dissolved concentrations of major anions (F, Cl, NO_3 and SO_4) and cations (K, Na, Ca, and Mg) in collected water samples were analyzed using Ion

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