DETERMINATION OF URANIUM IN DRINKING WATER OF THE THIRD BIGGEST TOWN OF GREECE (PATRAS, NW PELOPONNESE) AND IN THREE FAMOUS GREEK SPA WATERS

ATHANASOPOULOS D.[1], EFSTATHIOU M.[2], BALIKOS C.[1], PASHALIDIS I.[2] and SYMEOPOULOS B.D.[1]

[1]University of Patras, Department of Chemistry, Radiochemistry Lab, Patras 26500, Greece
[2]Department of Chemistry, University of Cyprus,P.O. Box 20537, 1678 Nicosia, Cyprus
E-mail: athanasopoulosd@gmail.com

ABSTRACT

Uranium is a radioactive toxic metal. It is widespread in nature, occurring mainly in granites and various other mineral deposits. Natural processes and many anthropogenic activities have resulted in re-distribution of this element, which can cause contamination of hydrosphere with uranium. Moreover, ^{222}Rn, is generated from the decay chain of ^{238}U. In case of inhalation, it is a dangerous radioactive gas. Spa waters may contain uranium as well as other metal salts in high concentrations, because the water comes from deep inside the Earth's crust. The occurrence of uranium in spa waters implies the occurrence of ^{222}Rn, especially under poor aeration conditions. Consequently, it is of great importance to identify the human health risks, which are associated with occurrence of uranium either in drinking water samples or in spa waters.
The aim of this work was to determine uranium content in:

1) drinking water of Patras, which is the third biggest city of Greece, with a population of about 200 000 people
2) three famous spa waters, namely natural thermal springs of Kaiafas, Edipsos and Kyllini spa, which are well known from ancient times.

Twenty one samples of drinking water were collected from an equal number of water reservoirs that provide potable water all over the city of Patras. Additionally, eight samples from different brands of bottled water produced in Greece and one imported mineral water, were analyzed for comparison reasons. 1 L from each sample was spiked with known amount of ^{232}U, and the total content of uranium was isolated by using Chelex-100 resin at pH=4.5. Uranium content was eluted from the resin by 15 mL of 2 M HNO_3. The latter volume was then evaporated to dryness in a water bath. Thereafter, uranium was re-dissolved in a solution of ammonium sulphate. After electro-deposition of uranium on stainless steel discs, the latter was counted for 5 days.
Uranium concentration in the drinking water of Patras was found to be tenths or even hundreds of times below WHO guideline and the maximum contaminant level (MCL) of EPA. Furthermore, an assessment was made of the annual uranium radiation exposure of population, which uses the studied waters for human consumption.

Uranium concentration in the studied spa waters was found as low as in potable water.

Keywords: Uranium, ^{238}U, ^{234}U, drinking water, Edipsos spa, Kyllini spa, Kaiafas spa, bottled water

1. Introduction

Uranium is widespread in nature occurring mainly in granites and various other mineral deposits (Roessler *et al.*, 1979). Natural processes and many anthropogenic activities have resulted in re-distribution of uranium. Uranium is present in water supplies as a result of leaching from natural deposits, releases in mill tailings, emissions from nuclear industry and combustion of coal and other fossil fuels (Naja & Volesky, 2009). Another source of uranium could be the use of phosphate fertilizers that contain uranium (WHO, 2012).

Uranium has three naturally occurring isotopes: ^{234}U (progeny of ^{238}U), ^{235}U and ^{238}U. ^{234}U and ^{238}U are in radiological equilibrium, namely activity ratio of ^{234}U to ^{238}U should be 1.0, if the uranium was placed in a closed system. $^{234}U/^{238}U$ ratio is widely described as uranium isotopic signature and could used to characterize ground and surface waters (Riotte & Chabaux, 1999).
Radon-222 (^{222}Rn) is a chemically inert gas, which is formed through the radioactive decay of ^{226}Ra. Both ^{222}Rn and ^{226}Ra are members of the ^{238}U decay series. Rocks containing natural uranium, release continuously radon into ground waters. Spa waters may contain uranium as well as other metal salts in high concentrations, because the water comes from deep inside the Earth's crust. The occurrence of uranium in spa waters implies the occurrence of ^{222}Rn, especially under poor aeration conditions.

The toxicity of both uranium and radon is significant. Uranium is a radioactive toxic metal. The most important effect of uranium is the damage to the kidneys. It affects nervous system and also induces some damage to liver and muscle tissues (Naja & Volesky, 2009). There are insufficient data regarding the carcinogenicity of uranium in humans (WHO, 2004). ^{222}Rn is a dangerous gas, in case of inhalation and consists the major source of naturally occurring radiation exposure for humans (Naja & Volesky, 2009).

Intake of uranium through drinking-water is normally low. However, in circumstances in which uranium is present in a drinking-water source, its contribution could be significant (WHO, 2012). Consequently, it is of great importance to identify the human health risks, which are associated with occurrence of uranium either in drinking water samples or in spa waters.

The purpose of this study was to determine uranium content in:

1) drinking water of Patras, which is the third biggest city of Greece, with a population of about 200 000 people,
2) three famous spa waters known from ancient times, namely thermal springs of Kaiafas, Edipsos and Kyllini spa,
3) a few brands of Greek bottled water for comparison reasons.

2. Experimental part

2.1. Sampling

Twenty one samples of drinking water were collected from an equal number of water reservoirs, that provide potable water all over the city of Patras (figure 1). Additionally, five samples of three spa waters (shown in figure 2), eight samples from different brands of bottled water produced in Greece, as well as one imported mineral water, were analyzed for their uranium content.
Bottled waters were purchased from local market, whereas all the other water samples were collected in 1 L polypropylene bottles and were acidified (pH<2) with concentrated HNO_3 on the spot. Immediately after sampling, they were transferred to the lab, where they were filtered through a 0.45 μm membrane filter.

Figure 1: Location map of the region around Patras showing the sampling sites.

Figure 2: Location of three famous spa waters, namely natural thermal springs of Edipsos (A), Kaiafas (B) and Kyllini spa (C).

2.2. Uranium determination

The analytical procedure including radioisotopes was performed in the University of Cyprus, Laboratory of Radioanalytical and Environmental Chemistry. According to Kiliari and Pashalidis (2010), each sample of water (1 L) was placed in a polypropylene beaker and it was spiked with a known activity (50 mBq) of ^{232}U. 2.5 g of Chelex-100 resin and 4.0 g CH_3COONH_4 were added and the suspension was maintained at pH=4.5, under continuous stirring at room temperature for at least 2 hours, correcting the pH from time to time. The resin was isolated by filtration using a glass filter (G3), and the uranium content of resin was eluted by 15 mL of 2 M HNO_3. This volume was evaporated to dryness in a water bath. Thereafter, uranium was re-dissolved in 15 mL of 0.15 M ammonium sulphate solution. Finally, uranium was electro-deposited on stainless steel discs and was counted for 5 days, using a high-resolution alpha-spectrometer (Alpha Analyst Integrated Alpha Spectrometer, Canberra) equipped with semiconductor detectors. The alpha spectrometer was calibrated in the region 3 - 9 MeV and the recorded spectrum included three main peaks due to ^{238}U, ^{234}U and ^{232}U.

3. Results and discussion

From the count rate of ^{232}U recorded on the spectrum and its known activity, which had been added into each sample, the efficiency of ^{232}U determination during the whole analytical procedure, was calculated*.* Based on this value, the activity concentrations of other uranium isotopes (^{238}U and ^{234}U) were estimated.

The activity concentrations of ^{234}U and ^{238}U in the samples were summarized in table 1. Uranium concentration in drinking water of Patras was found to be tenths or even hundreds of times below WHO guideline (WHO, 2012), and the maximum contaminant level (MCL) of EPA (30 μg/L) (EPA, 2015). Uranium concentrations in the studied bottled and spa waters were also found very low.

The concentrations (Bq/L) of ^{234}U and ^{238}U found in the water reservoirs that provide with potable water the city of Patras, varied from 0.0024 (Pititsa/ sample 12) to 0.038 (Rodini/ sample 9) and from 0.0014 (Pititsa/ sample 12) to 0.022 (Perivola/ sample 19) respectively whereas, their relevant concentrations in spa waters, varied from 0.00055 (Edipsos/ sample 3) to 0.0086 (Kaiafas) and from 0.0011 (Edipsos/ sample 3) to 0.0096 (Kaiafas) respectively.
The concentrations (Bq/L) of ^{234}U and ^{238}U in different brands of bottled water, varied from 0.00030 (Brand 7) to 0.025 (Brand 9/ Imported mineral water) and from 0.00040 (Brand 7) to 0.012 (Brand 9/ Imported mineral water) respectively. The imported mineral water contains three times higher uranium concentration than the other Greek bottled waters studied, as expected, because of its "mineral water" characteristics.

Under the restriction of the limited number of samples analyzed, it seems that:

- uranium content decreases according to the order:
  reservoirs of drinking water of Patras > spa waters > bottled waters and
- thermal springs of Kaiafas contains more dissolved uranium than the other two spa waters (Edipsos and Kyllini).

Values of the $^{234}U/^{238}U$ ratio, which also included in table 1, is of specific interest for understanding hydrological and geochemical processes. In natural waters the $^{234}U/^{238}U$ activity concentration ratio can differ from 1, due to environmental processes and human activities (Ivanovich & Harmon, 1992). Typically, the activity ratio $^{234}U/^{238}U$ in natural water varies from 1 to 2, but it can range up to 30 in extreme cases (Osmond *et al.*, 1983). High $^{234}U/^{238}U$ ratios correspond to old type waters, whereas relatively low ratios $^{234}U/^{238}U$ are related to relatively young waters with a strong local recharge component to the groundwater (Ivanovich & Alexander, 1987). In the majority of samples, radioactive disequilibrium was observed between uranium isotopes. The $^{234}U/^{238}U$ ratio in the samples of water reservoirs of Patras, varied from 0.60 (Arachovitica/ sample 8) to 3.0 (Agios Vasileios (Tseleika)/ sample 7). Similarly, the range of $^{234}U/^{238}U$ ratio in the bottled waters was almost the same as in water reservoirs, varied from 0.33 to 2.6.

Table 1: Uranium activity concentration and activity ratio $^{234}U/^{238}U$ in: a) drinking water of Patras, b) three famous spa waters and c) a few brands of bottled water. The annual uranium radiation exposure of population is also included.

Sample number/ code	Sampling site	Activity concentration ^{238}U (Bq/L)	Activity concentration ^{234}U (Bq/L)	$^{234}U/^{238}U$ ratio	Activity concentration ^{238}U + ^{234}U (Bq/L)	Annual radiation dose, *D* (μSv/year) based on U content	Times below WHO guideline (30 μg/L) for uranium in drinking-water
	All over the city of Patras (NW Peloponnese)						
1	Rio (Agios Georgios)	0.0073	0.013	1.8	0.020	0.68	25
2	Rio (Antrikopoulos)	0.0075	0.011	1.5	0.019	0.61	24
3	Rio (ERT)	0.0088	0.014	1.6	0.023	0.74	21
4	Akteo	0.0089	0.023	2.6	0.032	1.0	21
5	Agios Vasileios (Tsapaleika)	0.0035	0.0090	2.6	0.012	0.41	52
6	Agios Vasileios(Panahaikou)	0.0054	0.0092	1.7	0.015	0.48	34
7	Agios Vasileios(Tseleika)	0.0059	0.018	3.0	0.024	0.78	31
8	Arachovitica	0.010	0.0060	0.60	0.016	0.64	18
9	Rodini	0.021	0.038	1.8	0.059	1.9	9
10	Platani	0.0021	0.0045	2.1	0.0066	0.22	87
11	Sella (Agia Marina)	0.0021	0.0032	1.5	0.0053	0.18	87
12	Pititsa	0.0014	0.0024	1.7	0.0038	0.13	131
13	Velvitsi	0.0054	0.0071	1.3	0.012	0.41	34
14	Anthoupoli	0.0041	0.0044	1.1	0.0085	0.28	45
15	Castro	0.0037	0.0043	1.2	0.0080	0.26	49
16	Tarampoura	0.0047	0.0053	1.1	0.010	0.33	39
17	Riganocampos	0.0020	0.0050	2.5	0.0070	0.22	92
18	Neo Souli	0.0025	0.0042	1.7	0.0067	0.22	73
19	Perivola	0.022	0.021	0.95	0.043	1.4	8
20	Karia	0.015	0.016	1.1	0.031	1.0	12
21	Pournari (Bala)	0.0042	0.0064	1.5	0.011	0.35	44
	Spa waters						
SPA-A1	Edipsos	0.0032	0.0042	1.3	0.0074	-	-
SPA-A2	Edipsos	0.0032	0.0030	0.94	0.0062	-	-
SPA-A3	Edipsos	0.0011	0.00055	0.50	0.0017	-	-
SPA-B	Kaiafas	0.0096	0.0086	0.89	0.018	-	-
SPA-C	Kyllini	0.0023	0.0024	1.0	0.0047	-	-
	Bottled water						
BW1	Brand 1	0.0029	0.0055	1.9	0.0084	0.28	63
BW2	Brand 2	0.0037	0.0079	2.1	0.012	0.38	49
BW3	Brand 3	0.0022	0.0058	2.6	0.0080	0.26	83
BW4	Brand 4	0.0064	0.0065	1.0	0.013	0.42	29
BW5	Brand 5	0.0037	0.0033	0.89	0.0070	0.23	49
BW6	Brand 6	0.0034	0.0064	1.9	0.0098	0.32	54
BW7	Brand 7	0.00040	0.00030	0.75	0.00070	0.024	458
BW8	Brand 8	0.0012	0.00040	0.33	0.0016	0.050	153
BW9	Brand 9 (Imported mineral water)	0.012	0.025	2.1	0.037	1.2	15

Table 1 also included the estimated annual radiation dose, (*D*), corresponding to the alpha-radioactivity of drinking water, due to uranium content exclusively.
D, (μSv/ year), was estimated using the equation:

$$D = A \cdot I \cdot DCF$$

where, *A* is the uranium activity concentration in Bq/L,

I is the mean annual water consumption (730 L) and
DCF is the corresponding dose coefficient for ingest uranium (4.5 x 10^{-2} μSv/Bq) (IAEA, 1996 ; Efstathiou *et al.*, 2011).

The estimated values of *D*, varied from 0.024 to 1.9. These values are extremely low, even thousands of times below the WHO (2004) guideline, which is equivalent to 100 μSv/year. However, it is worth noticing that besides uranium, other alpha emitting radionuclides (^{226}Ra and ^{210}Po) should also be determined in order the annual alpha radiation dose of drinking water to be fully estimated.

4. Conclussions

Samples taken from reservoirs providing drinking water to population of Patras (the third biggest town of Greece) were analyzed and their uranium content was found very low (tenths or hundreds of times below 30 μg/L, that is recommended by WHO and EPA).
The uranium content found in three known Greek spa waters (Edipsos, Kaiafas and Kyllini), as well as in eight brands of bottled waters produced in Greece, was also very low.

REFERENCES

1. Efstathiou M., Kiliari T., & Pashalidis I. (2011), Uranium analysis in Cypriot groundwaters by total alpha-radiometry and alpha-spectroscopy, Radiation Measurements, **46**, 626–630.
2. EPA, URL:http://water.epa.gov/drink/contaminants/basicinformation/radionuclides.cfm (*accessed on April* 2015).
3. IAEA (1996), International basic safety standards for protection against ionizing radiation and for safety of radiation sources, Safety series no. 115.
4. Ivanovich M., & Alexander J. (1987), Application of uranium-series disequilibrium to studies of groundwater mixing in the Harwell region, U.K., Chem. Geol. **66**, 279–291.
5. Ivanovich M., & Harmon RS (1992), Uranium series disequilibrium, application of earth, marine and environmental sciences, 2nd ed. Clarendon Press, Oxford.
6. Kiliari T., & Pashalidis I. (2010), Simplified alpha-spectroscopic analysis of uranium in natural waters after its separation by cation-exchange, Radiation Measurements, **45**, 966–968.
7. Naja M. G., & Volesky B. (2009), Toxicity and sources of Pb, Cd, Hg, Cr, As, and radionuclides in the environment. In L. K. Wang, J. P. Chen, Y. Hung, & N. K. Shammas (Ed.), Heavy metals in the environment (pp. 13–61). Boca Raton, FL, CRC Press.
8. Osmond J. K., Cowart J. B., & Ivanovich, M. (1983), Uranium isotopic disequilibrium in ground water as an indicator of anomalies, International Journal of Applied Radiation and Isotopes, **34**, 283–308.
9. Riotte J., & Chabaux F. (1999), (^{234}U/^{238}U) Activity ratios in freshwaters as tracers of hydrological processes: The Strengbach Watershed (Vosges, France). Geochim. Cosmochim. Acta,**63(9)**, 1263–1275.
10. Roessler CE, Smith ZA, Bolch WE, & Prince RJ. (1979), Uranium and radium-226 in Florida phosphate materials, Health Physics, **37**, 267–269.
11. WHO (2003) Uranium in drinking-water, Background document for preparation of WHO Guidelines for drinking-water quality. Geneva, World Health Organization (WHO/SDE/WSH/03.04/118).
12. WHO (2004) Guidelines for drinking-water quality, Third Edition, Volume 1, Recommendation, Geneva, World Health Organization.
13. WHO (2012) Uranium in Drinking-water, Background document for development of WHO, Guidelines for drinking-water quality **(**WHO/SDE/WSH/03.04/118/Rev/1).