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Natural radionuclides content and radioactive series disequilibrium in drinking waters from Balkans region

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Abstract Natural radioactivity of drinking water with various geological origin in Balkans region has been studied. Collected water samples are analyzed for total alpha and total beta activities and specific alpha- and gamma-emitting radionuclides content using low-background proportional counting and alpha and gamma-spectrometry techniques. Obtained activity concentrations of ^{238}U, ^{234}U, ^{235}U, ^{226}Ra, ^{232}Th, and ^{40}K in water samples and radioactive disequilibrium between members of the natural radioactive series, based on the isotopic ratios, has been discussed.

Keywords Drinking water · Uranium · Radioactive disequilibrium · Alpha-spectrometry · Isotopic ratios

Introduction

The significance of drinking water for life and human health and rapid water resources use and perspectives has posed water quality in the focus of many investigations. Requirements for radiological properties of drinking waters are set by World Health Organization (WHO) in its guidelines for drinking water quality based on the average daily water consumption and annual effective dose limit of 0.1 mSv y^{-1} [1]. Since the dose contribution of drinking water to the overall effective dose for public is mainly due to the contents of radionuclides from natural uranium and thorium decay series (^{238}U, ^{234}U, ^{234}Th, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th, ^{228}Th, ^{228}Ra, etc.) guidelines and national regulations are stipulating the threshold values for total alpha and total beta activities and specific radionuclides content limits [2]. Natural radionuclides appearance in water basins is due to physical and chemical processes resulting with dissolution and leaching of solid rock material into liquid phase in certain geochemical environment [3–5]. Recent geochemical and radiological studies of water resources in Balkans region revealed that radiological properties of drinking water are influenced more by chemical composition of igneous intrusions in rock complexes of the geological aquifers (neogene sediments, limestone, flysch, schist, etc.) than the basic geo-tectonic structure [6, 7]. Regardless of radionuclide concentration levels in drinking water, radioactive disequilibrium between members of both ^{238}U- and ^{232}Th- natural radioactive series may be observed [8, 9]. Here will be presented results of a study on natural radionuclides content and radioactive series disequilibrium in different types of drinking water in water basins of Balkans metamorphic region. For that purpose, total alpha and total beta radioactivity, content of alpha- and gamma-emitting radionuclides and their ratios are determined and discussed with other data obtained for this region.

Materials and methods

Drinking water samples were collected at Interior Dinarides and Vardar zone in Balkans metamorphic region [10].

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Selected samples of tap water (TW1–TW3), spring water (SW1–SW8) and well water (WW1–WW4) were subjected to total alpha and total beta activities determination, alpha-spectrometric analysis and gamma-spectrometric analysis.

Total alpha and total beta activities determination

Total alpha and total beta activities were determined for all water samples by low-background proportional counting. Samples are collected into 3 L volume PET bottles and acidified to pH 2. After evaporation to dryness and mineralization at 450 °C, residues were transferred into stainless steel carriers of Thermo Eberline FHT 770T gas-flow (Ar/Mt) proportional counter. Counting time for samples and background was 3,600 s. Calibration was done using ^{90}Sr (EM 145, Prague) and ^{241}Am (EM445, Prague) certified reference sources. Counting efficiencies were 23 % for alpha- and 33 % for beta-radiation. The accuracy and reproducibility of measurements were verified on a weekly basis.

Alpha-spectrometric analysis

Alpha-spectrometric analysis was performed for all water samples. Samples are collected into 15–20 L volume PET bottles and acidified to pH 2. After evaporation to 50 ml, water sample is transferred to ceramic dish, evaporated to dryness and mineralized at 550 °C. Dry residue is dissolved in 8 mol dm^{-3} solution of HNO_3, filtered (W-389) and treated by 30 % H_2O_2 with heating for oxidation. The co-precipitation was done using 20 % NaOH to pH > 10. Voluminous precipitate was heated, filtered (W-388) and dissolved in 8 mol dm^{-3} HNO_3 solution. Uranium and thorium are transferred into higher oxidation state with 8 mol dm^{-3} HNO_3 and $NaNO_2$. Separation was done using the ion-exchange chromatography with anionic resin DOWEX 1 × 4 100–200 mesh, NO_3^- conditioned, with flow rate of 1 ml min^{-1}. The ^{232}U and ^{229}Th tracer solutions were used for analytical yield recoveries, with efficiency up to 90 %. Uranium and thorium have been eluated by 8 mol dm^{-3} solution of HNO_3 and 10 mol dm^{-3} HCl solutions, respectively. Further purification involved ether-extraction for iron removal from the uranium fraction. Modified Talvitie's electroplating procedure was applied for homogeneous thin-layer alpha-sources preparation [11, 12]. Thorium sources were covered with VYNS foil. Measurements were performed using the Canberra 2004 vacuum chamber with PIPS detector, 100 mm^2 surface, counting efficiency 7 % and resolution 20 keV for ^{241}Am 5,484 keV line. Calibration was done using alpha source of ^{229}Th with daughters. Counting time for sample and background measurements was 3–5 days. The reliability of the alpha-spectrometric determinations was evaluated by analysis of reference or certified materials as IAEA-326 soil, within 95 % confidence interval of the recommended values.

Gamma-spectrometric analysis

Gamma-spectrometric analysis was performed for determination of ^{238}U, ^{235}U, ^{226}Ra, ^{232}Th and ^{40}K contents in all water samples. Water samples have been evaporated from 5 to 8 L to 200 ml volume, sealed into PET vials and stored 1 month to reach secular equilibrium between ^{226}Ra and daughters. Measurements were performed using HP-Ge Canberra detector with Genie 2000 software. Counting efficiency was 23 % and calibration was done by a certified reference material: Czech Metrological Institute, Prague, 9031-OL-116/8 ERX, spiked with ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{88}Y, ^{113}Sn, ^{65}Sr, ^{137}Cs and ^{210}Pb. The activities of ^{226}Ra and ^{232}Th were determined by their decay products: ^{214}Bi (609. 1,120 and 1,764 keV), ^{214}Pb (295 and 352 keV) and ^{228}Ac (338 and 911 keV), respectively. ^{40}K activity was determined using 1,460 keV line. Counting time for sample and background measurements was 60,000 s. The accuracy and reproducibility of measurements were verified on a weekly basis.

Results and discussion

Results obtained for total alpha and total beta activities have shown that prescribed reference values 0.5 Bq L^{-1} and 1 Bq L^{-1} respectively, were not exceeded in the most of analyzed water samples. However, total beta activity of spring water SW8 had value 2.62 Bq L^{-1} and total alpha activity of the same sample was 0.12 Bq L^{-1}. High dissolved mineral matter content, characteristic for underground waters due to their transport through the mineral-rich geological layers, was observed. A very good correlation between the mass of dry residue after mineralization and enhanced total alpha and/or beta activities in water was found as reported elsewhere [13, 14].

Calculated concentrations of natural uranium in water samples (in μg L^{-1}) are presented in Fig. 1.

Figure shows that analyzed waters may be grouped according to the water type rather than to their geological origin. Tap water and well water samples have considerably higher uranium content in the range (0.83–3.06) and (1.06–2.23) μg L^{-1} respectively comparing to values in interval (0.06–0.33) μg L^{-1} for analyzed spring water samples of various geological areas. On the other hand, water samples belonging to different water types and coming from the same geological area do not have similar uranium content. Results presented in Fig. 1 show that natural uranium content differ a lot in tap water samples

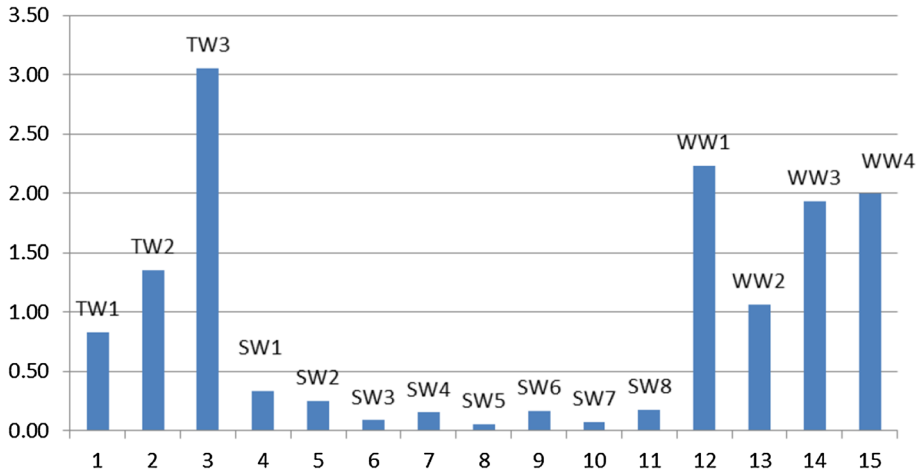

Fig. 1 Natural uranium content (μg L^{-1}) in 15 analyzed water samples

TW1 and TW2 taken from two cities waterworks coming from Sava and Danube river, respectively. Natural uranium concentration 1.35 μg L^{-1} was determined for tap water sample TW2 (Belgrade) comparing to natural uranium content 0.63 μg L^{-1} in Danube river water (at Belgrade) not subjected to procedures for drinking water supply [15]. Significantly higher natural uranium content value 3.06 μg L^{-1} was determined for tap water sample TW3 collected in Vranje waterworks and coming from granite metamorphic rock underground aquifer. This value is much higher than the mean value 0.301 μg L^{-1} obtained for 14 analyzed water samples from city water supply systems in Serbia [16]. Recent research on European waterworks, based on analysis of 579 tap water samples have shown the mean value 0.307 μg L^{-1} of natural uranium concentration being in the interval (0.001–65.2) μg L^{-1} [17, 18].

In that research, natural uranium content in European spring water covers 5–7 orders of magnitude concentration range and confirmed earlier obtained data [19–23]. Spring waters analyzed within this study had relatively low natural uranium content being in interval 0.08–0.33 μg/L. Low uranium content is characteristic for analyzed spring waters originated from three geo-tectonic structures: SW1, SW2, SW3 and SW5 from Inner Dinarides, SW6-SW7 from Vardar metamorphic area and SW8 from the north Vardar zone. Obtained concentrations in all analyzed water samples are far below the reference level of 30 μg/L, given by WHO [1] and in compliance with data reported for this region.

Contents of specific radionuclides ^{238}U, ^{234}U, ^{235}U, ^{226}Ra, ^{232}Th and ^{40}K (in mBq L^{-1}) obtained by alpha- and gamma-spectrometric analysis of water samples are presented in Table 1.

Data presented in the table show activity concentration values of ^{238}U within interval (0.70–37.9) mBq L^{-1}, ^{232}Th within (3–17) mBq L^{-1}, ^{226}Ra within (3–50) mBq L^{-1} with exception of value 96 mBq L^{-1} for SW8. Activity concentration of ^{40}K is up to 20 mBq L^{-1} except for SW8 and WW4 samples with maximum value 1,710 mBq L^{-1} contributing probably the most to enhanced total beta activity of SW8 water sample. Obtained data show relatively low values of radionuclides in three groups of water, comparable with data from the region: Slovenia [24], Croatia [25, 26], Hungary [27], Austria [28] and Romania [29].

Although the radiological quality requirements are fulfilled, more or less disturbed radioactive equilibrium between members of ^{238}U series may be observed in analyzed waters. In Fig. 2 are shown uranium activity ratios $^{234}U/^{238}U$ (Bq/Bq) versus natural uranium content (μg L^{-1}). In the most of samples the radioactive disequilibrium exist between first members of ^{238}U radioactive series as the ratio of progeny and predecessor nuclide activity concentrations were not equal. Values of $^{234}U/^{238}U$ activities ratio are in the range 0.80–3.81 with maximum values for TW1 and SW5.

^{234}U access in regard to ^{238}U may be present in open systems due to several reasons. First members of ^{238}U series are: ^{238}U, ^{234}Th, ^{234m}Pa and ^{234}U. During the radioactive decay of ^{238}U to ^{234}U in solid geological material, one alpha and two beta particles are emitted and the crystal lattice with parent uranium atoms may be damaged so that incurred ^{234}U atoms become dislocated and more susceptible to corrosive fluids. As a result, these atoms are more easily taken by slightly acid underground waters, hydrothermal solutions and precipitates. Additional reason for ^{234}U runoff from the lattice may be oxidation from U (IV) to much more soluble U (VI) ions due to ejection of orbital electrons during the decay. Formed uranyl ions dissolve within a wide range of Eh - pH values and built up highly soluble carbonate complexes such as $[UO_2(CO_3)_2(H_2O)_n]^{2-}$ or s $[UO_2(SO_4)_2(H_2O)_n]^{2-}$ in an oxidizing slightly acid or alkaline medium. [4, 30–32].

A reverse dependence of disequilibrium level and natural uranium concentration in waters may be noticed in

Table 1 Activity concentrations (A, mBq L^{-1}) of radionuclides in water samples

Water type	A (^{238}U) mBq L^{-1}	A (^{234}U) mBq L^{-1}	A (^{235}U) mBq L^{-1}	A (^{232}Th) mBq L^{-1}	A (^{226}Ra) mBq L^{-1}	A (^{40}K) mBq L^{-1}
TW1	10.3 ± 0.59	8.27 ± 0.49	0.34 ± 0.07	10 ± 4	50 ± 20	<20
TW2	16.8 ± 0.80	17.2 ± 0.75	<0.08	3 ± 1	50 ± 20	<20
TW3	37.9 ± 2.0	45.0 ± 2.4	1.44 ± 0.19	17 ± 10	50 ± 20	<20
SW1	4.10 ± 0.6	5.63 ± 0.7	<0.08	<10	<50	<20
SW2	3.1 ± 0.3	5.1 ± 0.6	0.2 ± 0.1	<10	<50	<20
SW3	1.08 ± 0.2	2.21 ± 0.8	<0.07	<10	<50	<20
SW4	1.9 ± 0.3	5.0 ± 0.6	<0.12	<10	<50	<20
SW5	0.70 ± 0.15	2.67 ± 0.4	<0.12	<30	<50	<20
SW6	2.09 ± 0.50	2.56 ± 0.10	0.12 ± 0.05	<30	<30	<20
SW7	0.95 ± 0.06	1.25 ± 0.07	0.04 ± 0.01	<30	<30	<20
SW8	2.23 ± 0.33	2.15 ± 0.29	<0.1	0.9 ± 0.3	96 ± 30	1,710 ± 120
WW1	27.6 ± 1.7	31.64 ± 1.89	1.33 ± 0.02	<30	<30	<20
WW2	13.2 ± 0.6	17.9 ± 0.7	0.55 ± 0.05	<30	<30	<20
WW3	23.95 ± 2.58	27.32 ± 2.93	0.93 ± 0.15	6.76 ± 0.76	3.0 ± 0.6	6.0 ± 0.6
WW4	24.71 ± 2.77	34.44 ± 3.80	0.67 ± 0.17	4.13 ± 0.76	20 ± 4	1,130 ± 80

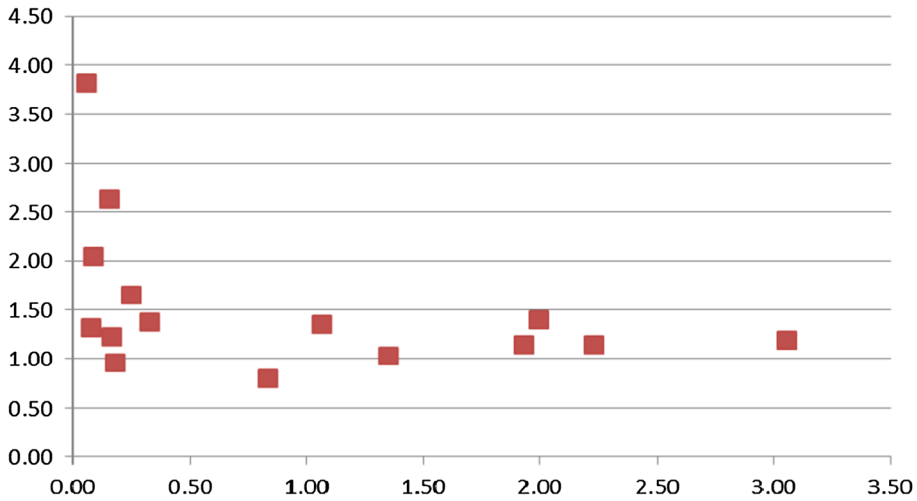

Fig. 2 Uranium activity ratio ^{234}U/^{238}U (Bq/Bq) versus natural uranium content U (μg L^{-1}) in water samples

Fig. 2. The radioactive disequilibrium or the ^{234}U activity excess in regard to^{238}U activity level is more expressed for waters with lower natural uranium content. For spring water SW8 uranium activity ratio ^{234}U/^{238} was slightly below 1 that confirms our previous findings on radioactive disequilibrium case in the ^{238}U radioactive series [33]. Isotopic ratios determined from radium and thorium isotopic concentrations were 38.5 for ^{226}Ra/^{230}Th ratio, 12.4 for ^{228}Ra/^{228}Th ratio and 54.3 for ^{228}Th/^{232}Th ratio. Radium excess in regard to expected values from parent isotopes ^{232}Th and ^{230}Th is the evidence of disequilibrium in both ^{238}U and ^{232}Th natural radioactive series. It may be attributed to the different solubility of thorium and radium and a partly upward diffusion from the surrounding sediments [4]. Due to a significant disequilibrium in ^{238}U series, relatively high ^{226}Ra concentration obtained was not the indication of high uranium content in SW8.

Conclusions

Result of this study has shown that, based on the natural uranium content, waters may be grouped according to the water type rather than to their geological origin. Tap waters and well waters have considerably higher uranium content in the range (0.83–3.06) and (1.06–2.23) μg L^{-1} respectively, comparing to values in interval (0.06–0.33) μg L^{-1} for spring waters of various geological areas.

The radioactive disequilibrium in both natural radioactive series (^{238}U and ^{232}Th), was observed in analyzed water samples. It was shown that radioactive disequilibrium or the ^{234}U activity excess in regard to ^{238}U activity concentration was more expressed for waters with lower natural uranium content. In general, local geochemical environment and change of properties such as solubility, adsorption and diffusion coefficients, the processes at the phase edges and transport medium properties are decisive for radioactive series disequilibrium. As a result, it may be more or less disturbed in underground, spring, mineral, well, tap, bottled and running waters regardless their geotectonic origin.

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References

1. World Health Organization WHO (2011) Guidelines for drinking water quality: radiological aspects, 4th edn. WHO, Geneva
2. Rulebook on limits of radionuclides content in drinking water, foodstuffs, feeding stuffs, medicines, general use products, construction materials and other goods that are put on market. Official Gazette of Republic of Serbia No. 86/11, 97/13
3. Ivanovich M, Harmon RS (1982) Uranium series disequilibrium applications to environmental problems. Clarendon Press, Oxford
4. Nikic Z, Kovacevic J, Papic P (2008) Uranium in the groundwater of Permo-Triassic aquifers of the Visok region, Stara Planina, Eastern Serbia. Water Air Soil Pollut 192:47–58
5. Reyes E, Marques LS (2008) Uranium series disequilibria in ground waters from a fractured bedrock aquifer (Morungaba Granitoids—Southern Brazil): implications to the hydro-chemical behavior of dissolved U and Ra. Appl Radiat Isot 69(1):196–200
6. Petrovic T, Zlokolica-Mandic M, Veljkovic N, Vidojevic N (2010) Hydro-geological conditions for the forming and quality of mineral waters in Serbia. J Geochem Expl 107:373–381
7. Tanaskovic I, Golobocanin D, Miljevic N (2012) Multivariate statistical analysis of hydrochemical and radiological data of Serbian spa waters. J Geochem Explor 112:226–234
8. Gunten HR, Surbeck H, Rossler E (1996) Uranium series disequilibrium and high thorium and radium enrichments in karst formations. Environ Sci Technol 30:1268–1274
9. Vesterbacka P (2005) ^{238}U series radionuclides in Finnish groundwater-based drinking water and effective doses. Radiation and Nuclear Safety Authority, STUK, Helsinki
10. Dimitrijevic MD (1994) In: Dimitrijević MD (ed) Geological Map 1:2 000 000 in Geological atlas of Serbia. Serbian Ministry of Natural Resources and Environmental Protection, Belgrade
11. Talvitie NA (1972) Electrodeposition of actinides for.alpha. spectrometric determination. Anal Chem 44(2):280–283
12. Radenković M, Vuković D, Šipka V, Todorović D (1996) Ion-exchange separation of uranium, thorium and plutonium isotopes from environmental samples. J Radioanal Nucl Chem 208(2):467–475
13. Desideri D, Roselli C, Feduzi L, Meli MA (2007) Radiological characterization of drinking waters in Central Italy. Microchem J 87:13–19
14. Jankovic MM, Todorovic DJ, Todorovic NA, Nikolov J (2012) Natural radionuclides in drinking waters in Serbia. Appl Radiat Isot 70:2703–2710
15. Vukovic Z, Sipka V, Vukovic D, Todorovic D, Markovic L (2006) Behavior of long-lived radionuclides in the Danube river ecosystem in Serbia. J Radioanal Nucl Chem 268(3):647–649
16. Petrovic T, Zlokolica-Mandic M, Veljkovic N, Papic PJ, Poznanovic MM, Stojkovic JS, Magazinovic SM (2012) Macro- and micro-elements in bottled waters and waterworks in Serbia. Chem Ind 66(1):107–122 in Serbian
17. Birke M, Rauch U, Lorenz H, Kringel R (2010) Distribution of uranium in German bottled and tap water. J Geochem Explor 107:272–282
18. EuroGeoSurvays (EGS) Geochemistry Expert Group (2010) European Groundwater Geochemistry, Part 1: Bottled water. Schweizerbartsche Verlagsbuchhandlung, Stuttgart
19. Jobbagy V, Kavasi N, Somlai J, Dombovari P, Kardos R, Kovacs T (2010) Radioanalytical investigations of uranium concentrations in natural spring, mineral, spa and drinking waters in Hungary. J Radioanal Nucl Chem 286:417–422
20. Jia G, Torri G, Sansone U, Innocenzi P, Rosamilia S, Di Lullo A, Gaudino S (2006) Concentrations and characteristics of uranium isotopes in drinking waters collected in Italy and the Balcan regions and their radiological impact on the public. In: Povinec PP, Sanchez-Cabeza JA (eds) Radioactivity in the environment. Elsevier, UK, pp 223–234
21. Kozlowska B, Walencik A, Dorda J, Przylibski TA (2007) Uranium, radium and ^{40}K isotopes in bottled mineral waters from Outer Carpathians, Poland. Radiat Meas 42:1380–1386
22. Palomo M, Penalver A, Borrul F, Aguilar C (2007) Measurement of radioactivity in bottled drinking water in Spain. Appl Radiat Isot 65:1165–1172
23. Taskin H, Asliyuksek H, Bozkurt A, Kam E (2013) Natural radioactivity in bottled mineral and thermal spring waters of Turkey. Radiat Prot Dosim 157(4):575–578
24. Benedik L, Jeran Z (2012) Radiological of natural and mineral drinking waters in Slovenia. Radiat Prot Dosim 151(2):306–313
25. Rozmaric M, Rogic M, Benedik L, Strok M (2012) Natural radionuclides in bottled drinking waters produced in Croatia and their contribution to radiation dose. Sci Total Environ 437:53–60
26. Bituh T, Marovic G, Petrinec B, Sencar J, Franulovic I (2009) Natural radioactivity of ^{226}Ra and ^{228}Ra in thermal and mineral waters in Croatia. Radiat Prot Dosim 133(2):119–123
27. Jobbagy V, Kavasi N, Somlai J, Mate B, Kovacs T (2010) Radiochemical characterization of spring waters in Balaton Upland, Hungary, estimation of radiation dose to members of public. Microchem J 94(2):159–165
28. Wallner G, Wagner R, Katzlberger C (2008) Natural radionuclides in Austrian mineral water and their sequential measurement by fast methods. J Environ Radioact 99:1090–1094
29. Calin MR, Ion AC, Radulescu I (2014) Evaluation of quality parameters and natural radionuclides concentrations in natural mineral water in Romania. J Radioanal Nucl Chem. doi:10.1007/s10967-014-3401-x
30. Krestou A, Panias D (2004) Uranium (VI) speciation diagrams in the $UO_2^{2+}/CO_3^{2-}/H_2O$ system at 25 °C. Euro J Min Proc and Environ Prot 4(2):113–129
31. Chu TC, Wang JJ (2000) Radioactive disequilibrium of uranium and thorium nuclide series in hot spring and river water from Peitou hot spring basin in Taipei. J Nucl Radiochem Sci 1(1):5–10
32. Romberger SB (1984) Transport and deposition of uranium in hydrothermal systems at temperatures up to 300 °C. In: De Vivo B (ed) Uranium geochemistry, mineralogy, geology, exploration and resources. Institution of Mining and Metalurgy, London, pp 12–17
33. Joksic JD, Radenkovic MB, Miljanic SS (2007) Natural radioactivity of some spring and bottled mineral waters from several central Balkan sites as a way of their characterization. J Serb Chem Soc 72(6):621–628