Radioactivity and hydrochemical properties of certain thermal Turkish spa waters

Muazzez Çelik Karakaya, Mahmut Doğru, Necati Karakaya, Fatih Kuluöztürk and Mahmut Tahir Nalbantçılar

ABSTRACT

The study aims to determine the radioactivity levels of thermal waters which have been used seasonally or permanently in spas for therapeutic intentions. Samples were collected from spas in different regions of Turkey. Some radionuclides (^{40}K, ^{232}Th, ^{226}Ra, ^{137}Cs), gross alpha (GA) and gross beta (GB) activities, and physical and some chemical parameters were measured. Gamma radiation measurements for ^{226}Ra, ^{232}Th and ^{40}K radionuclides were performed by using a high purity germanium (HPGe) detector. The results of the gamma spectrometry ranged from 1.385 to 11.025 Bql^{-1} for ^{226}Ra, <minimum detectable activity to 3.477 Bql^{-1} for ^{232}Th and 9.679 to 36.989 Bql^{-1} for ^{40}K. GA and GB activity concentrations were detected by using ultra-low level α/β counter. The GA and GB activity ranged from 43 to 3,182 mBql^{-1} and 54 to 1,950 mBql^{-1}, respectively. Based on calculated annual effective dose equivalent, the total dose originated mostly from ^{226}Ra and slightly from ^{40}K. Furthermore, waters with high Cl content were enriched with ^{40}K, ^{226}Ra isotopes, and the source of GA and GB activity in these waters was mostly ^{226}Ra. Strong high positive correlation between Cl, ^{226}Ra and total dissolved solids in Cl-enriched samples indicated that the nuclides formed from dissolved minerals in these waters.

Key words | gamma radiation, gross alpha and beta, hydrochemistry, natural radioactivity, therapy, thermal water

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INTRODUCTION

Turkey is very rich in thermal waters that originate from rocks in different chemical composition and age, and these waters commonly have been used in spas (thermal springs) since ancient times. The physical and major chemical properties of some natural thermal waters have already been studied while their radioactivity is less known.

Radionuclides are the main reason of radiation exposure of human beings and constitute background radiation levels (Bozkurt *et al.* 2007). The presence of radioactivity in nature is related to the radionuclides sourced by naturally decay chains, cosmic rays and artificial radionuclides.

The determination of radionuclide dispersion in the environment and calculation of the harmful effects of radiation exposure from the background is required. Natural radioactivity levels of a certain environment radionuclide depend on concentrations in air, water and rock that vary relative to geological and geochemical features of the source rocks. Cosmic rays from space also contribute to the background relating to altitude of the environment. Determination of the radionuclide concentrations of the thermal water samples in spas is very important for human health because of the diversity of the background radiation. After the Chernobyl accident, studies about determination of environmental radioactivity levels have been performed, especially in the northern parts of Turkey (TAEK 1998).

doi: 10.2166/wh.2017.263

The determination of radioactivity is important in waters which have a significant role on dispersion of radionuclides in nature. Natural waters are known as alpha, beta and gamma emitters and in a wide range of concentrations (Akyıl *et al.* 2009; Zorer *et al.* 2009; Janković *et al.* 2012; Görür & Camgöz 2014; Kuluöztürk & Doğru 2015). Radiation emitters in water are accountable for a small rate of the total dose exposed from natural and artificial radioactivity (UNSCEAR 2000). Transition of the chemical elements from rocks into the water depends on the geochemical characteristics of aquifers and period of the interaction between water and rocks (Janković *et al.* 2012).

Several thermal spring waters having different characteristics formed throughout the western and eastern parts of Turkey, located mostly around active volcanism and fault zones. The aim of the present study is to determine the radioactivity of thermal spa waters with gross alpha (GA)/gross beta (GB) counting, and gamma emitter radionuclide activity concentrations; and also to determine some physical and hydrochemical characteristics of the waters and find a relationship with radioactivity properties. In accordance with this purpose, a total of 31 thermal water samples were collected at spas from different parts of Turkey. The activity concentrations of ^{226}Ra, ^{232}Th, ^{40}K and gross α/β in the samples were determined and annual effective dose (AED) was calculated. Additionally, the concentrations of main cations, anions and physical parameters of water samples were determined.

MATERIALS AND METHODS

Thermal water samples were collected from 31 points of 20 spas in June 2011 and 2012 (Figure 1). Polypropylene bottles which were carefully washed in the laboratory with bi-distilled water were used for sampling. Three bottles of samples were taken from each spa. The first and second bottles were acidified with 3 N nitric acid to a pH of ≈2 to avoid biological contamination, precipitation of cations and adsorption of radionuclides onto the container material (Görür & Camgöz 2014). The third bottle was taken for anion analysis and no additional treatment was carried out on the bottle. For all of the samples, 500 mL of water was passed through a 0.2 μm filter. Then, the first bottle water samples were used for major cation analysis. The total abundances of the major cations, e.g., Na, Ca, Mg and K of the waters were determined by ACME Laboratories (Vancouver, British Columbia, Canada) using inductively coupled plasma and mass spectrometry (Spectro ICP-MS and

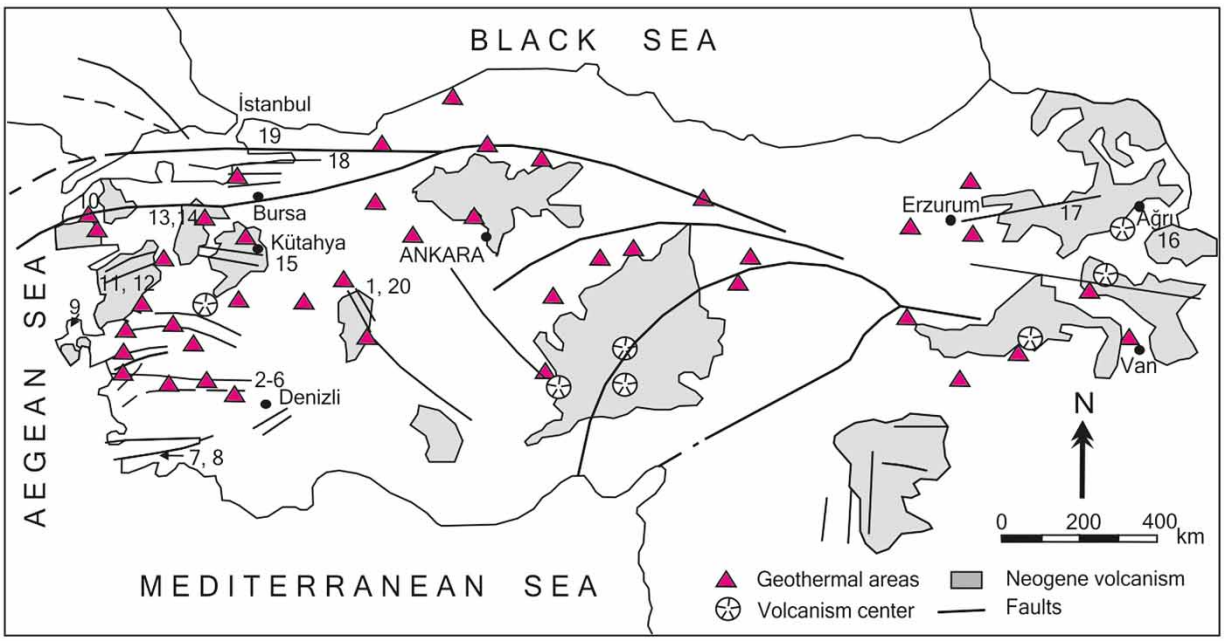

Figure 1 | Location of the thermal water samples and main tectonic lineaments, volcanic centres and geothermal areas of Turkey (simplified from Şimşek (2015)).

Perkin Elmer ELAN 9000 ICP-MS, USA, respectively). Anion contents of the thermal waters were determined by ion chromatography in the Hydrogeology Laboratory of Hacettepe University (Ankara, Turkey). Chemical analyses were achieved and the physical features of the water using international standards (APHA-AWWA-WPCF 1989). Some *in-situ* parameters, such as pH, electrical conductivity (EC, μS/cm) and temperature (T, °C) were measured on-site using a portable multi-parameter water meter (WTW 340i). The pH and EC meters were calibrated using pH 2, 4, and 7 buffer solutions and 0.01 mol/L KCl conductivity standard (1,278 at 20 °C and 1,413 at 25 °C), respectively. The third water samples were evaporated without boiling at 70 °C temperature in a volume of 600 mL for GA and GB analyses. The remnant in the vessel was scraped out and put in a planchette of 5.1 cm diameter (Zorer *et al.* 2009). The gamma measurements were made on loaded water samples into 1 L Marinelli beakers for one month to reach the secular radioactive equilibrium (Janković *et al.* 2012).

The radioactivity analyses were made at the Science and Technology Application and Research Center of Bitlis Eren University (Bitlis/Turkey). The GA and GB activity concentrations in the water samples were measured by ultra-low level α/β counter MPC 9604-1 (Protean Instrument Corporation). The detectors were calibrated for α and β energies using ^{241}Am (185 Bq) and ^{90}Sr (172 Bq) standard sources, respectively. Background counting was performed with empty steel planchets at 720 min intervals for each detector. Sample counting was made at 600 min intervals for all samples (Kuluöztürk & Doğru 2015).

The activity of ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs were determined by using a n-type HPGe (high purity germanium) detector with energy resolution of 2.10 keV at 1.33 MeV and relative efficiency 50%. Energy and efficiency calibrations of the detector were performed by using reference gel multinuclide material with total activity of 1.347 μCi (^{57}Co, ^{60}Co, ^{88}Y, ^{109}Cd, ^{113}Sn, ^{139}Ce, ^{137}Cs, ^{203}Hg, ^{210}Pb, ^{241}Am) and 1 kgl^{-1} density, and the energy and efficiency calibration curves were obtained (Figure 2). Sample spectra were taken at 24 h intervals. Spectra analyses and activity concentrations of ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs radionuclides were obtained by GammaVision (ORTEC) software. To protect the detector, a 10 cm thick lead covering lined with 2 mm thick Cu and Cd foils was used (Karakaya *et al.* 2015).

The activity (Bql^{-1}) of a sample for a given radionuclide was calculated as follows:

$$A\left(Bq\,l^{-1}\right) = \frac{N_S - N_B}{\varepsilon \times P_\gamma \times t} \times \frac{1}{V} \quad (1)$$

where A, N_S, N_B, ε, Pγ, t and V are sample activity (Bql^{-1}),

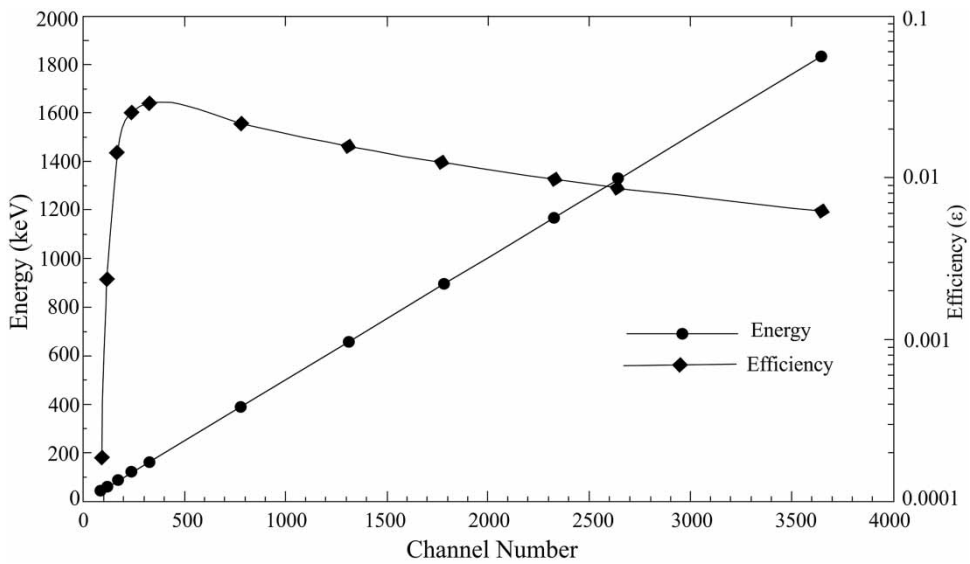

Figure 2 | Energy and efficiency calibrations of the HPGe detector.

count of sample, count of background, absolute efficiency, branching ratio, counting live time (s) and volume of the sample, respectively.

For the determination of specific activities, the daughter radionuclide gamma ray lines of 351.93 and 609.32 keV (^{214}Pb and ^{214}Bi) for ^{226}Ra and 911.2 keV (^{228}Ac) for ^{232}Th were used, respectively. Characteristic gamma peaks at 1,460.8 keV and 661.66 keV were used for the determination of ^{40}K and ^{137}Cs, respectively. The activity determination of ^{226}Ra and ^{232}Th was made by using the peaks of the decay products in equilibrium with their parent. Minimum detectable activity (MDA) was calculated using Equation (2):

$$MDA = \frac{271 + 4.65\sqrt{N_B}}{\varepsilon \times P_\gamma \times t} \quad (2)$$

where N_B, ε, Pγ and t are count of background, absolute efficiency, branching ratio, counting live time for certain radionuclides in gamma ray with energy E, respectively.

The AED of the thermal waters was calculated by using ^{226}Ra, ^{232}Th, ^{40}K, gross α and β activity values. The suggested conversion factors for ^{226}Ra, ^{232}Th, ^{40}K, GA and GB by Kurnaz *et al.* (2007), UNSCEAR (2008) and Khan *et al.* (2010) were used in calculations as follows in Equation (3) (Görür & Camgöz 2014):

$$DR_w = A_w \times IR_w \times ID_F \quad (3)$$

where DR_w is AED equivalent ($mSvy^{-1}$), A_w is activity (Bql^{-1}), and IR_w is drinking water for a person in a year (40 litres during a treatment cure for adults). The equation is used for drinking water. The therapeutic thermal water is not for drinking but its maximum dose could cause some health problems if it is drunk. ID_F is the AED equivalent conversion factor, which is 2.8×10^{-4}, 2.3×10^{-4}, 5.0×10^{-6} and 3.58×10^{-4} for ^{226}Ra, ^{232}Th, ^{40}K, and GA, GB, respectively ($mSvBq^{-1}$) (EPA 1988; WHO 2004).

RESULTS AND DISCUSSION

The studied thermal waters were collected around the tectonically active zones, geothermal areas and young volcanic centres. Most of the thermal springs are located roughly parallel to active fault systems, e.g., normal, oblique, horst-graben, and around Neogene aged volcanic areas (Figure 1). In the western part of Anatolia, the main tectonic features are extensional E–W-trending horst-graben systems (Bozkurt 2003). All of the thermal sources in western Anatolia, low temperature springs (>65 °C), are related to the low-angle detachment fault while high temperature geothermal fields developed along E–W-trending high angle normal faults (Karakuş & Şimşek 2013). Precambrian aged basement rocks, which are the reservoir of the springs, are composed of gneiss, metagranite, schist, paragneiss and metagabbro, whereas marble and schist cover Paleozoic to Early Tertiary aged rocks (Karakuş & Şimşek 2013 and references therein). The basement rocks are composed of marble and schist of the Paleozoic age in the western part of central Anatolia. Neogene carbonates unconformably cover the basement rocks and they are the reservoir rocks of the samples W-1 and W-20 together with Paleozoic aged rocks (Mutlu & Güleç 1998). Tertiary granodioritic rocks are covered by Neogene rocks which are formed from volcanics, different sized detrital sediments, basaltic rocks and Quaternary alluvium which are the reservoir rocks of the samples W-9 to 12. Paleozoic to Early Mesozoic aged metamorphics, e.g., gneiss, schist, marble and ophiolites and Upper Cretaceous mélange form the reservoir rocks while Upper Miocene-Pliocene detrital sediments form the cover rocks of the reservoir for the samples W-2 to 6 and W-13 to 15 (Mutlu 2007). The occurrence of thermal springs (W-7 and W-8) in the study area is linked to the young normal faults (Gökgöz & Tarcan 2006 and references therein). The authors indicate that karstic limestones and Lycian nappes are the reservoir rocks and there is no cap rock for geothermal systems of the samples W-7 and W-8. The reservoir rocks of sample W-16 formed from Paleozoic to Mesozoic aged metamorphic rocks and Miocene to Pliocene aged sedimentary and carbonate rocks. The Pliocene-Quaternary volcanic and volcanoclastic rocks are the cap rocks of the sample (Pasvanoğlu & Güler 2010). The Upper Miocene units formed from basaltic and andesitic lavas and volcanoclastic rocks are the oldest units and are overlain unconformably by the Pliocene units (Kalkan *et al.* 2012 references therein). The spring water sample W-17 lies on the Late Miocene fault zone, which is one of the most active fault belts of the Eastern Anatolian Region. Sample W-18 represents outflow of deep groundwater that has been recharged and circulated in a

possible fracture zone of flysch and sandstone of the Eocene age (Saner 1978). The Paleozoic aged detrital sedimentary rocks, limestones and granitic rocks which form the reservoir rocks of the sample W-19, show poor or very poor aquifer characteristics, covered unconformably by Pleistocene to Quaternary sediments (Yalçın *et al.* 2007 and reference therein).

The total dissolved solids (TDS) of the studied waters varies in a wide range between 590 and 29,212 mg/L and may be related to long residence time and circulation. The pH of the waters range from 6.40 to 9.21, the EC values range from 0.88 to 43.6 mS/cm, and temperatures of the thermal water samples vary from 26.5 to 87.0 °C (Table 1). The wide range variation of the above-mentioned properties may be related to distance from the main fault zone, penetrating depth, circulation time and/or source rocks' temperature. The thermal waters are slightly acidic/neutral to alkaline in character. From the hydrogeochemical point of view, the following four water types were defined as Na^+-HCO_3^-, Na^+-Cl^-, Na^+-SO_4^{2-}, Mg^{2+} and/or Ca^{2+}-HCO_3^- (Table 1). EC values and Cl content are high in especially samples (W-7, 8, 9 and 19) taken from near the coast which may reflect mixing with sea water or deep water circulation and partially long residence time (Table 1). Also, Gökgöz & Tarcan (2006) suggested that Cl-rich waters were sourced from the sea water contribution. On the other hand, Mutlu & Güleç (1998) indicated that the Cl-rich character related to the presence of connate fossil waters at depth. Additionally, Gökgöz & Tarcan (2006), who studied in the same area from which came the samples W-7 and W-8, suggested that these waters are of meteoric origin and sea waters percolated to the reservoir through the karstic voids and fractures. Additionally, the spring waters are mixed water which are heated at depth and ascend to the surface via major faults. High HCO_3 content with Na were determined in especially W-17, 18 and 20, and may be related to the reaction of cold meteoric water with carbonate rocks and ion exchange in the aquifers (Özen *et al.* 2012). Therefore, variations of HCO_3 concentrations among the studied waters may be related to dissolution and precipitation of carbonate minerals in reservoir and cover rocks. Additionally, Tarcan *et al.* (2009) stated that enrichment of thermal waters with Na reflects rock dissolution and ion exchange reactions in deep aquifers at high temperatures. Although a strong positive correlation ($r = 0.97$) was determined between Ca and SO_4 in samples W-1, 2, 7-9, 16 and 19, sulphate is not determined as the main anion in any sample. In addition, high levels of sulphate concentration may be related to oxidation of metallic sulphides and/or escape of H_2S from a deep hot-water system and dissolution of sulfate minerals. The processes mentioned regarding rising sulfate concentration were not thoroughly developed in the studied reservoir rocks. The negative trend of Ca with SO_4 can be attributed to calcite and/or aragonite dissolution in parallel with gypsum and/or anhydrite precipitation.

The characteristics of the waters were affected by many parameters, e.g., extensive volcanism, different active fault systems, mixing sea water, penetrating time and depth, type of the reservoir/cap rock, etc. Some water samples having nearly the same reservoir and cap rocks show different physical, chemical and radioactivity properties (2, 5 and 6, and 11 and 12, Figure 1). Additionally, different concentrations of natural radioelements in groundwater can be related to temperature, dissolved inorganic salts, geological composition of the rocks and other factors such as conductivity and pH, etc.

The measured activity concentrations range from 1.385 to 11.025 Bql^{-1} for ^{226}Ra, <MDA to 3.477 Bql^{-1} for ^{232}Th, <MDA to 0.244 Bql^{-1} for ^{137}Cs, 9.679 to 36.989 Bql^{-1} for ^{40}K, 0.043 to 3.182 Bql^{-1} for GA and 0.054 to 1.950 Bql^{-1} for GB in the water samples (Table 2, Figure 3(a) and 3(b)). Due to the low solubility of thorium, GA activity is mostly caused by mainly ^{226}Ra, ^{224}Ra, ^{210}Po and in specific circumstances uranium isotopes (^{234}U, ^{235}U and ^{238}U) and occasionally ^{232}Th in natural water (Osmond & Ivanovich 1992; Jobbágy *et al.* 2011 and references therein), whereas beta positive decay is probably sourced from ^{40}K, ^{226}Ra and ^{210}Po (Osmond & Ivanovich 1992; Örgün *et al.* 2005; Değerlier & Karahan 2010; Jobbágy *et al.* 2011 and references therein; Görür & Camgöz 2014). The GB activity is commonly higher than the GA activity possibly reflecting the geochemical composition of the source rocks where radionuclides of the thorium series are more abundant than those of the uranium series. Most of the measured GA and some of the GB activity is higher than the recommended limit for drinking water (WHO 2004, Table 2, Figure 3(b)). Therefore, the use of this water for drinking is not suitable. In the chloride-rich waters, samples W-7, 8, 9 and 19, a strong positive correlation is found between the Cl concentration and ^{226}Ra activity ($r = 0.98$), but no correlation was found when all samples

Table 1 | Some physical properties, chemical compositions (mg/L) and water types of the thermal waters

Sample	Temp. (°C)	pH	EC (μS/cm)	TDS (mg/L)	Na	K	Ca	Mg	HCO_3	Cl	SO_4	Water types
W-1	40.1	7.9	1,243	833	147	21	139	20	405	57	279	Ca-Na-HCO_3-SO_4
W-1/1	67.9	6.6	1,780	1,193	816	91	129	13	981	65	930	Na-SO_4-HCO_3
W-2	39.5	7.2	4,300	2,881	106	25	511	139	1,274	25	837	Ca-Mg-HCO_3-SO_4
W-2/2	50	6.8	3,020	2,023	96	24	566	127	1,417	22	785	Ca-Mg-HCO_3-SO_4
W-3	52	6.8	4,020	2,693	517	55	521	146	1,389	60	1,781	Ca-Na-SO_4-HCO_3
W-5	70	8.8	3,700	2,479	617	78	158	18	1,115	66	660	Na-Ca-HCO_3-SO_4
W-5/1	34	9.2	3,850	2,580	877	113	144	14	951	83	1,047	Na-SO_4-HCO_3
W-6	87	8	4,900	3,283	915	92	161	18	865	90	1,496	Na-SO_4-HCO_3
W-6/1	58	8.6	4,520	3,028	980	86	72	11	716	72	1,667	Na-SO_4-HCO_3
W-7/1	30	6.8	27,000	18,090	4,206	159	843	533	876	7,798	960	Na-Cl
W-7	31	6.9	22,600	15,142	4,529	188	845	589	888	8,467	1,021	Na-Cl
W-8/1	36	7	43,600	29,212	9,093	332	1,394	897	362	17,037	2,280	Na-Cl
W-8	35	7	43,500	29,145	8,951	309	1,450	884	356	16,765	2,285	Na-Cl
W-9/1	38	7.2	39,200	26,264	7,947	277	1,299	683	242	14,868	1,658	Na-Cl
W-11	36	7.4	39,600	26,532	545	35	92	15	1,105	67	425	Na-HCO_3-SO_4
W-12/1	65	7.3	3,300	2,211	196	9	151	18	290	37	512	Na-Ca-SO_4-HCO_3
W-14	37	7.8	3,400	2,278	516	16	145	30	583	685	84	Na-Ca-Cl-HCO_3
W-14/1	52	7	3,200	2,144	604	18	138	32	665	775	96	Na-Cl-HCO_3
W-14/2	31	8	3,400	2,278	529	15	158	28	589	680	82	Na-Ca-Cl-HCO_3
W-15	54	7.6	3,075	2,060	256	27	98	13	640	34	261	Na-Ca-HCO_3-SO_4
W-15/1	55	7.7	1,520	1,018	132	14	93	16	483	21	128	Na-Ca-HCO_3-SO_4
W-16	34	8.3	1,096	734	133	54	224	85	999	138	217	Ca-Na-Mg-HCO_3
W-16/1	47	6.8	2,350	1,575	129	50	194	78	1,017	113	101	Ca-Na-HCO_3
W-16/2	39	7.2	2,150	1,441	187	50	234	70	988	162	259	Ca-Mg-HCO_3-SO_4
W-17	31.4	6.8	1,510	1,012	199	35	134	58	1,005	116	5	Na-Ca-Mg-HCO_3
W-18	26.5	6.4	1,095	734	34	6	167	27	649	5	18	Mg-HCO_3
W-18/1	31	7.2	880	590	33	5	168	27	640	5	19	Ca-HCO_3
W-18/2	32	6.9	900	603	34	6	147	26	622	5	16	Ca-HCO_3
W-19	37	6.8	930	623	1,469	37	428	217	393	2,953	352	Na-Ca-Cl
W-20	37	6.8	8,600	5,762	920	81	123	28	2,715	106	7	Na- HCO_3
W-20/1	65.2	7.14	4,160	2,787	922	83	136	31	2,196	107	7	Na- HCO_3
MDL	0.1	0.01	0.01		0.05	0.05	0.05	0.05	0.01	0.01	0.01	

MDL: Method detection limit.

were taken into consideration. Furthermore, Cl shows strong positive correlation with GA (r = 84) and negative correlation with GB (r = 90). Additionally, ^{40}K presents strong negative correlation with GB (r = 0.81) but positive correlation with GA (r = 0.78). In the same samples, moderately positive correlations are presented between ^{226}Ra activity-GA (r = 0.51) and ^{226}Ra activity-GB (r = 0.50). The results indicated that most of the GB was sourced from decay of ^{226}Ra not ^{40}K. The correlation between Cl^- concentration, TDS values and the ^{226}Ra activity may be related to dissolution of minerals and radium-Cl complex enriched in Na-Cl-rich waters (Labidi *et al.* 2010).

The highest ^{40}K was measured for peloid samples P-11, 20 and 20/1 and is 1,698, 1,516 and 1,041 Bq/kg,

Table 2 | Activity concentrations (Bql^{-1}) of radionuclides in the water samples

Sample	^{226}Ra	^{232}Th	^{137}Cs	^{40}K	Gross-α	Gross-β
W-1	2.97 ± 0.45	0.53 ± 0.19	0.18 ± 0.06	21.78 ± 2.76	0.28 ± 0.07	0.33 ± 0.05
W-1/1	4.26 ± 0.48	1.38 ± 0.22	0.11 ± 0.05	14.00 ± 2.76	0.62 ± 0.08	0.34 ± 0.05
W-2	1.62 ± 0.36	0.53 ± 0.19	<MDA	15.21 ± 6.22	0.44 ± 0.07	0.80 ± 0.06
W-2/1	3.60 ± 0.45	0.89 ± 0.20	0.24 ± 0.10	16.94 ± 2.42	0.33 ± 0.07	0.45 ± 0.05
W-3	3.06 ± 0.48	1.60 ± 0.45	0.12 ± 0.05	23.51 ± 2.94	0.07 ± 0.02	0.58 ± 0.06
W-4	2.90 ± 0.49	0.98 ± 0.22	0.11 ± 0.06	22.12 ± 2.77	0.12 ± 0.03	0.64 ± 0.06
W-4/1	1.38 ± 0.46	1.92 ± 0.56	<MDA	23.16 ± 2.94	0.12 ± 0.03	0.71 ± 0.06
W-5	2.73 ± 0.46	1.25 ± 0.24	0.05 ± 0.03	25.58 ± 2.77	0.23 ± 0.07	0.66 ± 0.06
W-5/1	2.61 ± 0.45	0.94 ± 0.22	<MDA	17.28 ± 2.77	0.28 ± 0.07	1.29 ± 0.10
W-7	8.27 ± 0.57	0.62 ± 0.24	0.11 ± 0.05	18.67 ± 3.11	0.29 ± 0.07	1.49 ± 0.12
W-8	7.79 ± 0.56	0.98 ± 0.20	<MDA	35.09 ± 3.46	0.13 ± 0.03	0.12 ± 0.05
W-8/1	9.90 ± 0.63	0.76 ± 0.24	0.08 ± 0.05	36.99 ± 3.28	0.37 ± 0.07	1.05 ± 0.10
W-8/2	5.22 ± 0.51	<MDA	0.21 ± 0.08	21.78 ± 2.77	0.35 ± 0.08	1.17 ± 0.10
W-9	4.13 ± 0.74	<MDA	0.07 ± 0.03	29.40 ± 3.28	0.31 ± 0.07	1.11 ± 0.10
W-9/1	7.16 ± 0.53	0.98 ± 0.20	<MDA	28.17 ± 3.28	0.14 ± 0.03	0.43 ± 0.05
W-11	2.35 ± 0.45	0.89 ± 0.21	0.04 ± 0.03	12.62 ± 3.28	0.10 ± 0.02	0.30 ± 0.05
W-12	2.54 ± 0.50	<MDA	0.08 ± 0.05	19.19 ± 5.88	0.07 ± 0.02	0.14 ± 0.05
W-14	6.37 ± 0.56	0.62 ± 0.24	0.15 ± 0.08	16.77 ± 6.74	0.35 ± 0.07	0.35 ± 0.05
W-14/1	7.26 ± 0.57	1.34 ± 0.27	0.06 ± 0.03	15.56 ± 2.59	0.52 ± 0.08	0.10 ± 0.04
W-14/2	3.79 ± 0.59	0.76 ± 0.24	<MDA	18.67 ± 2.77	0.41 ± 0.07	0.24 ± 0.05
W-15	2.39 ± 0.51	1.60 ± 0.42	0.02 ± 0.02	21.26 ± 2.94	0.20 ± 0.07	0.49 ± 0.06
W-15/1	7.86 ± 0.63	0.80 ± 0.24	0.07 ± 0.03	13.65 ± 2.77	0.08 ± 0.02	0.14 ± 0.04
W-16	7.32 ± 0.64	1.02 ± 0.31	0.03 ± 0.02	10.37 ± 3.11	1.25 ± 0.15	0.76 ± 0.06
W-16/1	6.72 ± 0.57	0.80 ± 0.27	0.07 ± 0.05	18.84 ± 2.94	3.18 ± 0.46	1.95 ± 0.16
W-16/2	7.74 ± 0.62	1.78 ± 0.52	0.02 ± 0.01	15.56 ± 3.11	0.55 ± 0.08	1.00 ± 0.08
W-17	3.51 ± 0.58	<MDA	0.18 ± 0.08	13.48 ± 6.39	0.12 ± 0.04	0.42 ± 0.05
W-17/1	7.64 ± 0.65	<MDA	0.03 ± 0.02	17.11 ± 2.94	0.12 ± 0.03	0.42 ± 0.06
W-18	6.75 ± 0.61	0.53 ± 0.19	<MDA	13.65 ± 7.26	0.22 ± 0.03	0.23 ± 0.05
W-18/1	7.23 ± 0.57	<MDA	0.02 ± 0.01	10.54 ± 2.59	0.06 ± 0.02	0.05 ± 0.04
W-18/2	6.24 ± 0.58	0.53 ± 0.19	0.09 ± 0.05	14.35 ± 2.77	0.47 ± 0.08	0.42 ± 0.05
W-19	4.26 ± 0.57	<MDA	0.03 ± 0.01	9.68 ± 2.94	0.04 ± 0.01	0.14 ± 0.04
W-20	11.02 ± 0.84	3.48 ± 0.68	<MDA	11.58 ± 3.28	0.50 ± 0.08	0.60 ± 0.06
W-20/1	4.59 ± 0.60	2.94 ± 0.62	0.02 ± 0.02	19.88 ± 3.11	0.64 ± 0.08	1.30 ± 0.10
Minimum	1.38	<MDA	<MDA	9.68	0.04	0.05
Maximum	11.02	3.48	0.24	36.99	3.18	1.95
Mean	5.25	0.99	0.09	18.86	0.39	0.61
MDA	0.29	0.52	0.02	5.40	0.02	0.01
UNSCEAR (2000)	32	45		420		
WHO (2004)					0.1	1.0

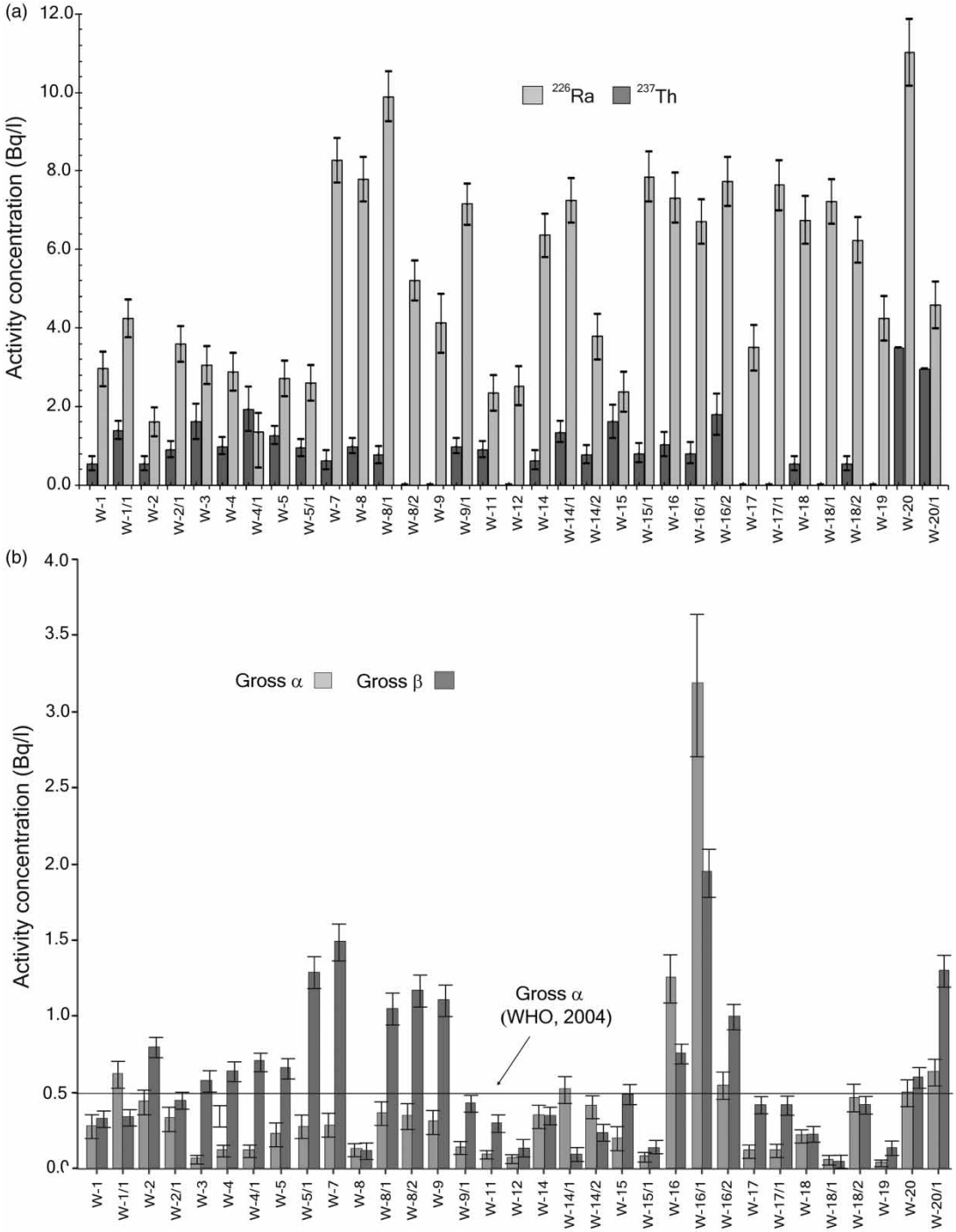

Figure 3 | (a) The activity concentration of ^{226}Ra and ^{232}Th of water samples. The error bars correspond to the measurement error. (b) The activity concentration of gross-α and -β of water samples. The error bars correspond to the measurement error.

respectively (Karakaya *et al.* 2015). Content of K_2O % wt and ^{40}K of the peloids shows moderately positive correlation ($r = 0.65$), and K (ppm) and also ^{40}K activity of the waters presents positive correlation ($r = 0.79$) which indicates that the K activity originates from source rocks (Table 2). However, there is no correlation between K_2O % and ^{40}K

activity of the peloids with some parameters of the water samples. As well, no statistically significant correlation was found between GA and GB activities when compared to concentrations of ^{226}Ra, ^{232}Th and ^{40}K measured in peloids and waters. The lack of correlation may be related to geochemical composition of the source rocks, redox conditions and circulation time due to easy dissolution of some nuclides (Vesterbacka 2007). The highest ^{40}K activities were determined in the chloride-rich waters samples W-7, 8, 9 and 19, and in these samples strong positive correlation ($r = 0.98$) is found between ^{40}K and Cl^-. Thorium activity concentration of the thermal waters varies from 0.089 to 3,477 Bql^{-1} (mean 1.027 Bql^{-1}) and is usually lower than other radionuclides. The low concentration of thorium is due to being a relatively insoluble element in natural waters and found generally within soils or rocks (Labidi *et al.* 2002).

It was determined that GA and GB activity concentrations are generally lower than recommended values for drinking water by WHO (2004), and the measured GA and GB values are generally in similar ranges of other spring waters in the world (Table 2, Figure 3(b)).

Recommended activity limit values for gamma emitters (32, 45 and 420 Bql^{-1} for ^{226}Ra, ^{232}Th and ^{40}K, respectively) by UNSCEAR were not exceeded (Figure 3(a)). Recommended activity limit values for GA and GB by WHO (2004) were exceeded by 82% and 21% of samples, respectively. Total calculated AED values were given as the sum of the ^{226}Ra, ^{232}Th, ^{137}Cs, ^{40}K, GA and GB dose values (Table 3). The largest and lowest contribution to the total dose was sourced from ^{226}Ra and ^{40}K, respectively. The total AED is between 0.040 and 0.173 $mSvy^{-1}$ and mean value is 0.086 $mSvy^{-1}$. The recommended AED value is 0.1 $mSvy^{-1}$ (WHO 2011) and 33% of samples exceed this value (Tables 2 and 3).

Table 3 | AED ($mSvy^{-1}$) of the water samples

	AED equivalent ($mSvy^{-1}$)					
Sample	**^{226}Ra**	**^{232}Th**	**^{40}K**	**Gross-α**	**Gross-β**	**Total dose**
W-1	0.033	0.005	0.004	0.004	0.005	0.051
W-1/1	0.048	0.013	0.003	0.009	0.005	0.077
W-2	0.018	0.005	0.003	0.006	0.011	0.044
W-2/1	0.040	0.008	0.003	0.005	0.006	0.063
W-3	0.034	0.015	0.005	0.001	0.008	0.063
W-4	0.033	0.009	0.004	0.002	0.009	0.057
W-4/1	0.016	0.018	0.005	0.002	0.010	0.050
W-5	0.031	0.011	0.005	0.003	0.009	0.060
W-5/1	0.029	0.009	0.003	0.004	0.018	0.064
W-7	0.093	0.006	0.004	0.004	0.021	0.128
W-8	0.087	0.009	0.007	0.002	0.002	0.107
W-8/1	0.111	0.007	0.007	0.005	0.015	0.146
W-8/2	0.058	0.004	0.004	0.005	0.017	0.089
W-9	0.046	0.001	0.006	0.004	0.016	0.074
W-9/1	0.080	0.009	0.006	0.002	0.006	0.103
W-11	0.026	0.008	0.003	0.001	0.004	0.043
W-12	0.028	0.005	0.004	0.001	0.002	0.040
W-14	0.071	0.006	0.003	0.005	0.005	0.090
W-14/1	0.081	0.012	0.003	0.007	0.002	0.106
W-14/2	0.042	0.007	0.004	0.006	0.003	0.062
W-15	0.027	0.015	0.004	0.003	0.007	0.056
W-15/1	0.088	0.007	0.003	0.001	0.002	0.101
W-16	0.082	0.009	0.002	0.018	0.011	0.122
W-16/1	0.075	0.007	0.004	0.046	0.028	0.160
W-16/2	0.087	0.016	0.003	0.008	0.014	0.128
W-17	0.039	0.003	0.003	0.002	0.006	0.053
W-17/1	0.086	0.001	0.003	0.002	0.006	0.098
W-18	0.076	0.005	0.003	0.003	0.003	0.090
W-18/1	0.081	0.003	0.002	0.001	0.001	0.088
W-18/2	0.070	0.005	0.003	0.007	0.006	0.090
W-19	0.048	0.004	0.002	0.001	0.002	0.056
W-20	0.123	0.032	0.002	0.007	0.009	0.173
W-20/1	0.051	0.027	0.004	0.009	0.019	0.110
Minimum	0.016	0.001	0.002	0.001	0.001	0.040
Maximum	0.123	0.032	0.007	0.046	0.028	0.173
Mean	0.059	0.009	0.004	0.006	0.009	0.086

CONCLUSION

In this study, physical properties, major element compositions and radioactivity profiles (^{226}Ra, ^{232}Th, ^{137}Cs, ^{40}K, GA and GB) of some therapeutic spa waters in Turkey were investigated. According to their major anion and cation content, water types were classified as Na^+-HCO_3^-, Na^+-Cl^-, Na^+-SO_4^{2-}, Ca^{2+} and/or Mg^{2+}-HCO_3^-. The investigated properties of the waters vary over a wide range, depending on the nature of the aquifer, e.g., mixing sea

water, penetrating time and depth, conductivity, temperature, etc. The water types and the wide range of TDS (190 to 29,200 mg/L) and EC values (0.88 to 43.6 mS/cm) of the waters indicate that the thermal waters originated from different geochemical processes in Turkey. The water samples with high Cl concentration showed the highest mean value of ^{226}Ra concentration resulting from seawater contribution and leading to proper conditions of ^{226}Ra mobilization. At the same time, these waters also are enriched with ^{40}K and ^{226}Ra isotopes, and GA and GB activities are mostly sourced from the ^{226}Ra. Close affinity of Cl-TDS indicated that the nuclides formed from dissolved minerals in these waters.

Most of the GA and some of the GB radioactivity concentrations are higher than the recommended guideline activity concentrations by WHO (1993) for drinking water. Values of GA in 82% and GB in 21% of the samples were higher than the recommended limit values. 33% of the samples exceed the recommended activity and AED values. ^{226}Ra is the main contributor to the AED. The thermal waters are not used for drinking purposes, however, based on the radiological properties of the investigated waters, some problems can be caused when using therapeutic treatments with peloids.

ACKNOWLEDGEMENTS

The project was funded by The Scientific and Technological Research Council of Turkey (TÜBİTAK 110Y033) and the Selçuk University Scientific Research Projects support program (BAP 11401045).

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First received 11 October 2016; accepted in revised form 15 February 2017. Available online 5 April 2017