Environ Monit Assess (2018) 190: 265
https://doi.org/10.1007/s10661-018-6643-1

Radiological and hydrochemical study of thermal and fresh groundwater samples of northern Euboea and Sperchios areas, Greece: insights into groundwater natural radioactivity and geology

C Kanellopoulos · P Mitropoulos · A Argyraki

Received: 6 November 2017 / Accepted: 26 March 2018 / Published online: 4 April 2018
© Springer International Publishing AG, part of Springer Nature 2018

Abstract A radiological and hydrochemical study has been conducted on thermal and fresh groundwater samples of northern Euboea Island and eastern central Greece. Both areas are characterized by complex geology and are renowned since antiquity for their hot springs, that are exploited for therapeutic spa purposes until today. The aim of the study was to combine radiological and hydrochemical data in order to achieve a holistic water quality assessment with insights into the geology of the study areas. All samples were characterized with respect to their major and trace ion and element composition, as well as activity concentrations of ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{40}K. The samples demonstrated elevated natural radioactivity and U concentrations, especially in some locations of the Kamena Vourla area, reaching 179 Bq/L ^{222}Rn, 2.2 Bq/L ^{226}Ra, 2.9 Bq/L ^{228}Ra, and 17 μg/L U. The estimated circulation depth of thermal groundwater ranges between 250 m in central Greece and 1240 m in north Euboea study area, whereas the calculated water residence times range between 27 and 555 years. Our data suggest the possible presence of an unknown until know U-rich plutonic rock formation in Kamena Vourla area and immiscibility of the fresh and thermal groundwaters in the studied areas.

C. Kanellopoulos (✉) · P. Mitropoulos · A. Argyraki
Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Panepistimiopolis, Ano Ilissia, 15784 Athens, Greece
e-mail: ckanellopoulos@gmail.com
e-mail: argyraki@geol.uoa.gr

Keywords Natural radioactivity · Hydrochemistry · Groundwater · Hot springs-spa · Dosimetry

Introduction

Natural radioactivity levels and the associated external exposure due to gamma radiation depend mainly on the local geological setting of an area and differ from region to region (United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) 2000; Florou et al. 2007; Jia and Torri 2007). The United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) has studied the exposure due to local geological settings (natural sources) and concluded that it contributes over 98% of the radiation dose to the population (excluding medical exposure). Whereas, the nuclear power production and nuclear weapons testing have only limited contribution. The global average human exposure from natural sources is 3.0 mSv/year (United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) 2008).

Thus, the determination of naturally occurring radionuclides in groundwater is essential in order to assess the environmental and public health impact (Isam et al. 2002). Furthermore, radiological studies of groundwater combined with geological and hydrochemical studies are of high importance, since (i) they provide valuable information leading to an integrated assessment of groundwater quality (United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) 2000; Isam et al. 2002; Jia et al. 2009) and, (ii) they can reveal important geological information, since the presence of natural radionuclides in groundwater is determined by their concentrations in the bedrock (Walencik et al. 2010).

In several cases, hot springs have been identified to be related with high natural radiation areas (Danali et al. 1986; Mishra 1990; Sohrabi 1990). In Greece, occurrence of hot springs is common due to the geological setting of the country. Specifically, presently active volcanic and hydrothermal locations occur mainly along the South Aegean Active Volcanic Arc which is related to the subduction of the African plate beneath the Aegean micro plate. The magmatic and volcanic processes and the tectonic setting which includes active graben and continental rift systems favor the rise of deep groundwater solutions that are discharged at the surface as hot springs. As a result of this geological setting, natural radioactivity in groundwater samples presents elevated concentrations compared with worldwide samples. Concentrations of up to 6289 Bq/L ^{222}Rn, 5 Bq/L ^{226}Rn, and 2.4 Bq/L ^{228}Rn have been reported in the literature (Trampidou 2004; Florou et al. 2007; Athansoulis et al. 2009; Athanasoulis et al. 2016). Inactive volcanism occurs also further north, within the North Euboean Gulf and in a back-arc position with respect to the South Aegean Active Volcanic Arc. Hot spring occurrences in this area are related to the Plio-Pleistocene volcanic center of Lichades (Georgalas 1938; Pe-Piper and Piper 2002).

Here, we report on the radiological and hydrochemical characteristics of thermal and fresh groundwater samples, from the northern part of Euboea island and the neighboring part of the mainland, eastern central Greece. Natural radionuclide concentrations (^{222}Rn, ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{40}K) have been measured and are assessed in combination with temperature, pH, and major and trace ions and elemental concentrations in groundwater. The data are interpreted within the context of local geology in order to provide new information concerning the groundwater circulation and reveal new geological information. Also, a holistic water quality assessment is attempted combining both the radiological and hydrochemical data.

Study area

The study area includes the northern part of Euboea Island and the neighboring part of the mainland, eastern central Greece (Fig. 1). The volcanic center of Lichades islands lies in the center of the investigation area, in North Euboean Gulf. Sampling sites are located on-shore, on both sides of the North Euboean Gulf. Specifically, samples were collected from springs and boreholes at Ilia, Aedipsos, and Agios Georgios located on Euboea Island as well as from Atalanti, Arkitsa, Kamena Vourla, and Thermopylae located on mainland Greece. The selected sampling locations represent all main hot springs in the area, while fresh water samples were obtained from water points (springs and boreholes) that are used mainly for irrigation purposes in the area. Hot springs are scattered on both sides of the North Euboean Gulf (Kanellopoulos et al. 2017a, 2017b), in mainland and northern Euboea Island and they have been exploited for therapeutic spa purposes since the antiquity. Fresh groundwater samples were collected from springs and boreholes in close proximity to hot springs/boreholes.

Lichades islands consist of trachyandesite lava flows, dated at 0.5 Ma. Volcanic rocks dating 1.7 Ma also outcrop in the Kamena Vourla area and comprise lavas of trachyandesite composition (Georgalas 1938; Pe-Piper and Piper 2002). The volcanic rocks are related to the neo-tectonic activity, since they are located along one of the main shear zones of the area (Kranis 1999). Innocenti et al. (2010) based on Sr–Nd–Pb isotopic data relate this volcanic center with the large volcanic belt that developed north of the Pelagonian–Attic–Cycladic–Menderes massifs, encompassing a 35-Ma time span. This belt is widespread over a large area from NW Greece–Macedonia to the Aegean–western Anatolia. Karastathis et al. (2011) showed that there is a magma chamber under the North Euboean Gulf area, at 7–8 km depth.

Bedrock geological formations of the Alpine orogenic cycle in the study area belong to the western part of the Geotectonic Units of the internal zones of Greece i.e. Pelagonian and Sub-Pelagonian (Mountrakis 1986; Jolivet et al. 2013). The eastern central part of mainland, were Thermopylae and Kamena Vourla are located, belong to the Sub-Pelagonian Geotectonic Unit. The basement consists mainly of carbonate rocks (limestone and dolomite) of Middle Triassic-Middle Jurassic age. An ophiolitic thrust sheet representing a relic of Thethian oceanic crust is overthrusted onto the carbonates. Drilling and geophysical data in Kamena Vourla indicate that a shale-chert formation rich in serpentinized ophiolite

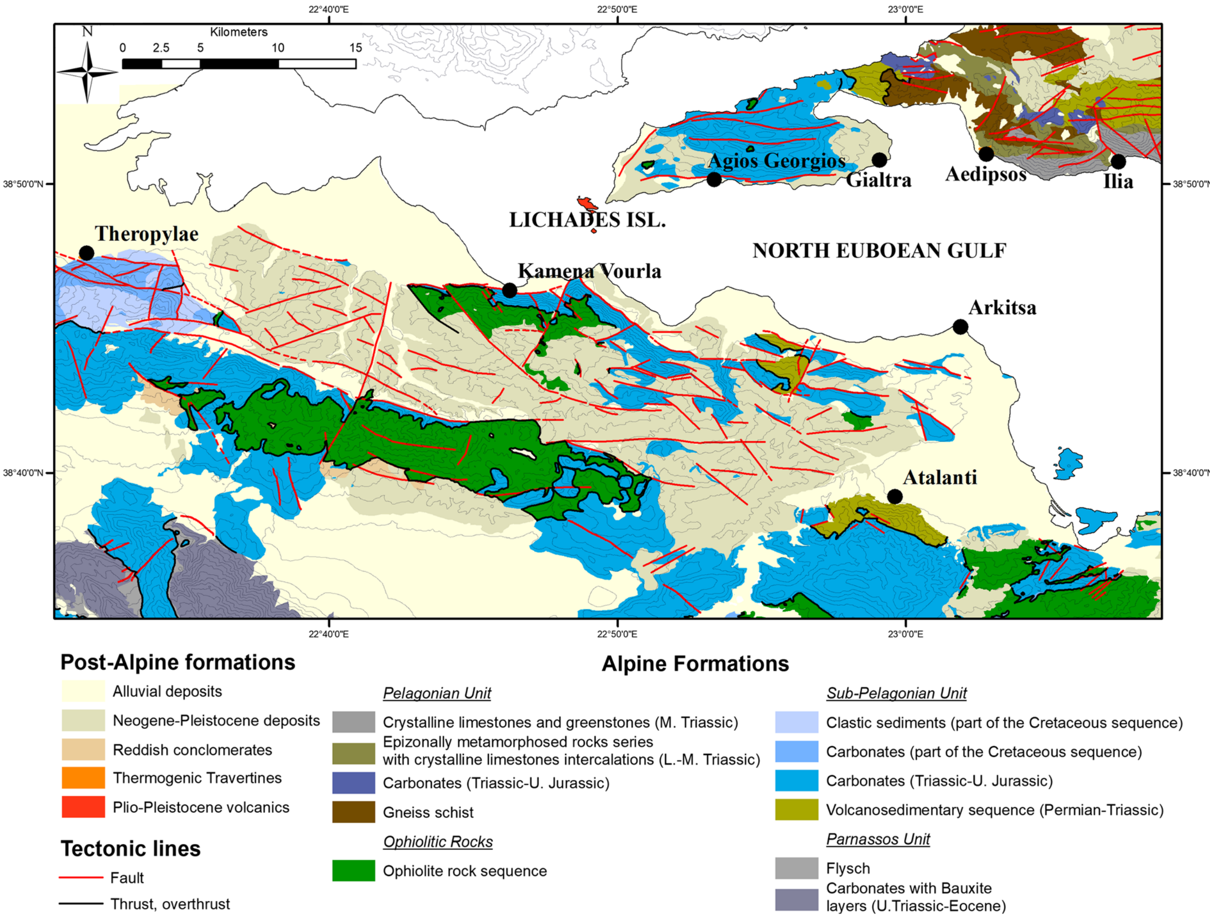

Fig. 1 Simplified geological map (modified after Kanellopoulos 2011)

rocks exists at depth of 90–250 m (Orphanos and Sfetsos 1975). Post-Alpine surface deposits include a sequence of fluvio-lacustrine marls, clays, conglomerates, sands, as well as some lignite layers of late Miocene-Pleistocene age (Kranis 2007).

The northern Euboea, consist of both Pelagonian and Sub-Pelagonian Geotectonic Units. In the studied area, a lower series, with a Permian–Triassic volcaniclastic complex overlie a pre-middle to middle Carboniferous metamorphic basement and is overlain by middle Triassic shallow marine clastic and carbonate rocks intercalated with volcanic rocks best developed at the southeast part of Aedipsos (Katsikatsos et al. 1984). On top of this sequence, Jurassic limestone and Late Jurassic–Early Cretaceous ophiolite rocks occur (Katsikatsos et al. 1984; Scherreiks 2000). The Paleozoic and Mesozoic sequences were folded or imbricated as the result of two main tectonic events (Alpine and Eo-Alpine). In the greater area of northern Euboea, lignite layers have been identified inside Neogene-Lower Pleistocene lake sediments (Vakalopoulos et al. 2000).

The whole area is highly faulted due to the prevailing extensional tectonics. The Northern Euboean Gulf occurs at the western extremity of the North Anatolian Fault and is one of the most neotectonically active areas in Greece dominated by extensional tectonics as the rest of the Aegean Sea (Pe-Piper and Piper 2002; Jolivet et al. 2013). It is characterized dominantly by ENE-WSW to E-W and to a lesser degree by NNE-SSW to NE-SW trending normal and transtensional faults (Angelopoulos et al. 1991; Vavassis 2001; Kranis 1999, 2007), representing two graben structures, responsible for the formation of northern Euboea coastline (Northern Euboean Gulf Graben–Oreoi Strait) and of the Sperchios basin (Sperchios Graben).

Materials and methods

A total of 12 groundwater samples were collected (Table 1). The thermal groundwater samples were collected from the main hot springs and boreholes providing water for spa therapy and thermal baths in the study areas and the fresh groundwater samples were collected from representative fresh water springs and boreholes providing groundwater, mainly used for irrigation purposes. Fresh water sampling points are in most cases in close proximity to the hot spring/ boreholes.

Chemical analysis

The borehole samples were collected after adequate time of pumping in order to flush out the residual groundwater. All samples were collected in a 1-L and 100-mL polyethylene bottles for laboratory analyses. The 100-mL samples intended for the determination of metals were filtered through 0.45-μm membrane filters and acidified to pH < 2, with HNO_3 (Suprapur 65%). All samples were stored in a portable cooler containing ice packs, transported to the laboratory and refrigerated at ~4 °C until analysis. The 1-L polyethylene bottles used for major ion determinations were filtered upon arrival at the laboratory, but not acidified.

Parameters such as pH, electrical conductivity (E.C.), total dissolved solids (T.D.S.), and temperature were measured in situ using portable multiparameter instruments of the Department of Geology and Geoenvironment, National and Kapodistrian University of Athens (N.K.U.A.). Analyses for total concentrations of four major ions (HCO_3^-, NO_3^-, Cl^-, SO_4^{2-}) and some major and trace elements (Cd, Co, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, Zn) were carried out at the Department of Geology and Geoenvironment, N.K.U.A. according to the Standard Methods for the Examination of groundwater and wastewater (Clesceri et al. 1989). Alkalinity (as HCO_3^-) was measured using the titration method [2320-B]. Nitrate ions were measured by the cadmium reduction method [4500-NO_3 E], SO_4^{2-} by the turbidimetric method [4500-SO_4 E] and Cl^- by the mercuric nitrate method [4500-Cl C], using a spectrophotometer (Hack DR/2000 or DR/4000). Multi-element standard solutions prepared by serial dilution of single certified standards were used for calibration of analytical instruments. The concentrations of K^+ and Na^+ were determined by flame emission photometry (Jenway PFP 7, see 3500-K B and 3500-Na B, Clesceri et al. 1989). Calcium ions and Mg^{2+} were determined by flame atomic absorption spectroscopy (see 3500-Ca and 3500-Mg, Clesceri et al. 1989) using a Perkin Elmer

Table 1 Samples locality, physiochemical parameters measured in situ and hydrochemical type

Sample ID	Location	T (°C)	pH	T.D.S. (g/L)	E.C. (mS/cm)	Hydrochemical type
Fresh groundwaters from Euboea						
F-GLT-1	Gialtra	21.3	6.96	0.69	1.36	Na-SO_4
F-AGG-1	Agios Georgios	19.9	6.96	1.18	2.37	Na-Cl
F-AEP-1	Aedipsos	12.2	6.99	0.47	0.96	Ca-HCO_3
Fresh groundwaters from eastern central Greece						
F-ATL-1	Atalanti	18.5	7.36	0.26	0.3	Mg-HCO_3
F-ATL-2	Atalanti	18.5	7.45	0.31	0.59	Mg-HCO_3
F-ARK-3	Arkitsa	19.4	7.1	0.44	0.88	Ca-HCO_3
F-KMV-1	Kamena Vourla	20.2	7.18	0.62	1.27	Na-HCO_3
Thermal groundwaters from Euboea						
T-AEP-2*	Aedipsos	80.5	6.43	54.52	27.12	Na-Cl
T-ILA-1*	Ilia	60.9	6.07	9.3	18.5	Na-Cl
Thermal groundwaters from eastern central Greece						
T-THP-1*	Thermopylae	40.4	5.95	7.55	15.13	Na-Cl
T-KMV-2*	Kamena Vourla	32.8	6.24	22.54	11.3	Na-Cl
T-KMV-3*	Kamena Vourla	35.5	5.92	11.53	16.6	Na-Cl

* Kanellopoulos et al. 2017a

603 instrument and trace metal elements by graphite furnace atomic absorption spectroscopy (Perkin Elmer 1100B). Elements Cd, Co, Cr, Mn, Pb, Ni, Fe, and Zn were determined by Atomic Absorption Spectrometry (AAS, Perkin Elmer 1100B), with Graphite Furnace (HGA-400). When concentrations were high (> 0.1 mg/L), Flame Atomic Absorption Spectrometry (F-AAS) was used instead for these elements (Table 2). Multi-element standard solutions prepared by serial dilution of single certified standards were used for calibration of analytical instruments.

Additionally, all samples were analyzed by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) and by inductively coupled plasma-mass spectrometry (ICP-MS) at the accredited ACME Analytical Laboratories Ltd., Canada, for a series of major and trace elements.

Radiological analysis

Groundwater samples were collected in 1-L Marinelli beakers for the determination of ^{222}Rn. The pH was adjusted to 1 by adding nitric acid and the beakers were sealed air tightly in order to avoid the diffusion of radon. About 4.5 L of groundwater samples were collected in plastic bottles for the determination of ^{226}Ra, ^{228}Ra, ^{40}K, and ^{228}Th and the pH was adjusted to 1 by adding nitric acid.

The radiological analyses were carried out at the National Centre for Scientific Research "Demokritos" (NCSRD)—Institute of Nuclear Technology—Radiation Protection. In the laboratory, Gamma-spectroscopy was applied, in order to determine the composition of these samples in ^{226}Ra, ^{228}Ra, ^{228}Th, ^{222}Rn, and ^{40}K radionuclides (see Florou et al. 2007). A high-resolution gamma-spectrometry system was used to measure gamma-ray spectra in an energy range between 50 and 2000 keV. The system comprises a high-purity germanium (HPGe) detector with an efficiency of 20% relative to a 3" x 3" NaI (Tl) scintillator. The calibration of the HPGe detector was made by use of simulated multi gamma sources (in the same geometry). The multi-channel analyzer emulation software Maestro2 (ORTEC) allowed data acquisition, display, storage, and analysis of the acquired spectra. The samples were measured for 70,000 s, whereas the relative statistical error (1σ) was kept always to within 10%. So, the radionuclides activity concentrations were determined from the analysis of gamma lines of their decay products (Florou 1992; Trampidou 2004; Florou et al. 2007). This required a parent daughter secular equilibrium within the samples that was achieved through their sealing in containers and a time delay prior to gamma-spectroscopy. The quality assurance of the laboratory is ensured per year as Environmental Radioactivity Laboratory (ERL) participates to the Analytical Laboratories for the Measurement of Environmental Radioactivity of International Atomic Energy Agency (ALMERA-IAEA) proficiency tests.

Estimation of groundwater circulation depth and residence time

The geothermal reservoirs in most of the studied areas have not been verified by drilling data yet, so any information concerning the underground circulation of the geothermal fluids such as the depth of the groundwater circulation and residence time is of high interest.

The depth of groundwater circulation (Z_{circ}) has been estimated by the following equation (Wang et al. 2015):

$$Z_{cicr} = -\frac{T_r - T_o}{GradT} + Z_o$$

where T_r = reservoir temperature (in °C); T_o = temperature of initial fresh groundwater (in °C); Zo = depth of the constant-temperature zone (in m), and $GradT$ = temperature gradient (in m/°C).

Based on the ^{226}Ra and ^{222}Rn concentrations, the residence time (T_{res}) of the geothermal fluids has been estimated (Cherdyntsev 1971; Zhou et al. 2008; Liu et al. 2015), by applying the following equation:

$$T_{res} = -\frac{1}{\lambda} \ln\left(1 - \frac{N_{Ra}}{N_{Rn}}\right)$$

where λ = decay constant of ^{226}Ra, i.e., 0.00043; N_{Ra} and N_{Rn} = ^{226}Ra and ^{222} Rn contents (in Bq/L) respectively.

Radiological dose estimation

In order to estimate the equivalent dose to humans from ingestion of radionuclides by water drinking, the following parameters are required: (i) the concentration of the radionuclides in water (measured in Bq/L), (ii) the daily consumption rate of groundwater (L/day), and (iii) the dose conversion factor for each radionuclide.

Table 2 Geochemical analysis of groundwater samples

		Thermal groundwater samples					Fresh groundwater samples							E.U.
		T-ILA-1*	T-AEP-2*	T-THM-1*	T-KMB-2*	T-KMB-3*	F-ATL-1	F-ATL-2	F-ARK-3	F-KMB-1	F-AGG-1	F-GLT-1	F-AEP-1	P.V.
SO_4^{2-}	mg/L	740	1500	510	740	960	16	15	17	28	80	620	26	
Cl^-	mg/L	12,400	16,130	4400	6720	7250	24	40	32	118	478	78	66	
HCO_3^-	mg/L	480	558	756	540	567	312	285	390	280	330	272	381	
PO_4^{3-}	mg/L	0.51	0.12	0.29	0.84	0.06	0.12	0.2	0.14	0.05	0.1	0.25	0.24	
NO_3^-	mg/L	12	7	13	0.7	4	35	36	34	4	7	*225*	20	*50*
Al	μg/L	218	< 100	16	17	< 10	6	14	7	10	8	7	10	
As	μg/L	*84*	*69*	*100*	*28*	*30*	0.5	1.5	2.5	3	3	4	0.5	*10*
B	μg/L	*10,700*	*9850*	*2920*	*3510*	*3290*	< 20	23	< 20	48	193	409	< 20	*1000*
Ba	μg/L	270	340	130	150	190	14	23	53	19	26	124	258	
Br	μg/L	4380	67,500	14,700	24,600	25,100	84	122	130	330	1692	242	134	
Ca	mg/L	1070	1140	470	510	720	62	66	103	73	114	117	120	
Cd	μg/L	< 0.003	1	1	< 0.003	0.2	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	*5*
Co	μg/L	4	< 0.02	1	6	9	0.09	0.09	0.13	0.11	0.15	0.18	0.21	
Cr	μg/L	12	< 0.01	0.3	3	< 0.01	4.3	4	5.2	< 0.5	< 0.5	0.7	1.1	*50*
Cs	μg/L	460	390	260	190	200	< 0.01	0.12	1.7	4.3	13.38	0.09	0.03	
Cu	μg/L	54	54	15	20	23	3.3	18.3	2	1	1.8	2.8	4.1	*2000*
Fe	μg/L	4900	270	5	1040	290	310	330	460	340	600	520	570	
K	mg/L	210	350	75	83	170	1	2	0.9	2	8	21	1.2	
Li	μg/L	300	1520	890	390	360	0.6	1.3	5.6	5.4	21.5	9.2	5.6	
Mg	mg/L	240	300	220	270	320	47	46	54	32	62	45	31	
Mn	μg/L	490	17	1	780	1490	0.34	0.42	1.3	0.25	1.36	0.29	0.37	
Na	mg/L	6900	10,600	2750	3800	5900	21	20	18	70	286	86	58	
Ni	μg/L	< 0.1	< 0.1	3	*35*	*37*	0.7	0.6	< 0.2	2.4	< 0.2	< 0.2	0.4	*20*
Pb	μg/L	4	4	3	4	2	1.2	1.5	0.1	0.1	0.1	< 0.1	< 0.1	*10*
S	mg/L	310	507	140	250	250	5	5	5	5	21	24	7	
Sb	μg/L	< 5	< 5	< 0.5	< 0.5	< 0.5	< 0.05	< 0.05	< 0.05	0.2	< 0.05	0.07	0.21	*5*
Sr	μg/L	29,900	17,300	11,900	5800	6100	138	153	184	151	368	222	324	
U	μg/L	< 2	< 2	< 0.2	12	10	1.25	0.75	1.3	17	2.82	0.98	2.73	
V	μg/L	50	76	20	28	30	10	7	2.5	1.3	3	3.8	0.6	
Zn	μg/L	61	< 50	19	8	6	13.5	23	25	7	11	11	27	

P.V. = parametric value set by Directive 98/83/EC; with italicized are the values exceed P.V.

* Kanellopoulos et al. 2017a

According to WHO, adults consume an average of 2 L of water per day. So, the annual dose of radionuclide consumed in groundwater for an adult is calculated using the following equation:

Annual dose (mSv/year) = dose per unit intake (mSv/Bq) × annual groundwater consumption (L/y) × radionuclide concentration (Bq/L).

Results

Hydrochemical characteristics of groundwater samples

The physiochemical parameters measured in situ at each location and the hydrochemical types of each sample are presented in Table 1, while concentrations of major and trace ions and elements are presented in Table 2.

The chemical analyses data were plotted on a Piper diagram (Fig. 3), in order to evaluate the hydrochemistry of the studied groundwater samples. All thermal groundwater samples are plotted in the same area and belong to the Na-Cl hydrochemical type (Table 1). In contrast, the fresh groundwater samples are plotted separately and are scattered, indicating a variety of hydrochemical types.

Temperatures of the thermal groundwater samples range from 33 up to 80 °C; the maximum values were observed for the Euboea samples (Table 1, Fig. 2a). The fresh groundwater samples show distinctly lower values, varying from 12 up to 20 °C.

Total dissolved solids (T.D.S.) and electrical conductivity (E.C.) in thermal groundwater samples vary from 7.5 to 54.5 g/L and from 11.3 to 27.1 mS/cm respectively. Aedipsos samples present the maximum values (Table 1). The fresh groundwater samples present noticeable lower values to T.D.S. and E.C. (0.3–1.2 g/L, 0.3–2.4 mS/cm, respectively).

Similarly, the physicochemical and chemical parameters show distinctive differentiation between the thermal and the fresh groundwater samples (Tables 1 and 2, Fig. 3a–c). All thermal groundwater samples show pH values below 7 (5.9–6.4) and all fresh groundwater samples approximate to and mostly above 7 (6.9–7.4, Table 1). All thermal groundwater samples show high Cl concentrations from 4400 up to 16,100 mg/L and the fresh groundwater samples from 24 up to 478 mg/L (Table 1). All thermal groundwater samples show high Ca concentrations from 470 up to 1140 mg/L and the fresh groundwater samples from 62 up to 120 mg/L (Table 1).

All samples from Euboea show low concentrations in Ni (most of them even below detection limit), in contrast with the samples from eastern central Greece (up to 35 μg/L, Fig. 3d). Similarly, even though all samples, present low concentration of U, the samples from Kamena Vourla, both fresh and thermal ones, present distinctive higher uranium concentration (Table 2). These results indicate that for the specific elements of Ni and U, the lithological characteristics of the aquifer play the major role in determining water sample composition irrespectively their high or low temperature.

Radiological characteristics of groundwater samples

The radiological analysis results and selected ratios between natural radionuclides are presented in Table 3. The concentrations of naturally occurring radionuclides in the studied groundwater samples vary widely, with higher concentrations recorded in the thermal groundwater samples.

In hot springs, the concentrations of ^{222}Rn, ^{226}Ra, and ^{228}Ra range from < 0.5 up to 179 Bq/L for ^{222}Rn, from <0.025 up to 5.2 Bq/L for ^{226}Ra and from < 0.025 up to 2.91 Bq/L for ^{228}Ra. In all samples, ^{222}Rn concentrations are higher than the parental ^{226}Ra, with only exception the T-AED-2 sample. In Kamena Vourla area, that phenomenon is particularly intense. The ^{222}Rn/^{226}Ra ratio varies from 1 to 917.

Circulation depth and groundwater residence time

In order to estimate the thermal groundwater circulation depth (Z_{circ}), for reservoir temperatures, representative estimated temperatures of geochemical and isotopic geothermometers were applied (Dotsika 2015; Kanellopoulos et al. 2016). Based on the study of Kanellopoulos and Mitropoulos (2013) and using representative fresh groundwater samples from the area near Aedipsos and Ilia, the average temperature of the local fresh groundwater is considered to be 14.5 °C. For Thermopylae and Kamena Vourla, based on Kanellopoulos (2011), the average temperature of the local fresh groundwater is assumed to be 11 and 19 °C, respectively.

As far as the geothermal gradients are concerned, data from the most recent and representative geothermal drills conducted by the Greek Institute of Geology and Mineral

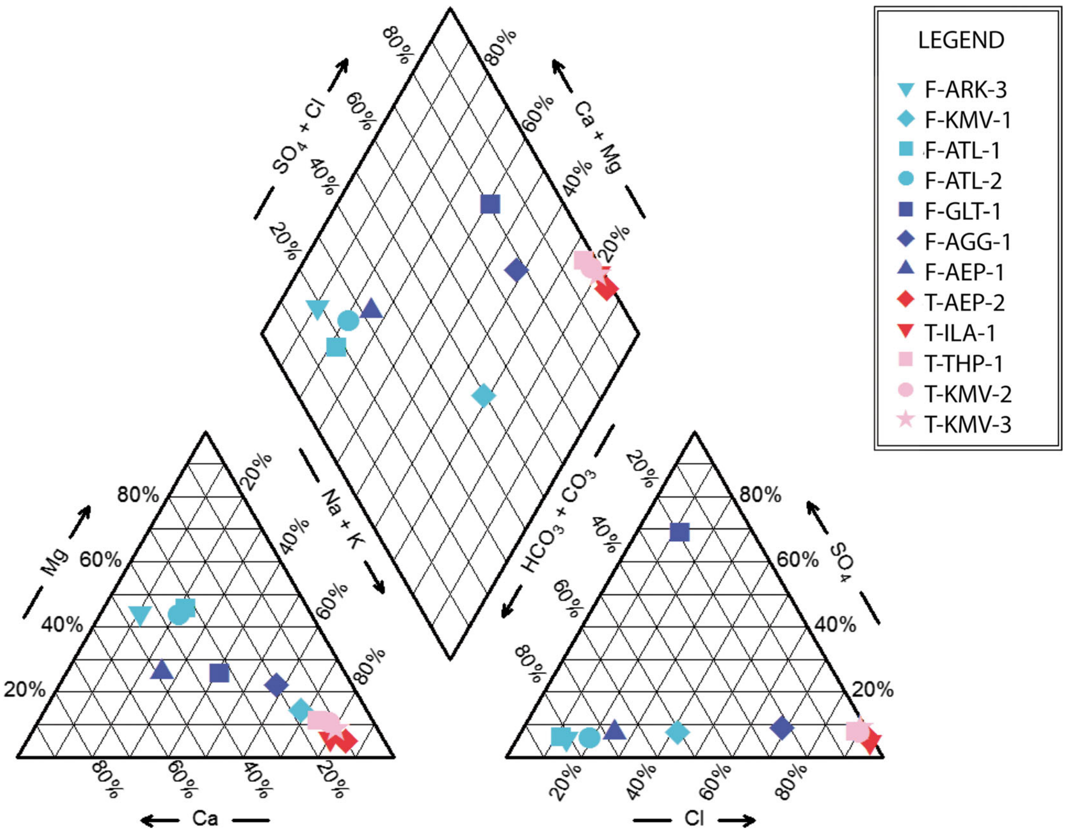

Fig. 2 Chemical composition of groundwater samples plotted in Piper diagram. (With turquoise color are symbolized the fresh groundwater samples from eastern central Greece, with blue color the fresh groundwater samples from Euboea, with pink color are symbolized the hot groundwater samples from eastern central Greece and with red fresh the fresh groundwater samples from Euboea)

Exploration (I.G.M.E.) were calculated and applied. So, the average geothermal gradient is 18.7 °C/100 m for Aedipsos (based on AD-L-4 borehole, Chatzis et al. 2008), 10.4 °C/100 m for Ilia (based on G-18 borehole, Gkioni-Stavropoulou 1998), 20.08 °C/100 m for Thermopylae (based on SP-D-2 borehole, Metaxas et al. 2008), and 38.37 °C/100 m for Kamena Vourla (based on G11/72 borehole, Orfanos and Sfetsos 1975).

The estimated circulation depths (Table 4) are (i) ~1240 m for Ilia, (ii) ~800 m for Aedipsos, (iii) ~250 m for Kamena Vourla, and (iv) ~480 m for Thermopylae area.

Based on the ^{226}Ra and ^{222}Rn concentrations, the estimated residence time (T_{res}) for the geothermal fluids (Table 5) is ~555 years for Ilia, ~27 years for Kamena Vourla, and ~ 403 years for Thermopylae. Because of the higher concentration of ^{226}Ra to ^{222}Rn, the residence time for the Aedipsos thermal water could not be estimated.

Radionuclide dosimetry

Since groundwater contains more than one radionuclide, the doses arising from each radionuclide must be summed to give the total dose.

Different dose per unit intake (dose factors) were utilized for the ingestion of each radionuclide, i.e., for ^{226}Ra is 2.8×10^{-4} mSv/Bq, for ^{228}Ra is 6.9×10^{-4} mSv/Bq, for ^{228}Th is 7.2×10^{-5} mSv/Bq, and for ^{40}K is 6.2×10^{-6} mSv/Bq (International Atomic Energy Agency (IAEA) 1996; World Health Organization (WHO) 2002). For ^{222}Ra dose per unit intake, there are several models estimating radon doses due to ingestion (Lopez et al., 2004). The main problem in order to estimate the committed effective dose and the dose equivalent in stomach is the fact that there are no internationally accepted dose factors. For adults, a committed effective dose per unit intake of groundwater dissolved radon has been estimated at 10^{-8} Sv/Bq (United

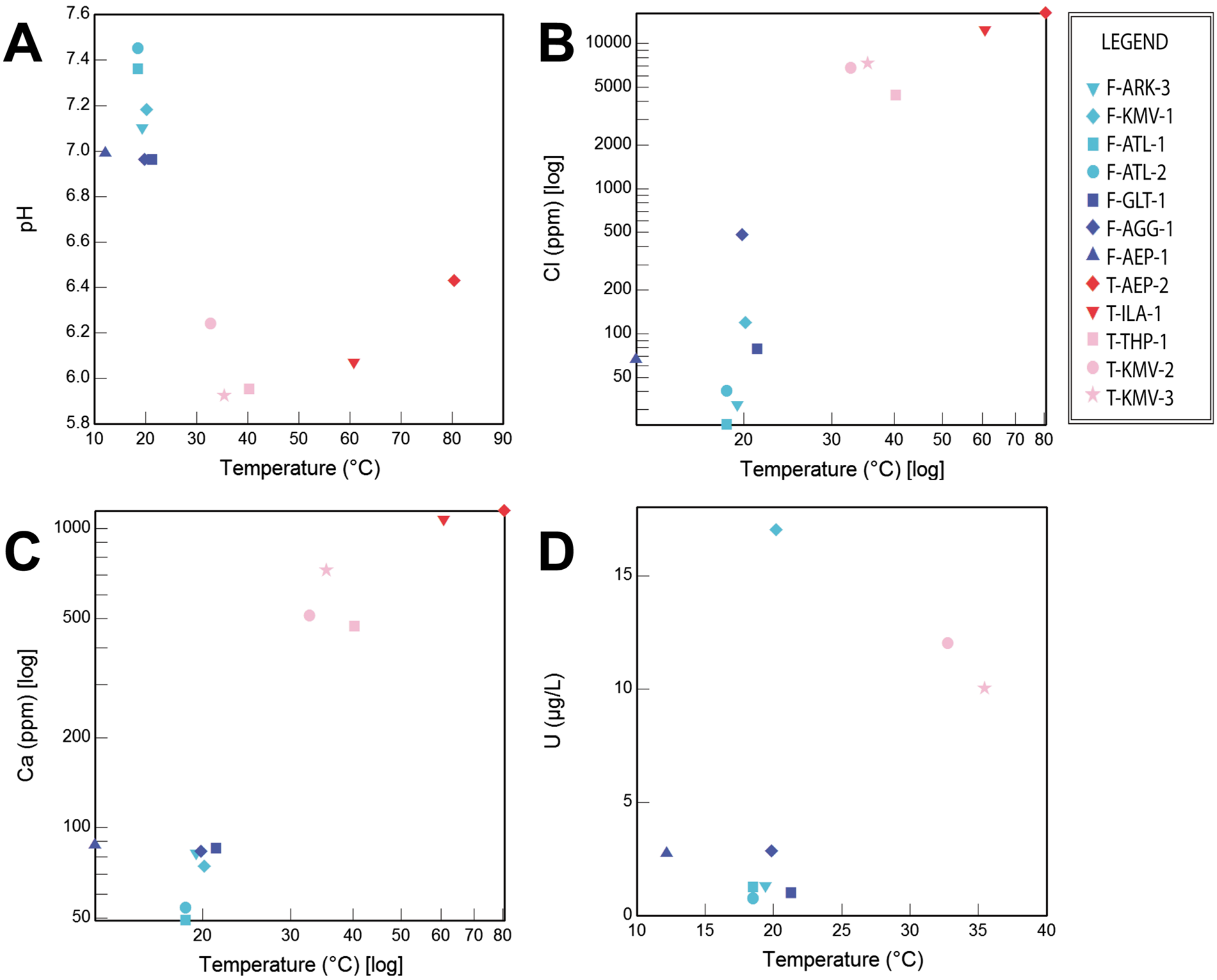

Fig. 3 Diagrams presenting the **a** temperature vs pH values, **b** temperature values vs Cl concentrations, **c** temperature values vs Ca concentrations, **d** temperature values vs U concentrations. (With turquoise color are symbolized the fresh groundwater samples from eastern central Greece, with blue color the fresh groundwater samples from Euboea, with pink color are symbolized the hot groundwater samples from eastern central Greece and with red color the fresh groundwater samples from Euboea)

Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) 1993) and slightly higher for children. The estimation has been calculated by the application of a modified ICRP model for the ingestion of radon in groundwater (Kendall et al. 1988). The National Research Council of USA (Wallström 2001) proposed a conversion factor of 0.38×10^{-8} Sv/Bq for the committed effective dose. The estimates for the dose equivalent to stomach per unit activity ranged between 5×10^{-8} and 2×10^{-7} Sv/Bq and an average value of 10^{-7} Sv/Bq has been adopted (Oliveira et al. 2001; Lopez et al. 2004).

This estimation is believed to be an appropriate average for Greece, giving an annual consumption of 730 L for each Greek adult, assuming a 2 L oral consumption of water per day. Based on the abovementioned parameters, the dose estimations from ingestion were calculated and presented in Table 6.

Discussion

Geological origin of radionuclides

Based on the combined radiological and hydrochemical data, the thermal groundwater samples usually show small variation in their values and compared with the fresh groundwater samples show distinctive higher concentrations in natural radionuclides and major and trace

Table 3 Radiological analysis and radionuclide ratios

	Activity concentration (Bq/L)					Ratios		
	^{222}Rn	^{226}Ra	^{228}Ra	^{228}Th	^{40}K	$^{222}Rn/^{226}Ra$	$^{226}Ra/^{228}Ra$	$^{228}Th/^{228}Ra$
Fresh groundwaters from Euboea								
F-GLT-1	3.4 ± 0.5	< LLD**	< LLD**	0.01 ± 0.04	0.392 ± 0.297	566.7	1	1.7
F-AGG-1	1.3 ± 0.65	0.085 ± 0.055	< LLD**	0.095 ± 0.055	0.99 ± 0.303	15.3	14.2	15.8
F-AEP-1	6.0 ± 0.12	0.043 ± 0.053	< LLD**	0.063 ± 0.047	0.655 ± 0.278	139.5	7.2	10.5
Fresh groundwaters from eastern central Greece								
F-ATL-1	5.5 ± 0.8	< LLD**	< LLD**	0.013 ± 0.04	0.115 ± 0.315	917	1	2.2
F-ATL-2	< LLD*	0.02 ± 0.4	< LLD**	< LLD**	0.42 ± 0.273	0.3	3.3	1
F-ARK-3	6.7 ± 1.01	0.25 ± 0.35	< LLD**	0.082 ± 0.032	0.497 ± 0.323	26.8	41.8	13.7
F-KMV-1	40.8 ± 2.0	0.17 ± 0.05	0.065 ± 0.14	0.052 ± 0.045	0.18 ± 0.25	240	2.6	0.8
Thermal groundwaters from Euboea								
T-AEP-2	2.8 ± 0.4	5.2 ± 0.11	1.63 ± 0.245	0.767 ± 0.075	12.5 ± 0.665	0.5	3.2	0.5
T-ILA-1	1.6 ± 0.16	0.34 ± 0.06	0.52 ± 0.177	0.19 ± 0.055	6.95 ± 0.63	4.7	0.6	0.4
Thermal groundwaters from eastern central Greece								
T-THP-1	2.26 ± 0.89	0.36 ± 0.07	< LLD**	< LLD**	4.69 ± 0.435	6.3	60	1
T-KBV-2	179 ± 3	2.06 ± 0.045	< LLD**	0.102 ± 0.04	5.42 ± 0.26	86.9	343.3	17
T-KMV-3	–	2.23 ± 0.09	2.91 ± 0.195	< LLD**	6.12 ± 0.36	–	0.8	0
EU*1	100	–						
WHO*2	100	1						
UNSCEAR*3	40	–						
EPA*4	11	0.185*5	0.185*5					

* LLD (for ^{222}Rn): 0.5 Bq/L; ** LLD (for ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K): 0.025 Bq/L (From 4 L); *1 = European Union (EU) 2001; *2 = World Health Organization (WHO) 2011; *3 = United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) 2008; *4 = Environmental Protection Agency (EPA) 2000; *5 = the limit refers to total Ra from ^{226}Ra and ^{228}Ra

ions and elements, indicative of an immiscible regime between fresh and thermal aquifers.

This clear differentiation, between the fresh and thermal samples and at the same time the close spatial relation between the thermal samples, could be explained by accepting the hypothesis that the hot springs in eastern central Greece (Kamena Vourla and Thermopylae) and northern Euboea (Aedipsos and Ilia) belong to a single geothermal system, as suggested by previous studies such as Kanellopoulos (2011) and Kanellopoulos et al. (2017a, 2017b). All hot springs from both Euboea island and eastern central Greece areas are the surface manifestation of a medium-, possible high- enthalpy geothermal field (Chatzis et al. 2008; Kanellopoulos et al. 2016, 2017b). Their occurrence is the result of the combination of the active tectonic

Table 4 Groundwater circulation (Z_{circ}) time of thermal groundwater samples

Sample	To	Tr	GradT	Zo	Z_{circ}
Aedipsos	14.5	160*	0.187	30	808
Ilia	14.5	140*	0.104	30	1237
Thermopylae	11	105**	0.2008	10	478
Kamena Vourla	19	110**	0.3837	18	255

*From Kanellopoulos et al. 2016; **from Dotsika 2015

Table 5 Thermal groundwater residence time (T_{res})

Sample	T_{res} (years)
Thermal groundwaters from Euboea	
T-AEP-2	cannot be calc. (Ra > Rn)
T-ILA-1	556
Thermal groundwaters from eastern central Greece	
T-THP-1	404
T-KBV-2	27
T-KMV-3	–

Table 6 Dose estimations for ingestion

	^{222}Rn (mSv/year)	^{226}Ra (mSv/year)	^{228}Ra (mSv/year)	^{228}Th (mSv/year)	^{40}K (mSv/year)	Total (mSv/year)
Fresh groundwaters from Euboea						
F-GLT-1	0.25	–	–	–	–	0.25
F-AGG-1	0.09	0.02	–	–	–	0.12
F-AEP-1	0.44	0.01	0	–	–	0.45
Fresh groundwaters from eastern central Greece						
F-ATL-1	0.40	–	–	–	–	0.40
F-ATL-2	–	0.004	–	–	0.002	0.006
F-ARK-3	0.49	0.05	0	–	–	0.55
F-KMV-1	2.98	0.03	0.03	–	0.00	3.05
Thermal groundwaters from Euboea						
T-AEP-2	0.20	1.06	0.82	0.04	0.06	2.19
T-ILA-1	0.12	0.07	0.26	0.01	0.03	0.49
Thermal groundwaters from eastern central Greece						
T-THP-1	0.16	0.07	–	–	0.02	0.26
T-KMV-2	13.07	0.42	–	0.01	0.02	13.52
T-KMV-3	–	0.46	1.47	0	0.03	1.95

regime and the Plio-Pleistocene magmatic activity in the area. The thermal groundwater is circulating through the major fault systems of the northern Euboea graben. All thermal groundwater samples show a Na-Cl hydrochemical type, irrelevant of their distance from the sea, indicating the high participation of seawater in that geothermal system. This is in agreement with previous isotopic studies (e.g., Dotsika 2015). In contrast, the fresh groundwater samples show several different hydrochemical types reflecting the lithological variety of the related aquifers.

Based on the geochemical analyses, elements like Ni and U present similar concentrations, at both fresh and thermal groundwater samples from some areas, which differs from the rest of the studied samples. In these cases, the local geology controls the presence and concentration of these trace elements in both fresh and thermal groundwater aquifers.

All samples from Euboea show low concentrations of Ni, in contrast with samples from eastern central Greece (i.e., Kamena Vourla, Thermopylae and Atalanti), which show concentrations up to 35 μg/L, as a result of the large occurrences of ultramafic rocks of the ophiolitic sequence in the greater area (Fig. 1) and their impact on the hydrochemical composition of the thermal and fresh groundwaters. Kanellopoulos et al. (2014, 2015) have identified similar geochemical anomalies in the groundwater-soil-plant system in the neighboring area of Atalanti and have attributed them to the weathering of ophiolite rock occurrences.

Combining the radiological and geochemical results (Tables 2 and 3), it is revealed that uranium and a number of natural radionuclides, show maximum concentrations in both, fresh and thermal groundwater samples from Kamena Vourla. The measured concentrations of natural radionuclides from Kamena Vourla hot springs are among the highest concentrations recorded in Greece (Trampidou 2004; Florou et al. 2007; Athansoulis et al. 2009; Athanasoulis et al. 2016). In previous studies, the highest concentrations of natural radionuclides have been recorded in hot springs located mainly in the Aegean Islands, where the hot springs are closely related to recent volcanic activity and plutonic rock emplacement, such as in Santorini and Ikaria Islands.

Uranium in the fresh and thermal groundwater samples of Kamena Vourla could be attributed to a plutonic intrusion rich in uranium minerals, unknown until now. This hypothesis is supported even farther by the radiological data, especially for the samples collected in Kamena Vourla, as ^{222}Rn concentrations are higher than the parental ^{226}Ra. This high imbalance between ^{226}Ra and ^{222}Rn could be explained by the high diffusion factor of ^{222}Rn, especially when it is compared with the low solubility of ^{226}Ra in groundwater. Consequently, the existence of ^{222}Rn in groundwater indicates the surrounding rocks that are enriched in uranium minerals as its sources. Also, a small percentage of ^{222}Rn probably emanates from the decay of the parental ^{226}Ra.

Hot groundwater boreholes and springs in Kamena Vourla presenting the highest values of radioactivity are in close proximity to boreholes and springs with very low values (Orfanos and Sfetsos 1975). This observation is suggesting a significant influence of radiation with small spatial impact radius. Small occurrences (few m^3) of traciandesite lava in the seaside of Kamena Vourla area, related to the volcanic center of Lichades provide further evidence of the presence of a plutonic intrusion at depth.

The low concentrations of ^{226}Ra, especially in the thermal groundwater samples, could be associated with the presence of high concentrations of SO_4^{-2} and Ca^+ in these samples (Tables 2 and 3, Fig. 4), as suggested by Lopez et al. 2004. The presence of these ions in concentrations close to the $CaSO_4$ solubility degree causes precipitation of the $CaSO_4$ and consequently parallel co-precipitation of the $RaSO_4$. It is noted that the vast thermogenic travertine deposits at Aedipsos and Thermopylae, characterized as the biggest active thermogenic travertine systems in Greece, also contain gypsum (Kanellopoulos et al. 2017a).

In the studied samples, the ^{222}Rn/^{226}Ra ratio varies from 0.3 to 917, which is among the highest values recorded in Greek hot springs (Trampidou 2004; Florou et al., 2007). Ikaria's hot springs which are among the highest radioactive in Greece and worldwide, show ^{222}Rn/^{226}Ra ratios up to 967 (Trampidou 2004; Florou et al. 2007). In other Greek hot springs such as Loutraki, the values are as low as 105–160 (Trampidou 2004; Florou et al. 2007). Among the studied samples, the highest ^{222}Rn/^{226}Ra ratios were recorded in the fresh groundwater samples, compared to thermal groundwater sample ratios of 0.5 to 86.9. The high imbalance of ^{222}Rn/^{226}Ra indicates that only a small percentage of the dissolved ^{222}Rn emanates from groundwater ^{226}Ra. The ^{222}Rn is inactive and easily dissoluble gas. So, most of the ^{222}Rn originates from the surrounding rocks. It is released in the groundwater from the surrounding rocks with rate that depends on their porosity and other characteristics of the rocks (Bettencourt et al. 1988).

The ^{226}Ra/^{228}Ra ratios also present large variation, from 0.6 to 343 (Table 3). But in this case, the highest ratios, i.e., from 0.6 to 343, are observed for the thermal groundwater samples. In Ikaria's hot springs, the

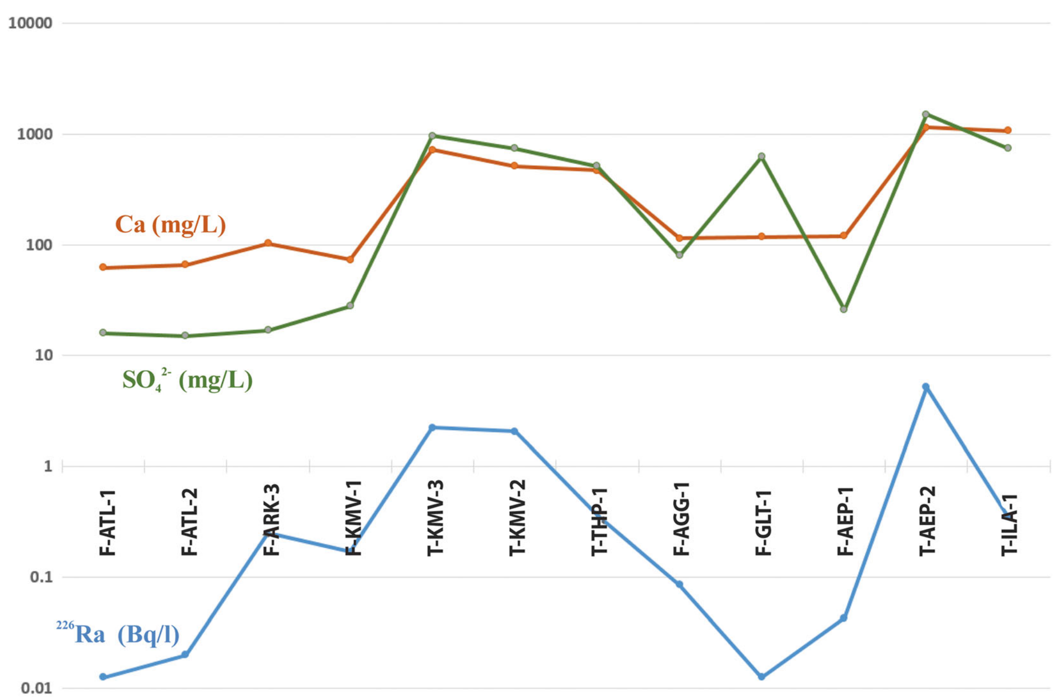

Fig. 4 Concentrations of ^{226}Ra (in Bq/L; with blue color), Ca (in mg/L; with red color) and SO_4^{2-} (in mg/L; with green color)

^{226}Ra/^{228}Ra ratio ranges from 1 to 7 and in Loutraki's hot springs from 0.8 to 16 (Trampidou 2004; Florou et al. 2007). That large variation of ratios could be attributed to the geochemistry of parent isotopes. According to Cherdyntsev theory, ^{226}Ra and ^{228}Ra exist in groundwater, specifically in old-fossil groundwater, in ratios equal to the median concentration of ^{226}Ra and ^{228}Ra in bedrock. In regions where uranium enrichment exists, the ^{226}Ra prevails. When the uranium concentration is low, ^{228}Ra prevails.

Consequently, occurrences of uranium, which are not linked with important concentrations of thorium, give a high ratio of ^{226}Ra/^{228}Ra (Asikainen 1981). In the studied samples, most of the ^{226}Ra/^{228}Ra ratios are higher than unity, so it can be assumed that they are related with bedrock lithologies, that contain more uranium than thorium minerals. The highest ^{226}Ra/^{228}Ra ratio is 343 and was found in a thermal groundwater sample (T-KMV-2) from Kamena Vourla. Also, a high imbalance of ^{222}Rn/^{226}Ra ratio was recorded in the same sample. However, high concentrations of ^{222}Rn and ^{226}Ra or high ratios of ^{226}Ra/^{228}Ra (Table 3, Fig. 5) are not related essentially to high concentrations of uranium minerals in the aquifer's surrounding area, but could also originate from intense migration of Ra or from the parent ^{238}U in the greater region.

The geothermal reservoirs in the studied areas have not been validated by drilling data yet. So, any estimations concerning the depth of the geothermal fluid circulation and residence time, is valuable. With respect to the estimated circulation depths, it seems that the geothermal fluids in northern Euboea are circulating in greater depth (up to ~1240 m) compared to eastern central Greece's geothermal fluids and consequently they present longer residence times (up to ~550 years). However, the circulation depth and the residence time at Thermopylae are comparable (~480 m and ~400 years). Exception to these estimations is the area of Kamena Vourla, where the estimated residence time is ~30 years and the circulation depth is considerable lower, i.e., 255 m. It is interesting that stable isotopic studies (Dotsika 2015) have suggested that the heating of the geothermal systems at Sperchios (e.g., Thermopylae) could be due to strong and deep circulation, probably

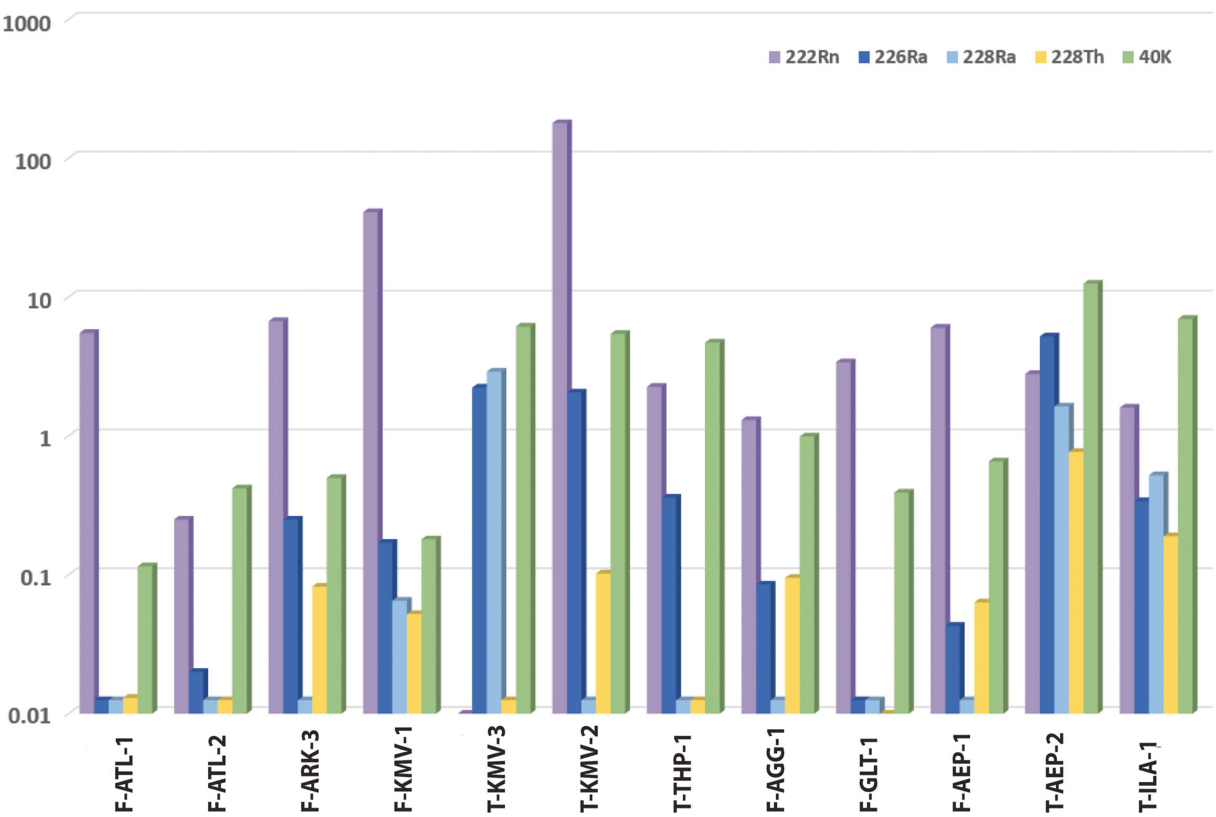

Fig. 5 Histogram presenting activities (in Bq/L) of the analyzed radionuclides

with low velocity to allow the water time for the chemical change in the major fracture zone of the area. This hypothesis is in accordance with the Thermopylae circulation depths and residence time, but it contrasts with the Kamena Vourla estimations. The geothermal fluids of Kamena Vourla probably circulate using mainly the costal E-W fault system, and especially its intersections with some local fault systems. It could be assumed that the even though Kamena Vourla belong to the greater geothermal system of Euboea-Sperchios, it is presenting some distinctive characteristics. The empirical method of radioactive isotope tritium could be also applied in the future, in order to estimate the residence time from the recharge area to the discharge point.

Health implications of groundwater chemistry

In order to assess the possible suitability of the studied groundwater samples, for human consumption, the analytical values were compared with the parametric levels, imposed by the current relative legislation (Directive 98/83/EU). It is noted that the National Greek law is in agreement with European Union (EU) Directive 98/83/EU. All the thermal groundwater samples are exceeding the As and B parametric values and two of them are exciting also the Ni parametric value (Table 2). So, all of them are not suitable for drinking. Concerning the fresh groundwater samples, only the F-GLT-1, from Gialtra area, exceeds the NO_3 parametric value.

Health and state agencies such as World Health Organization (WHO), United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) in an attempt to assess the impact of radiation in human health, have recommended specific guideline limits for isotopic concentration in drinking groundwater. These limits were based on the possible impact on human health and they must be considered as trigger values for further investigations (World Health Organization (WHO) 2011). For that reason, these values vary, for example, in relevance to ^{222}Rn concentrations in groundwater, the United States Environmental Protection Agency (US-EPA) has defined a value of 11 Bq/l (Environmental Protection Agency (EPA) 2000), the UNSCEAR, has defined a value of 40 Bq/l (United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) 1993) and the WHO and EU have defined a value of 100 Bq/l (World Health Organization (WHO) 2011; European Union (EU) 2001; see Table 3). The studied samples are below these limits, with only exceptions being one fresh water sample (F-KMV-1) and one thermal water sample (T-KMV-2), both from Kamena Vourla area.

In order to achieve a more realistic and integrated approach about the radiological impact to human health, since we are recipients of a combination of radionuclides, the estimated annual dose has been calculated, revealing high estimated doses, in some cases. The global average annual dose per person was estimated by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (2008) to be about 3.0 mSv/year, with 19.6% derived from medical diagnosis and 0.4% from other anthropogenic sources. So, European Union (EU) (2013) has suggested to the member states to set the limit on the effective dose for public exposure at 1 mSv/year. United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (1988) has estimated the total effective dose equivalent, from the natural origin radiological impact through all the pathways of internal irradiation, in areas of normal background for ^{222}Rn to be 0.85 mSv/year. Although, water supplies with high ^{222}Rn concentration could be used after special treatment, since ^{222}Rn gas is characterized by high volatility and quickly dissipates when exposed to the atmospheric conditions. The calculated mean dose of ^{222}Rn for the fresh and thermal groundwater samples is below the suggested value. Exception to that are both fresh and thermal groundwater samples from Kamena Vourla, which show values of 2.98 and 13.07 mSv/year ^{222}Rn respectively.

The elevated values in natural radionuclides are closely related to the geological background of the studied areas, further studies ought to be conducted focusing especially on Kamena Vourla groundwaters, in order to further understand the geochemical behavior of radioisotopes. Also, further research is needed in order to better assess the levels of internal irradiation taking into account food consumption in this area, e.g., consumption of fish. However, no such data are available at the moment to allow a comparison between different regions in the world and Greece.

Conclusions

Combining the results from the radiological and hydrochemical analysis and the geology of the studied areas, the following conclusions arise:

- All the studied thermal groundwater samples, from all regions, share similar hydrochemical characteristics, to such degree that could be categorized as one group, clearly distinguished from the fresh groundwater samples. The thermal and fresh groundwater samples show no mixing.

- The hydrochemical characteristics of all groundwater samples were associated with the local rock formations.
- High concentrations of ^{222}Rn are mainly due to the enrichment of groundwater from the surrounding rocks.
- A U-rich plutonic body at depth probably controls the natural radiation of groundwaters in the greater area of Kamena Vourla. Radionuclide ratios indicate that it has high-influence factor with small spatial radius impact.
- The geothermal fluid in Euboea makes a deeper journey (up to ~1240 m) during its circulation, compared to eastern central Greece. The shallowest depth circulation was estimated for Kamena Vourla area (255 m).
- The estimated residence time of the geothermal fluid is quite long (up to ~550 years), with only exception the Kamena Vourla areas (~30 years). These estimations are considered as indicative, until drilling data reveal the details of the geothermal fluid circulation.
- Based on the Directive 98/83/EU and the estimated effective radiation doses for ingestion by adults, most of the fresh groundwater samples are suitable for drinking, with only few exceptions.
- Based on the Directive 98/83/EU, all thermal groundwater samples are exceeding the parametric values of As and B and some of them exceed the Ni parametric value. Additionally, estimated effective radiation doses for ingestion of several thermal groundwater samples, by adults are in general above 1 mSv/year, making them not suitable for drinking.

Acknowledgements The authors would like to thank the local population for their co-operation during the field work. The two anonymous reviewers are thanked for their comments and suggestions that greatly improved the manuscript.

Funding information This research was supported by the "Kapodistrias" research funding program of National and Kapodistrian University of Athens and by the Earthquake Planning and Protection Organization (EPPO) of Greece.

References

Angelopoulos, I., Mitropoulos, D., Perissoratis, C., Zimianitis, E. (1991). Pagasitikos sheet, 1: 200,000. Surficial sediment map of the Aegean Sea floor. I.G.M.E., Athens.

Asikainen, M. (1981). Radium content and the $^{226}Ra/^{228}Ra$ activity ratio in groundwater from bedrock. *Geoch. et Cosmoch. Acta., 45*, 1375–1381.

Athanasoulis, K., Bakalopoulos, P., Xenakis, M., Persianis, D., Taktikos, S. (2009). Periodical monitoring of the Greek hot springs. IGME, Athens (in Greek).

Athanasoulis, K., Vougioukalakis, G., Xenakis, M., Kavouri, K., Kanellopoulos, C., Christopoulou, M., Statha, F., Rigopoulos, P., Spagakos, N., Tsigkas, Th., Papadatou, M. (2016). Diachronic monitoring of hot springs and geothermal fields of Greece. I.G.M.E., Athens (in Greek).

Bettencourt, A. O. De, Teixeira, M. M. G. R., Faisco, M. C., Vleira, I. A. & Ferrardo, G. C. (1988). Natural radioactivity in Portuguese mineral waters. *Radiation Protection Dosimetry, 24*(1-4), 139–142.

Chatzis, M., Kavouridis, Th., Bakalopoulos, P., Xenakis, M. (2008). Investigation and determination of northern Euboea geothermal fields. IGME, Athens (in Greek).

Cherdyntsev, V. V. (1971). Uranium-234. Jerusalem, Israel program for scientific translations, 234 pp.

Clesceri, L., Greenberg, A., Eaton, A., 1989. Standard methods for the examination of water and wastewater. 20th edition. APHA-AWWA-WEF, Washington, DC.

Danali, S., Margomenou, G., & Veldeki, K. (1986). The radioactivity of spas on the Greek Island Ikaria and influencing factor. *Health Physics, 50*, 509–513.

Dotsika, E. (2015). H-O-C-S isotope and geochemical assessment of the geothermal area of Central Greece. *Journal of Geochemical Exploration, 150*, 1–15. https://doi.org/10.1016/j.gexplo.2014.11.008.

Environmental Protection Agency (EPA), (2000). National primary drinking groundwater regulations, radionuclides; 40 CFR parts 141 and 142. Environmental Protection Agency, Washington, DC, USA, 65, 21575–21628.

European Union (EU), (2001). Commission recommendation of 20th December 2001 on the protection of the public against exposure to radon in drinking groundwater. In Official Journal of the European Commission; 2001/982/Euratom. European Commission, Brussels, Belgium.

European Union (EU), (2013). Council directive 2013/59/ Euratom of 5 December 2013 laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation, and repealing directives 89/ 618/Euratom, 90/641/Euratom, 96/29/Euratom, 97/43/ Euratom and 2003/122/Euratom. European Commission, Brussels, Belgium.

Florou, H. (1992). Natural and artificial radioactivity in marine ecosystems. Ph.D. thesis, National and Kapodistrian University of Athens, Athens (in Greece).

Florou, H., Trampidou, G., & Nicolaou, G. (2007). An assessment of the external radiological impact in areas of Greece with elevated natural radioactivity. *Journal of Environmental Radioactivity, 93*, 74–83.

Georgalas, G.C. (1938). Le volcan des les Likhades et de Hagios Ioannis (Kammena Vourla). Proceedings of Academia Athinon, 13, 86–98.

Gkioni-Stavropoulou, G. (1998). Hydrogeological study of hot and mineral springs of Euboean—Maliac gulf. IGME, Athens (in Greek).

Innocenti, F., Agostini, S., Doglioni, C., Manetti, P., & Tonarini, S. (2010). Geodynamic evolution of the Aegean: constraints from the Plio-Pleistocene volcanism of the Volos–Evia area. *Journal of the Geological Society, London, 167*, 475–489.

International Atomic Energy Agency (IAEA), (1996). International basic safety standards for protection against ionizing radiation and for the safety of radiation sources. International Atomic Energy Agency, safety series 15, Vienna.

Isam, S. M. M., Pettersson, H. B. L., & Lund, E. (2002). Uranium and thorium-series radionuclides in drinking groundwater from drilled bedrock wells: correlation to geology and bedrock radioactivity and dose estimation. *Radiation Protect. Dosimetry, 102*(3), 249–258.

Jia, G., & Torri, G. (2007). Estimation of radiation doses to members of the public in Italy from intakes of some important naturally occurring radionuclides (^{238}U, ^{234}U, ^{235}U, ^{226}Ra, ^{228}Ra, ^{224}Ra and ^{210}Po) in drinking water. *Applied Radiation and Isotopes, 65*(7), 849–857.

Jia, G., Torri, G., & Marco, L. (2009). Concentrations of ^{238}U, ^{234}U, ^{235}U, ^{232}Th, ^{230}Th, ^{228}Th, ^{226}Ra, ^{228}Ra, ^{224}Ra, ^{210}Pb, ^{210}Pb and ^{212}Pb in drinking groundwater in Italy: reconciling safety standards based on measurements of gross a and b. *Journal of Environmental Radioactivity, 100*, 941–949.

Jolivet, L., Faccenna, C., Huet, B., Labrousse, L., Le Pourhiet, L., Lacombe, O., Lecomte, E., Burov, E., Denèle, Y., Brun, J.-P., Philippon, M., et al. (2013). Aegean tectonics: strain localisation, slab tearing and trench retreat. *Tectonophysics, 597-598*, 1–33.

Kanellopoulos, C. (2011). Geochemical research on the distribution of metallic and other elements in the cold and hot groundwater, soils and plants in Fthiotida prefecture and N. Euboea. Environmental impact. Ph.D. Thesis, National and Kapodistrian University of Athens, (in Greek with English abstract).

Kanellopoulos, C. and Mitropoulos, P. (2013). Geochemical effect of the rock chemistry and the anthropogenic activities on groundwater: the case of NW Euboea, Greece. Bull. Geol. Soc. Greece, XLVII/2, 942-952, DOI: https://doi.org/10.12681/bgsg.11134, 2017.

Kanellopoulos, C., Mitropoulos, P., Argyraki, A. (2014). Geochemical effect of ultrabasic ophiolitic rock chemistry and anthropogenic activities on groundwater contamination: The case of Atalanti area, Greece. Bul. Shk. Gjeol., Special Issue 2/2014, Proceed. 20th CBGA Congress, Tirana/Albania, 329–332.

Kanellopoulos, C., Argyraki, A., & Mitropoulos, P. (2015). Geochemistry of serpentine agricultural soil and associated groundwater chemistry and vegetation in the area of Atalanti, Greece. *Journal of Geochemical Exploration, 158*, 22–33.

Kanellopoulos, C., Christopoulou, M., Xenakis, M., Vakalopoulos, P. (2016). Hydrochemical characteristics and geothermometry applications of hot groundwater in Edipsos area, NW Euboea (Evia), Greece. Greece. Bull. Geol. Soc. Greece, ISSN: 0438–9557, L, 720–729.

Kanellopoulos, C., Mitropoulos, P., Valsami-Jones, E., & Voudouris, P. (2017a). Fluid characteristics and mineralizing processes of an active low-sulfidation epithermal (geothermal) system of northern Euboea and eastern Central Greece. *Journal of Geochemical Exploration, 179*, 9–24. https://doi.org/10.1016/j.gexplo.2017.05.003.

Kanellopoulos, C., Stouraiti, C., Xenakis, M., Vakalopoulos, P., & Vougioukalakis, G. (2017b). The geothermal system of northern Euboea Island and eastern Sperchios areas, Greece: Geological characteristics and suggested direct use applications. *11th International Hydrogeological Congress of Greece, 2*, 263–273.

Karastathis, V. K., Papoulia, J., Di Fiore, B., Makris, J., Tsambas, A., Stampolidis, A., & Papadopoulos, G. A. (2011). Deep structure investigations of the geohot field of the north Euboean gulf, Greece, using 3-D local earthquake tomography and curie depth point analysis. *Journal of Volcanology and Geohot Research, 206*, 106–120. https://doi.org/10.1016/j.jvolgeores.2011.06.008.

Katsikatsos, G., Mettos, A., Vidakis, M. (1984). Geological map of Istiea, scale 1: 50,000. Institute of Geological and Mineral Exploration (I.G.M.E.), Athens.

Kendall, G. M., Fell, T. P., & Phipps, A. W. (1988). A model to evaluated doses from radon in drinking groundwater. *Radiol. Prot. Bull., 97*, 7–8.

Kranis, H. (1999). Neotectonic activity of fault zones in central-eastern mainland Greece (Lokris). Ph.D. thesis, GAIA, no 10, National and Kapodistrian University of Athens (in Greek).

Kranis, H. (2007). Neotectonic basin evolution in central-eastern mainland Greece. *Bull. Geol. Soc. Greece, 40*, 360–373.

Liu, Y., Zhou, X., Deng, Z., Fang, B., Tsutomu, Y., Zhao, J., & Wang, X. (2015). Hydrochemical characteristics and genesis analysis of the Jifei hot spring in Yunnan, southwestern China. *Geothermics, 53*, 38–45.

Lopez, R., Garcia-Talavera, M., Pardo, R., Deban, L., & Nalda, J. C. (2004). Natural radiation doses to the population in a granitic region in Spain. *Rad. Prot. Dos., 111*(1), 83–88.

Metaxas, A., Varvarousis, G., Karidakis, G. (2008). Geothermal study of Sperchios area. IGME, Athens (in Greek).

Mishra, U. (1990). Exposures due to high natural radiation background and radioactive springs around the world. Proceeding of International Conference on High Levels of Natural Radiation (ICHLNR), Ramsar, Iran.

Mountrakis, D. (1986). The Pelagonian zone in Greece: A polyphase deformed fragment of the Cimmerian continent and its role in the geotectonic evolution of the eastern Mediterranean. *Journal of Geology, 94*, 335–347.

Oliveira, J., Mazzilli, B. P., Sampa, M. H. O., & Bambalas, E. (2001). Natural radionuclides in drinking groundwater supplies of Sao Paulo state Brazil and consequent population doses. *Journal of Environmental Radioactivity, 53*, 99–109.

Orfanos, G. and Sfetsos, K.S. (1975). Hydrogeological study of Kamena Vourla area, IGME, Athens (in Greek).

Pe-Piper, G. and Piper, D. (2002). The igneous rocks of Greece, the anatomy of an orogen, Gebruder Borntraeger, Berlin.

Scherreiks, R. (2000). Platform margin and oceanic sedimentation in a divergent and convergent plate setting (Jurassic, Pelagonian zone, NE Evvoia, Greece). *International Journal of Earth Sciences, 89*, 90–107.

Sohrabi, M. (1990). Recent radiological studies of high background radiation areas of Ramsar. Proceeding of

International Conference on High Levels of Natural Radiation (ICHLNR), Ramsar, Iran.

Trampidou, G. (2004). Radiological study in radioactive springs areas. Ph.D. thesis, University of Athens, Athens, Greece (in Greek).

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), (1993). Sources and effects of ionizing radiation. Report to the general assembly. United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York.

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), (2000). Sources and effects of ionizing radiation. Report to the general assembly. United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York.

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), (2008). Sources and effects of ionizing radiation. Report to the general assembly. United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York.

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), (1988). Sources and effects of ionizing radiation. Report to the general assembly. United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York.

Vakalopoulos, P., Metaxas, A., Xenakis, M. (2000). Research and evaluation of lignite resources in Euboea Island: northern Euboea basin. Report of IGME, p. 35 (in Greek).

Vavassis, I. (2001). Geology of the Pelagonian zone in northern Evia Island (Greece): implications for the geodynamic evolution of the Hellenides. These de doctorat, Univ. de Lausanne, Switzerland.

Walencik, B., Kozlowska, J., Dorda, W., & Zipper, W. (2010). Natural radioactivity in underground groundwater from the outer Carpathians in Poland with the use of nuclear spectrometry techniques. *Appl. Radiat. Isotopes, 68*, 839–843.

Wallström, M. (2001). Commission Recommendation of 20 December 2001 on the protection of the public against exposure to radon in drinking groundwater supplies. 2001/928/EURATOM (DOCE L 344/85 of 28/12/01, Brussels).

Wang, J., Jin, M., Jia, B., & Kang, F. (2015). Hydrochemical characteristics and geothermometry applications of thermal groundwater in northern Jinan, Shandong, China. *Geothermics, 57*, 185–195.

World Health Organization (WHO), (2002). Guidelines for drinking groundwater quality: radiological aspects. World Health Organization, available in www.who.int/water_sanitation_health/GDWQ/Radio/radioasp.htm.

World Health Organization (WHO), (2011). Guidelines for drinking-water quality, fourth edition. World Health Organization, Library Cataloguing-in-Publication Data.

Zhou, Q., Birkholzer, J. T., Tsang, C. F., & Rutqvist, J. (2008). A method for quick assessment of CO_2 storage capacity in closed and semi-closed saline formations. *International Journal of Greenhouse Gas Control, 2*(4), 626–639.