

Characterization of a karstic system by examining the occurrence of radioactive nuclides and trace elements (*)

C. PAPASTEFANOU, M. MANOLOPOULOU, S. STOULOS

A. IOANNIDOU and E. GERASOPOULOS

Nuclear Physics Department, Aristotle University of Thessaloniki - Thessaloniki 54006, Greece

(ricevuto l'8 Giugno 1999; revisionato il 6 Novembre 1999; approvato il 3 Febbraio 2000)

Summary. — Naturally occurring primordial radionuclides, particularly those of the uranium-radium series, in a karstic system like that of Maras in the Drama area, Northern Greece, were examined using gamma-ray spectrometry. Radon in karstic waters was monitored by alpha scintillation detectors (Lucas cells), Clipperton-type detectors (silicon diodes) and solid state nuclear track-etch detectors (LR-115). Trace elements were determined using the instrumental nuclear activation analysis (INAA) method. Although the specific activities of the natural radionuclides in bedrocks (marbles) were at the level of the earth's crust average abundance, they were enhanced in the clay materials (soil intrusions), soils and sediments of the karstic system. Radon in karstic waters increased in the spring and summer periods (water crisis period) and decreased in the fall and winter periods. Of the major elements, the occurrence of calcium, iron and potassium, and of the minor elements, the occurrence of strontium and zinc in significant concentrations characterized the karstic system.

PACS 92.40.Kf – Groundwater.

PACS 91.65.Dt – Isotopic composition/chemistry.

PACS 91.65.Nd – Trace elements.

PACS 91.65.Vj – Major element composition.

1. – Introduction

Karstic systems are irregular limestone regions with sinks, underground streams, and caverns. It shows a pattern of denudation in limestone and dolomite rocks produced not by normal surface run-off but by percolating ground waters and underground streams. Limestones are normally well jointed, allowing water to follow a restricted path and not penetrating the rock as a whole. The ground water reappears at the surface as a stream issuing at the base of the limestone, having carried out its

(*) The authors of this paper have agreed to not receive the proofs for correction.

solution work. An adequate rainfall is of course necessary to provide the continual passage of water. The leaching action of the ground water as it passes through the limestone produces a residual deposit, "terra rossa", a red clay-like soil.

The most characteristic feature of a karstic system is the sink (swallow-hole) in the limestone. Water disappears underground through the hollows and by enlarging the joints and cavities in the limestone produces caverns and galleries. As the water percolates downwards some of the excess calcium carbonate, CaCO_3 , may be deposited on the ceilings and floors of the caverns, forming stalactites and stalagmites, respectively. Karstification of limestones due to dissolution by circulating ground water greatly enhanced permeability and such bedrock could act as a very efficient radon conduit (O'Connor 1993). Radon-222, an intermediate decay product radionuclide in the ^{238}U decay series with half-life 3.84 days and immediate decay product of ^{226}Ra , has been extensively used as a tracer for the study of ground water hydrology particularly in karstic systems (Eisenlohr and Surbeck 1995).

The karstic system of the present work is located at Maras, Drama area ($41^\circ 31' \text{N}$, $24^\circ 2' \text{E}$), 185 km from the city of Thessaloniki ($40^\circ 38' \text{N}$, $22^\circ 58' \text{E}$), Northern Greece (fig. 1). Its bedrock is mostly metamorphised limestone (marbles) lying onto granite (Dimadi 1988). Terra rossa does not cover the limestone surface and the bedrock is bare, type III in karstic classification (fig. 2). Part of the underground innerflows seem to occur in contact with granites. In turn, due to their very characteristic chemical composition, granites are able to label waters (radon and trace elements).

The purpose of this work is the investigation of characterization of a karstic system by measuring radioactive elements as well as trace elements in bedrocks (marbles), clay materials (soil intrusions), soils and sediments, and radon in karstic waters.

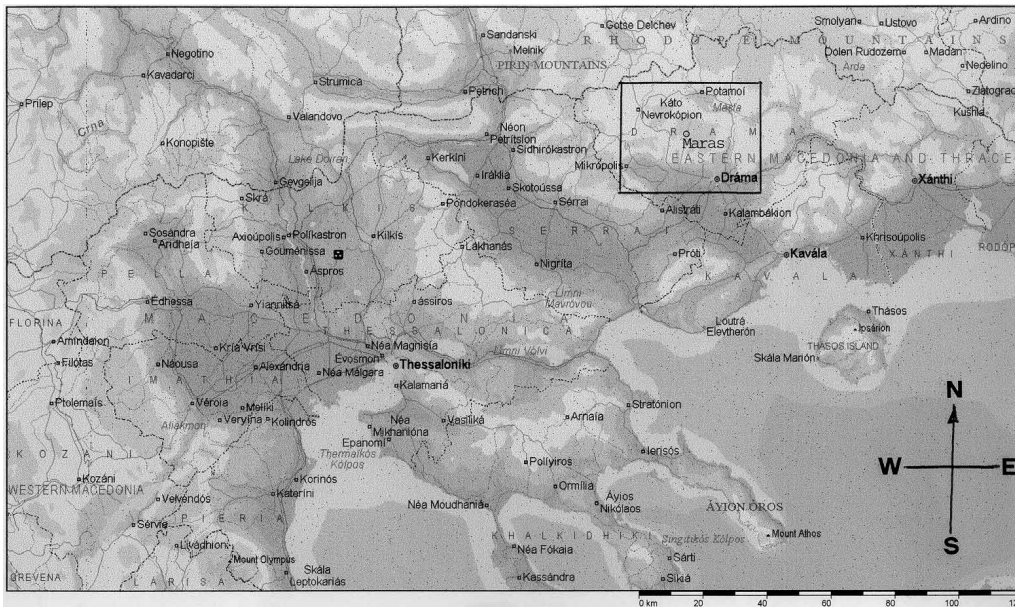


Fig. 1. – A map of Macedonia, Northern Greece, showing in the frame the karst aquifer of Maras in the Drama area.

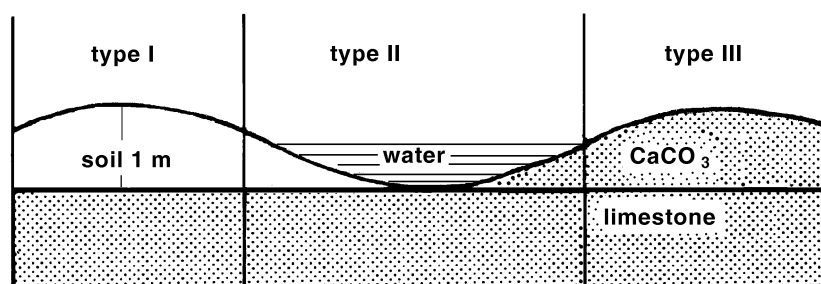


Fig. 2. – Classification of karstic systems. The Maras karstic system is of type III.

2. – Experimental procedures

The radioactivity of solid samples, such as soil, sediments, clay material and bedrock samples, and of liquid samples, such as waters from the karstic springs, was measured by gamma spectrometry using high-resolution (1.9 keV at 1.33 MeV, ^{60}Co), high-efficiency (42%), low-background HPGe detectors in gamma-ray energy ranging from 5 to 186 keV for ^{210}Pb , ^{226}Ra and ^{238}U (via its decay product ^{234}Th) and from 240 to 2614 keV for ^{226}Ra (via its decay products ^{214}Pb and ^{214}Bi), ^{232}Th (via its decay products ^{228}Th , ^{228}Ac and ^{228}Ra) and ^{40}K , etc., in a standard geometry 40 g plastic can of 6 cm diameter or in a Marinelli beaker of 1 litre (volume) or about 1 kg (mass). The overall efficiency of the counting system was known to accuracy of better than 5% for the plastic can geometry and about 12% for the Marinelli beaker (Papastefanou *et al.* 1994a).

Radon-222 in waters as well as in soil gas was measured by alpha spectrometry using appropriate Lucas scintillation cells⁽¹⁾. The spectrometer consisted of a water degassing unit (kit) and was linked to a portable radon monitor⁽²⁾, a trace environmental level radon gas detector which detects radon levels as low as 11 Bq m^{-3} , and a data acquisition unit (instantaneous radon measurements). The technique for water sampling was developed using specially made bubblers with appropriate stopcocks to avoid any radon entry of atmospheric origin. The volume of Lucas cells was 270 ml coated with $\text{ZnS}(\text{Ag})$. The active area was 27700 mm^2 . The counting efficiency was $0.75 \pm 0.02 \text{ cpm dpm}^{-1}$. The sensitivity was $0.037 \text{ cpm Bq}^{-1} \text{ m}^3$. The radon detection levels were as low as 11 Bq m^{-3} .

For continuous monitoring of radon gas in karstic waters, two Clipperton-type detectors (silicon diodes) were applied. The distance between the detectors was 115 m and about 130 m from the entrance of the cave of Maras karst aquifer (fig. 3). The sensitivity of the detectors was 1 count h^{-1} per 362 Bq m^{-3} (Pane *et al.* 1995). A response-function test of Clipperton-type detectors was performed using a calibrated radon source of 20 kBq ⁽³⁾. The data storage units were far away from the radon detectors that were inside the waters, to avoid any influence of electric fields on the detectors. Specially made Clipperton detector supporters were provided when the

⁽¹⁾ Type 300A (PYLON).

⁽²⁾ Type AB-5 (PYLON).

⁽³⁾ Type RN-1025-20 (PYLON).

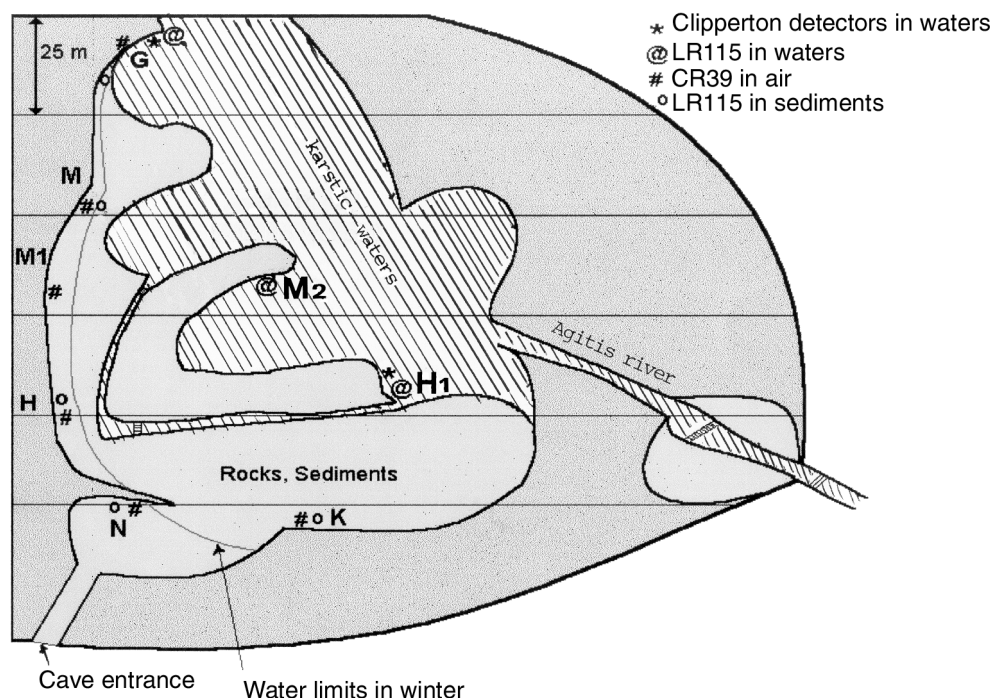


Fig. 3. – Schematic diagram of the Maras karstic cave with the aquifer showing the locations of experimental measurements. The springs of the Agitis river are in the mid of the cave.

waters were very deep, particularly in the winter period. Registrations of radon were performed every 15 minutes.

Radon in waters and in soil gas was also monitored by three LR-115 Kodak type-II, non-strippable nuclear track-etch detectors (integrated radon measurements) in specially made devices consisting of plastic tubes, 44 mm inner diameter, 50 mm outer diameter and 300 mm in length. The detectors were put on top of the tubes. The sensitivity of the detectors was $0.03 \text{ tr cm}^{-2} \text{ kBq}^{-1} \text{ m}^3 \text{ h}^{-1}$ for radon detection. The time of exposure of the detectors was 1 month.

Radon in air was monitored by six CR-39 nuclear track-etch detectors (integrated radon measurements) which were set in specially made devices consisting of cylindrical plastic pots which were put upside down inside the karstic cave (Papastefanou *et al.* 1994b). The sensitivity of the detectors was $0.09 \text{ tr cm}^{-2} \text{ kBq}^{-1} \text{ m}^3 \text{ h}^{-1}$ for radon detection. The time of exposure of the detectors was 1 month.

Trace element analysis of solid samples was performed by the instrumental neutron activation analysis (INAA) method using thermal neutrons in the nuclear reactor of 5 MeV at the National Center for Research of Physical Sciences “Democritos”, Athens, Greece, at neutron fluxes ranging from $10^{14} \text{ n cm}^{-2}$ (reactor power 100 kW for 9 min) for high elemental concentrations to $10^{16} \text{ n cm}^{-2}$ (reactor power 5 MW for 17 min) for low elemental concentrations. This method was first applied for detection and measurement of ^{238}U and ^{232}Th by n, γ reactions: $^{238}\text{U} (n, \gamma) ^{239}\text{U} \rightarrow ^{239}\text{Np}$ and $^{232}\text{Th} (n, \gamma) ^{233}\text{Th} \rightarrow ^{233}\text{Pa}$, respectively (Charalambous and Papastefanou 1977). The INAA method for trace

element analysis was newly developed by using IAEA⁽⁴⁾ soil-7 calibrated samples of known concentrations of trace elements, which were irradiated together with the samples in the reactor. For evaluating the spectra of irradiated samples, a Monte Carlo program was developed for the summation effect of gamma peaks that were observed at the spectra on the one hand, and on the other hand for the self-absorption effect when ²¹⁰Pb was determined by a planar Ge detector (47 keV gamma photons).

Mineralogical analysis of solid samples was performed by X-ray diffraction using a diffractometer with Cu *K α* nickel-filtered radiation. The diffraction pattern was recorded over a 2θ range from 2° to about 60° (Charalambous and Papastefanou 1977).

3. – Results and discussion

3.1. Radioactivity of solid phase materials in karstic systems. – With respect to the radioactivity of the karstic system of Maras aquifer in the Drama area, Northern Greece, the naturally occurring primordial radionuclides were determined in bedrocks, such as marbles, in clays (soil intrusions), in soils and in sediments from the field of research, with focus on uranium-radium and their decay products. Beside these, other radionuclides such as thorium and potassium-40 were detected and measured (table I).

The results showed that uranium-238 ranged from 4 to 29 Bq kg⁻¹ (average 12 Bq kg⁻¹) in bedrocks and from 45 to 72 Bq kg⁻¹ (average 58 Bq kg⁻¹) in clay materials. In soils, uranium-238 ranged from 19 to 43 Bq kg⁻¹ (average 32 Bq kg⁻¹), and from 20 to 66 Bq kg⁻¹ (average 44 Bq kg⁻¹) in sediments. The radium-226 content ranged from 1.6 to 21 Bq kg⁻¹ (average 9.5 Bq kg⁻¹) in bedrocks and from 36 to 122 Bq kg⁻¹ (average 65 Bq kg⁻¹) in clay materials. In soils, radium-226 ranged from 37 to 117 Bq kg⁻¹ (average 83 Bq kg⁻¹), and from 44 to 91 Bq kg⁻¹ (average 65 Bq kg⁻¹) in sediments. Lead-210 ranged from 9.3 to 52 Bq kg⁻¹ (average 24 Bq kg⁻¹) in bedrocks, and from 52 to 152 Bq kg⁻¹ (average 97 Bq kg⁻¹) in clay materials. In soils, lead-210 ranged from 109 to 1135 Bq kg⁻¹ (average 776 Bq kg⁻¹), and from 37 to 93 Bq kg⁻¹ (average 68 Bq kg⁻¹) in sediments.

TABLE I. – Average activity concentrations (Bq kg⁻¹) of naturally occurring radionuclides of solid phase materials of the karstic system of Maras in the Drama area, Northern Greece (the range is given within brackets).

Radionuclide or decay series	Bedrocks	Clay materials	Soils	Sediments
²³⁸ U	12.0 (3.96–28.8)	58.1 (44.8–71.6)	32.1 (19.0–42.8)	43.8 (20.4–65.5)
²²⁶ Ra	9.5 (1.58–20.58)	65.3 (36.3–122.0)	82.8 (36.6–117.0)	65.2 (44.1–90.5)
²¹⁰ Pb	23.6 (9.31–51.9)	97.3 (52.0–151.9)	775.8 (109.1–1135.1)	68.2 (36.9–93.2)
²³² Th	6.31 (0.32–22.9)	112.0 (92.9–132.0)	44.25 (20.3–61.5)	60.7 (16.4–117.6)
⁴⁰ K	60.6 (5.94–147.0)	665.4 (514.0–874.0)	525.6 (287.0–695.0)	1052.25 (929.0–1130.0)

⁽⁴⁾ International Atomic Energy Agency, Vienna, Austria.

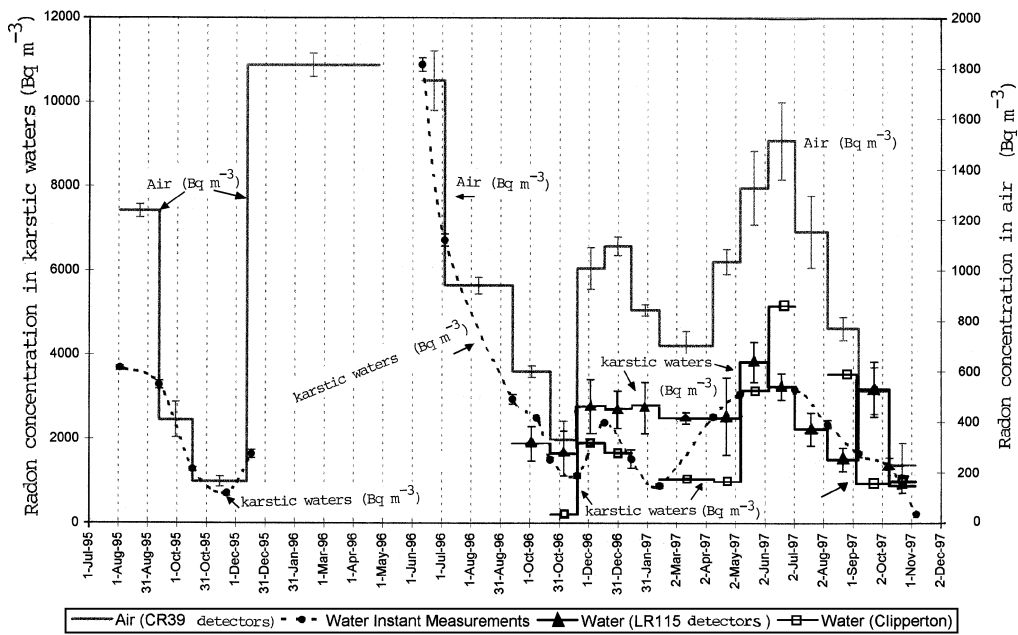


Fig. 4. – Radon variations in air and in waters at the Maras karst aquifer. Error bars are of 1σ .

The above results show that in bedrocks almost radioactive equilibrium did exist between uranium-238, radium-226 and lead-210, all members of the uranium series, while enrichment of radium-226 as well as of lead-210 produced by the decay of radium-226 occurred in clay materials, soils and sediments, because radium was diluted in the infiltrated waters of the karstic system and, therefore, concentrated producing lead-210 by decaying.

3.2. *Radon in waters of karstic aquifers.* – Radon was measured in karstic waters for 15 months (1 1/3 years) as follows:

a) Instantaneous measurements of radon in the waters of Maras aquifer performed by alpha scintillation detectors (Lucas cells) are presented in fig. 4. Integrated radon measurements performed by solid state nuclear track-etch detectors (LR-115) are also presented in fig. 4. Radon concentrations in karstic waters varied between 771 and 4373 $\text{Bq} \cdot \text{m}^{-3}$ (mean value 2475 $\text{Bq} \cdot \text{m}^{-3}$), table II. The data shows that radon increased during the spring and summer periods (water crisis) and decreased in the fall and winter periods with increasing precipitation (rainfalls). It could be explained by dilution of radon in a water table whose volume has increased.

b) The results of continuous monitoring of radon in the waters of Maras aquifer performed by Clipperton-type detectors are presented in fig. 5. Precipitation and temperature data in the Drama area for the period of radon measurements (January 1995 to September 1997) are presented in fig. 6. The data show that radon in waters increased during the period from May to July 1997 and decreased following the high precipitation rates occurred in November and December 1996. Heavy rainfalls induce a

TABLE II. – Radon concentrations (Bq m^{-3}) in karstic waters of the Maras aquifer (fig. 3). Numbers in italics are not included in the calculation of the mean value.

Time period		Point G (No 1) ($\text{Bq m}^{-3} \pm \sigma$)		Point M1 (No 2) ($\text{Bq m}^{-3} \pm \sigma$)		Point H (No 3) ($\text{Bq m}^{-3} \pm \sigma$)		Average ($\text{Bq m}^{-3} \pm \sigma$)	
13-Sep-96	22-Oct-96	2183	150	1597	129	<i>346</i>	<i>69</i>	1890	415
22-Oct-96	19-Nov-96	2237	181	1527	152	1206	137	1657	528
19-Nov-96	17-Dec-96	3275	211	2042	168	2993	202	2770	646
17-Dec-96	14-Jan-97	2303	124	3174	218	2599	200	2692	443
14-Jan-97	12-Feb-97	2303	124	3169	205	<i>4565</i>	<i>245</i>	2736	612
12-Feb-97	09-Apr-97	2371	104	2478	131	2632	135	2494	131
09-Apr-97	07-May-97	2371	104	1701	158	3523	222	2532	922
07-May-97	05-Jun-97	3584	217	3519	215	4373	239	3825	475
05-Jun-97	03-Jul-97	2880	415	3389	573	3443	822	3237	311
03-Jul-97	06-Aug-97	2504	335	640	678	1953	487	2228	390
06-Aug-97	07-Sep-97	1817	339	1430	368	1278	363	1508	278
07-Sep-97	09-Oct-97	2901	186	2713	180	<i>3932</i>	<i>214</i>	2807	133
09-Oct-97	05-Nov-97	771	107	1021	122	<i>451</i>	<i>84</i>	896	177
(Sep '96 - Sep '97) MEAN $\pm \sigma$								2475	140

decrease in radon concentration which could be explained by dilution of radon in a water table whose volume has increased.

Radon concentrations in the air inside the karstic cave at Maras aquifer were presented in fig. 4. Equilibrium equivalent radon (EER) concentrations in the air inside

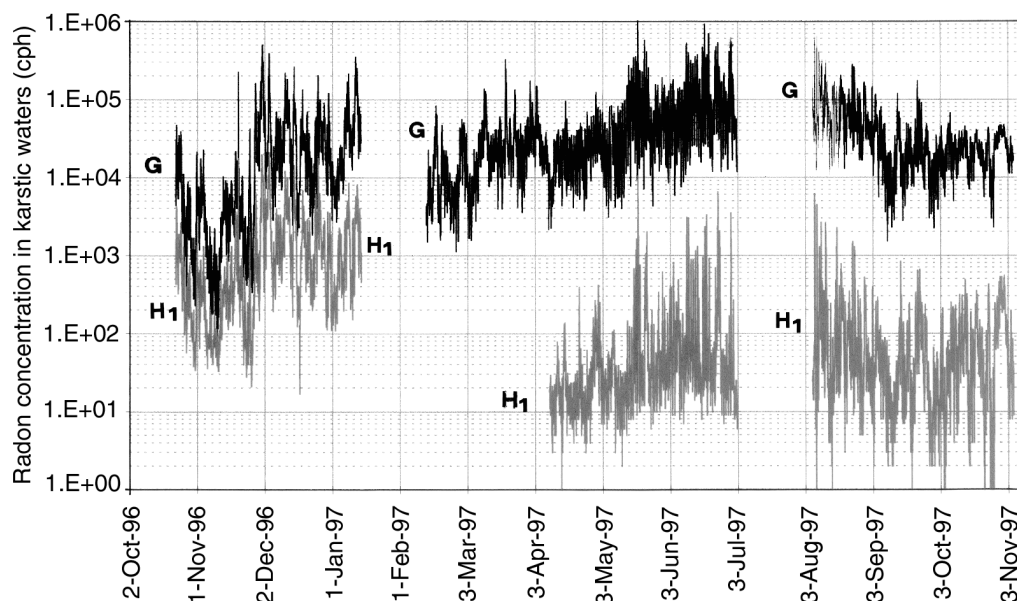


Fig. 5. – Results of radon continuous monitoring in waters by Clipperton-type detectors at the Maras karst aquifer (fig. 3).

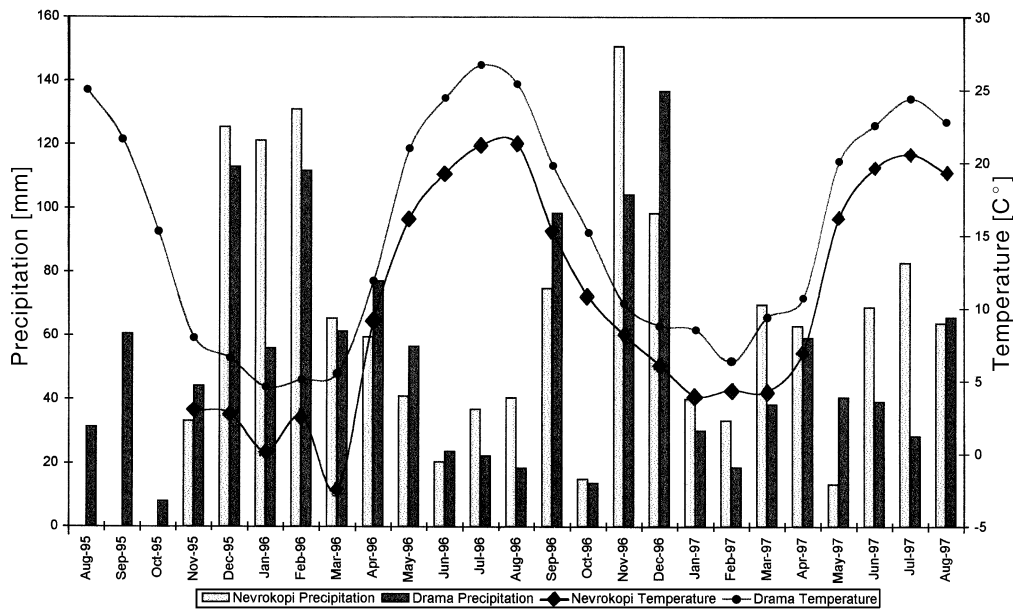


Fig. 6. – Precipitation and temperature data in the Drama area. Nevrokopi altitude: 560 m. Drama altitude: 110 m (fig. 1).

the cave (indoors) varied between 160 and 2054 Bq m^{-3} (mean value 930 Bq m^{-3} for the period from September 1995 to September 1996 and 917 Bq m^{-3} , almost the same, for the next period from September 1996 to September 1997), table III. The corresponding EER value in the normal atmospheric air (outdoors) is at the level of 5 Bq m^{-3} , while the average concentration of radon in the atmosphere is at the level of 10 Bq m^{-3} (UNSCEAR 1982). The high level of radon in the air inside the karstic cave is characteristic of indoor air radon level due to radon exhalation from the bedrock. The data show that the trend of increasing and/or decreasing radon is the same as that measured in waters, indicating that the radon in the air was originated from the karstic waters.

3.3. Trace element analysis of solid phase materials in karstic systems. – The results of the trace element analysis performed on bedrocks such as marbles, clay materials (soil intrusions), soils and sediments at the karstic system of Maras in the Drama area, using the instrumental neutron activation analysis (INAA) method, are presented in table IV. The data show enrichment of major elements, such as calcium, iron, potassium and sodium. In marbles, calcium was in very high concentrations, as expected. In clay materials, iron and calcium as well as potassium were at the same level. In sediments, all major elements were at the same level. Soils were richer in calcium than in iron and potassium.

Mineralogical analysis of these materials strongly showed the presence of calcite, particularly in marbles, while clay materials from the underlayers, sediments and soils showed the presence of quartz chlorite (kaolinite), micas (illites) and feldspars. Iron was not in limonite form but rather in goethite or hematite form, giving the soil a red color. Radium-226 in such cases is caught by $\text{Fe}(\text{OH})_2$ producing high radon levels as well in the karstic systems (Surbeck 1995).

TABLE III. — *Equilibrium equivalent radon (EER) concentrations (Bq m⁻³) in the air of the Maras karstic cave (fig. 3). Numbers in italics are not included in the calculation of the mean value.*

Time period	Point G (No 5) (Bq m ⁻³ ± σ)	Point M (No 6) (Bq m ⁻³ ± σ)	Point MI (No 8) (Bq m ⁻³ ± σ)	Point H (No 9) (Bq m ⁻³ ± σ)	Point K (No 10) (Bq m ⁻³ ± σ)	Point N (No 7) (Bq m ⁻³ ± σ)	Average (Bq m ⁻³ ± σ)
02-Ago-95			1220	71	1256	79	1238
12-Sep-95			361	51	461	39	411
17-Oct-95			152	12	180	9	166
12-Dec-95			1814	47			1814
11-Jun-96			1851	109	1753	49	1752
04-Jul-96	1801	1553	91	1801	49	2054	52
13-Sep-96	940	890	20	939	33	957	30
22-Oct-96	588	624	23	567	22	609	23
19-Nov-96	325	413	23	350	21	855	22
17-Dec-96	351	886	30	1054	33	1050	33
14-Jan-97	535	1054	51	1103	52	1144	52
12-Feb-97	535	851	32	861	32	819	31
09-Apr-97	646	698	49	664	37	705	27
07-May-97	1053	990	34	1102	36	982	34
05-Jun-97	1508	42	1267	39	1309	39	1127
03-Jul-97	1325	154	1709	99	1614	133	1424
06-Aug-97	1024	106	1143	34	1143	38	1417
07-Sep-97	715	42	748	76	841	66	1500
09-Oct-97	471	28	426	27	532	29	1066
05-Nov-97	360	25	197	21	175	21	782
(Sep '95 - Sep '96) MEAN ± σ							
930							
(Sep '96 - Sep '97) MEAN ± σ							
917							
26							

TABLE IV. – Average amounts of trace elements (ppm) of solid phase materials of the karstic system of Maras in the Drama area, Northern Greece (the range is given within brackets).

Element	Bedrocks	Clay materials	Soils	Sediments
Ca	372130 (291100–439390)	39644 (22210–64040)	78280 (34950–117640)	17793 (12790–23580)
Fe	2509 (190–11460)	49660 (25110–66230)	28425 (13440–37930)	20365 (9950–32840)
K	984 (130–3090)	20022 (16210–24010)	13158 (7430–17980)	25108 (23270–27310)
Na	142 (30–770)	8830 (620–23630)	3518 (2320–5270)	18713 (16830–21450)
Zn	30.0 (2.2–69.4)	173.4 (68.1–249.8)	163.6 (119.5–184.0)	44.0 (28.6–59.3)
Rb	7.5 (0.8–32.0)	150.8 (111.9–202.1)	104.6 (57.5–152.5)	125.7 (113.0–143.7)
Sr	111.8 (28.5–161.0)	180.7 (62.3–364.0)	108.6 (71.4–150.0)	291.1 (264.0–324.5)
Ba	18.9 (6.2–51.1)	389.2 (232.5–544.2)	292.3 (183.1–342.9)	648.6 (520.3–768.5)
Sc	1.33 (0.13–4.68)	15.80 (8.99–21.08)	9.87 (4.27–14.44)	3.71 (0.05–7.30)
Cr	13.20 (2.67–45.98)	78.03 (43.30–102.61)	70.68 (30.66–107.80)	31.51 (15.05–54.23)
Co	0.93 (0.08–4.64)	23.51 (11.30–31.94)	11.07 (5.16–15.42)	7.46 (4.68–10.63)
Ga	1.29 (0.09–4.69)	25.23 (13.84–32.50)	12.16 (5.59–18.70)	—
As	2.05 (0.36–6.15)	22.67 (3.29–35.20)	12.54 (5.59–19.80)	14.43 (2.26–40.15)
Br	0.37 (0.13–1.10)	1.63 (0.75–2.94)	6.73 (3.05–10.81)	2.69 (0.81–3.97)
Mo	1.18 (0.23–5.10)	3.88 (0.47–9.68)	1.54 (0.08–4.41)	3.94 (1.18–7.21)
Sb	0.29 (0.07–0.56)	1.75 (0.52–2.52)	1.91 (1.68–2.57)	0.40 (0.19–0.61)
Cs	1.35 (0.04–7.01)	10.47 (2.61–17.79)	4.96 (2.28–7.38)	2.53 (1.93–3.44)
Hf	0.81 (0.02–4.06)	6.52 (3.55–9.56)	5.00 (1.86–7.61)	4.99 (1.93–11.31)
Ta	0.08 (0.01–0.35)	1.60 (1.39–1.76)	1.04 (0.50–1.43)	1.19 (0.54–1.62)
La	5.55 (0.61–16.00)	42.51 (31.46–48.29)	32.75 (14.96–46.06)	29.88 (17.66–59.50)
Ce	6.26 (0.94–22.36)	98.53 (73.75–125.78)	61.60 (28.86–83.77)	58.09 (21.01–87.01)
Nd	5.47 (0.98–15.87)	38.87 (36.51–43.77)	33.21 (16.40–45.06)	24.11 (8.45–36.27)
Sm	0.94 (0.04–2.74)	6.14 (3.80–8.44)	4.88 (2.14–6.61)	3.37 (1.49–6.94)
Eu	0.17 (0.01–0.57)	1.37 (1.12–1.87)	1.14 (0.49–1.73)	0.98 (0.43–1.41)
Tb	0.11 (0.01–0.33)	0.70 (0.36–0.93)	0.55 (0.24–0.79)	0.44 (0.17–0.73)
Ho	0.43 (0.09–0.98)	1.66 (1.33–2.14)	1.24 (0.54–1.72)	4.38 (2.11–6.65)
Yb	0.45 (0.05–1.25)	3.23 (2.77–3.80)	2.33 (1.12–3.21)	1.85 (1.64–2.89)
U	1.55 (0.08–5.62)	27.48 (22.63–32.55)	8.36 (4.09–15.09)	14.90 (4.03–28.87)
Th	0.97 (0.32–2.33)	4.22 (3.63–5.80)	2.60 (1.60–3.47)	3.55 (1.65–5.30)

Minor elements such as Sc, Cr, Co, Zn, Ga, As, Br, Rb, Sr, Mo, Sb, Cs, Ba, Hf, and Ta as well as the lanthanides La, Ce, Nd, Sm, Eu, Tb, and Yb and the actinides Th and U were determined in the solid phase materials of the karstic system of Maras in the Drama area. Strontium was in high concentrations in marbles, clays, soils and sediments. Zinc was in high concentrations in clays, soils and sediments, but not as high as in marbles. The same result was obtained for rubidium and barium (table IV).

4. – Conclusions

The karstic system of Maras in the Drama area, Northern Greece, consists of a metamorphosed limestone (marbles) lying onto granite. It is a bare bedrock including a cavern with stalactites and stalagmites giving rise to the springs of the river Agitis in the middle of the cave.

Naturally occurring primordial radionuclides such as ^{238}U and its decay products were present in high concentrations particularly in clay materials (soil intrusions) embedded in bedrocks and in sediments of the karstic system. Radon-222 was enriched in the air inside the karstic cave reaching the level of $2 \times 10^3 \text{ Bq m}^{-3}$ (average level $9 \times 10^2 \text{ Bq m}^{-3}$). Radon-222 in karstic waters increased in the spring and summer periods (water crisis) reaching the level of $4 \times 10^3 \text{ Bq m}^{-3}$ (average level $2.5 \times 10^3 \text{ Bq m}^{-3}$) and decreased in the fall and winter periods due to high precipitation rate.

Of the major elements, calcium in bedrocks reached up to $4.4 \times 10^5 \text{ ppm}$ (average $3.7 \times 10^5 \text{ ppm}$), while of the trace elements, the occurrence of strontium and zinc in significant concentrations was very important and characterized the karstic system.

* * *

This work was sponsored by the European Commission under contract no. CHRX-CT94-0567.

REFERENCES

- CHARALAMBOUS S. and PASTEFANOU C., *Nuclear Instrum. Methods*, **142** (1997) 581-588.
- DIMADI A., *Comportement hydrogeologique des marbres de la bordure du Rhodope hydrogeologique du secteur Sud-Ouest du massif du Falacro Macedoine Orientale-Grece*, These de Doctorat, Université Scientifique, Technologique et Medicale de Grenoble, France (1998), p. 214.
- EISENLOHR L. and SURBECK H., *C. R. Acad. Sci. Paris, Ser. IIa*, **321** (1995) 761-767.
- O'CONNOR P. J., GALLANGER V., MADDEN J. S., VAN DEN BOOM G., MCLAUGHLIN J. P., MCAULEY I. R., BARTON K. J., DUFFY J. T., MULLER R., GRIMLEY S., MARSCH D., MACKIN G. and MACNIOCAILL C., *Geological Survey of Ireland, Rep. Ser.*, 93/2 (1993).
- PANE M. B., SEIDEL J. L., MONNIN M. and MORIN J. P., *Radon as a tracer of fluid motion in fractured aquifers*, in *Proceedings of the 2nd International Colloquium on Gas Geochemistry, Besançon, France, 5-9 July 1993* (Science Reviews, Northwood) 1995, pp. 325-334.
- PAPASTEFANOU C., MANOLOPOULOU M., STOULOS S. and IOANNIDOU A., *J. Radioecology*, **2** (1994a) 13-18.
- PAPASTEFANOU C., STOULOS S., MANOLOPOULOU M., IOANNIDOU A. and CHARALAMBOUS S., *Health Phys.*, **66** (1994b) 270-273.
- SURBECK H., personal communication (1995).
- UNSCEAR, *Ionizing Radiation: Sources and Biological Effects*, United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York, 1982.