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Radionuclides Concentration in Water and Mud of Euganean Thermal District

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ABSTRACT: The geothermal phenomena in the area nearby the Euganean Hills (near Padua, in Italy) are known and exploited for therapeutic purposes since ancient times, and recently also for aesthetic purposes. This paper presents the first characterization of the radionuclides content in the Euganean thermal waters and mud, extended to a great number of spas. In particular the radionuclides content of both the ^{238}U and ^{232}Th series in water and mud samples was determined. Moreover, for the first time the transfer of ^{226}Ra and of ^{228}Ra from water to mud during the maturation process was demonstrated and the comparison of ^{226}Ra and of ^{228}Ra activity concentration between mud and water was studied. An excess of "unsupported" ^{222}Rn in water was measured. ^{226}Ra enrichment was observed in "mature" mud, with respect to the "raw" mud. The absorption of radium through skin from mud application was evaluated. Also, it was possible to distinguish some muds prepared from different starting materials.

Key words: Geochemistry, Gamma-ray spectroscopy, Thermal water, Thermal mud, Pelotherapy, Radon

INTRODUCTION

The Euganean thermal waters represent the most significant thermal phenomenon in the Veneto region. This phenomenon is mainly located in the so called "Euganean Thermal District", on the eastern side of the Euganean Hills (near Padua), which includes the small towns of Abano, Montegrotto, Battaglia and Galzignano; over 200 spas are present in this area. The thermal water is valuable for its content of sodium, bromine and iodine; its temperature ranges between 60°C and 87°C. The presence of unsupported radon is known (Biancotto *et al.,* 1991; GUBIOCE web-site). This water is widely used in swimming pools, in rehabilitation therapies and in particular for therapeutic mud preparation.

The thermal phenomena in the Euganean area are known and exploited since prehistoric times. They are not related to the pseudo-volcanic origin of the Hills, but to a simple geothermal gradient. The meteoric precipitations fallen on the Piccole Dolomiti area (North of Vicenza province) seep until they reach the pre-Permian impermeable basement, where waters warm up. The hot waters in contact with volcanic rocks leach out some mineral components, including also U, Th, and their decay products. When the deep hot thermal waters reach the valley around Euganean Hills, they can rise to the surface through a system of impermeable fractured rocks. The time needed to run the entire path from the Piccole Dolomiti to the Euganean Hills was estimated (through ^{3}H decay determination) in some decades (Astolfi and Colombara, 1990; Dal Prà and Sedea, 1976). Further studies based on ^{14}C indicate greater times, maybe thousands of years (Fabbri and Trevisani, 2005; Boaretto *et al.,* 2003; GUBIOCE web-site). The hot thermal waters do not spring up spontaneously since decades; nowadays the extraction requires relatively deep wells.

The thermal mud preparation process is performed putting the mud into contact with a continuous flow of thermal water. The fresh mud is collected from the bottom sediments of the small lake Costa, near Arquà Petrarca, and, in lesser amount, from the even smaller lake Lispida, between Battaglia and Monselice (all these sites are in the neighbourhood of the Euganean Hills). The fresh mud is put into concrete basins and fluxed with thermal water for at least 2-3 months; during this time, a complex bio-geochemical process, defined as "maturation", takes place. During maturation, some organic compounds and trace elements are transferred from the water to the mud; moreover, particular thermophiles microorganisms grow up and accumulate their metabolites in the mud. The anti-inflammatory properties of these substances were reported (Galzigna *et al.,* 1995; Galzigna *et al.,* 1996; Jobstraibizer, 1999;

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Veniale *et al.,* 2004; Veniale et al, 2007; Tateo and Summa, 2007; Tateo *et al.,* 2009). The "mature" mud is now called also "thermal" mud, and can be used both for therapeutic and aesthetic applications. After each treatment on patients the "exhausted" mud must be regenerated: it is mixed with fresh mud (if needed), and put again in contact with flowing hot thermal water for at least a few months. However, the processes of mud maturation and regeneration are not yet fully standardized: they depend mostly on each spa experience and tradition.

The radionuclides (mainly ^{222}Rn) content in thermal water is measured in many places in the world, for research study and for workers radioprotection (Marovic *et al.,* 1996, Forte *et al.,* 2003, Losana *et al.,* 2006, Steinhäusler, 1988, Lovric and Strohal, 1972, Martin Sanchez *et al.,* 1995, Clemente, Renzetti and Santori, 1979; Desideri *et al.,* 2004; Marovic *et al.,* 1996a; 1996b; Soto *et al.,* 1995; Varga *et al.,* 1995; Vogiannis *et al.,*2004). About the Euganean thermal district, there are data from Biancotto et al. (1991), and from GUBIOCE web site; the measurement of ^{222}Rn activity concentration in air in Italian spas is required by the Italian law D.Lgs. 241/2000, then it will not be treated in this paper.

The radionuclides content in thermal mud is less studied, and only some sparse literature information are available. Manic et al. (2006) explain the high ^{226}Ra content in the soil used for the preparation of therapeutic mud in Niska Banja spas (Serbia) as due to the geological structure of the region. The sand taken from Red Sea and used for the same purpose at Safaga and Hurgada (Egypt) presents a low content of ^{226}Ra and ^{232}Th (El-Arabi, 2005). The mud used in Pinar del Rio spas, in Cuba, is prepared from river sediments collected in San Diego River; these sediments undergo a maturation process, similar to the Euganean mud (Diaz Rizo *et al.,* 2013). Anyway, in all these cases only the starting materials were analysed, and no radionuclides data are available about the "mature" mud, nor the eventually regenerated mud.

The present paper reports the first *"wide-ranging"* characterization, extended to a large number of spas (25), of radionuclides in mud and water utilized in the Euganean Thermal District. The results of the chemical characterization of water and mud used in the same 25 spas (carried out together with radiochemical analyses) are reported in Cantaluppi *et al.,* 2012. Former studies (Bertolo and Manduchi, 1990; Doretti *et al.,* 1992; Jobstraibizer, 1999) were restricted to a very small number of spas.

MATERIALS & METHODS

The mud and water samples were collected from 25 spas evenly distributed in the Euganean Thermal District, so they can be considered representative of the entire spas population.
In each spa both water and mud samples were analysed; because of privacy, in this paper the original spas names are replaced with a progressive label: S1÷S25.

The water samples were collected when possible directly at the well font; otherwise they were collected at the surface of the first mud's maturation basin. The water samples were labelled W1÷W25. For the determination of gamma-emitting radionuclides (and particularly for the determination of ^{222}Rn daughters) the water samples were collected directly in 0.5 L Teflon® bottles and immediately tightly sealed; for all other analytical determinations the water samples were stored into 10 L HDPE containers. The water temperature was measured at sampling. The first sampling campaign was completed during summer (June-July) 2003; about six months later (December 2003) a second sampling was performed, with the aim to merely determine possible variations, during time, in the concentration of ^{226}Ra and ^{222}Rn in water.

The mud samples (labelled M1÷M25) were collected through PE tools directly from the concrete basins in which the mud was deposited after the maturation period. In laboratory each mud sample was accurately homogenized; part of each sample was dried at 30°C and then at 110°C to determine the loss of water and, in sequence, the loss on ignition. The radionuclides activity concentration determinations were measured through high resolution gamma spectrometry, without further pre-treatments, in Marinelli beakers (for the determination of all gamma emitting radionuclides, except ^{232}Th and ^{226}Ra); the results were referred to the dry-weight at 30°C. Only for the analysis of ^{226}Ra, the mud samples were put in tightly sealed aluminium bottles and kept closed until the radioactive equilibrium was reached (see details in subsection 2.3). The mud samples were measured again about eight years later to determine ^{228}Ra *via* ^{228}Ac. The complete list of the measured radionuclides and the analytical techniques used is reported in Table 1. Immediately after water sampling, pH and conductivity (at 25°C) were measured in untreated water samples. Suspended particulate matter (SPM) content was determined after filtration on preconditioned 0.45 µm cellulose filters. The determination of the radionuclides activity concentration in the water and mud samples (except ^{232}Th) was achieved through High Resolution Gamma Spectrometry with high purity germanium detectors (a coaxial n-type, FWHM at 1332 keV = 1.73 keV; and a planar, FWHM at 122 keV = 0.548 keV); the detectors are located in a lead well shield 100 mm thick

for external background reduction, with two internal sheets respectively of Cd and Cu for X-rays reduction. Counting times were different for each sample: they were chosen in order to achieve less than 10% (1 standard deviation) counting statistics uncertainty in the photopeaks of interest. Minimum detectable activities are reported in tables of results. Genie 2000 ® (by Canberra) software was in operation for spectral analysis.

Table 1a. Radionuclides determination in mud

	$t_{1/2}$	main decay mode	detected γ emissions energy (keV), yield (%)	measurement error at 2 σ (%)	notes:
"4n+2" series					
^{238}U	4.5 10^9 a	α	---	---	α emitter
^{234}Th	24 d	γ	63.3 keV, 4.8 %	< 20 %	
^{234m}Pa	1.2 min	γ	(1001 keV, 0.84 %)		(rarely used)
^{226}Ra	1600 a	γ	186.2 keV, 3.59 %	(see ^{214}Pb and ^{214}Bi)	this peak is used seldom, and must be corrected for ^{235}U (185.7 keV, 52 %); ^{226}Ra is measured through its daughters ^{214}Pb and ^{214}Bi at radioactive equilibrium
^{222}Rn	3.8 d	α	---	(see ^{214}Pb and ^{214}Bi)	α emitter; measured through its daughters ^{214}Pb and ^{214}Bi at radioactive equilibrium
^{214}Pb	27 min	γ	351.9 keV, 37.6 %	< 8 %	
^{214}Bi	20 min	γ	609.3 keV, 46.1 %	< 8 %	
^{210}Pb	22 a	γ	46.5 keV, 4.24 %	< 15 %	
"4n" series					
^{232}Th	1.4 10^{10} a	α	---	---	measured through EDP-XRF
^{228}Ac	6.1 h	γ	911.2 keV, 25.8 %	< 10 %	
^{212}Pb	11 h	γ	238.6 keV, 43.3 %	< 10 %	
^{212}Bi	61 min	γ	727.3 keV, 6.58 %	< 15 %	
^{208}Tl	3.1 min	γ	2614.5 keV, 99 %	< 15 %	
Others					
^{40}K	1.27 10^9 a	γ	1460.8 keV, 11 %	< 5 %	
^{137}Cs	30 a	γ	661.7 keV , 85 % (see note)	< 7 %	from fallouts (nuclear tests and accidents); its 32-keV (5.8 %) peak is not used, this emission is from its daughter ^{137m}Bi
^{235}U	7 10^8 a	γ	185.7 keV, 52 %		from "4n+3" series

Table 1b. Radionuclides determination in waters

	$t_{1/2}$	main decay mode	detected γ emissions energy (keV), yield (%)	measurement error at 2 σ (%)	notes:
"4n+2" series					
^{226}Ra	1600 a	γ	186.2 keV, 3.59 %	(see ^{214}Pb and ^{214}Bi)	this peak is used seldom, and must be corrected for ^{235}U (185.7 keV, 52 %); ^{226}Ra is measured through its daughters ^{214}Pb and ^{214}Bi at radioactive equilibrium
^{222}Rn	3.8 d	α	---	(see ^{214}Pb and ^{214}Bi)	α emitter; measured through its daughters ^{214}Pb and ^{214}Bi at radioactive equilibrium
^{214}Pb	27 min	γ	351.9 keV, 37.6 %	< 8 %	
^{214}Bi	20 min	γ	609.3 keV, 46.1 %	< 8 %	
^{210}Po	138 d	α	---	---	α emitter, measured through α-spectrometry after deposition on Ag plate

In ^{222}Rn determination, it is defined as "supported" its activity concentration in radioactive equilibrium with the ^{226}Ra contained in the sample; the exceeding ^{222}Rn activity concentration, in the same sample, is defined as "unsupported".

The determination of ^{226}Ra and ^{222}Rn in water samples was carried through ^{222}Rn daughters ^{214}Pb (at 351.9 keV) and ^{214}Bi (at 609.3 keV); the samples were put in 0.5 L perfectly sealed Teflon ® bottles.

For the determination of total ^{222}Rn activity (supported + unsupported), the water contained in the bottles was initially measured in the first hours after collection (taking into account sampling time). A second measurement of the water samples was done after about 30-40 days, when the unsupported ^{222}Rn was completely decayed, and at the same time the equilibrium among ^{226}Ra, ^{222}Rn and daughters ^{214}Pb and ^{214}Bi was surely attained; this second measurement provided the "supported" ^{222}Rn activity concentration which is coincident with ^{226}Ra activity concentration. The measurement of ^{226}Ra was performed both in the unfiltered water (containing soluble + particulate ^{226}Ra) and in the filtered sample (after filtration on 0.45 μm cellulose filter).

In water samples, ^{228}Ra was only determined in unfiltered samples from both the first and the second sampling campaign; the water samples (about 1.5 L) were dried and the resulting salts were measured for ^{228}Ra ($t_{1/2}$= 5.75 y) through its short-lived daughter ^{228}Ac ($t_{1/2}$ = 6.13 h) after at least ten half-life times since sampling, for the achievement of the radioactive equilibrium. These salts were also measured by EDP-XRF to determine thorium, and then ^{232}Th, as described below.

Each mud sample was analysed "as it is" (after accurate homogenisation) without any chemical pre-treatment, in 1 L Marinelli beaker for the determination of all gamma emitters (except ^{232}Th and ^{226}Ra). As for water samples, also in mud samples ^{226}Ra was measured through ^{222}Rn daughters ^{214}Pb (at 351.9 keV) and ^{214}Bi (at 609.3 keV), after the attainment of the radioactive equilibrium: the samples were put in 0.25 L tightly sealed aluminium bottles for 30-40 days before the measurement. The results were referred to the dry-weight at 30°C.

^{232}Th decays basically *via* α to ^{228}Ra without significant gamma emissions; for this reason, it is usually determined indirectly through the 911.1 keV emission of the daughter ^{228}Ac, nevertheless this can be done only if the radioactive equilibrium with the daughter is guaranteed. In our case, the mobility of ^{228}Ra precludes this approach, therefore ^{232}Th activity concentration of mud samples was calculated from Th elemental concentration, through X-ray fluorescence analysis performed with an EDP-XRF (Energy Dispersive Polarized X-Ray Fluorescence) instrument, whereas ^{228}Ra was measured *via* ^{228}Ac.

The determinations of ^{232}Th were conducted with a SPECTRO X-LAB EDP-XRF spectrometer (s/n 4D/0013), equipped with a Si(Li) detector. For this measurement, the sample was dried at 30°C and grinded to obtain a very fine powder. The powder (~4 g) was mixed with paraffin wax (~0.9 g) and pressed in a tablet, which was used for analysis.

In only 3 water samples, also, ^{210}Po in water was determined, through spontaneous deposition on an Ag plate and measurement with an α-spectrometer with Si detector; the method used is described in Meli et al. (2013).

In gamma spectrometry the efficiency calibrations were obtained for each different container used (1 L Marinelli beakers, cylindrical 50 mL beakers, 0,25 L and 0,5 L bottles) through certified multi-gamma standard solutions (QCY48 and QCYB40 from Amersham).

The corrections for the self-attenuation of gamma rays in the mud samples, with respect to the calibration solution, were done through the method reported in Cantaluppi and Degetto (2003); the accuracy of the calibration efficiency of the measuring system is periodically checked through inter-laboratory and inter-calibration control tests planned by National Physics Laboratory of Teddington (UK).

The EDP-XRF instrument was calibrated with certified reference standard materials (MURST-ISS-A1 Marine sediment, GBW07310 Stream sediment, GBW08303 Farmland soil, LGC6138 Soil, SRM 12-3-12 Sludge, SRM 12-3-13 Sludge, SRM 12-3-14 Sludge, TD 12-1-12 Fly ash, BCR CRM 144R Sludge, CCRM PACS-2 Marine sediment, NIST SRM 2709 Agricultural soil, NIST SRM 2711 Montana soil, NIST SRM 1633b Fly ash). After calibration the Quality Assurance was performed measuring Lake sediment certified reference materials LKSD-1, LKSD-2, LKSD-3, LKSD-4 by CANMET Canada. The analytical precision for Th, measured as relative standard deviation, was < 8 %. ^{232}Th was calculated through its specific activity (4057 Bq g^{-1}; Pearce, 2008), from the total Th concentration.

RESULTS & DISCUSSION

For the sake of brevity, the complete physical data (temperature, pH, etc.) of thermal water samples are not reproduced here (see Fasson, 2004). The observed differences, in some parameters among the samples could be attributed to many reasons, above all: the extraction of water from each well catches strata of different depth, or anyway the paths followed by the

meteoric water from the input up to the sampling point are never the same.

The content of unsupported ^{222}Rn and ^{226}Ra in the water samples collected during the two sampling campaigns is reported in Table 2. The results of the first sampling campaign show that ^{226}Ra is present almost completely in dissolved form; for this reason in the samples from the second sampling campaign, only ^{226}Ra in unfiltered samples (i.e. the "total" ^{226}Ra) was measured.

^{226}Ra data of the two series of samples (summer/ winter 2003; listed in Table. 2) present a linear regression coefficient $R^2 = 0.88$; this implies that ^{226}Ra content in the waters collected from each well is roughly constant, at least in the time lag between the two sampling campaigns.

Table 2. ^{222}Rn, ^{226}Ra and ^{228}Ra content in the 25 water samples collected during the 1st and 2nd sampling (6 months later)

	1st sampling, June-July 2003			2nd sampling, December 2003		
Sample	Dissolved ^{226}Ra (Bq/kg)	Total ^{226}Ra (Bq/kg)	"Unsupported" ^{222}Rn (Bq/kg)	Dissolved ^{226}Ra (Bq/kg)	Total ^{226}Ra (Bq/kg)	"Unsupported" ^{222}Rn (Bq/kg)
W 1	2.1	2.1	6	n.d.	1.8	74
W 2	1.6	1.6	10	n.d.	2.4	59
W 3	2.1	2.4	71	n.d.	1.4	54
W 4	1.3	1.1	43	n.d.	2.8	51
W 5	2.0	1.8	34	n.d.	1.4	84
W 6	2.8	3.3	29	n.d.	3.2	16
W 7	3.5	3.9	169	n.d.	3.8	33
W 8	4.0	3.6	59	n.d.	7.1	4
W 9	4.5	3.9	31	n.d.	4.3	51
W 10	2.7	2.5	47	n.d.	3.8	21
W 11	1.3	1.8	103	n.d.	1.9	96
W 12	0.9	0.8	104	n.d.	1.1	43
W 13	6.2	6.2	141	n.d.	6.4	181
W 14	1.0	1.0	17	n.d.	1.4	86
W 15	6.6	6.6	3	n.d.	7.3	61
W 16	5.7	6.5	70	n.d.	6.7	97
W 17	5.8	5.4	3	n.d.	6.7	2
W 18	6.5	6.5	55	n.d.	5.5	100
W 19	2.5	2.2	72	n.d.	3.3	13
W 20	2.5	2.3	103	n.d.	3.2	85
W 21	3.3	3.2	11	n.d.	2.8	17
W 22	5.6	5.6	0	n.d.	6.3	9
W 23	3.7	3.7	29	n.d.	6.4	33
W 24	2.9	2.7	17	n.d.	3.5	46
W 25	2.8	2.5	97	n.d.	1.8	124
Mean	3.4	3.3	52.9		3.8	57.5
Std dev	1.8	1.8	45.6		2.1	42.6
Min	0.9	0.8	0.0		1.1	1.5
Max	6.6	6.6	169		7.3	181

MDA (both ^{226}Ra and ^{222}Rn) = 1 Bq/kg (measured through ^{214}Pb and ^{214}Bi).

In contrast, unsupported ^{222}Rn shows large variations between the 2 series of samples collected at the 25 spas in each of the two sampling campaigns (R^2 = 0.1829); also, a large data spread in the same sampling campaign is observed. This can be due to manufacturing works occurred in some spas at the thermal water sources and/or to possible differences in the meteorological conditions in the two sampling periods, circumstance to which ^{222}Rn concentration in water is particularly sensitive. The average ^{222}Rn activity concentration is however comparable in the two sampling campaigns, but with a wide standard deviation. On the contrary, no correlation is observed between supported ^{222}Rn (i.e. total ^{226}Ra) and unsupported ^{222}Rn: this underlines the different mobility and solubility of ^{222}Rn and ^{226}Ra (the precursor of the supported ^{222}Rn fraction).

The activity concentrations found for these radionuclides are in broad agreement with the literature data (very limited) regarding the same thermal district: Bertolo and Manduchi (1990) sampled water and mud from only 3 spas and mud from the Lake Costa; Doretti et al. (1992) analysed samples of water and mud from 6 spas and mud from the Lake Costa, and Biancotto et al. (1991) measured 11 samples of only water. In this paper, unsupported ^{222}Rn ranges from 0 to 181 Bq /L, while Doretti et al. (1992) reported data from 5 to 451 Bq /L, and Biancotto et al. (1991) from 7.7 to 481 Bq /L.

High unsupported ^{222}Rn activity concentration is a common feature for many mineral and thermal waters; values in low activity range (400÷2000 Bq /L) are found in Italy in Bormio, Bognaco, Nepo, Spezzano Albanese; in mean activity range (2000÷5000 Bq /L) in Montecatini and Merano; in high activity range (> 5000 Bq /L) in Lurisia and Ischia (Forte *et al.*, 2003). Among the highest activities in Europe there are Lurisia in Italy (40000 Bq /L), Bad Gastein in Austria (1900 Bq /L) and Jachymov in Czech Republic (5000-20000 Bq /L) (Forte *et al.*, 2003).

For ^{226}Ra, in this work values in the range 0.8 ÷ 7.3 Bq /L were found, quite close to those (0.07 ÷ 4.4 Bq / L) found in some mineral and thermal waters in Croatia (Marovic *et al.*, 1996b); in Lurisia spring 0.0176 ÷ 0.0388 Bq /L were found (Losana *et al.*, 2006). Anyway, the comparison among different spas is not very significant, because generally the radionuclides content of underground waters depend on their "geological history", i.e. their origin, the composition of the rocks they pass through, with the respective chemical and physical conditions, etc.

The activity concentration of ^{228}Ra and ^{232}Th (via elemental thorium) in water salts are reported in Table 3. The average activity concentration of ^{228}Ra in water is about 1/3 ÷ 1/4 of the ^{226}Ra content. ^{232}Th and ^{228}Ra are not correlated (R^2=0.0114): this might be a consequence of their different solubility in water. Moreover, ^{226}Ra and ^{228}Ra are not correlated (R^2=0.0067). This can be explained as they come from two different decay chains, and have different $t_{1/2}$. In some water samples from the 25 spas also ^{210}Po was measured through alpha spectrometry: the results showed very low ^{210}Po concentrations in this samples (mean value about 2.7 mBq /L), so it was not studied in depth in this work.

Table 3. ^{228}Ra and ^{232}Th (*via* EDP-XRF) content in salts from the 25 water samples collected during the 1st and 2nd sampling

Sample	Total ^{228}Ra (Bq/L)	^{232}Th (Bq/L)
W 1	1.53	0.24
W 2	1.16	0.20
W 3	1.37	0.21
W 4	0.87	0.25
W 5	1.27	0.22
W 6	0.87	0.28
W 7	0.80	0.24
W 8	0.45	0.22
W 9	0.85	0.28
W 10	0.81	0.25
W 11	0.74	0.21
W 12	1.19	0.12
W 13	3.45	0.28
W 14	0.84	0.15
W 15	0.55	0.30
W 16	0.58	0.29
W 17	< MDA	0.16
W 18	0.51	0.38
W 19	0.45	0.22
W 20	0.91	0.21
W 21	0.44	0.14
W 22	1.29	0.12
W 23	0.24	0.16
W 24	0.73	0.22
W 25	1.40	0.26
MDA	0.22	0.03
Mean	0.97	0.22
Std dev	0.63	0.06
Min	1.24	0.06
Max	3.45	0.38

About mud samples, the radionuclides content of mud in use in the 25 spas is showed in Table 4; in the same table the radionuclides content of an untreated mud sample from the Lake Costa is reported. For the sake of brevity, the loss of water and loss on ignition data are here omitted and reported in Fasson (2004).

In the 25 mud samples, an extensive disequilibrium can be noticed in the ^{238}U decay chain; the mean ^{226}Ra

activity concentration is 5 times higher with respect to ^{238}U (the latter decays basically *via* α to ^{234}Th without significant gamma emissions, so it is measured through the 63 keV emission of ^{234}Th, which is considered to be in equilibrium with its parent), while the mean ^{210}Pb activity concentration is about three times higher than ^{238}U. A large data variability is observed for ^{226}Ra which ranges from the level found in neighbouring soils (about 30 Bq kg^{-1}; Marani, 2000) to over 500 Bq kg^{-1} (referred to dry samples); ^{210}Pb presents a wide variability too, that includes also the contribution from atmospheric deposition of unsupported ^{210}Pb. On the contrary, ^{232}Th activity concentrations are quite homogeneous, but again for ^{228}Ra a large data spread is observed. The radionuclides belonging to the decay chain from ^{228}Ra to ^{208}Tl present an activity concentration almost double with respect to ^{232}Th. It is to notice that ^{226}Ra and ^{228}Ra, identical from the chemical point of view, are not correlated in these samples (R^2=0.2705); this is due to their different origins (respectively, from ^{238}U and from ^{232}Th).

A comparison of these data with the radionuclides content of the mud of Lake Costa is not fully significant, because some spas sometimes use different starting materials for preparing the therapeutic mud. Anyway, comparing the mean value of the 25 mud samples, a substantial enrichment (about 5 times) in ^{226}Ra with respect to Lake Costa mud (and respect to values normally found in soils) can be found. This can be due to "accumulation" phenomena: ^{226}Ra coming from water can be fixed to some substrates present in mud, i.e. organic matter and/or the silica skeleton of microorganisms, so it might accumulate at each mud regeneration.

About ^{137}Cs, its activity concentration in thermal mud is coherent with the low values found in Lake Costa mud, originated from the radioactive fallout. As an exception, in M12 and M25 samples ^{137}Cs was not found.

^{40}K values are all very similar to Lake Costa "raw" mud, with a very low spread of values; but again M12 and M25 samples make exception showing the higher values among the set of samples. These two mud samples were most probably prepared in the spas from different starting materials.

^{235}U was not measured, due to its small isotopic abundance (~ 0.72% *vs.* 99.2% of ^{238}U).

About the radionuclides content of thermal mud, the most significant remark is related to the increased ^{226}Ra concentration with respect to the untreated mud from Lake Costa. Fig. 1a shows the direct proportionality between ^{226}Ra in mud and in water with a linear regression coefficient R^2 = 0.62 (or R^2=0.68 considering ^{226}Ra measured in water salts).

The ratio between the mean ^{226}Ra activity concentration in the thermal mud and the same mean activity concentration in the water samples is 86; as seen above, the ^{226}Ra mean activity concentration in the thermal mud is 5 times higher respect to the one found in the original mud of Lake Costa. The range of ^{226}Ra values observed in the spas mud samples should be attributed to the different number of maturation treatments undergone by the thermal mud. ^{228}Ra behaves in the same way, but with a less relevant activity ratio between thermal mud and fresh mud (ratio = 1.3). At the same time even the correlation between ^{228}Ra in water and in thermal mud is less evident (see Fig. 1b, R^2=0.44).

As already observed (Cantaluppi *et al.,* 2012), the ^{226}Ra and the ^{228}Ra content in thermal mud does not correlate with any other chemical element present in the mud: this underlines their different origin, in fact they are taken up from the thermal water during the maturation process. This hypothesis was confirmed measuring again some mud samples after about 8 years from sampling for the determination of ^{228}Ac (^{228}Ra). The results reported in Table 5 show the partial decay of ^{228}Ra and confirm that part of ^{228}Ra was unsupported, i.e. not supported by the presence of ^{232}Th (half-life =5.7 years).

The comparison with literature data of radionuclides in thermal mud (Bertolo and Manduchi, 1990; Doretti *et al.,* 1992), is unfortunately limited to a small number of cases; in this research the maximum ^{226}Ra activity concentration found in the mud was 553 Bq kg^{-1}, but in one case (Doretti *et al.,* 1992) a ^{226}Ra activity concentration corresponding to 1208 Bq kg^{-1} was reported, which is above the limit of 1000 Bq kg^{-1} set in order to state a material as "radioactive" in Italian law (D.Lgs. 230/95). Also it is noteworthy the variability observed for ^{226}Ra activity concentration, which is connected to the mud "story".

About the radioprotection aspects, it is to notice that a high ^{222}Rn content in thermal waters (unsupported and supported), if not adequately controlled, could turn out in dangerous indoor activity concentrations. This aspect is regulated in Italy by D.Lgs. 230/95 and was not discussed here, because it is treated by many other works about indoor Rn in spas.

The thermal waters of the Euganean District are not used for drinking purposes, nevertheless some radioprotection aspects should be considered in bathing in thermal waters and in therapeutic treatments with mud. In this respect the percutaneous migration

Table 4.Radionuclide content in mud samples from 25 spas and (for comparison) from the lake near Arquà Petrarca (data in Bq/kg, samples dried at 110°C)

	^{234}Th	^{226}Ra (*)	^{210}Pb	^{232}Th (**)	^{228}Ra (***)	^{212}Pb	^{208}Tl	^{40}K	^{137}Cs
	(Bq/kg)	(Bq/kg)	(Bq/kg)	(Bq/kg)	(Bq/kg)	(Bq/kg)	(Bq/kg)	(Bq/kg)	(Bq/kg)
M1	60.4	215	190.0	34.1	121.9	87.0	39.5	432.0	1.9
M2	25.2	97	76.6	29.6	65.7	49.0	21.8	392.1	0.7
M3	27.7	227	199.1	40.6	126.0	101.4	43.4	492.0	2.3
M4	46.1	116	128.6	37.3	66.8	59.7	27.1	438.6	1.8
M5	41.6	168	155.7	35.3	95.9	75.8	33.6	409.5	0.7
M6	46.7	253	227.4	35.3	68.8	57.1	24.8	440.1	4.5
M7	55.9	221	103.5	30.0	65.7	40.8	25.0	382.7	0.8
M8	60.8	414	267.7	29.2	37.8	30.6	14.5	370.4	1.2
M9	38.9	209	150.1	38.6	58.8	47.0	19.2	410.7	1.3
M10	13.3	278	179.7	36.5	58.5	42.9	19.4	410.3	1.5
M11	73.0	305	393.9	39.8	103.4	82.5	36.7	485.6	3.2
M12	21.2	35	23.7	44.2	56.8	35.6	14.6	507.8	<0.6
M13	51.3	391	321.8	35.3	30.5	29.5	12.4	420.8	2.4
M14	56.6	145	139.2	34.9	87.5	107.6	30.4	422.2	1.4
M15	58.2	396	165.3	31.3	53.9	60.3	19.2	361.1	1.8
M16	70.2	547	309.9	34.5	48.9	61.2	19.3	459.6	4.4
M17	101.3	553	251.9	31.7	34.1	51.2	16.0	385.8	2.4
M18	53.5	466	216.9	33.3	42.6	51.0	14.7	409.6	1.6
M19	82.4	266	188.6	34.1	67.1	82.9	25.5	415.4	1.6
M20	126.1	229	165.9	30.0	69.5	89.2	25.2	357.8	1.2
M21	61.9	412	226.4	30.0	64.6	84.0	25.9	358.4	1.9
M22	52.6	287	188.8	36.5	35.9	51.2	16.1	404.9	2.3
M23	95.3	462	206.9	34.9	39.4	57.7	18.3	436.3	1.5
M24	60.7	264	197.0	34.5	71.6	98.7	28.2	412.9	2.5
M25	44.4	187	65.4	44.2	102.3	128.4	35.5	549.7	<0.5
MDA	4	5	4	10	1	0.5	0.4	7	0.5
Mean	57.0	285.6	189.6	35.0	67.0	66.5	24.3	422.6	2.0
Std. Dev.	25.3	137.6	81.9	4.2	26.4	25.9	8.5	47.5	1.0
Min.	13.3	34.5	23.7	29.2	30.5	29.5	12.4	357.8	0.0
Max.	126.1	553.0	393.9	44.2	126.0	128.4	43.4	549.7	4.5
Arquà P.	---	61	127	34	53	---	---	432	3.0

(*) ^{226}Ra was measured from ^{214}Bi and ^{214}Pb at radioactive equilibrium

(**) ^{232}Th was calculated from total Th content measured through EDP-XRF

(***) ^{228}Ra was measured from ^{228}Ac at radioactive equilibrium through gamma spectrometry

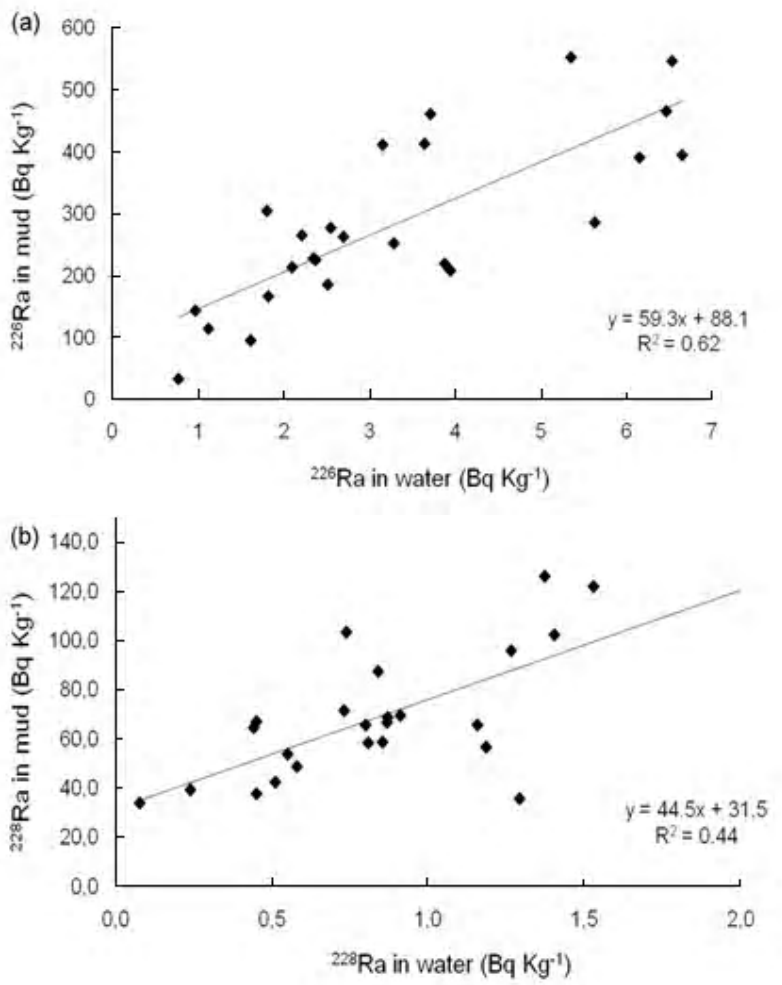

Fig. 1. (a) ^{226}Ra activity concentration in mud *vs* ^{226}Ra in water; (b) ^{228}Ra activity concentration in mud *vs* ^{228}Ra in water

Table 5. ^{228}Ra content in some mud samples (data in Bq kg^{-1}, samples dried at 110°C)

Sample	^{228}Ra (^{228}Ac) (2003 measurement) (Bq kg^{-1})	^{228}Ra (^{228}Ac) (2011 measurement)(Bq kg^{-1})
M1	121.9	38.0
M3	126.0	41.0
M5	95.9	34.2
M11	103.4	39.2
M14	87.5	32.4

of radium from the thermal waters during bathing should be evaluated. Specific literature data was not found, but from Tateo et al. (2009), it is possible to consider some chemical analogies between Ra and the periodic group of elements containing Ca, Sr and Ba (all belonging to the II group of the Periodic Table) (Table 6). On this basis it is possible to deduce an indication of the amount of ^{226}Ra passing from water to body during bathing (Table 7). Assuming for ^{226}Ra the lower ratio (concentration/amount passed) found for Ba, Ca and Sr (i.e. 14.7 /L), and a mean ^{226}Ra concentration in thermal waters of 3.55 Bq kg^{-1}, (see Table 2), it is possible to evaluate in 0.24 Bq the maximum amount of ^{226}Ra expected to be absorbed through the skin in 1 hour bath. As data on absorbed dose from percutaneous absorption of ^{226}Ra are lacking, for a rough estimation of the absorbed dose, cautelatively, the most severe dose coefficient for ^{226}Ra in D.Lgs. 230/95 (inhalation coefficient) was used. The result is an absorbed dose of 0.85 μSv, which is at least one order lower that the reference value of 10 μSv under which the exposure is considered not relevant by Italian legislation.

Data regarding ^{226}Ra transfer from mud through skin during therapeutic treatment are unknown. However, according to Tateo et al (2009), the figures are quite comfortable; in fact the exchange from mud is always lower, of at least one order of magnitude, with respect to the amount exchanged from water.

Table 6.Second group elements transfer from thermal water to body (source: Tateo *et al.*, 2009)

Element	Concentration in water(mg/L)	Amount that passes in 1 hour(mg)	Ratio for 1 hour bath (concentration/amount passed)(L)
Ba	10.92	0.6	18.2
Ca	4477.96	303	14.8
Sr	435.24	29.7	14.7

Table 7. Absorbed dose derived for ^{226}Ra in one hour bathing (see also Table 6)

^{226}Ra in water(Bq/L)	Estimated ratio for 1 hour bath (concentration/amount passed) (L)	^{226}Ra absorbed in 1 hour(Bq)	Inhalation coefficient(Sv/Bq)	Absorbed dose in 1 hour bathing (μSv)
3.55	14.7	0.24	3.5 E-6	0.85

CONCLUSION

In this paper the first characterisation of radionuclides content in Euganean thermal mud is reported. For the first time it is highlighted that during the maturation process ^{226}Ra and ^{228}Ra gradually transfer from the thermal water to the mud and can be found in the mature mud. This process can become more relevant with time as the acquirement of fresh mud is becoming more and more problematical and as a consequence the spas are inclined to reuse almost completely the mud after the application on patients. The estimation of the ^{226}Ra and ^{228}Ra transfer from water and mud to the skin seems not to present adverse effects as regards radiation protection, however a more detailed and accurate evaluation should be done. Also the process by which Ra transfers from water to mud should be studied in detail. Moreover, radionuclides analysis evidenced muds of different composition.

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