



Investigations on chemical composition and natural radioactivity levels from salt water and peloid used in pelotherapy from the Techirghiol Lake, Romania

M. R. Calin · I. Radulescu · A. C. Ion · L. Capra · E. R. Almasan

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Abstract The work presents the historical evolution, objectives, goals, concepts, chemical and radiometric methods, results and conclusions for salt waters and natural peloids used in pelotherapy. This study assesses chemical composition, natural radioactivity concentrations and the radiological hazard in peloid and salt water samples, from ten places in the Techirghiol Lake from Romania. Pelotherapy is a very important procedure, and thus, the materials used for this purpose must be well characterized to guaranty safety use. Concentrations of elements such as Sr, Ba, Mn,

Fe, Sb, Zn, Cu, Pb, Ti, Ni, Cr, As have been measured using ICP-OES analytical technique. The natural radionuclides such as ^{238}U , ^{226}Ra , ^{232}Th and ^{40}K have been determined by gamma-ray spectrometry. The average activity concentrations were of 0.48 ± 0.10 Bq/kg for ^{238}U , 0.60 ± 0.10 Bq/kg for ^{226}Ra , 0.30 ± 0.08 Bq/kg for ^{232}Th and 17.5 ± 1.3 Bq/kg for ^{40}K for salt water samples. Also, the mean activity concentrations for peloids were: 5.70 ± 1.00 Bq/kg for ^{238}U , 6.85 ± 1.60 Bq/kg for ^{232}Th , 15.3 ± 3.7 Bq/kg for ^{226}Ra and 95.8 ± 5.5 Bq/kg for ^{40}K . The results from this study contribute to the identification of possible contaminants in the salt water and peloid, and their association with the potential ecological and human health risk. In this context, of using salt water and peloid in a relatively long treatment period, several radiological indices have been calculated, to determine if the radionuclide's content can be also harmful to human health. The assessment indicates that humans are not exposed to concentrations of metal contaminants higher than the international recommended values.

M. R. Calin · I. Radulescu (✉)
“Horia Hulubei” National Institute for Physics and Nuclear Engineering - IFIN HH, 30 Reactorului Str.,
P.O. Box MG-6, 077125 Bucharest-Magurele, Romania
e-mail: rileana@nipne.ro

A. C. Ion
Department of Analytical Chemistry and Environmental Engineering, University Polytechnic, Bucharest, 6 Polizu, Str. No. 1-7, 011061 Bucharest, Romania

L. Capra
National Research and Development Institute for Chemistry and Petrochemistry ICECHIM, Bucharest, Romania

L. Capra
Faculty of Applied Chemistry and Material Science, University Polytechnic, Bucharest, Romania

E. R. Almasan
Techirghiol Balneary and Recovery Sanatorium, 34 Victor Climescu Str., 906100 Techirghiol, Romania

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Introduction

Peloids as defined by Gomes et al. (2013) are used for therapeutic treatments, rheumatic pathologies,

arthritis, muscle and bone traumas, and for dermatological pathologies or aesthetic purposes (Baschini et al. 2010). Thus, the external application of peloids is called pelotherapy, which is a worldwide used method to treat numerous diseases (Kikouama and Balde 2010). The most known Romanian peloid is Techirghiol's peloid. Due to its therapeutic effects, locals and people from all over the world have benefited from its healing effects (Ciobotaru et al. 2009; Marin et al. 2012).

The peloid of the Techirghiol Lake belongs to a group of organogenic underwater sediments, being characterized as a sapropelic coastal mud. This type of peloid is the product of extremely complex and long-lasting biochemical and chemical processes that mineral and organic substances from the lake suffer. The medical and scientific value Techirghiol Lake's water and peloid have been the subject of numerous studies in the most diverse research areas. From a historical perspective, Alphons Saligny (1893) was the first researcher who studied the complex problems raised by the lake and the therapeutic use of the peloid with solid scientific proof, regarding its therapeutic actions and the methodology of treatments. In addition to this, professor Paul Bujor was the author of a complete study on the peloid followed by others (Munteanu and Dumitrascu 2011).

Subsequently, the peloid has been the subject of numerous research and clinical trials conducted by the physicians of the Spa, Balneary and Recovery Sanatorium Techirghiol, where many diseases are treated: degenerative rheumatic diseases or inflammatory type, post-traumatic sequelae, central and peripheral nervous system disorders, gynaecological disorders, dermatological disorders, peripheral vascular diseases, chronic back pain, fibromyalgia, ankylosing, spondylitis, rheumatoid arthritis, osteoarthritis, etc. (Ciobotaru et al. 2009; Marin et al. 2012).

One of the most intensive treatments is peloid packs—consisting of the application of 1–2-cm-thick layers of heated peloid to 38–46 °C on a limited region or on the entire body surface for 20–40 min, up to 10–14 days. This procedure can expose the patient to the ionizing radiation present in the peloid, mostly originating from radionuclides such as ^{238}U and ^{232}Th and from ^{40}K . These primordial radionuclides and their progenies are of special interest because they are α -, β - and γ -ray emitters. The public exposure to the ionizing radiation is considered undesirable at all

levels. From this point of view, the knowledge and understanding of natural radioactivity and induced doses of radiation along with the physico-chemical composition of the peloid and salt water are important and draw considerable attention from both physicists and physicians.

During the last decade, several studies on the chemical and radiometric characterization of peloids have been carried out in different regions of the world. For example, Carretero et al. (2014) compared the properties of three Spanish clays from the point of view of their mineralogy, geochemistry and physico-chemical properties to find out which is the most suitable for thermotherapy and pelotherapy. Quintela et al. (2012) investigated the clay sediments in order to achieve quality criteria establishment and certification of clayey products intended to be used, especially for peloids which have therapeutic actions. Diaz-Rizo et al. (2013) have studied radioactivity levels and radiation hazard of healing mud from the San Diego River, Cuba, showing the necessity of finding the geochemical abundance of toxic elements in peloids, including radioactive elements. Muñoz et al. (2015) provided a physico-chemical characterization and elemental specification of the complex system that composes the San Diego de los Baños peloid from Thermal Center, Cuba. Knorst-Fouran et al. (2012) have described the properties of the Dax peloid and its evolution when mixed with thermal and mineral water. Da Silva et al. (2015) looked into Peruibe Black Mud characterization *in natura* and matured forms by determining some of its physical properties, mineralogical and chemical composition, radioactivity content, as well as the assessment of radiation doses arising from the mud application over the human skin during the treatment. In Italy, Cantaluppi et al. (2014) have described radionuclides concentration in water and mud of Euganean Thermal District, and Veniale et al. (2007) analysed thermal muds. Karakaya et al. (2015) studied the radioactivity concentrations and dose assessments of therapeutic peloids from some Turkish spas. In Slovenia, Glavaš et al. (2017) presented the mineralogical, geochemical and thermophysical characterization of healing saline mud for use in pelotherapy and established quality criteria necessary for safe use. Shaltout et al. (2017) studied quantitative elemental analysis and natural radioactivity levels of mud and salt collected from the Dead Sea, Jordan. All these concerns for the determination

of chemical and radioactive elements in peloids show their importance, from the point of view of the risks associated with human health and estimating doses for patients during treatment.

Thereby, the main objective of the study is to determine the activity concentrations of natural radionuclides and on this basis to estimate the doses received by the patients. The assessment of the gamma radiation dose from natural sources is of major importance as being one large contributor to the external dose of the population (Diaz-Rizo et al. 2013). In addition to this, the importance of determining the concentrations of some metals represents also a goal of this study, due to the fact that physico-chemical parameters such as salinity, pH, conductivity and temperature may influence these concentrations up to a toxic level. Some of these metals are becoming toxic when forming complexes with organic compounds, modifying the therapeutic properties, involving the transfer of chemical elements from the peloid to the human body, across the skin (Baron et al. 1990; Tateo et al. 2009).

Materials and methods

The study area

Situated on the Black Sea shore, between Techirghiol, Eforie Nord and Eforie Sud, Lake Techirghiol is the largest salt lake in Romania with a length of 7500 m (Fig. 1). It is located South–South–West from Constanta City and 150 m away from the Black Sea, in a climate specific to the Caspian–Pontic sea steppe. The lake has an irregular shape, consisting of a central basin and three branches. The Techirghiol Lake is fundamentally different from other lakes through its physico-geographic aspects, although the genesis is similar (river sea coast). From the point of view of origin, Lake Techirghiol is a former Black Sea lagoon, today separated from it. The complete disconnection of the sea is with the relatively recent date. The lake is 1.5 m below the Black Sea level, and it has a varying depth from 0.5 m to 5 m, sometimes reaching 9–10 m. The fauna consists of several species of arthropods, worms and protozoa. The flora consists of several algae species, and down to the bottom of the lake colourless sulphur bacteria predominate. Glossy and black peloid of Techirghiol Lake has a characteristic

smell. It possesses physico-chemical properties that make it extremely useful in the treatment of various diseases along with salt water.

A general overview of the chemical composition of the lake shows, in the central part, homogeneous mineralization and salinity both horizontally and vertically of approximately 90 g/L. The general characteristics of water remain constant, being a chlorine–bromine–sodium sulphate and magnesium water. Chlorine is found in the form of sodium chloride and magnesium chloride. There is an appreciable amount of bromine, its presence being another indication of the marine origin of the lake (Munteanu 2012; Gâstescu et al. 2016). The absence of iodine seems to be related to metabolic actions of the zoo- and phytoplankton.

Sampling area and analytical techniques

Salt water samples preparation

Ten water samples were collected from Techirghiol Lake, mainly from the central part of the lake, where specific peloid exploitation areas exist. Most part of the lake is under the administration of the sanatorium, which also has the right to exploit the peloid. To observe the physical parameters of salt water samples, the pH was measured with a pH meter Consort P 901 on a 10% solution according to the SR EN ISO 10523:2012. The conductivity was measured with an Electrochemical Analyzer Consort K 912, according to SR EN 27888:1997, and the density according to SR ISO 758:1995. To determine the presence of metals in salt water samples, the Optima 2100 DV ICP-OES System (PerkinElmer) with dual-view optical (axial and radial) system was used. The calibration curves were obtained by dilution from the stock solutions of 1000 mg/L ICP Multi-Element Standard Certipur (Merck) and 100 mg/L Quality Control Standard 21 (PerkinElmer) (Sarojam and PerkinElmer 2010), according to the working procedures. These analyses focused on several elements, such as concentrations of strontium, barium, manganese, antimony, iron. Other metals were also considered such as copper, lead, titan, nickel, chromium, arsenic. However, these couldn't be quantitatively determined in the salt water samples; the values obtained were below the quantification limit of the methods for determining the metals (Capra et al. 2016; Tanase et al. 2007). The optimized

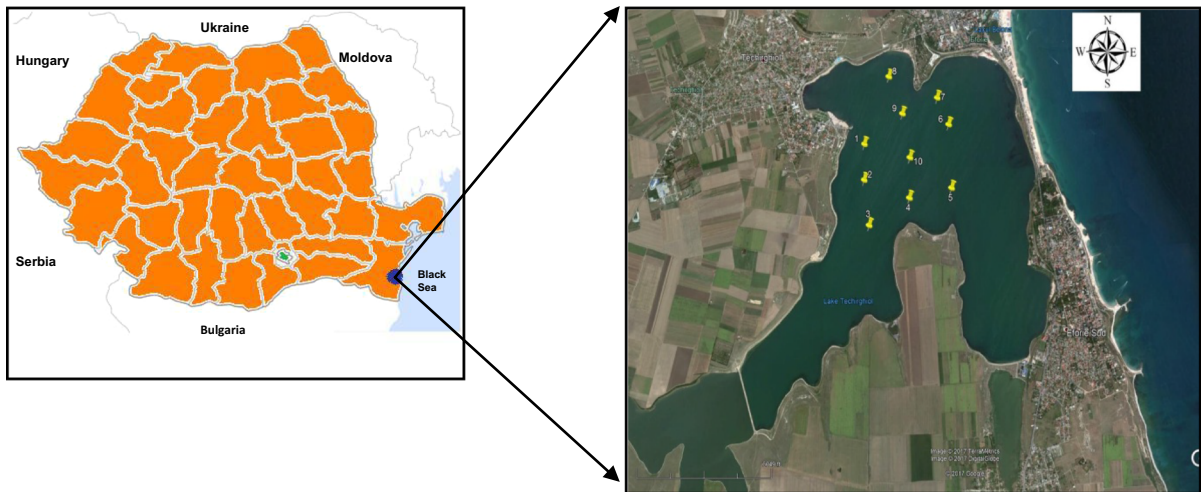


Fig. 1 Map of the studied samples from Techirghiol Lake situated on the Black Sea coast

parameters for the operation of ICP-OES equipment are presented in Capra et al. (2016). Sample analysis was performed in duplicate, keeping the same conditions as for generating the calibration curve. The correlation coefficients of the calibration curves are between 0.9970 and 0.9999, fulfilling the acceptance criterion of $r \geq 0.997$ (Tanase et al. 2007).

The major anions and cations, in salt water samples, have been determined using an ion chromatograph 850 Professional IC AnCat-MCS from Metrohm equipped with a Metrosep C4-150/4.0 column, ideal for the analysis of alkaline and earth alkaline metals in aqueous media and Metrosep C4-250/4.0 column for anions, being able to determine fluoride, hypophosphate, chlorite, bromate, chloride, nitrite, bromide, chlorate, nitrate, phosphate, sulphate and iodide anions (EPA 2007; Meng et al. 2008; Calisevici et al. 2009).

Peloid samples preparation

The peloid samples have been collected from the same points as the water samples, from depths between 6 and 9 m. These were dried at room temperature for 5 days, after which they were dried at 40 °C for 8 h, finely grounded, and then, 10 g was weighed to determine humidity at 105 °C. Subsequently, for the determination of metals by ICP-OES System (PerkinElmer), about 0.1 g of dried peloid at 105 °C was mineralized into the microwave digester (Multiwave 3000, Anton Parr GmbH, Austria) with a mixture of

HNO_3 (65%): HCl (37%): HF (50%) = 6: 2: 2 mL. As expected, more metals were found in peloid samples than in the salt water samples.

All physical–chemical analyses were performed in a RENAR accredited laboratory (gravimetric, volumetric, electrochemical, ICP-OES, etc., samples of fertilizers, biocides, waste water and drinking water, etc.) from The National Research and Development Institute for Chemistry and Petrochemistry—ICECHIM.

Radiometric analyses: experimental set-up

For gross alpha and gross beta analysis, small quantities with masses between 3.4 g and 5.6 g of both salt water and peloid samples have been measured with alpha–beta global PROTEAN ORTEC MPC-2000-DP system, in *UP ALPHA–BETA* measurement geometry. The full system is described by Calin et al. (2013) and consists of a scintillation radiation detector ZnS dual detector phosphor. The system was calibrated regarding its efficiency using sets of standard radioactive sources of ^{241}Am and of $^{90}\text{Sr-Y}$ (Calin et al. 2013) and reference samples of KCl prepared in the laboratory in two sets, each containing 7 samples. Efficiency determination as a function of sample mass geometry was used. The samples were placed in metallic trays located at 3 mm below the probe detector, inside the lead castle system, directly facing the probe detector. These were measured in 10 intervals of 100 min, the total acquisition time being of 16.7 h. In addition, a

measurement with an empty metallic tray for this specific geometry was performed to establish the background count rate (Calin et al. 2016; Radulescu et al. 2017; Pintilie et al. 2017). In order to calculate the gross α – β activity from samples, the following equation is used, Eq. 1 (Pintilie et al. 2017):

$$A(\alpha, \beta) = [(R - R_0) \times m] / (M \times \varepsilon \times m_1) \quad (1)$$

where $A(\alpha, \beta)$ is the gross α or β activity of the measured sample (Bq/kg), R is the rate of alpha or beta measurement for the sample (counts/s), R_0 is the rate of α or β , respectively, measured for background (counts/s), m is the entire mass of the sample resulted after the evaporation of water from the sample (kg), M is the mass of the fresh sample (kg), ε is the efficiency of the detector and m_1 is mass of sample transferred to a stainless steel tray for measurements (kg).

For the assessment of activity concentrations of ^{40}K , ^{238}U , ^{232}Th and ^{226}Ra , a low background coaxial p-type HPGe detector was used, with a relative efficiency of 35% and energy resolution of 1.85 keV at 1332.5 keV for ^{60}Co . The detector is used for certified activities such as radiological monitoring of the environment. The geometry used for gamma spectrometry measurements was a cylindrical plastic container of 7.5 cm diameter and 4 cm height. The samples are kept at room temperature for a month to reach secular equilibrium. The calibration of the detector for energy, peak shape and efficiency was carried out by using certified volume sources for ^{60}Co , ^{134}Cs , ^{137}Cs , ^{152}Eu and ^{241}Am supplied by the institute's Radiation Metrology Laboratory (Radulescu and Calin 2014). The spectra were acquired for the live time between 86400 s and 300000 s, in the energy range 40–2650 keV for 16384 channels. The measurements and calibration procedures were conducted in conformity with the procedures of the accredited SR EN ISO/CEI 17025: 2005 and according to designation certificate LI1653/2018 (in compliance with the criteria for the evaluation of the testing laboratories).

Results and discussion

Chemical analysis results

The water pH was 10 at 20 °C, fairly constant for all 10 samples, as well as the conductivity, at 25 °C,

where the average value was 139.2 ± 1.4 mS/cm. At the same time, the water density, for the selected points, did not vary statistically significant and the average value was 1.060 ± 0.004 kg/m³.

The concentrations of some of the elements Sr, Ba, Mn, Fe, Sb, Zn have been measured for the collected samples (Table 1). By analysing these concentrations determined in the salt water samples, it can be observed that in the case of strontium the recorded variation is not large, being between 80.8 mg/kg and 94.8 mg/kg, which is less than 15%. However, for the other metals the variations are higher than 50%, as in the case of manganese and antimony with variation between 0.16 mg/kg and 0.33 mg/kg, and 0.15 mg/kg and 0.32 mg/kg, respectively. Even greater variations are observed for barium and iron, that is 80%, from 0.15 mg/kg to 0.71 mg/kg and from 0.98 mg/kg to 4.91 mg/kg (Table 1). In terms of zinc concentrations, these were determined only in two salt water samples; thus, no variation could be highlighted. The values measured for the above elements are very low compared with international standards (Long et al. 1995), below which adverse biological effects are unlikely to occur. The determination of other metals, such as Co, Pb, Ti, Ni, Cr, As, was also desired, but their concentrations were below the quantification limit for this specific method.

Concentration values for several chemical parameters for naturally constituents present in salt waters such as ion concentrations: Na^+ , K^+ , Ca^{2+} , Mg^{2+} , F^- , Cl^- , Br^- , SO_4^{2-} , NO_3^- , NO_2^- , PO_4^{3-} , NH_4^+ are shown in Table 2. As expected, this is highlighting the character of the water, where high concentrations are observed for Na^+ , Cl^- , Mg^{2+} and SO_4^{2-} , while for K^+ , Ca^{2+} and Br^- concentrations are in the order of a few tens. Instead, concentrations of nitrates, nitrites and phosphates are rather low, since in some samples these were not determined, meaning that those values were lower than the determination limit. These samples were subject to assay the ammonium concentration. For the first three cations, namely Na^+ , K^+ and Ca^{2+} , the variations in their values are within 30%; for Mg^{2+} , F^- , Cl^- , the variations are between 45 and 64%; for Br^- , SO_4^{2-} these are lower, around 16%. Three anions, namely NO_3^- , PO_4^{3-} and NH_4^+ , have large variations of 98%, 83% and 77%, respectively. Ammonium anions are a waste product of the metabolism of animals, from fish and aquatic invertebrates, and its concentrations are normal values for the type of water.

Table 1 Element's concentrations (mg/kg) in Techirghiol Lake's salt water samples

Samples	Strontium $\lambda = 407.771$ nm (mg/kg) $\pm 1\sigma$	Barium $\lambda = 233.527$ nm	Manganese $\lambda = 257.610$ nm	Iron $\lambda = 238.204$ nm	Antimony $\lambda = 206.836$ nm	Zinc $\lambda = 213.587$ nm
WS 1	89.2 \pm 0.8	0.50 \pm 0.03	0.33 \pm 0.02	1.63 \pm 0.06	0.22 \pm 0.06	2.57 \pm 0.06
WS 2	88.0 \pm 0.7	0.70 \pm 0.04	0.24 \pm 0.01	2.56 \pm 0.06	0.26 \pm 0.06	< 0.61*
WS 3	86.2 \pm 0.7	0.18 \pm 0.02	0.16 \pm 0.01	1.34 \pm 0.05	0.26 \pm 0.06	< 0.61*
WS 4	90.7 \pm 0.8	0.22 \pm 0.03	0.21 \pm 0.01	4.90 \pm 0.07	0.20 \pm 0.05	< 0.61*
WS 5	87.7 \pm 0.8	0.16 \pm 0.02	0.16 \pm 0.01	< 0.9*	0.27 \pm 0.06	< 0.61*
WS 6	94.8 \pm 0.8	0.20 \pm 0.02	0.17 \pm 0.01	< 0.9*	0.32 \pm 0.07	< 0.61*
WS 7	80.8 \pm 0.7	0.15 \pm 0.02	0.16 \pm 0.01	n.p.**	n.p.**	n.p.**
WS 8	84.2 \pm 0.7	0.18 \pm 0.02	0.29 \pm 0.02	4.50 \pm 0.07	0.26 \pm 0.06	< 0.61*
WS 9	85.0 \pm 0.7	0.16 \pm 0.02	0.20 \pm 0.01	1.00 \pm 0.04	0.15 \pm 0.04	< 0.61*
WS 10	90.0 \pm 0.8	0.32 \pm 0.03	0.16 \pm 0.01	3.60 \pm 0.06	0.20 \pm 0.05	1.86 \pm 0.06
Mean	87.7 \pm 1.2	0.28 \pm 0.06	0.21 \pm 0.02	2.8 \pm 0.6	0.24 \pm 0.06	2.22 \pm 0.36

Copper (mg/kg), $\lambda = 327.393$ nm, < 2.1*, lead (mg/kg), $\lambda = 220.353$ nm, < 1.0*, titanium (mg/kg), $\lambda = 334.940$ nm, < 1.2*, nickel (mg/kg), $\lambda = 231.604$ nm, < 0.32*, chromium (mg/kg), $\lambda = 267.71$ nm, < 2.2*, arsenic (mg/kg), $\lambda = 228.812$ nm, < 0.47*

*Values represent the limit of quantification (LoQ) of metal determination methods

**n.p. not presented

Table 2 Concentrations for anions and cations (mg/L) of Techirghiol Lake's salt water samples

Samples	Na ⁺ (mg/L)	K ⁺	Ca ²⁺	Mg ²⁺	F ⁻	Cl ⁻	Br ⁻	SO ₄ ²⁻	NO ₃ ⁻	NO ₂ ⁻	PO ₄ ³⁻	NH ₄ ⁺
WS 1	3804	97.6	41.2	479	0.13	1383	14.0	618	0.01	0.01	0.07	0.10
WS 2	3200	83.5	35.5	403	0.27	625	14.7	701	0.10	n.d.	0.16	0.25
WS 3	3346	87.0	37.2	422	0.28	723	15.7	742	0.01	n.d.	0.42	0.12
WS 4	3236	84.0	35.5	409	0.30	714	15.0	728	0.01	0.52	0.20	0.10
WS 5	2888	75.0	31.4	365	0.25	558	13.7	661	0.20	n.d.	n.d.	0.35
WS 6	2920	76.3	32.2	370	0.27	627	14.0	679	0.40	0.40	0.17	0.40
WS 7	2571	67.8	28.2	262	0.23	495	13.0	634	0.01	0.20	0.20	0.15
WS 8	2991	78.0	33.0	377	0.30	1018	15.4	745	0.01	0.02	0.10	0.16
WS 9	2896	75.4	31.4	363	0.30	1016	15.5	744	0.02	n.d.	n.d.	0.20
WS 10	2910	76.2	32.7	366	0.30	1017	15.5	744	0.01	n.d.	n.d.	0.16

n.d. not determined

The average concentration values for major elements such as magnesium, calcium, potassium and iron (Table 3) are $(27.6 \pm 1.3) \times 10^3$ mg/kg, $(94.7 \pm 7.5) \times 10^3$ mg/kg, $(12.1 \pm 0.3) \times 10^3$ mg/kg and $(19.9 \pm 0.5) \times 10^3$ mg/kg, respectively. According to the presented data, there are positive correlations between the concentrations of magnesium/calcium and iron/potassium, since between the magnesium/potassium and iron/magnesium the

correlations are negative (Fig. 2). Values of continental crust (CC) and upper continental crust (UCC) for the major element's concentrations are presented for comparison (Table 3), but these are different and only the magnesium values are close to the CC concentrations, most likely due to variations in regional background levels. Quantitative analysis results of peloids for Dead Sea (Shaltout et al. 2017) show similar values of $(32.5 \pm 9.8) \times 10^3$ mg/kg for Mg,

Table 3 Concentrations for major elements (mg/kg) ± 1σ in peloid samples from the Techirghiol Lake, Romania

Samples	Magnesium λ = 279.077 nm × 10 ³ (mg/kg)	Calcium λ = 317.933 nm	Potassium λ = 766.490 nm	Iron λ = 238.204 nm
PS 1	35.0 ± 0.2	131 ± 0.5	10.0 ± 0.1	16.7 ± 0.2
PS 2	24.3 ± 0.1	80 ± 0.4	12.7 ± 0.2	21.7 ± 0.3
PS 3	20.4 ± 0.1	52 ± 0.3	13.0 ± 0.2	21.0 ± 0.3
PS 4	24.8 ± 0.2	69.3 ± 0.3	13.0 ± 0.1	20.7 ± 0.2
PS 5	26.2 ± 0.2	90 ± 0.1	13.0 ± 0.1	20.2 ± 0.2
PS 6	30.7 ± 0.3	118 ± 0.3	11.2 ± 0.1	18.2 ± 0.1
PS 7	29.4 ± 0.2	111 ± 0.2	12.3 ± 0.2	20.5 ± 0.2
PS 8	28.3 ± 0.2	11 ± 0.2	11.4 ± 0.1	19.0 ± 0.1
PS 9	30.0 ± 0.2	94 ± 0.1	12.0 ± 0.1	19.7 ± 0.2
PS 10	26.6 ± 0.2	91.7 ± 0.1	12.5 ± 0.2	20.8 ± 0.2
CC*	23.3	41.5	20.9	56.3
UCC**	15.0	25.7	23.2	39.2
Mean	27.6 ± 0.13	94.7 ± 0.8	12.1 ± 0.3	19.9 ± 0.48

CC*: Continental crust (Taylor 1964)

UCC**: Upper continental crust (Rudnick and Gao 2003)

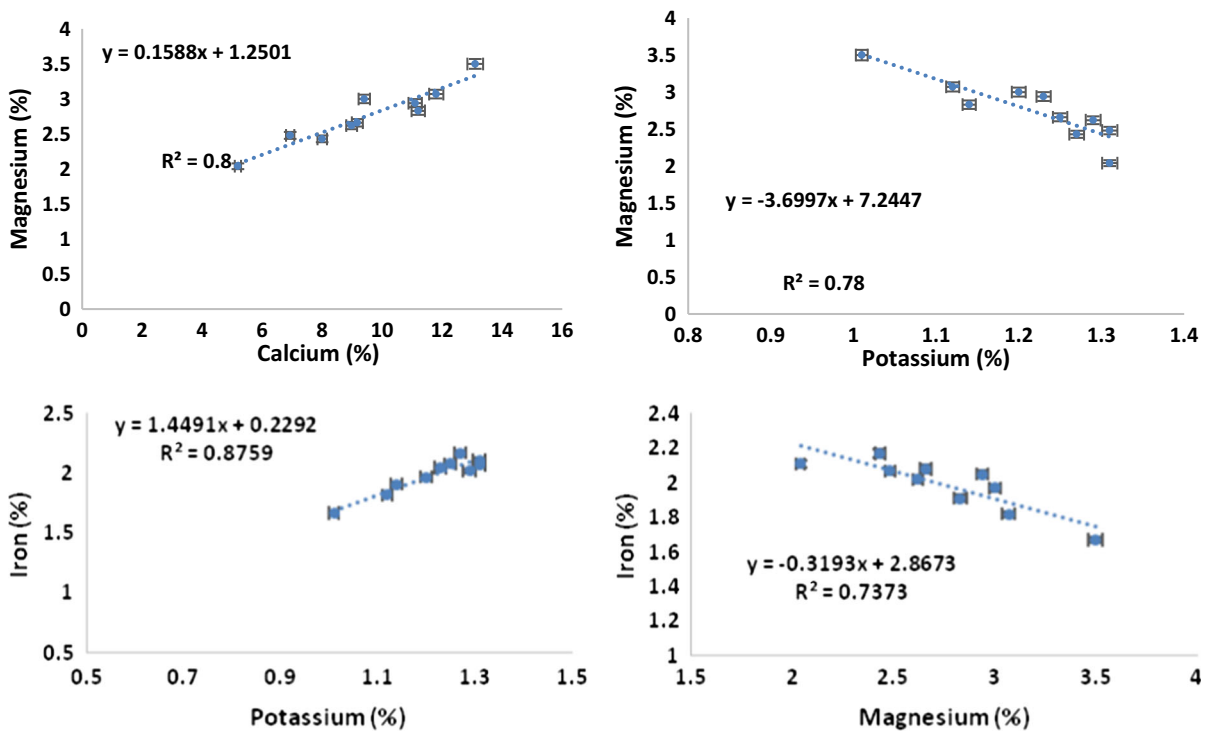


Fig. 2 Relations between concentrations of magnesium versus calcium, magnesium versus potassium, iron versus potassium and iron versus magnesium determined in peloid samples

(180 ± 17) × 10³ mg/kg for Ca, (22.2 ± 2.0) × 10³ mg/kg for K and (41.8 ± 4.1) × 10³ mg/kg for Fe.

Elements and metals concentrations measured in the Techirghiol Lake’s peloid samples (Table 4) were

in average 401 ± 38 mg/kg for Sr, 230 ± 7 mg/kg for Ba, 334 ± 25 mg/kg for Mn, 56.6 ± 1.5 mg/kg for Zn, 21.5 ± 0.8 mg/kg for Cu, 29.5 ± 1.1 mg/kg for Cr, 2.7 ± 0.6 mg/kg for Pb, 4.5 ± 1.0 mg/kg for

Ni and 2242 ± 82 mg/kg for Ti. Then, these concentrations were compared with other values reported by other authors for the peloid samples. A good agreement exists between values reported by Maor et al. (2006) for the Dead Sea black mineral mud and values reported in this paper for Sr, Ba, Mn, Zn, Cu and Pb. The values for Cr and Ni presented in Table 4 are lower than those in Dead Sea black mineral mud. Da Silva et al. (2015) found slightly higher values in Peruibe Black Mud than in Techirghiol peloid. The metals concentrations reported in soil and sediment samples from Bedimahi river by Zorer et al. (2009) are considerably higher than the values reported in this paper. Moreover, the threshold effect level (TEL) and probable effect level (PEL) were considered to quantify if adverse effects can occur for reported values. It can be easily observed that all values are well below TEL for which adverse biological effects rarely occur, except for copper. However, the average value of copper is below value considered by US EPA for marine sediment quality guidelines (SQGs), that is, 25 mg/kg for non-polluted sediments (EPA 2012).

A direct comparison of the measured elements and metals concentrations shows that the lowest are those specific to lead and nickel (Fig. 3). For these two metals, in some samples, the concentration values were lower than the limit of quantification for this specific determination method. The maximum determined value for lead was 4.9 mg/kg, which is lower than 12.1 mg/kg previously obtained by Radulescu et al. (2014). Also, in the case of nickel, the maximum value was 8.6 mg/kg which is two-fold smaller than 17.5 mg/kg reported by Radulescu (2014). Only in the case of manganese, their value of 92.5 mg/kg is five-fold smaller than the maximum value reported in this paper, 466.6 mg/kg. The elements and metals concentrations, in the peloids, do not have a strong correlation with each other, as shown in Fig. 3 and Table 5. Only in few cases, there are some relatively weak correlations, as can be observed from the Pearson correlation coefficients (Table 5).

The most obvious positive correlation is between manganese and strontium (Figs. 3, 4, Table 5) where the correlation coefficient is 0.75. Another positive correlation is seen between chromium and titanium (Fig. 4). Negative correlations are observed between chromium/strontium and zinc/strontium (Fig. 4). Other dependences are not observed for elements determined in peloid samples.

Differences in the results are due to the fact that trace metals in peloid may exist in different chemical forms or ways of binding. Trace metals may be recycled via chemical and biological processes, within the sedimentary compartment and back to the water media (Leschber et al. 1985; Tessier and Campbell 1987). Trace metals can be deposited and incorporated into peloid after entering the aquatic system, being an integral and dynamic part of the lake. The mobility and bioavailability of the metals varied significantly with the peloid properties: particle size, organic matter, carbonates, pH, redox potential and water dynamic.

Elements and metal concentrations and distributions are, in general, influenced by regional background levels (Grigoras et al. 2012), where geological factors are major controls for their distribution. These trace metals in the sediments have distinct geochemical behaviours, possibly originating from anthropogenic sources through inputs of water and air (Mardomingo et al. 2015; Kusin et al. 2018).

Radiometric results

Activity concentrations

The gross alpha and gross beta activity together with isotopes concentrations of ^{40}K , ^{238}U , ^{232}Th and ^{226}Ra in Techirghiol Lake is calculated for the salt water samples (WS1–WS10) and in peloid samples (PS1–PS10) (Table 6). The activity concentrations for all types of measurements have values considerable higher in peloid than in salt water samples. The average activity concentrations for ^{40}K , ^{238}U , ^{232}Th and ^{226}Ra in peloid samples are 95.8 ± 5.5 Bq/kg, 5.7 ± 1.0 Bq/kg, 6.85 ± 1.60 Bq/kg and 15.3 ± 3.7 Bq/kg, respectively. The activity concentrations measured for all ten points are rather similar and cannot be concluded that there is any measurement point that shows abnormal values or is influenced by anthropogenic activities. Comparing the activities reported in peloids for ^{226}Ra , the results are similar to data presented by Shaltout et al. (2017), where a value of 14 Bq/kg is measured for mud from the Dead Sea Jordan and also by Da Silva et al. (2015), wherein an average of 15 Bq/kg is obtained for Peruibe Black mud. Other authors reported values slightly higher (Diaz-Rizo et al. 2013; Jonas et al. 2018). All reported values for ^{40}K are higher than those presented in Table 6, the same situation occurring for ^{232}Th and

Table 4 Concentrations of elements and metals (mg/kg) in Techirghiol Lake’s peloid samples

Samples	Strontium $\lambda = 407.771$ nm (mg/kg) $\pm 1\sigma$	Barium $\lambda = 233.527$ nm	Manganese $\lambda = 257.610$ nm	Zinc $\lambda = 213.587$ nm	Copper $\lambda = 327.393$ nm	Chromium $\lambda = 267.716$ nm	Lead $\lambda = 220.353$ nm	Nickel $\lambda = 231.604$ nm	Titanium $\lambda = 334.940$ nm
PS1	626 \pm 8	191 \pm 9	372 \pm 4	48.0 \pm 0.6	19.2 \pm 0.3	21.4 \pm 0.2	0.8 \pm 0.1	< 1.43*	1869 \pm 4
PS2	313 \pm 4	233 \pm 11	285 \pm 3	60.5 \pm 0.8	26.7 \pm 0.4	30.5 \pm 0.3	3.0 \pm 0.5	6.0 \pm 0.3	2582 \pm 5
PS3	195 \pm 2	201 \pm 9	238 \pm 2	59.8 \pm 0.7	20.0 \pm 0.3	30.6 \pm 0.3	1.4 \pm 0.2	4.0 \pm 0.2	2164 \pm 4
PS4	294 \pm 4	224 \pm 10	272 \pm 3	55.7 \pm 0.7	21.0 \pm 0.3	31.8 \pm 0.4	< 0.3*	2.6 \pm 0.1	2296 \pm 4
PS5	333 \pm 4	237 \pm 11	277 \pm 3	55.7 \pm 0.7	24.0 \pm 0.4	28.5 \pm 0.3	3.3 \pm 0.5	5.2 \pm 0.3	2213 \pm 4
PS6	437 \pm 5	227.3 \pm 11	348 \pm 4	59.0 \pm 0.7	22.5 \pm 0.4	26.6 \pm 0.3	5.0 \pm 0.7	< 1.4*	2180 \pm 4
PS7	480 \pm 6	246 \pm 11	467 \pm 5	58.4 \pm 0.7	20.3 \pm 0.3	30.6 \pm 0.3	4.0 \pm 0.6	1.7 \pm 0.1	2308 \pm 4
PS8	483 \pm 6	234 \pm 11	453 \pm 5	52.0 \pm 0.6	20.0 \pm 0.3	30.6 \pm 0.3	< 0.28*	< 1.43*	2332 \pm 5
PS9	425 \pm 5	261 \pm 12	335 \pm 3	53.0 \pm 0.7	17.8 \pm 0.3	32.8 \pm 0.4	< 0.28*	3.7 \pm 0.2	2222 \pm 4
PS10	419 \pm 5	246 \pm 11	291 \pm 3	64.0 \pm 0.7	23.6 \pm 0.4	31.7 \pm 0.4	1.4 \pm 0.2	8.6 \pm 0.4	2257 \pm 4
Mean	401 \pm 38	230 \pm 7	334 \pm 25	56.6 \pm 1.5	21.5 \pm 0.8	29.5 \pm 1.1	2.7 \pm 0.6	4.5 \pm 1.0	2242 \pm 82
TEL	-	-	460	120–124	18.7	52.3	30.2–46.7	16.0	-
PEL	-	-	-	271	108	160	112	42.8	-

Antimony (mg/kg), $\lambda = 206.836$ nm, < 1.81*

TEL: threshold effect level (MacDonald et al. 1996); PEL: probable effect level (MacDonald et al. 1996)

*Values represent the limit of quantification (LoQ) of metal determination methods

Fig. 3 Distribution per samples of the concentration of metals (mg/kg) determined in Techirghiol Lake's peloid

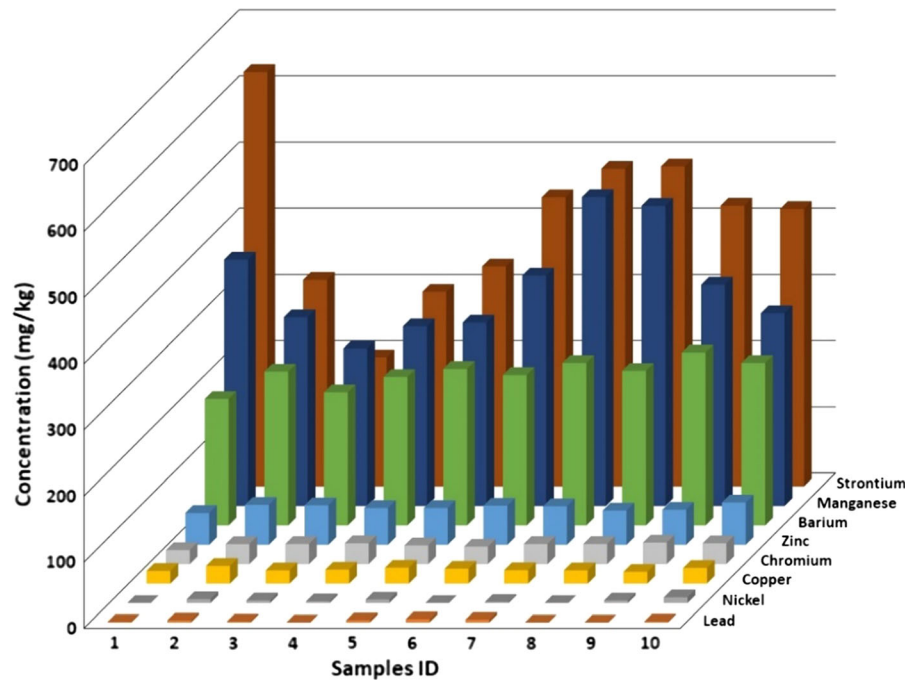


Table 5 Pearson correlation coefficient between elements in peloid samples with 95% level of confidence

Variable	Manganese	Copper	Zinc	Barium	Chromium	Strontium	Lead	Nickel	Titanium
Manganese	1								
Copper	− 0.39	1							
Zinc	− 0.41	0.61	1						
Barium	0.20	0.11	0.29	1					
Chromium	− 0.18	0.07	0.49	0.69	1				
Strontium	0.75	− 0.35	− 0.56	− 0.02	− 0.58	1			
Lead	0.39	0.29	0.24	0.56	0.17	− 0.04	1		
Nickel	− 0.47	0.60	0.63	0.13	− 0.04	0.00	− 0.61	1	
Titanium	− 0.54	0.58	0.52	0.55	0.70	− 0.48	0.42	0.14	1

^{238}U (Diaz-Rizo et al. 2013; Shaltout et al. 2017; Jonas et al. 2018). The concentration of each radionuclide is lower than the world average values (UNSCEAR 2000). As a novelty, gross alpha and gross beta activities were determined in these samples to provide basic information to consumers and competent authorities regarding the exposure risk due to accidentally intake of salt water. The values for gross alpha activities and gross beta activities were in the ranges of 0.13–0.22 Bq/kg and 0.99–4.52 Bq/kg, respectively. The composition of natural peloids depends on their origin, making comparison difficult with other

samples of peloids from other parts of the world. The results can serve, in the future, as a comparison when evaluating contribution from radionuclides released to the environment as a result of any human practices in the studied area.

Radiological hazard indices

In the context of radiological risk assessment of using salt water and peloid in relatively long treatment periods, few radiological indices are calculated to

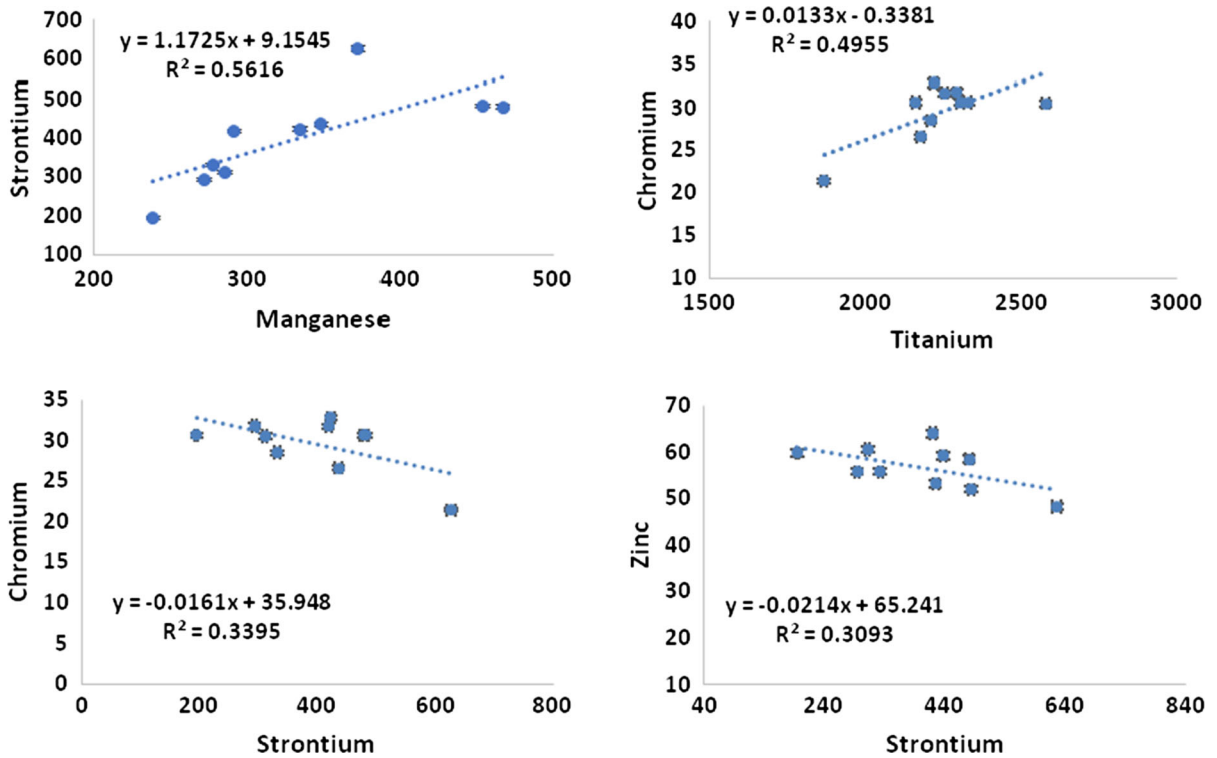


Fig. 4 Dependences between concentrations (mg/kg) of strontium versus manganese, chromium versus titanium, chromium versus strontium and zinc versus strontium

observe if the radionuclides content can be harmful to human health (Table 7).

Radium equivalent activity (Ra_{eq})

Due to the fact that radium can be strongly adsorbed in mineral oxides present in peloid or by organic material, the radium equivalent hazard index is first calculated. Few models have been developed in order to keep the radiation dose limit due to a certain material to 1.5 mGy (1 mSv). It has been concluded that an activity concentration of 370 Bq/kg (1 μ Ci/g) of ^{226}Ra , uniformly distributed in material, will give an annual dose of 1.5 mGy. This index has been in practice for the last 40 years for the assessment of the radiological hazard in environmental materials (Tufail 2012). It is also used when comparing specific activities of samples containing different concentrations of ^{226}Ra , ^{232}Th and ^{40}K . It is defined on the assumption that 10 Bq/kg of ^{226}Ra , 7 Bq/kg of ^{232}Th and 130 Bq/kg of ^{40}K produce the same gamma radiation exposure dose rate which is calculated as in

Eq. 2 (Shaltout et al. 2017; Beretka and Mathew 1985):

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \tag{2}$$

where C_{Ra} , C_{Th} and C_K are the activity concentrations for the three radionuclides in Bq/kg. It can be noted that all values of Ra_{eq} for peloid and salt water samples (Table 7) are lower than the recommended maximum value of 370 Bq/kg (ICRP 1991).

Absorbed gamma dose rate (D)

Another important index that takes into consideration the contribution of gamma radiations from naturally occurring radionuclides ^{226}Ra , ^{232}Th and ^{40}K is the absorbed dose rate calculated in Eq. 3, based on guidelines provided by ICRP and UNSCEAR (ICRP 1991; UNSCEAR 1993, 2000).

$$D_{out} = 0.462C_{Ra} + 0.604C_{Th} + 0.0417C_K \tag{3}$$

Equation 3 uses conversion factors to compute absorbed gamma dose rate (D) of 0.462 nGyh⁻¹/

Table 6 Gross alpha, gross beta and gamma activities concentrations ($\pm 1\sigma$) of the salt water and peloid samples

Sample code water/ peloid	Total residue $\times 10^{-3}$ [kg]	Residue for gross alpha and gross beta	Gross α [Bq/kg]	Gross β [Bq/kg]	^{40}K	^{238}U	^{232}Th	^{226}Ra
WS1	132	3.43	0.20 \pm 0.01	4.43 \pm 0.20	16.3 \pm 0.5	0.64 \pm 0.05	0.38 \pm 0.05	< 0.68 (MDA)
WS2	129	4.18	0.17 \pm 0.01	2.10 \pm 0.23	18.2 \pm 0.6	0.20 \pm 0.02	< 0.54 (MDA)	< 0.76 (MDA)
WS3	127	5.05	0.17 \pm 0.01	1.00 \pm 0.20	18.7 \pm 0.6	0.50 \pm 0.04	< 0.65 (MDA)	0.88 \pm 0.08
WS4	123	5.00	0.17 \pm 0.01	1.60 \pm 0.16	17.6 \pm 0.5	0.30 \pm 0.03	< 0.60 (MDA)	0.50 \pm 0.04
WS5	128	4.25	0.13 \pm 0.01	4.52 \pm 0.24	16.0 \pm 0.5	0.68 \pm 0.06	< 0.45 (MDA)	< 0.87 (MDA)
WS6	123	3.83	0.22 \pm 0.01	2.40 \pm 0.22	17.8 \pm 0.6	0.38 \pm 0.03	< 0.28 (MDA)	0.47 \pm 0.03
WS7	137	5.60	0.18 \pm 0.01	2.95 \pm 0.12	17.6 \pm 0.6	0.88 \pm 0.08	< 0.44 (MDA)	0.70 \pm 0.06
WS8	174	4.60	0.20 \pm 0.01	4.07 \pm 0.22	15.4 \pm 0.5	< 0.43 (MDA)	0.36 \pm 0.06	< 0.65 (MDA)
WS9	127	4.06	0.22 \pm 0.01	2.48 \pm 0.22	20.2 \pm 0.6	0.26 \pm 0.02	0.12 \pm 0.01	0.45 \pm 0.14
WS10	169	4.95	0.18 \pm 0.01	3.38 \pm 0.16	17.0 \pm 0.6	< 0.47 (MDA)	< 0.38 (MDA)	< 0.67 (MDA)
Mean $\pm 1\sigma$	137 \pm 6	4.50 \pm 0.20	0.18 \pm 0.01	2.90 \pm 0.40	17.5 \pm 1.3	0.48 \pm 0.10	0.30 \pm 0.08	0.60 \pm 0.10
Range	123–174	3.43–5.60	0.13 \pm 0.01–0.22 \pm 0.01	1.00 \pm 0.20–4.52 \pm 0.24	15.4 \pm 0.5–20.2 \pm 0.6	MDA–0.88 \pm 0.08	MDA–0.38 \pm 0.05	MDA–0.88 \pm 0.08
UNSCEAR 2008					420		45	35
PS1	194	4.10	5.56 \pm 0.44	134.7 \pm 2.2	95.4 \pm 3.2	6.30 \pm 0.70	6.40 \pm 0.85	17.2 \pm 1.2
PS2	194	2.52	7.50 \pm 0.77	210.4 \pm 4.7	96.1 \pm 3.2	6.87 \pm 0.40	5.84 \pm 0.67	15.2 \pm 1.0
PS3	189	2.68	4.40 \pm 0.38	175.9 \pm 2.3	68.8 \pm 2.4	4.33 \pm 0.36	4.43 \pm 0.74	8.3 \pm 1.0
PS4	198	3.98	4.95 \pm 0.46	172.3 \pm 3.3	88.8 \pm 2.7	4.37 \pm 0.33	5.50 \pm 0.75	11.0 \pm 0.5
PS5	192	3.82	5.25 \pm 0.36	192.7 \pm 2.2	78.9 \pm 2.6	4.25 \pm 0.30	7.60 \pm 0.87	14.7 \pm 1.0
PS6	204	4.19	6.13 \pm 0.55	162.3 \pm 2.0	99.2 \pm 3.2	5.96 \pm 0.35	5.30 \pm 0.57	20.8 \pm 1.2
PS7	210	4.60	3.20 \pm 0.35	124.4 \pm 1.1	128.0 \pm 4.1	5.80 \pm 0.30	9.60 \pm 0.80	18.7 \pm 1.1
PS8	217	3.56	5.80 \pm 0.35	203.4 \pm 6.1	116.6 \pm 3.6	6.68 \pm 0.67	9.50 \pm 1.14	18.9 \pm 0.8
PS9	198	3.89	3.10 \pm 0.26	128.4 \pm 1.4	100.66 \pm 3.3	6.50 \pm 0.60	6.70 \pm 0.80	15.9 \pm 1.0
PS10	193	2.97	6.80 \pm 0.55	231.2 \pm 4.3	85.54 \pm 2.8	6.00 \pm 0.30	7.60 \pm 0.75	12.4 \pm 0.8
Mean $\pm 1\sigma$	199 \pm 3.0	3.63 \pm 0.22	5.30 \pm 0.45	173.6 \pm 11.6	95.8 \pm 5.5	5.70 \pm 1.00	6.85 \pm 1.60	15.3 \pm 3.7
Range	192–217	2.52–4.61	3.09 \pm 0.26–7.49 \pm 0.77	124.4 \pm 1.1–231.2 \pm 4.3	68.8 \pm 2.4–128.0 \pm 4.1	4.25 \pm 0.30–6.87 \pm 0.40	4.43 \pm 0.74–9.59 \pm 0.83	8.3 \pm 1.0–20.8 \pm 1.2
UNSCEAR 2008					400		33	37

Table 7 Radiation hazard parameters—radium equivalent activity, absorbed dose rate, annual effective dose, gamma index, external hazard index, the excess lifetime risks of cancer for salt water and peloid samples

No.	Waters and sludges samples	R _{aq} [Bq/kg]	D [nCy/h]	AED [μ Sv/y]	I _{gr}	H _{ex}	ELCR ($\times 10^{-3}$)
1.	WS1	1.80	0.90	1.10	0.015	0.005	0.004
2.	WS2	1.40	0.76	0.93	0.012	0.004	0.004
3.	WS3	2.32	1.20	1.45	0.018	0.006	0.006
4.	WS4	1.85	0.96	1.20	0.015	0.005	0.005
5.	WS5	1.22	0.66	0.80	0.010	0.003	0.003
6.	WS6	1.84	0.96	1.18	0.015	0.005	0.005
7.	WS7	2.05	1.06	1.30	0.016	0.006	0.005
8.	WS8	1.70	0.86	1.06	0.014	0.005	0.004
9.	WS9	2.20	1.12	1.40	0.018	0.006	0.005
10.	WS10	1.30	0.70	0.87	0.010	0.004	0.003
	Mean	1.77	0.92	1.13	0.014	0.005	0.004
	Range	1.22–2.32	0.66–1.19	0.81–1.45	0.010–0.018	0.003–0.006	0.003–0.006
	World	–	60	–	–	< 1	0.07
11.	PS1	33.7	15.8	19.4	0.24	0.10	0.07
12.	PS2	31.0	14.5	17.8	0.22	0.08	0.07
13.	PS3	20.0	9.4	11.5	0.15	0.05	0.04
14.	PS4	25.7	12.1	14.8	0.20	0.07	0.06
15.	PS5	31.7	14.7	18.0	0.23	0.10	0.07
16.	PS6	36.0	17.0	20.8	0.26	0.10	0.08
17.	PS7	42.3	19.8	24.3	0.30	0.10	0.09
18.	PS8	41.5	19.3	23.7	0.30	0.10	0.09
19.	PS9	33.2	15.6	19.1	0.24	0.10	0.07
20.	PS10	29.8	14.0	17.0	0.22	0.08	0.07
	Mean	32.5	15.2	18.6	0.23	0.10	0.07
	Range	20.0–42.3	9.4–19.8	11.5–24.3	0.15–0.30	0.05–0.10	0.04–0.09
	World	–	60	70	–	< 1	0.07
	Otansev et al. (2016)	100.0	48.3	–	–	0.27	–
	El-Taher et al. (2018a)	69.5–102	34–49.5	42–60.5	0.22–0.33	–	0.15–0.21
	Shaltout et al. (2017)	118	57	69	0.9	–	–
	El-Taher et al. (2018b)	33.1	16.1	20	0.25	–	–
	Diaz-Rizo et al. (2013)	82	40	48.5	–	0.23	–
	Karakaya et al. (2015)	257	118	0.26–2.78	–	–	0.001–0.005

Bqkg⁻¹ for ²²⁶Ra, 0.604 nGyh⁻¹/Bqkg⁻¹ for ²³²Th and 0.0417 nGyh⁻¹/Bqkg⁻¹ for ⁴⁰K and the assumption that other radionuclides such as ¹³⁷Cs or ²³⁵U decay series have a negligible contribution to the total dose. C_{Ra} , C_{Th} and C_K from Eq. 3 have the same meaning as in Eq. 2.

The experimental results for the absorbed dose rate in the air are ranging from 0.66 nGy/h to 1.19 nGy/h for salt water samples and from 9.38 nGy/h to 19.77 nGy/h for peloid samples.

Annual effective dose (AED)

To estimate the annual effective dose, the conversion coefficient (0.7 SvGy⁻¹) from the absorbed dose in the air to the effective dose and the outdoor occupancy factor (20%) must be considered. The annual effective dose (AED) outdoors in units of μSv/y is calculated by the following formula, Eq. 4:

$$\text{AED } (\mu\text{Sv/y}) = D_{\text{out}}(\text{nGy/h}) \times 0.2 \times 24(\text{h}) \times 365.25(\text{d}) \times 0.7 \mu\text{Sv/y} \times 10^{-3} \quad (4)$$

The values for the annual effective dose in the air are in average of 1.13 μSv/y for salt water samples and of 18.6 μSv/y for peloid samples. The maximum calculated value for peloid sample was 24.3 μSv/y for the sample 7 because of the high values activities concentrations for ⁴⁰K and ²³²Th. The annual effective dose rate results are ranging from 0.80 to 1.45 μSv/y for salt water samples and from 11.50 μSv/y to 24.25 μSv/y for peloid samples. The annual equivalent world average for outdoor terrestrial gamma radiation is 70 μSv/y, higher than the presented values.

Gamma radiation hazard index ($I_{\gamma r}$)

Radiation hazards due to the natural radionuclides of ²²⁶Ra, ²³²Th and ⁴⁰K were assessed by another index called representative level index, $I_{\gamma r}$ (Beretka and Mathew 1985), calculated with Eq. 5:

$$I_{\gamma r} = C_{Ra}/150 + C_{Th}/100 + C_K/1500 \quad (5)$$

where C_{Ra} , C_{Th} and C_K are the activity concentrations (Bq/kg). The average $I_{\gamma r}$ in salt water and peloid samples is 0.014 and 0.23, respectively.

External hazard index (H_{ex})

The external hazard index (H_{ex}) for the samples under analysis is given by Eq. 6 (Beretka and Mathew 1985). The aim of this index is to keep the values less than unity in order to keep the health hazard risk as low as possible.

$$H_{ex} = C_{Ra}/370 + C_{Th}/259 + C_K/4810 \leq 1 \quad (6)$$

where C_{Ra} , C_{Th} and C_K (Bq/kg) are described above. This index has very low values for salt water samples with an average of 0.005, but for peloid samples the average value is 0.10.

Excess lifetime cancer risk (ELCR)

The excess lifetime risk of cancer (ELCR) was calculated using Eq. 7:

$$\text{ELCR} = \text{AED } (\mu\text{Sv/y}) \times \text{DL } (\text{y}) \times \text{RF } (1/\text{Sv}) \quad (7)$$

where AED is annual effective dose rate defined as in Eq. 4, DL is the lifetime (70 years) and RF is the risk factor (1/Sv) that is fatal cancer risk per Sievert. The 103 report of ICRP (2007) uses a value of 0.055 for the nominal risk coefficient adjusted to the detriment of cancer for stochastic effects after a small dose rate radiation exposure to the public (Gomes et al. 2018).

The highest values for excess lifetime risks of cancer are for samples 7 and 8 (Table 7). These samples are collected from the northern part of the lake, where increased activities concentrations of ²²⁶Ra are observed. This rise of values could be due to human activities in the coastal area. The lowest values were found in the southern part of the lake where there is less influence from human activities. Values presented in Table 7 are in the same order of magnitude or somewhat smaller than others presented in the literature Diaz-Rizo et al. (2013), Karakaya et al. (2015), El-Arabi (2005), Otansev et al. (2016), Shaltout et al. (2017) and El-Taher et al. (2018a, b).

All calculated values for the radiological indices (radium equivalent activity, absorbed gamma dose rate, annual effective dose, gamma radiation hazard index, external hazard index and excess lifetime cancer risk) are lower than world average or the maximum allowed level defined by UNSCEAR and ICRP.

Conclusions

In this paper, were analysed and investigated from both chemical and radiometric perspective ten samples of salt water and peloid originating from Techirghiol Lake, which represents the most known and intensively used area in Romania for therapeutic purposes. The chemical composition highlighted the chlorine–sodium, magnesium, sulphurous and brominated character of water, as these elements presented relatively high concentrations. The results of the chemical analyses of water and peloid samples show variations in the elements concentrations, but measured values are very low compared with international standards, for which adverse biological effects are unlikely to occur. These variations have rather weak correlations between the elements, but also between the water and peloid from the same point of measurement. By analysing the results presented in Tables 1, 3 and 4, can assert that the increase in element's concentrations does not highlight a clear influence from human activity, close to shore and settlements. The elements detected in peloids are within the limits, and their concentrations are below the maximum allowance level.

Pelotherapy is a very old therapeutic practice, whose efficacy can be documented by modern techniques and clinical observations. Experiments showed that the amount transferred across the skin depends on the element's concentration in the water and peloid. However, the exchangeable fraction is negligible with respect to the high salinity of the water, but still, after 20 min of peloid application only few chemical elements cross the skin.

Another objective of the study was to determine the activity concentration of natural radionuclides and based on them to estimate the doses received by patients. The assessment of the gamma radiation dose from natural sources is of major importance, being one large contributor to the external dose of the population. The annual effective doses to the public were between 11.5 $\mu\text{Sv}/\text{y}$ and 24.3 $\mu\text{Sv}/\text{y}$, representing two orders of magnitude lower than the reference level of 1 mSv per year. The radiological impact of natural radionuclides was estimated for the gamma-ray exposure of the full body. The measured specific activity concentrations for the ^{238}U , ^{232}Th decay series and ^{40}K and radiation hazard parameters are lower than the maximum allowance level defined by UNSCEAR and

ICRP. The salt water and peloid samples analysed from Techirghiol Lake do not pose a radiological threat to the population's health.

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