Indian Journal of Traditional Knowledge
Vol. 1 (1), January 2015, pp. 5-12

Physico-chemical and geochemical characterization of Makirina Bay peloid mud and its evaluation for potential use in balneotherapy (N Dalmatia, Republic of Croatia)

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Received 23 May 2014, revised 18 September 2014

Makirina Bay peloid mud was analysed in the interest of determining its physico-chemical and geochemical characteristics in order to assess the suitability of peloid mud use for cosmetic and/or therapeutic purposes as material for mud wraps or baths. The properties of Makirina Bay peloid mud were compared with various raw geological materials (Dead Sea mud, the mud of 'Capetta', Lo Pagán lagoon sediments, and peloid mud from Morinje Bay) already applied or with potential to be used in various spa centres. Makirina Bay peloid mud is represented mostly by sandy silt and has a relatively high C_{org} content (5%) and cation exchange capacity (CEC) value (63.82 meq/100g). The mineral composition of peloid mud is dominated by dolomite and quartz, followed by illite/muscovite, aragonite, halite, calcite, and pyrite. The calculated contamination factor (CF) and index of geoaccumulation (I_{geo}) values for the majority of heavy metals showed that the peloid mud had a low contamination status. The highest CF and I_{geo} values were for lead, at 2.2 and 0.5 respectively, but the pollution load index value was < 1, indicating that no heavy metal contamination of the peloid mud exists. Geochemical analyses have shown the adequate comparability of Makirina Bay peloid mud with raw materials already successfully used in purposes related to wellness and therapy.

Keywords: Makirina Bay peloid mud, Republic of Croatia, Grain size, CEC, Mineralogical and geochemical composition

IPC Int. Cl.[8]: A01C 23/04, E02F, A61K 8/00, A61Q, A61K, B63G 6/00, B63G 7/00, B03B 5/00, E04B, E04C, E04D, E04F, E04G

Peloids are commonly used in balneotherapy as mud baths and wraps. A new definition of peloid, proposed by Gomes *et al*.[1] is as follows: 'Peloid is a maturated mud or muddy dispersion with healing and/or cosmetic properties, composed of a complex mixture of fine-grained natural materials of geologic and/or biologic origins, mineral water or sea water, and commonly organic compounds from biological metabolic activity'. The application of peloids on different parts of the body or on the whole body is mainly intended for therapeutic treatment generally related to muscle-bone-skin pathologies and for the purposes of wellness and relaxation[2-4].

In the past years, several studies have been carried out in order to determine the basic physico-chemical characteristics of geological materials with potential therapeutic and/or cosmetic applications and geological materials already used in various spa centres around the world[5-14]. Most studies point out that the main factors determining the final characteristics of peloids are the chemical composition, mineralogy, cation exchange capacity (CEC), and grain size distribution of the initial geological material.

Makirina Bay represents one of the major and most important sites where organic-rich sediments accumulate along the eastern Adriatic coast. These sediments (hereafter named peloid mud), according to their organoleptic properties, are suitable for application as a raw material for different therapeutic, cosmetic, and wellness-related purposes[15]. In addition, Makirina Bay peloid mud is already frequently used by local people and tourists as pomades. Peloid mud is collected *in situ* from the bay, applied directly on the skin, and sundried.

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In this study, we determined the basic physical and chemical characteristics (grain size distribution, C_{org} content, CEC, and mineralogical and geochemical compositions) of Makirina Bay peloid mud and assessed its heavy metal pollution status by calculating several environmental indices (contamination factor, index of geoaccumulation, and pollution load index). We then compared these determined characteristics of Makirina Bay peloid mud with characteristics of raw geological materials already applied or with a potential to be used for cosmetic and/or therapeutic purposes (Table 1).

Table 1—Raw geological materials and their application used for comparative study with Makirina Bay peloid mud

Geological material	Application
Makirina Bay peloid mud	Local inhabitants and tourists as mud wraps
Mud samples from N basin of the Dead Sea	Dead Sea spa hotel's clinic for mud therapy[9, 16]
The mud of 'Cappetta' (Quaternary lacustrine sediments)	S Italian thermal centres[5]
Lo Pagán natural muddy lagoon sediment	Spanish spas[3, 17]
Peloid mud from Morinje Bay	Local inhabitants and tourists as mud baths[14]

Materials and methods

Study area

Makirina Bay is located in northern Dalmatia (Republic of Croatia), 18 km northwest of Šibenik (Fig. 1). It is a small bay, approximately 1250 m in length and 300 m in width. A cove with a North to South extension represents the southern part of Pirovac Bay. The depth of the sea in the southern part of the bay rarely exceeds 0.5 m and increases in the seaward direction to a depth of 4.5 m. The land which surrounds the bay is cultivated (olives, gardens, and vineyards) and sparsely populated[15].

The bottom of the bay is covered by 0–3 m thick peloid mud, overgrown mostly by sea grass (*Cymodocea nodosa*) and benthic algae (*Codium bursa*)[15]. The sediment body of Makirina Bay consists of about 410,000 m^3 of peloid mud[15].

The wider area of Makirina is built mostly of Early and Late Cretaceous carbonate rocks and Quaternary sediments[15]. According to the lithological features and microfossil assemblages discerned, researchers have found Ivinj dolomites (Albian–Cenomanian), Makirina limestones and dolomites (Cenomanian–Turonian), Kamena rudist limestones (Early Senonian), and Ivinj Draga deluvial deposits (Quaternary) lithostratigraphic units[18].

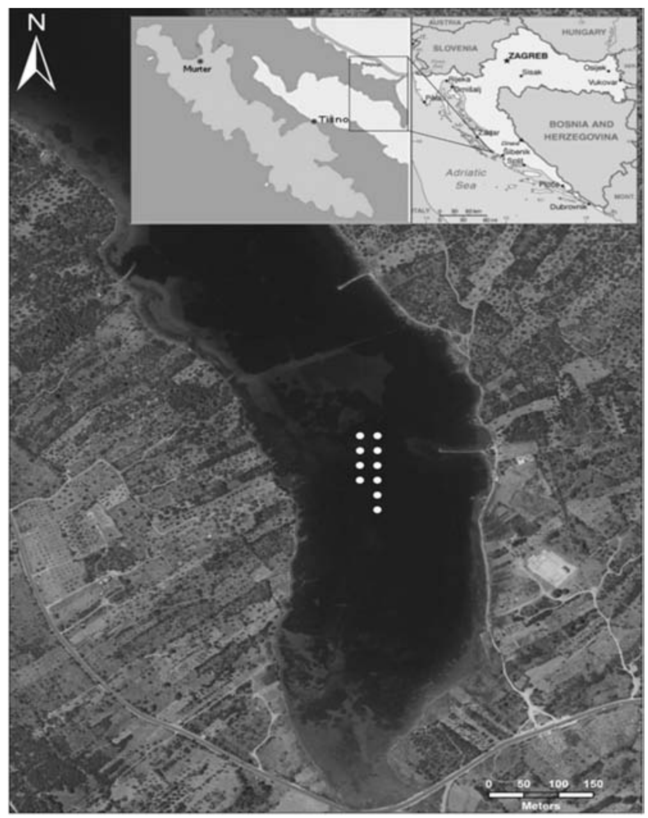

Fig. 1—Location map of Makirina Bay showing sampling sites (DOF 1:5000, DGU Croatia)

Sampling

Peloid mud samples were taken in summer 2010 from 10 different sites in the central part of the bay (Fig. 1). Samples were collected with hand-driven Plexiglas core samplers (40 cm long, 3.5 cm inner diameter) and were immediately frozen until subsequent analysis. In the laboratory, cores were divided into 5-cm-long sections and air-dried. Only surficial peloid mud (the top 5 cm) was used for further granulometric, C_{org}, CEC, mineralogical, and geochemical analyses. Non-representative debris (large rocks and organic debris) was removed by sieving and samples were then homogenized to a fine powder (< 63 μm) in an agate mortar.

Analytical methodology

The granulometric composition of peloid mud was specified at Salonit Anhovo d.d., Deskle, Slovenia, by a combination of wet sieving and a Malvern Mastersizer S laser diffractometer (fraction < 125 μm). Grain size boundaries were calculated using the program GRADISTAT (version 8.0) developed by Blott and Pye[19].

The CEC was determined at the Agricultural Institute of Slovenia (Kmetijski inštitut Slovenije – KIS) using ammonium acetate as the extraction agent. Peloid mud was washed through a 2 mm sieve and air-dried. CEC is given as the sum of exchangeable calcium, magnesium, potassium, and sodium cations and total exchangeable acidity. The procedure does not include the removal of soluble salts prior to extraction of exchangeable cations (KIS, personal communication).

The mineralogical composition of peloid mud was determined at the Faculty of Natural Sciences and Engineering, Department of Geology, Ljubljana (Slovenia) via X-Ray Powder Diffraction (XRD) using a Philips PW3710 X-ray diffractometer equipped with Cu Kα radiation and a secondary graphite monochromator. Data were collected at 40 kV and a current of 30 mA in the range from 2 to 70° 2θ with a speed of 3.4º 2θ /min. Diffraction patterns were identified with the X'Pert HighScore Plus program and Rietveld method, a full-pattern fit method where the measured profile and a calculated profile are compared.

The clay fraction identification was carried out with oriented samples prepared by the following procedure: the sample was first suspended in distilled water to eliminate excess salt. After 72 hrs, the distilled water was removed. The upper 5 mm of the sample was placed in a cuvette and mixed with distilled water. Forty five minutes later (according to Stoke's law), the suspension was pipetted (1 cm under the surface) and transferred to glass plates to dry. Next, samples were treated with ethylene-glycol and heated at 70°C for 24 hrs. Subsequently the oriented aggregates were thermally treated at 550°C.

The organic carbon and total S contents were analysed by a LECO carbon-sulfur analyser in the certified commercial Canadian laboratory Acme (Acme Analytical Laboratories). Induction flux was added to the prepared sample and then it was ignited in an induction furnace. Carrier gas sweeps up released carbon to be measured by adsorption in an infrared spectrometric cell. Results are totals and are attributed to the presence of carbon and sulfur in all forms. Organic carbon content was determined by subtraction, where: organic carbon = total C–inorganic (CO_2) carbon–graphite carbon (Acme, personal communication).

Geochemical analysis of peloid mud was carried out in the certified commercial Canadian laboratory Acme by extraction for 1 hour using 2-2-2-HCl-HNO_3-H_2O at 95°C with ICP/MS. The analytical precision and accuracy were better than ±5% for the investigated elements. This was assessed with in-house reference materials (STD SO-18) and by the results of the duplicate measurements of peloid mud samples and reference material.

Environmental indices

For the heavy metals analysed in this study, we calculated the contamination factor (CF), pollution load index (PLI), and index of geoaccumulation (I_{geo}). CF was proposed by Hakanson[20] in order to describe the contamination of a given heavy metal in an investigated area. CF is expressed as $CF = C_s/C_b$, where C_s is the mean content of the heavy metal in the sample and C_b is the heavy metal background value. Hakanson[20] classified CF into four categories: $CF < 1$ (low contamination), $1 < CF < 3$ (moderate contamination), $3 < CF < 6$ (considerable contamination), and $CF > 6$ (very high contamination).

We also assessed the heavy metal contamination of Makirina Bay peloid mud by using the index of geoaccumulation introduced by Müller[21]: $I_{geo} = \log_2(C_n/1.5B_n)$, where C_n is the measured concentration of heavy metal n in the sample and B_n is the geochemical background value for the heavy metal n. A factor of 1.5 is used because of possible variations of the background data due to lithological variations. The classification of I_{geo} is defined as: uncontaminated ($I_{geo} < 0$), uncontaminated to moderately contaminated ($0 < I_{geo} < 1$), moderately contaminated ($1 < I_{geo} < 2$), moderately to strongly contaminated ($2 < I_{geo} < 3$), strongly contaminated ($3 < I_{geo} < 4$), strongly to extremely contaminated ($4 < I_{geo} < 5$), and extremely contaminated ($I_{geo} > 5$)[21].

The PLI is an environmental index that provides a simple, comparative means of assessing the level of heavy metal pollution of the sediment[22]. The PLI is calculated by using the equation: $PLI=(CF1*CF2*CF3*\ldots*CFn)^{1/n}$. PLI > 1 means that pollution exists, while PLI < 1 means that there is no heavy metal pollution in the sediment[22]. In this study the mean concentrations of heavy metals in surficial sediments from the central Adriatic[23] were used as natural geochemical background values, listed as follows: As (10.5 ppm), Co (16 ppm), Cr (115 ppm), Cu (24.7 ppm), Ni (111 ppm), Pb (11 ppm), V (89 ppm), and Zn (73 ppm). Concentrations of Cd and Mo were generally lower than the detection limit of ICP analysis (1 ppm and 1 ppm respectively)[23].

Results and discussion

Grain size distribution

The granulometric analysis of Makirina Bay peloid mud (Table 2) showed that peloid mud is mostly represented by very poorly sorted sandy silt. In peloid mud samples, mud (silt + clay) dominates over sand, indicating a relatively calm depositional environment[24]. The lower content of clay and elevated content of sand particles in Makirina Bay peloid mud in comparison with other raw geological materials (Table 2) are related to the mineralogical composition of peloid mud, that is its origin, because quartz, organic debris, and broken bioclasts can increase peloid mud sand-sized particles.

Assessment of the granulometry of raw material involves determining its abrasiveness[17] and reactive surface and is related to the ease of handling and pleasantness of the sensation when the peloid mud is applied onto the skin of patients[2]. The granulometric composition of Makirina Bay peloid mud should not pose a problem, since a major proportion of the sand is fine sand sized (< 250 µm). Sand sized particles could also be separated by sieving before the potential application of peloid mud.

Cation exchange capacity (CEC)

The high CEC value of Makirina Bay peloid mud compared to other raw materials (Table 3) is linked to peloid mud organic matter (Table 4), as the CEC of materials is determined mostly by organic matter, clay particles, and Fe and Al oxides[25,26]. Organic matter in Makirina Bay peloid mud is mainly related to the accumulation of organic material associated with the decomposition of aquatic plants, which are abundant in Makirina Bay. Jobstraibizer[27] showed that increase in organic materials was accompanied by a rise in exchange capacity and plasticity although the peloid was low in clay minerals and contained little smectite.

CEC is one of the most important properties that make a peloid suitable for thermal therapy and other applications[6]. High CEC values of raw geological materials allow an exchange of nutrients to take place while the material is in contact with skin[28] and ensures that cleansing occurs through the absorption of toxins, bacteria, and unwanted substances from the skin during topical application[11]. Nevertheless a high CEC allows the retention of ions in peloids that may potentially be harmful to health[4].

Mineralogy

According to the XRD analysis, the mineral composition of Makirina Bay peloid mud is characterized by high quantities of dolomite (44%) and quartz (16%), followed by illite/muscovite (10%), aragonite (8%), Mg-rich calcite (7%), halite (6%), calcite (5%), and pyrite (2%). In some peloid mud samples, plagioclase, gypsum, and clinochlore were also detected. Oriented preparations (Fig. 2) of the clay fraction revealed illite/muscovite, chlorite, and kaolinite as the dominant clay minerals.

Khlaifat *et al*.[9] reported the bulk composition of **N Dead Sea mud** is mainly represented by total carbonates (40.21%), quartz (18.01%), and kaolinite (12.64%). Mud samples also contain clay (8.76%), dolomite (5.05%), gypsum (3.85%), pyrite (8.93%), and total feldspar (2.55%).

The mud of 'Cappetta' is composed of sheet silicates (43 wt.%), calcite (25 wt.%), quartz (19 wt.%), feldspars (11 wt.%), and dolomite (3 wt.%). The clay fraction corresponds to illite (38 wt.%), smectite (34 wt.%), chlorite (18 wt.%), and kaolinite (10 wt.%)[5].

The Bulk mineralogy of **Lo Pagán Lagoon sediment** is dominated by phyllosilicates (41 wt. %) and calcite (40 wt.%), followed by quartz (9 wt.%),

Table 2—Grain size distribution of Makirina Bay peloid mud, N Dead Sea mud, the mud of 'Capetta', Lo Pagán Lagoon sediments and peloid mud from Morinje Bay

Sample	% Sand [>63µm]	% Silt	% Clay [<2 µm]
Makirina Bay peloid mud	41.1	55.8	3.1
N Dead Sea mud[9]*	19.9	46.1	34
The mud of "Cappetta"[5]	7	68.8	24.2
Lo Pagán Lagoon sediment[17]	1.2	77.9	20.8
Peloid mud from Morinje Bay[14]	26.3	67.1	6.6

*Sand fraction>65 µm

Table 3—CEC of Makirina Bay peloid mud, N Dead Sea mud, the mud of 'Capetta', Lo Pagán Lagoon sediments and peloid mud from Morinje Bay

Sample	CEC [meq/100g]
Makirina Bay peloid mud	63.82
N Dead Sea mud[9]	45.75
The mud of 'Cappetta'[5]	n.a.
Lo Pagán Lagoon sediment[17]	11
Peloid mud from Morinje Bay[14]	18

(n.a.: not available)

Table 4—Major oxides and heavy elements content of Makirina Bay peloid mud, N Dead Sea mud, the mud of 'Capetta', Lo Pagán Lagoon sediments and peloid mud from Morinje Bay

Oxides and elements (wt.)	Makirina Bay peloid mud	N Dead Sea mud[9]	The mud of 'Cappetta'[5]	Lo Pagán Lagoon sediments[3]	Peloid mud from Morinje Bay[14]
SiO_2 [%]	27.06	29.65	44.29	18.41	
Al_2O_3[%]	8.17	8.41	11.80	3.58	
Fe_2O_3[%]	3.24	4.25	5.35	1.72	
MnO [%]	0.03	0.07	0.07	0.021	
MgO [%]	5.16	4.18	2.86	4.06	
CaO [%]	15.83	20.61	14.16	26.48	
Na_2O [%]	3.3	0.89	0.71	4.341	
K_2O [%]	1.49	1.10	1.99	1.103	
TiO_2 [%]	0.44	0.79	0.58	0.219	
P_2O_5 [%]	0.08		0.16		
LOI [%]	34.96		18.02	37.66	26
C org. [%]	5				
Tot S [%]	1.45			2.37	
As [ppm]	14.47		3.9	6.4	12-22
Cd [ppm]	0.27	81	0.11	<LD	0.5-0.7
Co [ppm]	7.05	25		4	
Cr [ppm]	82.10			42.3	84-160
Cu [ppm]	27.64	2	23	24.7	18-48
Mo [ppm]	13.82			3.1	
Ni [ppm]	26.51		63	20	47-78
Pb [ppm]	23.74	108	8.2	37.5	9-35
V [ppm]	80.23	250		41.8	
Zn [ppm]	47.67	72	65	85.9	57-95

Empty spaces: informations were not available, < LD: below detection limit

halite (6 wt.%), and gypsum (4 wt.%). Dolomite, plagioclase, and aragonite were detected in traces. Phyllosilicates are represented mainly by illite (35 wt. % in the total sample), kaolinite (4 wt.% in the total sample), and chlorite (2 wt.% in the total sample)[3].

The mineralogical analysis of **peloid mud from Morinje Bay** showed substantial amounts of primarily carbonate minerals (calcite) and quartz, while aragonite, illite, halite, dolomite, feldspar, and chlorite were also determined[14].

In Makirina Bay, peloid mud carbonate minerals predominate among the established mineral assemblage, which is in accordance with the catchment geology (dolomite-rich) of the study area. It can be determined that carbonate minerals also dominate in N Dead Sea mud, Lo Pagán sediment, and peloid mud from Morinje Bay.

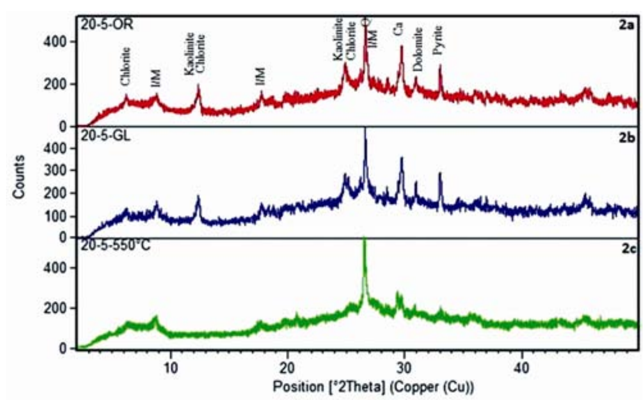

Fig. 2—XRD patterns of Makirina Bay peloid mud. 2a) Oriented preparation air-dried. 2b) Oriented preparation solvated with ethylene glycol. 2c) Oriented preparation thermally treateted at 550°C. (I/M=Illite/Muscovite, Q=Quartz, Ca=Calcite)

Geochemical characteristics

The major oxides and heavy elements content of Makirina Bay peloid mud and compared materials are presented in Table 4.

According to the results of the geochemical analysis, it can be seen that the concentrations of major oxides in Makirina Bay peloid mud do not exceed concentrations in the raw geological materials to which it was compared. The only exception is that MgO is present in higher concentrations due to the dolomitic background of Makirina Bay. The elevated concentration of MgO in Makirina Bay peloid mud should not be problematic since Mg is an essential macronutrient for all organisms. It activates over 100 enzymes and helps nerves and muscles to function[29]. It has also been reported that Mg is very important in the treatment of osteoporosis[29].

Concentrations of most heavy metals are comparable with those found in N Dead Sea mud, the mud of ‘Cappetta’, and Lo Pagán Lagoon sediments (Table 4). Values are slightly elevated for As, Cr, Cu, and Mo concentrations in Makirina Bay peloid mud, which is related to agricultural activity in the areas surrounding Makirina Bay (As and Cu), the source material of Makirina Bay peloid mud (Cr from Eocene flysch located 6 km northeast of Makirina[18]), and the anoxic condition even at the sediment/water interface (Mo). When the heavy metal concentrations of Makirina Bay peloid mud are compared with those of peloid mud from Morinje Bay, the values are lower in the Makirina Bay peloid mud.

To describe the contamination of heavy metals in Makirina Bay peloid mud, several environmental indexes were calculated (Table 5). The calculated CF and I_{geo} values for the majority of heavy metals show low contamination status according to CF and uncontaminated status according to I_{geo} (Table 5).. It can be seen that the CF values confirm slightly elevated As and Cu concentrations (moderate contamination), while the CF and I_{geo} values for Cr show low contamination and uncontaminated status, respectively. The heavy metal with the highest CF (2.2) and I_{geo} (0.5) values is Pb (Table 5), indicating moderate contamination (according to CF) and moderately contaminated status (according to I_{geo}). Despite the slightly elevated CF and I_{geo} values of Pb it is still present in lower concentrations than in N Dead Sea mud[9] and Lo Pagán Lagoon sediments[3]. It can be noted that the calculated PLI value is < 1 (Table 5), meaning that no heavy metal contamination of the peloid mud exists. CF and I_{geo} values for Cd and Mo were not calculated. According to their concentrations in surficial sediments of the central Adriatic (< 1 ppm) we can expect low CF and I_{geo} values for Cd but higher ones for Mo.

Molybdenum is an element that is strongly enriched in highly anoxic conditions and is accompanied by the accumulation of organic matter and the precipitation of iron sulfide[30]. It also shows the greatest degree of enrichment in reducing sediments relative to crustal values[31]. The results of Eh measurement in Makirina Bay peloid mud showed a highly reductive sedimentary environment at the sediment/water interference (Eh = –430 mV). Mo is considered toxic in large amounts as the element causes secondary Cu deficiency, but on the other hand, it is essential for all organisms except for some bacteria[32,33], since it contributes to normal growth and development[29].

Pharmaceutical and cosmetic regulations

Heavy metal impurities in dermatologic products are unavoidable due to the ubiquitous presence of these elements[4,34]. Currently, there is a lack of normative regulation of the quality of raw materials for peloids but, considering that peloids have similarities with both pharmaceutical products and cosmetics[4], we can use the same regulations.

According to ICH (International Conference on Harmonisation) Q3D[35], arsenic (As) is an element that is significantly toxic across all routes of administration; it typically has limited or no use in the pharmaceuticals and therefore belongs to Class 1. Health Canada (HC)[34] has proposed that the level of the As should be limited to < 3 ppm in cosmetic products. Arsenic is an element with no known useful biological function in humans or other organisms. Dermal exposure to arsenic may contribute less than 1% of the exposure from ingestion[36] and therefore the dermal uptake of arsenic is expected to be very limited[34]. Nevertheless, Quintela ***et al.***[4] compiled the characteristics of peloids in use at thermal centres,

Table 5—Calculated environmental indices for Makirina Bay peloid mud

Trace elements	CF	Description of peloid mud according to CF	I_{geo}	Description of peloid mud according to I_{geo}
As	1.4	Moderate contamination	-0.1	Uncontaminated
Co	0.4	Low contamination	-1.8	Uncontaminated
Cr	0.7	Low contamination	-1.1	Uncontaminated
Cu	1.1	Moderate contamination	-0.4	Uncontaminated
Ni	0.2	Low contamination	-2.7	Uncontaminated
Pb	2.2	Moderate contamination	0.5	Moderately
V	0.9	Low contamination	-0.7	Uncontaminated
Zn	0.7	Low contamination	-1.2	Uncontaminated
	PLI: 0.85			

including their geochemical composition, revealing that the maximum concentration of As was 39 ppm.

Chromium (Cr^{3+}) is essential in trace amounts for some organisms[32] including humans (e.g., the regulate blood sugar)[29] but is highly toxic in the Cr^{6+} oxidation state[32]. The European Medicines Agency (EMEA) placed Cr in Class 1C, which recommends a concentration of < 25 ppm[4,37]. ICH Q3D[35] put Cr in Class 3, which is similar to elemental impurities with relatively low toxicity and high PDE (permitted daily exposure) when administered by the oral route. These require consideration of the risk assessment for other routes of administration (inhalation and parenteral routes). Carretero *et al*.[3] studied the mobility of elements (including Cr) in interaction between artificial sweat and peloids used in Spanish spas. Cr was not leached by peloids or was leached in a lower concentration (below 0.05 µg/gm) in the case of natural lagoon peloid[3].

Copper (Cu) is an essential element for all organisms (e.g., it promotes the formation of red blood cells and connective tissue)[29], but is toxic at high doses[32]. Cu belongs to Class 2 according to EMEA, with recommended values of < 250 ppm[4, 37] and Class 3 according to ICH Q3D[35].

Mo falls into Class 1C according to EMEA (recommended concentration < 25 ppm)[37]. ICH Q3D[35] placed Mo in Class 2A (recommended concentration < 25 ppm) as an elemental impurity that is toxic to a greater or lesser extent based on the route of administration.

Conclusion

This paper has examined the physico-chemical (grain size distribution, CEC, mineral and geochemical composition) characteristics of Makirina Bay peloid mud. The comparative study of Makirina Bay peloid mud with several other raw materials already successfully used in cosmetics and/or for therapeutic purposes shows that Makirina Bay peloid mud has comparable examined properties. The exceptions are the granulometric composition, due to its high content of sand-sized particles, dominance of dolomite mineral, and consequently elevated Mg values and slightly increased As, Cu, Cr, and Mo concentrations. Our future work will focus on the determination of the mobility and bioavailability of heavy metals in Makirina Bay peloid, since these are among the most important properties which make peloids suitable for balneotherapy.

Acknowledgement

This research was financially supported by the Slovenian Research Agency (ARRS) under contract number 1000-11-310206 and Geoexp, d.o.o., Tržič, Slovenia. Special thanks go to Mr Boris Paškvalin, Director of BTP, d.d., Betina (Croatia).

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