Assessment of heavy metal content in peloids from some Cuban spas using X-ray fluorescence

Oscar Díaz Rizo[1], Margaret Suárez Muñoz[1], Patricia González Hernández[2], Alina Gelen Rudnikas[1], Katia D´Alessandro Rodríguez[1], Clara M. Melián Rodríguez[1], Alberto Pérez Martín[1], Juan R. Fagundo Castillo[2], Nadia V. Martínez-Villegas[3].

[1]Instituto Superior de Tecnologías y Ciencias Aplicadas (InSTEC), Ave. Salvador Allende y Luaces, Habana 10600, Cuba.
[2]Facultad de Química, Universidad de La Habana, Zanja esq. a G, Habana 10600, Cuba.
[3]Departamento de Geociencias Aplicadas. Instituto de Investigaciones Científicas y Tecnológicas, San Juan Potosí, México.
odrizo@instec.cu

Abstract

Heavy metal (Co, Ni, Cu, Zn and Pb) content in muds from some Cuban spas (San Diego, Elguea, Santa Lucía and Cajío) have been studied using X-ray fluorescence. The measured metal contents are in the same order of magnitude as those reported for average Earth's upper crust average shales and muds as well as with worldwide reported peloids. The comparison with sediment quality guidelines (SQGs) shows a different degree of pollution for peloids from each studied spa. Nevertheless, the estimated sum of metal/probable effect level value ratios (0,9 – 2,4) correspond to a low potential acute toxicity of contaminants. Therefore, the heavy metal content present in peloids from the studied Cuban spas is not an obstacle for its use with therapeutic purposes.

Key words: *sediment, x-ray fluorescence analysis, heavy metals, Cuba, therapeutic uses.*

Estimación del contenido de metales pesados en peloides provenientes de varios balnearios cubanos mediante Fluorescencia de rayos X

Resumen

Se estudia mediante la técnica de Fluorescencia de rayos X, el contenido de metales pesados (Co, Ni, Cu, Zn y Pb) en lodos terapéuticos provenientes de varios balnearios cubanos (San Diego, Elguea, Santa Lucía y Cajío). Los contenidos de metales pesados determinados en los lodos terapéuticos se encuentran en el mismo orden que los reportados para lodos y esquistos representativos de la corteza terrestre, así como para lodos utilizados en balnearios internacionalmente. La comparación con las Guías de Calidad de sedimentos muestran diferentes grados de polución para los lodos de cada balneario. Independientemente de ello, los valores de las razones suma de metales/nivel de efecto probable (0,9-2,4) corresponden a un bajo potencial agudo de toxicidad por contaminantes. De esta manera, el contenido de metales pesados presentes en los lodos de los balnearios estudiados no representa impedimento alguno para su uso con fines terapéuticos.

Palabras clave: *sedimentos, analisis por fluorescencia de rayos x, metales pesados, Cuba, usos terapéuticos.*

Introduction

Peloids are defined as 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 origin, mineral water or sea water, and common organic compounds from biological metabolic activity [1]. Peloids have been used in medicine since ancient times and more recently, applications of this old practice have been developed for wellness and relax purposes [2, 3]. The most important inorganic components of the peloid are clay minerals, which make them useful in spas due to their physical properties, i.e. rheology, absorption/adsorption capacity, cation exchange capacity, water saturation, swelling index, grain size, cooling index, etc. Some recent investigations demonstrated the necessity of studying the geochemical abundance of potential hazardous elements in peloids [3-7]. Although the use of healing mud is very old, specific criteria for the evaluation of their contamination by some trace elements (such as As, Pb, Hg, Cd, Zn or Cu), their toxicity are yet to be established.

In Cuba, mud application in pelotherapy use started at the end of the 19th century. The reference peloid user in Cuba is the San Diego de los Baños Thermal Center, located in the Western Cuban province of Pinar del Río. The peloid used there is a mud extracted directly from the estuary of San Diego River, and enriched later with inorganic and organic components, as well as with the microbiota of calcic sulfated, fluoric, radionic and sulfurous mesothermal waters (33 °C) of San Diego de los Baños Thermal Center. These waters, show low oxidation-reduction (Eh) potential values (-226 to -270 mV) and their electric conductivity (EC) values oscillate between 1 480 and 2 200 µS/cm [8]. The maturation process of the sediment is done using a static, open method during 15 days, and under environmental conditions. The gray peloid produced in this way (with high content in clays, and the presence of quartz, and Fe minerals) is classified as a clayed slime by Peláez [9], but according to the organic matter content can be classified as fangi or mud [8]. The peloid is routinely used to palliate inflammatory and dermatological processes, as an analgesic, in male and female infertility treatments, and in cosmetic products. The San Diego raw (non-maturated) mud was recently studied to assess the heavy metal content [10], showing that those are not an obstacle for its use in medical purposes. The rest of the Cuban spas use the so-called “natural” maturated peloids, i.e. muds taken directly from thermal or sulphated water sources.

The peloid used in Elguea is dark gray. Elguea´s waters are also hyperthermal (51 °C), calcic sulfated, magnesic, sulfurous ($SH_2 \geq 10$ mg/L), brominated and radioactive-radonic [11]. This peloid may be classified as fangi or mud, due to strong mineral composition and hydrothermal origin and the predominantly phases are composed by clay, carbonates and halite. The great tradition and experience of Elguea Thermal Center is aimed at using its waters and peloids in the treatment of different inflammatory and dermatological processes, both as analgesic and as a cosmetic.

In Santa Lucía, the original sediment is extracted directly from El Real salt pond deposit and later enriched with the sodium chlorine hypersaline waters (mineralization of almost 250 g/l) of the salt pond. The obtained dark gray peloid can be classified as sulfurous slime and the predominantly phases are composed by gypsum, carbonates and halite. The main uses of this peloid are related with psoriasis, acne, mycosis, seborrheic dermatitis, degenerative osteoarthritis and rheumatoid arthritis [12].

On the other hand, the Cajío original sediment is extracted directly from the coastal deposit. This gray mud is classified as sulfurous slime and is formed by the waters with mineralization of 39,5 g/l of the Batabano Gulf. These waters show Eh values of approximately 150 mV and their EC value is approximately of 49 700 µSm [13]. The peloid has sandy particles with poor development of clayed phases and high content of organic matter and carbonates. It is used in pathologies of SOMA, arthritis, dermatological diseases (psoriasis), among others.

The aim of the present study is to determine heavy metal contents (Co, Ni, Cu, Zn and Pb) in maturated peloids used in different Cuban spas, to assess the potential pollution and radiological risks for the users of peloid therapeutic practices.

Materials and methods

Five replicas were collected in each of the four main peloid-users spas in Cuba, located in four different Cuban provinces (see Figure 1). Samples for non-natural maturated peloids were taken from the San Diego spa, while those of natural maturated peloids were taken from spas in Elguea, Santa Lucía and Cajío. Every sample used in this study was dried at 60 °C. Large rock debris, mollusk skeletons and organic debris were removed before sieving. The fraction, smaller than 1 mm, was ground into a fine powder (<63 µm) in an agate mortar. The pulveri-

Figure 1. Location of studied Cuban spas.

zed samples were newly dried at 60 °C until obtaining a constant weight.

Heavy metal concentrations were determined by external standard method of X-Ray Fluorescence Analysis (XRF) using the Certified Reference Materials (CRM) IAEA-SL-1 "Lake Sediment", IAEA-Soil-5, IAEA Soil-7, BCR-2 "Basalt Columbia River" and BCSS-1 "Marine sediment" as standards. All samples and CRM were mixed with cellulose (analytical quality) in proportion 4:1 and pressed at 15 tons into the pellets of 25 mm diameter and 4 - 5 mm height. Pellets were studied using Canberra Si(Li) detector (150 eV energy resolution at 5,9 keV, Be window thickness = 12,0 μm) coupled to a multi channel analyzer. A ^{238}Pu (1,1 GBq) excitation source with ring geometry was used. All spectra were processed with WinAxil code [14]. Detection Limits were determined according to Padilla et al. [15] (in concentration units) as LD = 3σ/mt, where m is the sensibility in counts.seg-1 per concentration unit, σ is the standard deviation of the area of the background windows (peak window at 1,17 times the FWHM) and t is the measuring time (4 hours).

The accuracy was evaluated using the SR criterion, proposed by McFarrell et al. [16]:

$$SR = \frac{|C_X - C_W| + 2\sigma}{C_W}.100\,\%$$

where C_X is the experimentally determined concentration value, C_W is the certified concentration value and σ is the standard deviation of C_X. On the basis of this criterion the similarity between the certified value and the analytical data obtained by proposed methods is divided into three categories: SR ≤ 25% = excellent; 25 < SR ≤ 50% = acceptable, SR > 50% = unacceptable. The analysis of five replica of the CRM IAEA-356 "Polluted Marine Sediment" [17] is presented in Table 1. All heavy metals determined by XRF analysis, using the external standard method [17], qualify as "excellent" (SR ≤ 25 %) and the obtained results show a very good correlation (R = 0,999) between the certified and measured values.

Table 1. XRF analysis of CRM IAEA-356 (mean ± SD, n=5, mg.kg^{-1} dry weight), SR values and Detection Limits.

Metal	Certified value	Confidence interval	Measured value	SR (%)	L_D (mg.kg^{-1}) [18]
Co	15	14,1–16,4	14 ± 1	20	6
Ni	36,9	35,1–40,1	34 ± 3	24	11
Cu	365	351–375	360 ± 29	17	16
Zn	977	936–1019	958 ± 45	11	5
Pb	347	301–365	362 ± 22	22	4

Numerical sediment quality guidelines (SQGs) have been used worldwide for both freshwater and marine ecosystems, and to identify contaminants of concern in aquatic ecosystems as well [19]. SQGs have been developed for many potentially toxic substances (i.e., trace elements, chlorinated organics, and polynuclear aromatic hydrocarbons). SQGs were applied to this study for the assessment of the ecotoxicological sense of metal concentrations in peloids with the threshold effect level (TEL) and probable effect level (PEL) values.

Results and discussion

The average concentrations of heavy metals determined by XRF analysis in peloid samples from the studied Cuban spas are shown in Table 2, along with the concentrations of the elements under consideration in representative shales and muds [20]. The metal content ratios determined for peloid and raw healing mud [10] from San Diego spa were 0,4 for Co, 0,7 Ni, 0,6 for Cu, 1,0 for Zn and 0,7 for Pb, confirming that peloid maturation processes do not change the heavy metal content present in the raw mud, as it was also shown by Tateo and Summa [5].

The levels of the toxic metals examined in the Cuban spas peloids are, in general, in the same order of magnitude as those previously reported for average shales, Argillaceous sediments and muds [20, 21]. From a geochemical standpoint, the level of individual elements in shales and muds can be considered as a good approximation to the specific element in Earth's upper crust. In terms of potential toxicity of the Cuban spas peloids, it is important to note that none of the values of toxic element levels documented in the studied peloids are significantly higher than the terrestrial background values [20]. The only exception is the Cu content in Santa Lucía peloid, since the geochemical values are exceeded by 1,8 – 3,6 folds. On the other hand, except for Ni content in Elguea spa, the metal contents in the studied peloids are in the range of the concentration limits established by the U.S. Pharmacopeia [29] and the European Medicines Agency EMEA [30] for pharmaceutical formulations and cosmetics (see Table 2). The mentioned regulations were proposed by Quintela et al [28] for peloid chemical composition, considering that both pharmaceutical products and cosmetics have similarities with peloids. On the other hand, the comparison with metal contents reported worldwide for peloids (natural and commercial) used for different medical purposes, show that heavy metal concentrations in Cuban peloids are also in the same concentration ranges.

The comparison with SQGs values (Table 2), show that Ni contents in peloids from San Diego and Elguea are above Ni PEL value, while Cu content on peloids from Santa Lucía is above the Cu TEL value. Furthermore, the potential acute toxicity of contaminants in peloid samples could be estimated as the sum of the toxic units (ΣTUs), which is defined as the ratio of the determined concentration to PEL value [31]. A ΣTUs value larger than the number of studied metals, indicate the potential toxicity by metal content in the peloid sample. The estimated ΣTUs values (Figure 2), based on concentrations of Ni, Cu, Zn and Pb, are lower than 4 for all of the sampling spas, with the highest value obtained for peloids from Elguea spa (ΣTUs = 2,4) and the lowest (ΣTUs = 0,9) for Cajío's.

Table 2. Metal content in studied peloids (mean ± SD, n=5, in mg.kg-1 dry weight), baselines, SQGs values and comparison with results reported worldwide .

Peloid/Baseline		Co	Ni	Cu	Zn	Pb	References
San Diego (peloid), Cuba		6,9 ± 0,6	44 ± 5	33 ± 1	73 ± 4	20 ± 2	Present study
Elguea, Cuba		< 6	65 ± 6	30 ± 1	97 ± 4	14 ± 1	
Santa Lucía, Cuba		< 6	23 ± 5	107 ± 2	57 ± 4	6 ± 1	
Cajío, Cuba		< 6	20 ± 4	20 ± 1	25 ± 3	12 ± 1	
Average shale		19	50	45	95	20	[20]
River mud		14	32	32	78	23	
Hemipelagic mud		20	53	30	130	24	
Argillaceous sediments(1).		14–20	40–90	40–60	80–120	20–40	[21]
Shales(1)		11–20	50–70	40	80–120	18–25	
San Diego (raw), Cuba		18 ± 2	62 ± 8	52 ± 2	72 ± 4	28 ± 2	[10]
Calda, Italy		–	58	27	109	14	[22]
Cappeta, Italy		–	67	24	67	8,5	[22]
Archena, Spain		5,1	3,4	11,5	33,1	10,9	[7]
Arnedillo, Spain		16,8	50,8	52,3	89,8	37,0	[7]
Caldas de Boí, Spain		5,7	21,1	14,5	56,9	24,6	[7]
El Raposo, Spain		14,6	35,1	29,2	160,4	33,3	[7]
Lo Pagán, Spain		4,0	20,0	24,7	85,9	37,5	[7]
Vale das Furnas, Portugal		–	10	52	78	28	[23]
Laguna del Chancho, Argentina		9,5	15,9	601,1	48	16,1	[24]
Makirina Cove, Croatia		11	29	35	51	26	[25]
Makirina Bay, Croatia		7,05	26,51	27,64	47,67	23,74	[26]
Deep Sea Spa Hotel, Jordan(2)		6,1	16	8,0	23	5,1	[27]
Bentonite So.Mi.Es(3)		15,2	32	41,6	72	11,1	[28].
Fango sulfurado(3)		10,9	25,4	24,2	71	20,1	[28]
Fango sulfurado com agua sulfurada(3)		13,6	31,4	28,1	96	28,6	[28]
US Pharmacopeia		50	50	50	50	50	[29]
European Medicines Agency		–	25	250	1300	–	[30]
SQGs	TEL		18	35,7	123	35	[19]
	PEL		36	197	315	91,3	

(1) - Represents mean values of shales and A.S. from Kabata-Pendias and Mukherjee [21]; (2) - Sample from hotel's clinic for mud therapy; (3) - Commercial peloids from Portugal.

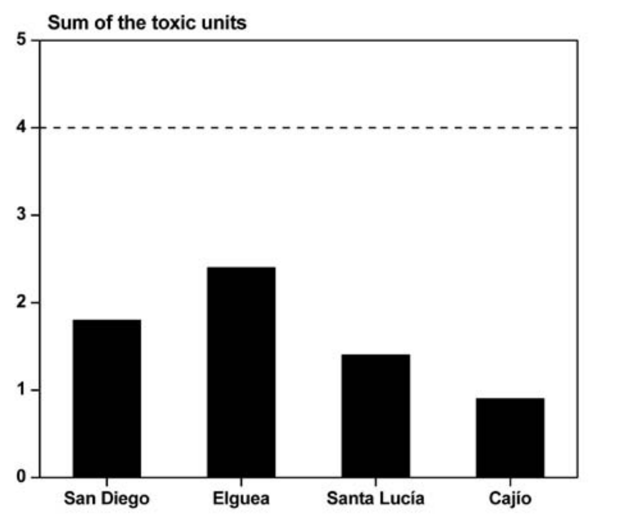

Figure 2. Estimated sum of the toxic units (ΣTUs) of healing muds from Cuban spas (dashed lines represent the Pedersen criteria in the present study).

Conclusions

Cuban regulations do not specify a maximum allowable limit for heavy metal content in peloids. However, according to the obtained results in the present study and its comparison with existing and in force international regulations, we can conclude that the heavy metal content determined in peloids from studied Cuban spas is not an obstacle for its use with therapeutic purposes.

References

[1] GOMES C, CARRETERO MI, POZO M, et. al. Peloids and pelotherapy: Historical evolution, classification and glossary. App Clay Sci. 2013; 75-76: 28-38.

[2] CARRETERO MI. Clay minerals and their beneficial effects upon human health: a review. App Clay Sci. 2002; 21(3-4): 155-163.

[3] VENIALE F, BARBERIS E, CARCANGIU G, et. al. Formulation of muds for pelotherapy: effects of "maturation" by different mineral waters. App Clay Sci. 2004; 25(3-4): 135-148.

[4] MASCOLO N, SUMMA V, TATEO F. In vivo experimental data on the mobility of hazardous chemical elements from clays. App Clay Sci. 2004; 25(1-2): 23-28.

[5] TATEO F, SUMMA V. Element mobility in clays for healing use. App Clay Sci. 2007; 36(1-3): 64-76.
[6] TATEO F, RAVAGLIOLI A, ANDREOLI C, et. al. The in-vitro percutaneous migration of chemical elements from a thermal mud for healing use. App Clay Sci. 2009; 44(1-2): 83-94.
[7] CARRETERO MI, POZO M, MARTÍN-RUBÍ JA, et. al. Mobility of elements in interaction between artificial sweat and peloids used in Spanish spas. App Clay Sci. 2010; 48: 506-515.
[8] SUÁREZ MUÑOZ M, MELIÁN RODRÍGUEZ C, GELEN RUDNIKAS A, et. al. Physicochemical characterization, elemental speciation and hydrogeochemical modeling of river and peloid sediments used for therapeutic uses. App Clay Sci. 2015; 104: 36-47.
[9] PELÁEZ R. Proyecto de Explotación Fangos Medicinales de Boca de San Diego, Pinar del Rio. In: Unión Geológica. Fondo Geológico Nacional, MINBAS, 2003. 26 p.
[10] DÍAZ RIZO O, GELEN RUDNIKAS A, D´ALESSANDRO RODRÍGUEZ K, et. al. Assessment of historical heavy metal content in healing muds from San Diego river (Cuba) using nuclear analytical techniques. Nucleus. 2013; (53): 19-23.
[11] FAGUNDO JR, GONZÁLEZ P, SUÁREZ M, et. al. Origen y composición química de las aguas minerales sulfuradas de Cuba. Su relación con el medio ambiente geológico. In: Contribución a la Educación y la Protección Ambiental. Vol. 3, 2002. Electronic Book. ISBN 959-7136-13-9
[12] MANCHADO A, CERVANTES P. InfoTER database. Version 1.0. Centro Nacional de Termalismo “Victor Santamarina” (CENTERVISA). La Habana, 2003.
[13] GONZÁLEZ HERNÁNDEZ P. Contribución al conocimiento hidroquímico de acuíferos cársicos costeros con intrusión marina. Sector Güira-Quivicán, Cuenca sur de La Habana [tesis para optar por el grado de Dr. en Ciencias Técnicas]. La Habana: ISPJAE, 2003.
[14] WinAxil code. Version 4.5.2 [software]. CANBERRA-MiTAC, 2005.
[15] PADILLA R, MARKOWICZ A, WEGRZYNEK D, et. al. Quality management and method validation in EDXRF analysis. X-Ray Spectrom. 2007; 36(1): 27-34.
[16] QUEVAUVILLER PH, MARRIER E. Quality assurance and quality control for environmental monitoring. Weinheim: VCH, 1995.
[17] IAEA. Polluted marine sediment. Reference material 356. IAEA/AL/080 Report. Vienna: International Atomic Energy Agency, 1994.
[18] DÍAZ ARADO O, DÍAZ RIZO O, LÓPEZ PINO N, et. al. Evaluation of the InSTEC´s EDXRF assembly for marine sediment pollution studies. AIP Conf Proc. 2009; 1139(1): 158-159.
[19] McDONALD DD, INGERSOLL CG, BERGER TA. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch Environ Contam Toxicol. 2000; 39(1): 20-31.
[20] LI YH. A compendium of geochemistry: from solar nebula to the human brain. Princeton: Princeton University Press, 2000.
[21] KABATA-PENDIAS A, MUKHERJEE AB. Trace elements from soil to human. Springer, 2009.
[22] SUMMA V, TATEO F. The use of pelitic raw materials in thermal centres: mineralogy, geochemistry, grain size and leaching test: examples from the Lucania area (southern Italy). App Clay Sci. 1998; 12(5): 403-417.
[23] TERROSO D, ROCHA F, FERREIRA DA SILVA E, et. al. Chemical and physical characterization of mud/clay from Sao Miguel and Terceira islands (Azores, Portugal) and possible application in pelotherapy. 9Th International Symposium on Metal Ions in Biology and Medicine. May 21-24, 2006. Metal vol 9. p. 85-92.
[24] BASCHINI MT, PETTINARI GR, VALLES JM, et. al. Suitability of natural sulphur-rich muds from Copahue (Argentina) for use as semisolid health care products. App Clay Sci. 2010; 49(3): 205-212.
[25] MIKO S, KOCH G, MESI□ S, et. al. Anthropogenic influence on trace element geochemistry of healing mud (peloid) from Makirina Cove (Croatia). Environ Geol. 2008; 55(3): 517-537.
[26] KOMAR D, DOLENEC T, DOLENEC M, et. al. Physico-chemical and geochemical characterization of Makirina Bay peloid mud and its evaluation for potential use in balneotherapy (N Dalmatia, Republic of Croatia). Indian Journal of Traditional Knowledge. 2015; 14(1): 5-12.
[27] ABDEL-FATTAH A, PINGITORE NE. Low levels of toxic elements in Dead Sea black mud and mud-derived cosmetic products. Environ Geochem Hlth. 2009; 31(4): 487-492.
[28] QUINTELA A, TERROSO D, FERREIRA DA SILVA E, et. al. Certification and quality criteria of peloids used for therapeutic purposes. Clay Minerals. 2012; 47(4): 441-451.
[29] US Pharmacopeia 29-NF 24. Rockville: US Pharmacopeial Convention, 2006.
[30] European Medicines Agency. Guideline on the specification limits for residual metal catalysts for metal reagents. London, 2008. Available at: http://www.ema.europa.eu/docs/en_GB/document_library/Scientific_guideline/2009/09/WC500003586.pdf [accessed: november, 2015].
[31] PEDERSEN F, BJØRNESTAD E, ANDERSEN HV, et. al. Characterizarion of sediments from Copenhagen harbour by use of biotests. Wat. Sci. Techn. 1998; 37(6-7): 233-240.

Recibido: 17 de octubre de 2016
Aceptado: 31 de enero de 2017