Assessment of historical heavy metal content in healing muds from San Diego river (Cuba) using nuclear analytical techniques

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Abstract

Behavior of heavy metals (Fe, Co, Ni, Cu, Zn and Pb) content in ^{210}Pb-dated healing mud profiles from San Diego river outlet (western Cuba) has been studied using X-ray fluorescence analysis. Iron-normalized enrichment factors indicate the Co, Ni, Cu and Zn natural origin (Enrichment Factor ≈ 1), reflecting a low anthropogenic impact to the area in the last 100 years. A minor lead enrichment (EF = 2) in the last few decades was determined. The heavy metal levels in most recent mud (0-5 cm, on mg.kg^{-1} dry weight) were: Co = 18 ± 2, Ni = 62 ± 8, Cu = 52 ± 2, Zn = 72 ± 4 and Pb = 28 ± 2. The comparison with reported Earth's upper crust average shales and muds, and with data reported for different muds used for medical purposes shows that heavy metal content in San Diego River mud is suitable for therapeutic purposes.

Key words: *sediments, X-ray fluorescence analysis, heavy metals, therapeutic uses, lead 210, rivers, Cuba*

Estudio del contenido historico de metales pesados en lodos medicinales del Río San Diego (CUBA) mediante técnicas analíticas nucleares

Resumen

Se determinan los niveles de metales pesados (Fe, Co, Ni, Cu, Zn y Pb) en perfiles de sedimentos del río San Diego, fechados con la técnica de ^{210}Pb y mediante la técnica de Fluorescencia de Rayos X. La normalización al hierro de los contenidos de metales pesados indicó el origen natural de los elementos Co, Ni, Cu y Zn, así como un muy moderado enriquecimiento en Pb, reflejando el bajo impacto antropogénico que ha tenido esta área en los últimos 100 años. Los niveles de metales pesados en los lodos más recientes (0-5 cm, en mg.kg^{-1} peso seco) fueron: Co = 18 ± 2, Ni = 62 ± 8, Cu = 52 ± 2, Zn = 72 ± 4 y Pb = 28 ± 2. La comparación con los contenidos de metales pesados, reportados en la literatura en lodos de uso medicinal, mostró que el contenido de metales pesados en los lodos del río San Diego es aceptable para su empleo con fines terapéuticos.

Palabras clave: *sedimentos, análisis por fluorescencia de rayos X, metales pesados, usos terapéuticos, plomo 210, ríos, Cuba*

Introduction

Thermal muds are hydrothermal or hydrothermalized pastes produced by primary or secondary mixing of clayey (geo) materials with salty thermo-mineral waters, accompanied by organic materials produced by the biological-metabolic activity of micro-organisms growing during the so-called "maturing" process [1]. Peloids have been used in medicine since ancient times and more recently such old practice has received applications also for wellness and relax purposes [2, 3]. The most important inorganic components of the peloids are clay minerals which make them useful in spas due to their physical properties (i.e. absorption/adsorption capacity, cation exchange capacity, water saturation, swelling index, grain size, cooling index, etc.). Some recent investigations showed the necessity of studying the geochemical abundance of potential hazardous chemical toxic elements in peloids [2, 4-5] and although the use of healing mud is very old, specific criteria for the evaluation of

their contamination by some trace metals (such as As, Pb, Hg, Cd, Zn, Cu, etc.) and their toxicity are yet to be established.

One of the big peloid users in Cuba is the San Diego de los Baños Thermal Center, located in Pinar del Río, western Cuban province. The peloid used there is a mud extracted from the San Diego river outlet (40 km from Thermal Center) and maturated with sulphated and radonic thermo-mineral waters. The present study was conducted in order to determine total concentrations of some heavy metals (Co, Ni, Cu, Zn and Pb) in the vertical sediment profile in an attempt to establish the pattern and history of their enrichment in San Diego river outlet and to assess the quality of peloids in medical uses at present and over time.

Materials and Methods

Three cores were collected in the San Diego river outlet (Figure 1) during the same journey. The core tubes were divided in 5 cm thick slices. All samples were dried at 60 °C. Large rock debris; mollusk skeletons and organic debris were removed before sieving. The fraction smaller than 1 mm was ground to a fine powder (< 63 μm) in an agate mortar. The pulverized samples were newly dried at 60 °C until obtaining a constant weight.

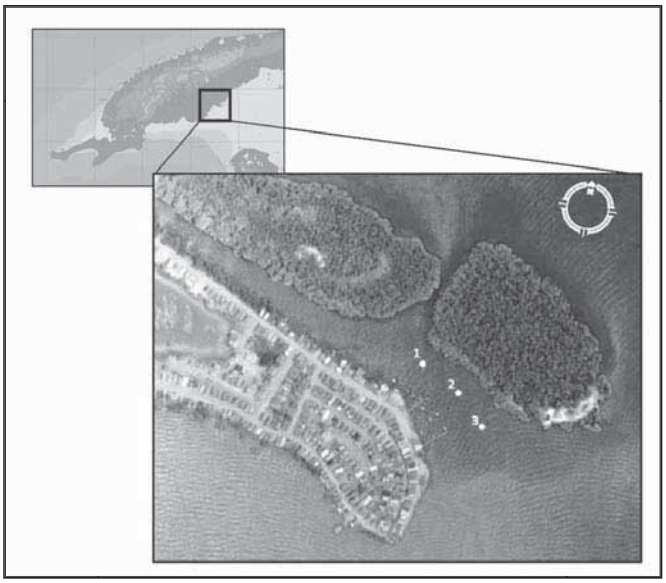

Figure 1. Location of studied stations in San Diego river outlet (1 – 22o19´35.06"N 83o16´06.11"W; 2 – 22o19´34.00"N 83o16´04.43"W; 3 – 22o19´32.77"N 83o16´02.89"W).

Heavy metal concentrations were determined by external standard method of X-Ray Fluorescence Analysis (XRF) using the Certified Reference Materials (CRM) IAEA-SL-1 [6], IAEA-Soil-5 [7], IAEA Soil-7 [8], BCR-2 [9] and BCSS-1 "Marine sediment" from the Canadian National Research Council 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 measured using Canberra Si(Li) detector (150 eV energy resolution at 5,9 keV, Be window thickness = 12.0 μm) coupled to a MCA. A ^{238}Pu (1.1 GBq) excitation source with ring geometry was used. All spectra were processed with WinAxil code [10]. Detection Limits were determined according to Padilla et al. [11] (in concentration units) as $L_D = 3\sigma/mt$, 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 (6 hours).

The accuracy was evaluated using the SR criterion, proposed by McFarrell et al. [12]:

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

where C_X – experimental value, CW – certified 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 [13] is presented in Table 1. All heavy metals determined by XRF analysis are "excellent" (SR ≤ 25%) and the obtained results show a very good correlation (R = 0.9999) between certified and measured values.

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

Element	Certified value	Measured value	SR (%)	L_D (mg.kg^{-1})
Fe (%)	2.41	2.57 ± 0.19	23	9
Co	15	14 ± 1	20	6
Ni	36.9	34 ± 3	24	11
Cu	365	360 ± 29	17	16
Zn	977	958 ± 45	11	5
Pb	347	362 ± 22	22	4

In order to asses the possible heavy metal pollution in mud, the element enrichment was estimated by normalizing the results to a reference element, using the Enrichment Factor [14]:

$$EF = (X/Y)_{sample} / (X/Y)_{background}$$

where X is the concentration of the potentially enriched element and Y is the concentration of the reference element. If the EF value of an element is close to unity, it means that its observed concentration in sediment samples can be considered as crustal material. Enrichment value higher than unity indicated abnormal behavior for the corresponding element concentration. The average elemental composition of the deepest core slices was used as background values, considering the recommendations taken from Vreca and Dolenec [15]. Iron was selected as reference element. The use of Fe to normalize the results is recommended because the

natural high levels of this element in the environment [16, 17].

The sediment age has been successfully achieved starting from the determination of the activity profiles of ^{137}Cs and ^{210}Pb and calculating by the constant rate of supply (CRS) model using the excess ^{210}Pb profile [18]. The activities of the radionuclide present in mud samples were determined by gamma spectrometry using the CRM UC-1 and UC- 2, prepared in the University of Cantabria (Spain) [19] as standards. Sample preparation was standardized at 50 grams (dry weight) and placed in the hermetic closed plastic container during 30 days so that a secular equilibrium between ^{226}Ra, ^{222}Rn and shorter half lives daughters of ^{222}Rn was assured. Spectra were measured during 24 hours in the Low-Background Gamma Spectrometer (LBGS) of the Nuclear Analytical Lab at InSTEC, composed by a Low-Background Chamber, an n-type closed-end coaxial high-purity germanium detector (DSG, NGC-3018, 130 cm^3, FHWM = 2.04 keV for 1332 keV ^{60}Co gamma line) equipped with an 8192 channel multichannel analyzer (webMASTER TARGET coupled to PC) [20]. The gamma spectra were processed using the Gamma-W version 18.03 code (Dr. Westmeier Gesellschaft für Kernspektrometrie GmbH). The minimum detectable activity (MDA) of the system for 24 hours count acquisition were 6.1 $Bq.kg^{-1}$ for ^{210}Pb and 0.6 $Bq.kg^{-1}$ for ^{137}Cs,. The Determination Limit was calculated according to Currie criteria [21].

Results and Discussion

The behaviour of excess ^{210}Pb and ^{137}Cs average activities measured in healing mud cores and the mud formation-year estimated by CRS model are shown in Figure 2. In Cuba, the presence of ^{137}Cs in sediments is only due to fallout from nuclear explosions [22, 23].The artificial radionuclide ^{137}Cs (T½ = 30.2 years) has been appearing in traces in the environment since the early 1950s, showing a characteristic activity maximum in sediments between 1962 and 1964 due to atmospheric nuclear weapon testing fallout maximum [24]. This ^{137}Cs activity maximum (see Figure 2) is usually used as data marker to verify the ^{210}Pb age sediment determination [25]. The latter is in correspondence with formation year estimation by excess ^{210}Pb CRS model.

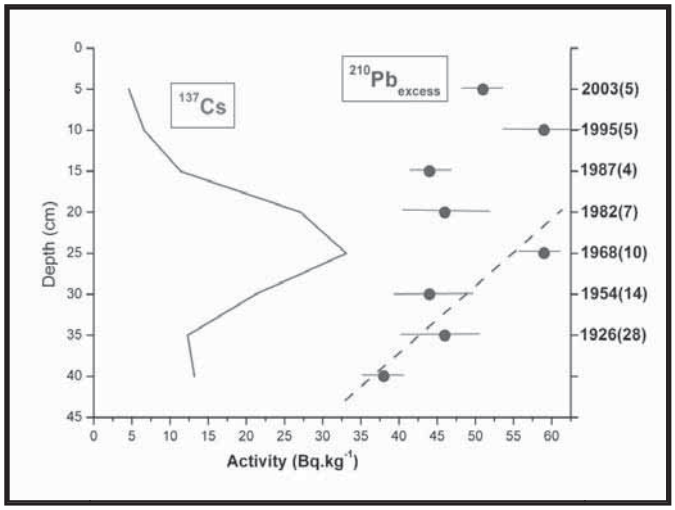

Figure 2. Downcore average ^{137}Cs and excess ^{210}Pb activities (in $Bq.kg^{-1}$) in sediment profile. Dashed line shows the non perturbed estimation for CRS model. Right axis shows the estimated mud formation year (Error in years)

The average concentrations of the heavy metals determined by XRF analysis in mud cores from San Diego river outlet are shown in Table 2. Low concentrations of all heavy metals in the mud reflect a low anthropogenic impact, practically, in the last 100 years, taking into the account the sediment age estimated by CRS method using the excess ^{210}Pb profile.

Calculating the Enrichment Factor respect to Fe for determined heavy metals using the deepest core slice concentrations as background (Figure 3), the chronological behavior of the metal enrichment in last 80 years was obtained. The result shows the natural Co, Cu, Ni and Zn origin (EF ≈ 1) and a minor enrichment for Pb (EF ~ 2) in the most recent mud. Taking into account the urban area located in the west side of the river (see Figure 1), Pb enrichment in the last decades should be associated with wastes from domestic diesel power plants and diesel kitchens, frequently used in Cuban small towns, and with motor boat traffic in the area.

Cuban regulations [26] do not specify a maximum allowable limit for heavy metal content in healing mud. The levels of the five toxic metals examined in the most recent San Diego River muds (top slice) are seen to be of the same order of magnitude as those reported by Li [27] for average shale and muds (Table 3). From a geochemical standpoint, the level of most individual elements

Table 2. Average concentrations* for heavy metals determined in healing mud profiles from San Diego river outlet

Metal	Core depths (in cm)							
	0-5	5-10	10-15	15-20	20-25	25-30	30-35	35-40
Fe (%)	3.6 ± 0.1	4.0 ± 0.1	3.8 ± 0.1	4.6 ± 0.1	5.0 ± 0.2	4.9 ± 0.2	4.1 ± 0.2	4.8 ± 0.2
Co	18 ± 2	16 ± 2	15 ± 1	19 ± 2	21 ± 3	22 ± 3	19 ± 3	20 ± 4
Ni	62 ± 8	56 ± 8	62 ± 8	67 ± 8	74 ± 14	77 ± 14	59 ± 14	78 ± 21
Cu	52 ± 2	49 ± 2	39 ± 1	45 ± 2	64 ± 3	48 ± 2	42 ± 2	62 ± 4
Zn	72 ± 4	82 ± 5	87 ± 5	95 ± 5	106 ± 8	107 ± 8	73 ± 7	113 ± 12
Pb	28 ± 2	32 ± 2	35 ± 2	38 ± 3	24 ± 2	21 ± 2	17 ± 2	22 ± 3
*- mean ± SD, in mg.kg-1 except the indicated.								

in shales and muds can be considered to approximate that of the specific element in Earth's upper crust. In terms of the toxic potential of the San Diego River muds, it is reassuring that none of the values of toxic element levels documented in the San Diego River muds are not significantly higher than Li's terrestrial background values. On the other hand, the comparison with some muds, worldwide used for different medical proposes; show that heavy metal concentrations in San Diego River are in the same concentration ranges. Taking into account that peloide maturation processes do not change the heavy metal content present in the mud [32, 33], the heavy metal content in San Diego River healing mud is not an impediment for its medical purposes.

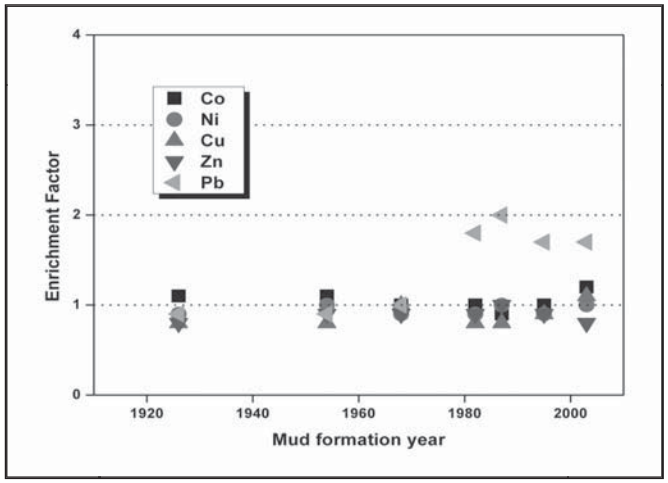

Figure 3. Historical heavy metal enrichment in healing mud from San Diego river outlet

Table 3. Heavy metal content (in $mg.kg^{-1}$) in healing muds used with medical proposes

Sample	Co	Ni	Cu	Zn	Pb
San Diego, Cuba (present study)	18 ± 2	62 ± 8	52 ± 2	72 ± 4	28 ± 2
Average shale **[27]**	19	50	45	95	20
River mud **[27]**	14	32	32	78	23
Hemipelagic mud **[27]**	20	53	30	130	24
Campomaggiore, Italy **[28]**	28	324	154	58	27
Calda, Italy **[29]**	-	58	27	109	14
Cappeta, Italy **[29]**	-	67	24	67	8.5
Genoa, Italy **[4]**	24	49	44	91	24
Archena, Spain **[30]**	5.1	3.4	11.5	33.1	10.9
Arnedillo, Spain **[30]**	16.8	50.8	52.3	89.8	37.0
Caldas de Boí, Spain **[30]**	5.7	21.1	14.5	56.9	24.6
El Raposo, Spain **[30]**	14.6	35.1	29.2	160.4	33.3
Lo Pagán, Spain **[30]**	4.0	20.0	24.7	85.9	37.5
Makirina Cove, Croatia **[31]**	11	29	35	51	26

Conclusions

The combination of the gamma spectrometry and XRFA allow to determine the practically constant levels of heavy metals in healing mud from San Diego River during the last 100 years. The comparison with some muds, worldwide used for different medical proposes; show that heavy metal content in San Diego River healing mud is suitable for its medical purposes.

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