Evaluation of the hurricanes Gustav and Ike impact on healing mud from San Diego river using nuclear and geochemical techniques

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Abstract
Effects induced by hurricanes Gustav and Ike on the characteristics of the San Diego River mud have been studied. X-ray fluorescence analysis, gamma spectrometry and the measurement of some physical andchemical characteristics in mud samples, collected before and after the hurricanes, show that the hurricanes induced changes not only in mud major composition but also in some other mud characteristics. The average sedimentation rate determined by gamma spectrometry in San Diego River outlet allowed to estimate that the original mud characteristics will be recovered no sooner // earlier than after 5-7 years. Further studies on the influence of changes in mud characteristics and in its therapeutic properties as a result of the impact of hurricanes are recommended as well.

Key words: *X-ray fluorescence analysis, Cuba, gamma spectroscopy, hurricanes, sediments*

Evaluación del impacto de los huracanes Gustav e Ike sobre los lodos medicinales del río San Diego mediante técnicas nucleares y geoquímicas

Resumen
Se estudian los efectos inducidos por los huracanes Gustav e Ike en las características principales de los lodos del río San Diego. La fluorescencia de rayos X, la espectrometría gamma y la medición de varios parámetros físico-químicos de lodos, colectados antes y después del paso de los huracanes en septiembre del 2008 mostraron que los huracanes provocaron cambios en la composición mayoritaria y en otras características de los lodos. La tasa de sedimentación promedio determinada por espectrometría gamma en la desembocadura del río San Diego permitió estimar que las características originales de los lodos medicinales no se recobrarán hasta dentro de 5-7 años. Se recomienda estudiar cómo influyen en las propiedades terapéuticas de los lodos, los cambios ocurridos en sus características producto del impacto de los huracanes.

Palabras claves: *análisis por fluorescencia de rayos X, Cuba, espectroscopía gamma, huracanes, sedimentos*

Introduction

Extreme natural event like hurricane (or series of hurricanes) can have substantial ecological ef-fects on coastal ecosystems. Physical effects of hurricanes on estuaries include increased sedi-mentation, sudden short term changes in salinity or dissolved oxygen [1], disturbance of shallow bottom habitats from storm-surge scouring [2,3] and remobilization of sediment contaminants [4]. Independently that hurricane impact is very local, usually, a long time is necessary to recover the original ecological status of the impacted area [5].

Peloide therapy have been used in medicine since ancient times and more recently such old practice has received applications also for wellness and relax purposes [6,7] due to their physical properties (i.e. absorption/adsorption capacity, cation exchange capacity, water saturation, swell-ing index, grain size, cooling index, etc.). The most important inorganic component of the peloide is clay minerals, mixed with salty thermomineral waters and accompanied by organic materials produced by the biological-metabolic activity of microorganisms growing during the so-called "maturation" process [8].

In September 2008, the San Diego River outlet (main mud source of San Diego de los Baños Thermal Centre) was impacted by two sequential strong hurricanes (a Category 4 on the Saffir-Simpson hurricane scale) named Gustav and Ike, respectively (figure 1). The aim of the present study was the evaluation of the effects induced by the hurricanes on San Diego River mud char-acteristics (major and heavy metal composition, radioactivity levels, electric conductivity, DO, etc.) for its therapeutic purposes.

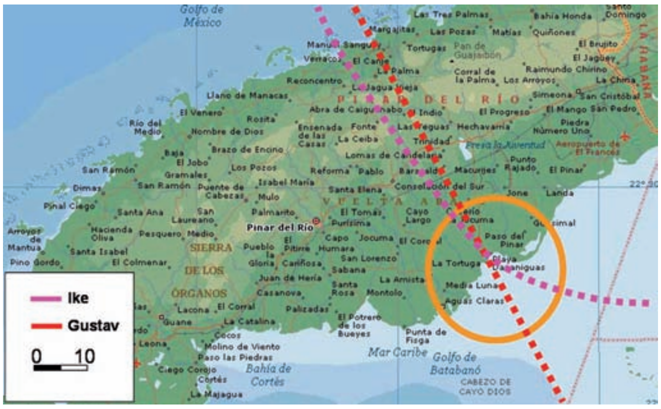

Figure 1. Trajectories of the hurricanes Ike and Gustav trough Pinar del Río province, western Cuba. San Diego river outlet is located in the centre of the circle.

Materials and methods

Samples were collected in five stations in the San Diego River outlet (figure 2) during the same journey and two weeks after the second hurricane. Stations were selected in the same places studied in 2007 when some mud samples were collected for their toxicological analysis [9]. Additionally, a 50 cm core was collected in station 3 for sedimentation rate determination. The core tube was cut 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.

Elemental concentrations were determined by external standard method X-ray fluorescence analysis (XRF) using the Certified Refereznce Materials (CRM) IAEA-SL-1 “Lake Sediment” [10], IAEA-Soil-5 [11], IAEA Soil-7 [12], BCR-2 “Basalt Columbia River” [13] 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) de-tector (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 [14]. Detection Limits were determined according Padilla *et. al*. [15] (in concen-tration 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).

Figure 2. Location of studied stations in San Diego River outlet.

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 – experimental value, C_W – 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 in three categories: SR ≤ 25% = excellent; 25 < SR ≤ 50% = ac-ceptable, 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 are “excellent” (SR ≤ 25%) and the obtained results shows a very good correlation (R = 0.9999) between certified and measured values.

Table 1. XRF analysis of CRM IAEA-356*, SR values and Detection Limits

Metal	Certified value	Measured value	SR (%)	LD (mg.kg-1)
K (%)	1.26	1.29 ± 0.06	12	308
Ca (%)	8.87	8.62 ± 0.14	14	105
Ti (%)	2190	^{210}4 ± 178	20	42
Mn	312	315 ± 34	23	21
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

* Mean ± SD, n = 5, mg.kg^{-1} except indicated

In order to assess the hurricane impact to sediment elemental composition and to mitigate the grain-size dependence; the element enrichment (or impoverishment) was calculated by normaliz-ing the results to a reference element, using the Enrichment Factor [18]:

$$EF = (X/Y)_{after} /(X/Y)_{before}$$

where X is the concentration of potentially enriched element and Y is the concentration of the reference element, using the corresponding to 2007 elemental concentrations as background. If EF value of an element is close to unity, it means that hurricanes do not induce to a concentra-tion increment Then, Enrichment value higher (lesser) than unity indicated a possible enrichment (impoverishment) of the element content induced by the hurricanes. 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 [19,20].

In radiometric study, CRM, standard and sample preparation was standardized as 50 grams (dry weight) and putted in the hermetic closed plastic container during 30 days so that a secular equi-librium between ^{226}Ra, ^{222}Rn and shorter half lives daughters of ^{222}Rn was assured. Samples, CRM and standards were measured during 24 hours in the Low-Background Gamma Spec-trometer (LBGS) of the Nuclear Analytical Lab at InSTEC [21]. LBGS is composed by a Low-Background Chamber (LBC), using 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). The gamma spec-tra were processed using the Gamma-W version 18.03 code (Dr. Westmeier Gesellschaft für Kernspektrometrie mbH). The minimum detectable activity (MDA) of the system for 24 hours count acquisition were 6.1 Bq.kg^{-1} for ^{210}Pb, 1.8 Bq.kg^{-1} for 234Th, 1.0 Bq.kg^{-1} for 214Pb, 0.6 Bq.kg^{-1} for ^{137}Cs, 1.9 Bq.kg^{-1} for ^{232}Th and 7.1 Bq.kg^{-1} for ^{40}K. The Determination Limit was calculated according Currie criteria [22].

The radionuclide activities present in sediment samples were determined by gamma spectrome-try using the CRM IAEA-375 [23] and UC-2 standard prepared in the University of Cantabria (Spain) [24] for calibration. The accuracy (table 2) was evaluated by UC-1 standard [24]. The application of relative method show “excellent” results (SR < 25% for all determined activities). The obtained deviation from the reference values is always less than 5%. It is an excellent preci-sion for environmental radioactivity measurements.

The sedimentation rate and age of recent sediments has been achieved starting from the deter-mination of the activity profile of ^{137}Cs and ^{210}Pb in Station 3. The ^{137}Cs isotope has an artificial origin; it results from the nuclear explosions since the 50´s, showing a characteristic activity maximum in sediments between 1962 and 1964 due to atmospheric nuclear weapon testing fallout maximum [25]. For this reason ^{137}Cs activity maximum (see figure 3) usually is used as data marker, to verify the ^{210}Pb age determination [26]. ^{210}Pb isotope is a natural radionuclide in the ^{238}U series which is deposited from the atmosphere. Taking into account the possible perturba-tion of the sediments from more superficial layers, the age of the sediments was calculated by the constant rate of supply (CRS) model using the excess ^{210}Pb profile [27]. For each layer, the sedimentation rate was calculated as layer-thickness/formation-time ratio (in cm. y^{-1}).

Table 2. Activities (Bq.kg^{-1}) determined in UC-1 standard by relative method

Nuclide	^{210}Pb	^{226}Ra	^{137}Cs	^{232}Th	^{40}K
Reference activity	75	24	45	30	480
Standard Deviation (%)	17	13	4	10	4
Measured activity	78	25	44	31	460
Standard Deviation (%)	9	8	9	10	7
Deviation from the reference value (%)	4.0	4.2	-2.2	3.3	-4.2
SR (%)	23	21	20	23	18

Measurements of mud physical properties (pH, temperature, redox, conductivity and dissolved oxygen) were obtained at each station, with a WTW 315i pH-meter (WTW TFK 325 temperature sensor, WTW SenTix 21 pH-electrode, SCHOTT Platinum Blue Line 32Rx redox-electrode), WTW LF 197 conductivity meter and HANNA Instruments HI 9142 DO-meter.

Results and Discussion

The average concentrations of the elements determined by XRF analysis, average activities of the radionuclides measured by gamma spectrometry and changes in mud properties, before and after the hurricanes impact to the studied area, are presented in tables 3-5, respectively.

The must significant differences in content are observed for K, Ca and Mn. In maturated peloids, Ca and K are not come from the mineral–medicinal water. There contents are mainly associated with the solid phase [28]. Potassium content usually is associated with soil particles dragged by river waters, i.e., K is an indicator of pluvial origin component in the sediment composition. On the other hand, Ca content is associated with the presence of marine sediment. Then, K impov-erishment (EF = 0.7) and Ca enrichment (EF = 1.5) must be associated with changes in the mud major composition because the hurricane impacts, which can change the river sediment from pluvial nature to marine. The high Mn content is usual in river outlets due it flocculation property in fresh-sea water border. The invariability of heavy metal enrichment was expected, because the historical low heavy metal content in San Diego River mud in the last 100 years [29], indicat-ing a small anthropogenic heavy metal pollution in the area.

Table 3. Average concentrations* and enrichment of elements determined in mud from San Diego River outlet

Element	2007	2008	EF
K (%)	1.2 ± 0.1	0.8 ± 0.1	0.7
Ca (%)	1.31 ± 0.05	1.82 ± 0.05	1.5
Ti (%)	0.63 ± 0.02	0.59 ± 0.02	1.0
Mn	817 ± 28	950 ± 30	1.3
Fe (%)	4.0 ± 0.1	3.6 ± 0.1	-
Co	18 ± 2	16 ± 2	1.0
Ni	68 ± 8	62 ± 8	1.0
Cu	56 ± 2	52 ± 2	1.0
Zn	77 ± 4	72 ± 5	1.0
Pb	32 ± 2	28 ± 2	1.0

* - Mean ± SD, in $mg.kg^{-1}$, except the indicated

Radiometric study confirms the potassium impoverishment. The ^{40}K activity determined in mud, collected after hurricane impacts, decrease around a 25% respect before one (table 4). The ac-tivity of the rest of natural and artificial radionuclides present in mud practically does not change.

A several increment in electric conductivity (~ 60%, see table 5) must be a good indicator of ma-rine sediment increment in San Diego River outlet. Usually, this increment is associated with sa-linity increment in the area.

The behaviour of excess ^{210}Pb and ^{137}Cs activities measured in mud core collected in station 3 and the mud formation-year estimated by CRS model are shown in figure 3. The ^{137}Cs presence in Cuban sediments is only due to fallout from nuclear explosions [30,31]. Then, its activity maximum (25 cm depth core slice) corresponds to 1962-1964 period. The last is in correspon-dence with formation year estimation by excess ^{210}Pb CRS model.

Table 4. Average activities* for radionuclides determined in mud from San Diego River outlet

Nuclide	2007	2008
^{210}Pb	61 ± 10	51 ± 10
^{238}U	11 ± 2	10 ± 2
^{226}Ra	19 ± 2	22 ± 2
^{137}Cs	5.0 ± 0.4	4.5 ± 0.4
^{232}Th	21 ± 2	18 ± 2
^{40}K	273 ± 21	208 ± 23

* - mean ± SD, in $Bq.kg^{-1}$

Table 5. Changes in physico-chemical mud characteristics before and after hurricanes impact.

	2007	2008
pH	7.4	7.8
Eh (mV)	-207	-180
T (°C)	26.5	24.3
DO ($mg\text{-}L^{-1}$)	1.0	0.8
Elec. Cond. ($mS.cm^{-1}$)	12.6	20.1

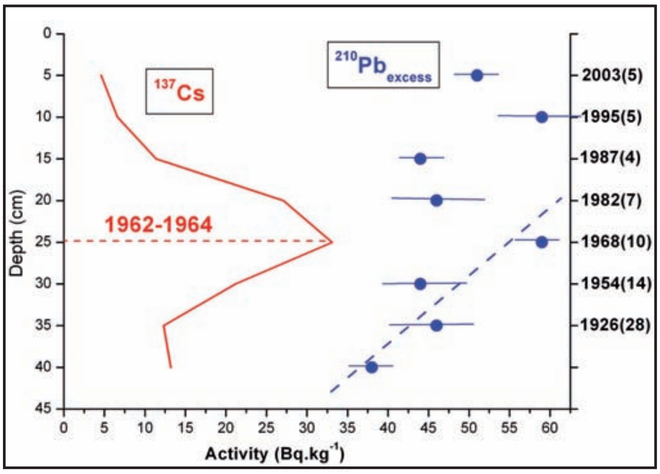

Figure 3. Downcore average ^{137}Cs and excess ^{210}Pb activities (in $Bq.kg^{-1}$) in sediment profile. Dashed line shows the non perturbed estimation for CRS model. Right axis shows the estimated mud formation year (Error in years).

A notable sedimentation rate increment in San Diego River outlet is determined in the last 50 years (figure 4). This increment must be associated with some anthropogenic activities (principally, due a considerable increment of cultivable areas along San Diego River) and natural ones (for example, soil erosion increment due an increment in rain regimes in the area) in the last few decades. Taking into account the average sedimentation rate in the last few decades (~ 0.7 $cm.y^{-1}$), the original mud characteristics in San Diego River outlet will be recovered never before than 5-7 years.

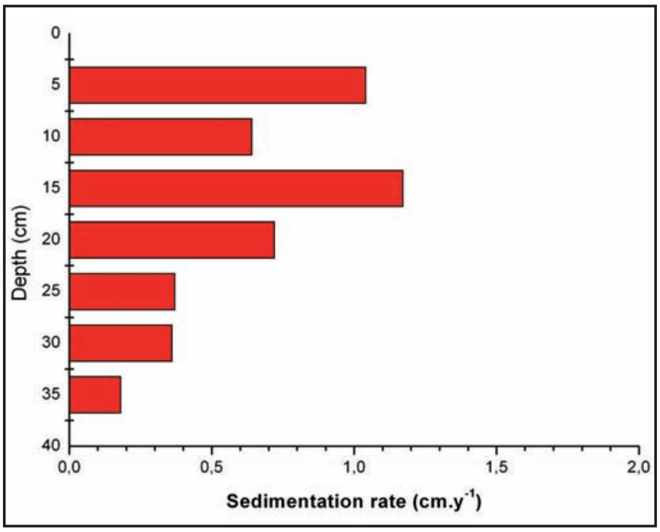

Figure 4. Sedimentation rate in San Diego River outlet.

Conclusions

Nuclear and geochemical techniques permit to evaluate that the direct impact of the strong hurri-canes to San Diego River outlet in September 2008, induced changes in mud major composition (Ca enrichment and K impoverishment) and in some mud physic-chemical characteristics (elec-tric conductivity, redox and DO). On the other hand, the sedimentation rate in San Diego river outlet, determined by gamma spectrometry, permit to estimate that the original mud characteris-tics will be recovered never before than 5-7 years.

Taking into account the importance of peloide therapy for different diseases treatments, further studies to quantitatively assess the changes within the mud main characteristics due to the hurri-cane impacts are recommended, with particular interest in its therapeutic properties and how these could result affected.

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