HISTORICAL TREND IN HEAVY METALS POLLUTION IN THE SEDIMENTS OF CIENFUEGOS BAY, DEFINED BY ^{210}PB AND ^{137}CS GEOCHRONOLOGY

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Abstract

Investigations on the concentration level of heavy metals in the sediments of Cienfuegos bay (Cuba) have been carried out, to reconstruct their "depositional history" by using radionuclide geochronology, to highlight the major changes occurred in the last century and to draw hypotheses on their origin. During two sampling campaigns (1999 and 2001) sediment cores and surface grab samples have been collected in the two basins of the bay. In this paper results on the horizontal and vertical distribution of arsenic, nickel and vanadium are discussed, along with data on concentrations of natural (excess ^{210}Pb) and anthropogenic (^{137}Cs) radionuclides, used as tools to "date" the sediment horizons. Results evidenced that important changes in the sedimentation regime of the bay occurred in the last forty years, in relation to changes in land uses and to the effects of some extreme meteorological events. The distribution of the heavy metals shows the influence of the recent industrialization of the area, as revealed by both the spatial and vertical concentration within the sediment horizons.

Key words: cesium 137, Cuba, bays, sediments, metals, radioecological concentration, sensitivity analysis, chemical analysis, absorption spectroscopy, Cienfuegos

TENDENCIA HISTÓRICA DE LA CONTAMINACIÓN POR METALES PESADOS EN SEDIMENTOS DE LA BAHÍA DE CIENFUEGOS, DEFINIDA CON LA GEOCRONOLOGÍA DEL ^{210}PB Y ^{137}CS

Resumen

En este trabajo se determinaron los niveles de metales pesados en cores de sedimentos de la bahía de Cienfuegos (Cuba), y con el uso de radiotrazadores para su datación, nos permitió reconstruir la historia de su deposición, así como la identificación de los principales cambios ocurridos en el último siglo. Durante dos campañas de muestreo (1999 y 2001) se colectaron cores y sedimentos superficiales en la bahía de Cienfuegos. En este artículo se presentan los resultados de la distribución horizontal y vertical de arsénico, níquel y vanadio y de los radionúclidos ^{210}Pb (en exceso) y ^{137}Cs, estos últimos usados como herramientas para la datación de los cores de sedimentos. Los resultados del trabajo evidencian un cambio en el régimen de sedimentación de la bahía de Cienfuegos en los últimos cuarenta años, atribuibles al uso de la tierra en el área y a eventos meteorológicos extremos. La distribución, tanto horizontal como vertical de los metales analizados, muestra la influencia de la industrialización reciente en la bahía de Cienfuegos.

INTRODUCTION

The sediments play a key-role in the distribution of heavy metals in a semi-enclosed environment (Fabris *et al.*, 1999; Mason *et al.*, 2004, Tolun, 2001), where the concentrations of heavy metals can reach as much as five orders of magnitude higher than those of the surrounding water (Birch, 1996; Bryan and Langston, 1992; Turner, 2000). The fate of particle-associated contaminants is primarily controlled by the energy released in the environment: fine-grained particles - in particular clay minerals, to which contaminants are preferentially associated. The distribution and bioavailability of metals in a semi-enclosed marine environment also depend on many other

processes, that include: geochemical behavior of the element (Algan *et al*., 2004, Wright and Mason, 1999); the presence of a salinity gradient (Riba *et al*., 2003, Wang and Liu, 2003); tidal dynamics (Yang, 2004) and hurricanes (Walker, 2001), that can re-suspend surface sediments.

The bay of Cienfuegos, located in the southern-central part of Cuba (figure 1), is an enclosed bay with a surface area of 90 km^2 and an average depth of 14 m. The bay is divided in two well-defined hydrographic basins. The northern basin receives most of the anthropic impact from the city sewage discharge, from the industrial area (thermoelectric power plant, fertilizer industry, oil refineries) and from the outflow of the Damuji and Salado rivers that drain an area where intense agriculture has been developed in the last forty years. The southern basin is subject to a smaller degree of anthropic pollution, mainly originated from the Caonao and Arimao rivers. The bay represents the most important natural resource in the Cienfuegos province, and the surrounding land has been intensively exploited.

In the last three decades some deleterious ecological signals have been observed in the Bay. For these reasons a large environment research programme has been initiated, to define the main physical, chemical and biological characteristics of the bay, whose knowledge will constitute the basis for the correct management of the area.
As part of this programme, dating techniques based on the natural and antropogenic radionuclides (^{210}Pb and ^{137}Cs) and mineralogical distribution were applied by Alonso Hernández *et al.* (2006) to study of the sedimentation regime in Cienfuegos bay. This study showed that in the last 40 years significant changes have affected sedimentation processes in the bay. These results are the base to evaluate the distribution of heavy metals in the bay.

The aims of the study are to reconstruct the "pollution history", using natural and anthropogenic radionuclides as tools for "dating" the sediment horizons; to identify the main processes responsible for the spatial and vertical distribution of heavy metals (As, V, Ni) in the

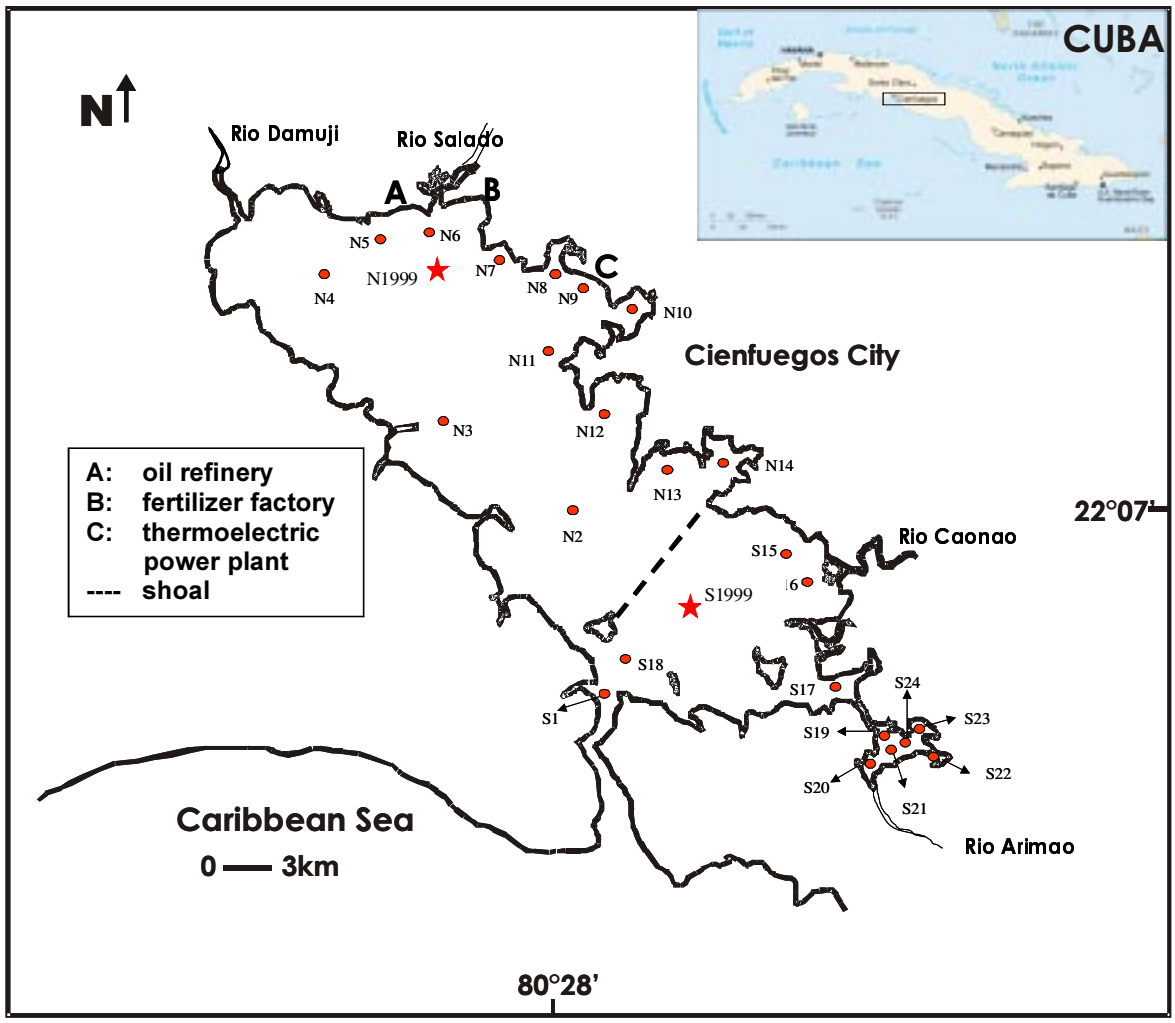

Figure 1 Sampling points. Dot: grabs, 2001; Star: cores, 1999.

sediments, and then to identify the major events related to the management of specific industries located in the bay.

MATERIAL AND METHODS

Sampling

Two sampling campaigns have been carried out in 1999 and 2001. The location of the sampling stations is reported in figure 1. Surface sediments have been collected in 24 stations. Sediment cores (N1999 and S1999) have been collected by a scuba diver carefully inserting a plastic tube, 12 cm in diameter and 100 cm in length, into the sediment. Cores have been quickly sliced into 1-cm intervals. All samples have been put in polyethylene cans and stored at 4°C. Samples were dried at 40°C until constant weight, sieved through 1-mm nylon sieve and grinded. The resulting powder was stored at room temperature in polyethylene cans until analysed. Porosity, Organic Matter, Grain Size, Radiochemical and Mineralogical composition in sediment cores collected in 1999 have been discussed by Alonso Hernández *et al*. (2006).

Chemical analyses of heavy metals

Analytical procedure, calibration, and quality control of results are described elsewhere (Perez Santana *et al.*, 2004, in press; Ipoly *et al*., 2002). Briefly, the total dissolution of 0.5 g of sediment was performed using strong acids and a CEM microwave pressurized digestor. Determinations of metals were carried out by ICP-MS (Perkin-Elmer ELAN 6000, equipped with a Ryton cross-flow nebuliser). The calibration standards were prepared diluting stock BDH Aristar solution with double-deionized Milli-Q water. Analyses have been performed on two aliquot of each sample, and on blanks. Performances of the analytical procedure were checked analysing Certified Reference Materials (NIST 1646a, PACS-1, MESS-1). All results were comprised within 90-110% of certified values.

Radiochemical analyses

Sub-samples of the surface sediments and of all core sections were analysed for ^{210}Pb, ^{226}Ra and ^{137}Cs contents by gamma spectrometry, using low background intrinsic germanium coaxial detectors (60% efficiency, 2.1 keV resolution at 1333 keV) coupled with a multichannel analyser. Twenty grams of the dried and homogenised samples were placed in sealed containers and left for three weeks before counting, to reach the ^{222}Rn/^{226}Ra equilibrium. ^{210}Pb was determined via its gamma emission at 46.5 keV; ^{226}Ra by the 295 keV, 352 keV and 609 keV gamma rays emitted by its daughters ^{214}Pb and ^{214}Bi; ^{137}Cs was measured at 662 keV. Efficiency calibration was performed using a CANMET Standard U-Ore and QCY44 AMERSHAM Certified Solution. NBS and IAEA Reference Materials were used to check the accuracy of the results that resulted within ± 10% of the certified values. The excess ^{210}Pb was calculated of the difference between the supported ^{210}Pb and the ^{226}Ra.

RESULTS AND DISCUSSION

Geochronology

The vertical profiles of ^{137}Cs in the cores collected in Northern (N 1999) and Southern (S 1999) basins are showed in figure 2 and have been used for "dating" specific sediment horizons. The vertical profiles, concentrations were plotted versus "mass depth" (g cm^{-2}), instead of depth ("cm"), to avoid correction for sediment compaction.

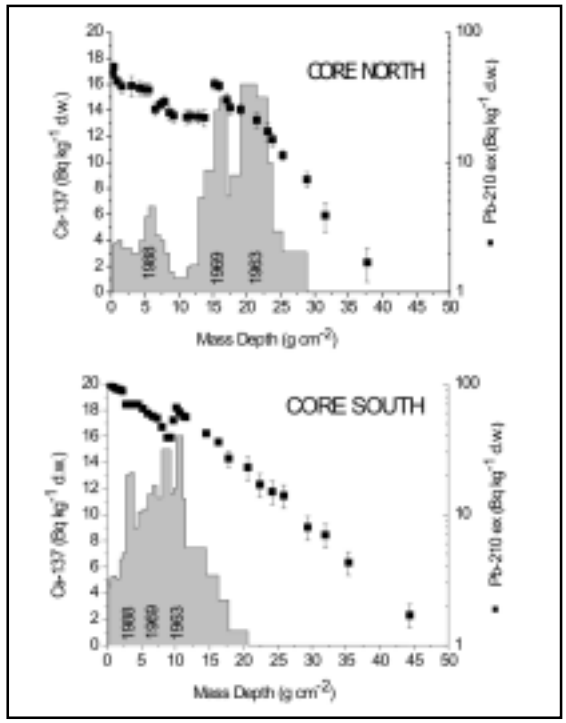

Figure 2. Vertical profiles of ^{137}Cs and ^{210}Pb$_{ex}$ in Core North and Core South, 1999.

^{137}Cs was introduced into the Caribbean environment mainly by fallout from nuclear weapon testing in the atmosphere. The input function of ^{137}Cs at the latitude of Cuba is well defined (Alonso Hernández, 2004), and shows a maximum in 1963 due the ban of nuclear testing explosions in the atmosphere and a sharp decrease in the following years: so it was realistic to attribute "1963" to the sediment layer corresponding to the maximum ^{137}Cs concentration in the vertical profiles. The profiles show also two additional peaks between the maximum concentration and the surface, that we attributed to extra-inputs of ^{137}Cs-reach particles into the Bay. In fact, the calculated inventory of ^{137}Cs in the sediment cores

(0.19 and 0.20 Bq cm^{-2}) are higher than the cumulative fallout deposition in the area, estimated from adjacent undisturbed soil (0.12 Bq cm^{-2}, Sibello Hernández *et al.*, 2002). This likely indicates a significant transport of ^{137}Cs from land to the bay. Moreover, two extreme meteorological episodes have been actually registered, after 1963, able to produce extra-input from the rivers: the hurricane "Camille", that crossed Cuba in 1969 with 500 mm of rain in 3 days and an exceptional period of heavy rain (1000 mm in 7 days) occurred in June 1988.

These events provided an extra-input of suspended load to the bay (carrying an enhanced ^{137}Cs content, associated to clay particles), from both the weathering of the catchment basins and the resuspension & transport of ^{137}Cs-rich sediment initially stored in the river bed. Finally, by crossing the data of the ^{137}Cs vertical profiles with those on the fallout deposition and with the meteo record for the region we reasonably hypothesised that the two extra-peaks could be dated at 1969 and 1988.

Results from the vertical profiles of excess ^{210}Pb have been used to integrate those of ^{137}Cs dating and to derive information on the sedimentation regime in the last 100 years. The vertical profiles of $^{210}Pb_{ex}$ suggest significant variations in the sedimentation regime, both spatially and temporally. A remarkable discontinuity was observed in the profiles (figure 2), corresponding to sedimentation processes occurred in the period 1963-1973. The CFCS/Constant Flux Constant Sedimentation model (Appleby *et al.*, 1992) was separately applied to the sediment layers below and above the observed discontinuity. While from the beginning of 1900 sediments were regularly accumulated at a rate of around 0.3 g cm^2 y^{-1}, beginning from early Seventies the sediment accumulation rate almost doubled (0.5 g cm^{-2} y^{-1}) in the northern basin. In addition, corresponding to the caesium peaks, there are "packages of sediment" having the same age, supporting the hypothesis that ^{137}Cs peaks are correlated to the meteo events that produced enhanced supply of particles into the bay, in a very short period of time. More information about the chronological results was discussed by Alonso Hernández *et al*. (2006).

Nickel, vanadium, arsenic in sediments

In figure 3 the spatial distributions of nickel, vanadium and arsenic are shown, whereas figure 4 and 5 show the vertical profiles of vanadium, nickel and arsenic in the two cores. All results are reported in table 1, 2 and 3.

Table 1. Concentrations of Ni, V and As in surface sediments (mg.kg^{-1})

Station	Ni	V	As
C1	27 ± 1.9	46 ± 2.9	5.15± 0.13
N2	37 ± 1.2	88.7 ± 1.3	7.6 ± 0.12
N3	64 ± 0.8	126 ± 1.2	8.04± 0.02
N4	60 ± 0.6	100 ±	8.3± 0.15
N5	58 ± 3.3	94 ± 0.3	8.1 ± 0.43
N6	41 ± 0.1	122 ± 0.5	11 ± 0.15
N7	25 ± 0.9	40 ± 12.7	5.8 ± 0.38
N8	38 ± 0.2	95 ± 0.3	6.7 ± 0.06
N9	124± 7.1	400 ±16.3	9.04± 0.45
N10	89 ± 4.8	392 ± 3.9	9.2 ± 0.17
N11	49 ± 2.1	111 ± 5.8	6.9 ± 0.23
N12	50 ± 0.3	112 ± 0.9	8.9 ± 0.13
N13	28 ± 0.9	80.8 ± 2.7	4.7 ± 0.13
N14	39 ± 0.3	113 ± 1.4	11 ± 0.13
S15	38 ± 0.3	145 ± 1.4	7.9 ± 0.07
S16	34 ± 0.7	137 ± 2.8	8.5 ± 0.01
S17	65 ± 1.9	154 ± 4.8	9.3 ± 0.48
S18	52 ± 0.4	124 ± 0.6	9.1 ± 0.01
S19	78 ± 5.1	182 ± 13.2	8.7 ± 0.41
S20	68 ± 3.4	173 ± 7.9	7.9 ± 0.35
S21	52 ± 3.5	150 ± 9.5	5.01± 0.28
S22	53 ± 2.8	162 ± 11.8	5.8 ± 0.24
S23	62 ± 3.8	184 ± 11.6	6.6 ± 0.39
S24	69 ± 0.7	192 ± 1.7	8.3 ± 0.09

Table 2. Concentrations of Ni, V and As in core N1999 (mg.kg^{-1})

Depth (cm)	Ni	V	As
5	57 ± 0.5	143 ± 0.4	73 ± 10
25	68 ± 0.2	125 ± 0.1	88 ± 9.6
32.5	60 ± 1.1	121 ± 3.5	11 ± 0.23
35.5	55 ± 2.2	118 ± 4.7	9.5 ± 0.36
40	51 ± 4.1	107 ± 8.4	11 ± 0.98
70.5	45 ± 0.9	83 ± 0.1	6.6 ± 0.31
72	46 ± 0.3	87 ± 2.3	7.5 ± 0.01
76.5	45 ± 0.5	83 ± 0.4	6.8 ± 0.16
78	48 ± 0.9	88 ± 1.8	6.9 ± 0.05

Table 3. Concentrations of Ni, V and As in the South core (mg.kg^{-1})

Depth (cm)	Ni	V	As
5	57 ± 0.8	143 ± 0.8	11 ± 0.09
12	51± 2.8	120 ± 1.0	9.4 ± 0.59
15	48 ± 0.6	114 ± 1.1	9.3 ± 0.13
18	51 ± 1.4	116 ± 4.0	8.8 ± 0.17
19.5	51± 2.5	116 ± 6.0	8.9 ± 0.33
59	36 ± 0.2	76 ± 0.2	6.4 ± 0.06
63.5	38 ± 2.7	80 ± 5.4	7.3 ± 0.30
66.5	38 ± 1.2	81 ± 3.5	6.8 ± 0.11
68	41 ± 4.2	88 ± 12	6.8 ± 0.34

In the case of nickel and vanadium (figure 3a and 3b) particularly high concentrations were found, as expected, in the surface samples collected in front of the thermoelectric power plant (figure 1, point "C"). Concentration levels are twice (nickel) and three times (vanadium) higher than the average value found in the surface sediments of the northern basin (Ni: 106 mg kg-1, in respect to 50; V: 400 mg kg-1, in respect to 137). This area can be considered as zone of preferential accumulation of the metals emitted by the plant, both in gaseous form and as wastewater. The plant was activated in 1939, but the substantial increase in power generation occurred in 1949. Actually the vertical profiles of vanadium and nickel in the sediment cores (figure 4) reveal enhanced concentrations in strata deposited after the early sixties. These differences are measured in both basins, demonstrating that the impact of the power plant has been redistributed on the whole bay territory, on a fifty years time-scale.

The spatial distribution of arsenic in 2001 is rather homogeneous in the two basins of the bay (figure 3), with concentrations around 5 mg kg^{-1}. On the contrary, the vertical profiles in the sediment cores (figure 5) gave an additional insight on impacts recently produced by the industry in the northern basin. While the profile gathered in the southern core shows values that can be considered as "background level", a significant increase in concentration – up to 88 mg kg^{-1}, more than one order of magnitude higher- was found down in the northern core, in strata corresponding to late-Seventies/early Eighties. This signal marks the management of a Nitrogen fertilizer industry, including the effect of a major accident occurred in 1979.

Summarizing, in fact, the re-distribution in the sediments is correlated to preferential pathways in wet and dry deposition for nickel and vanadium,

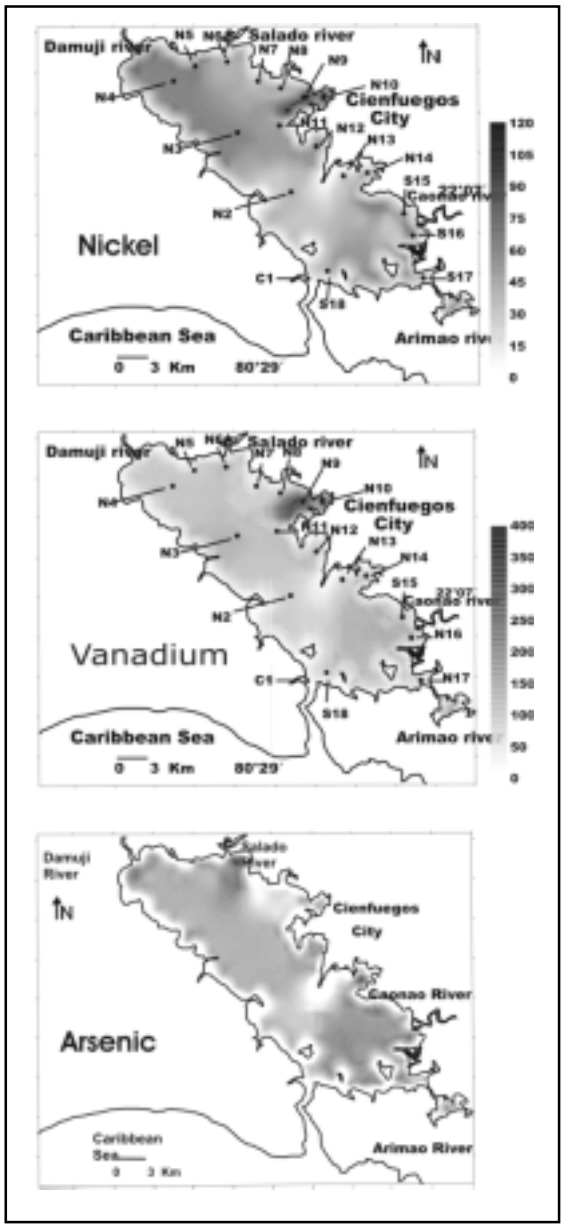

Figure 3. Spatial distributions of nickel (a), vanadium (b) and arsenic (c), 2001.

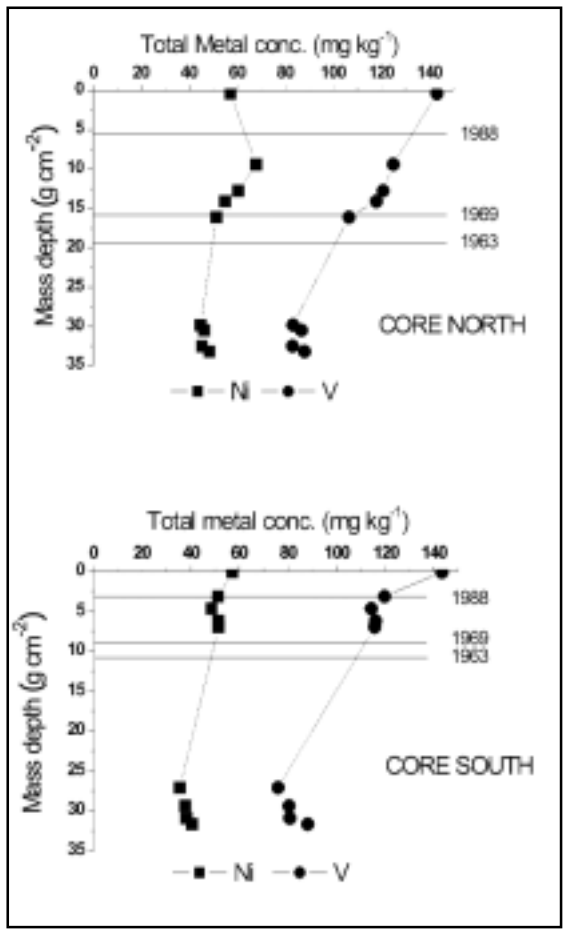

Figure 4. Vertical profiles of vanadium and nickel in Core North and Core South.

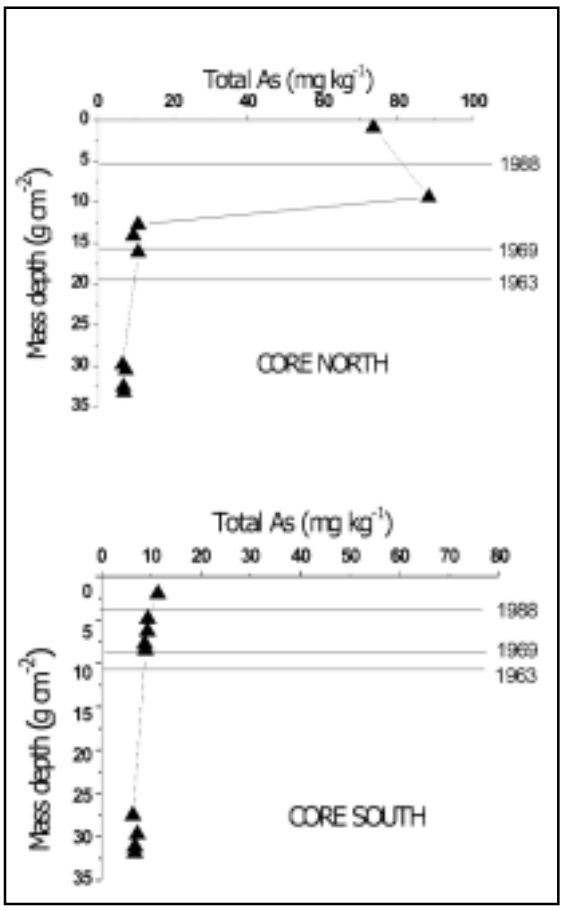

Figure 5. Vertical profiles of arsenic in Core North and Core South, 1999.

initially dispersed into the atmosphere from the thermoelectric power plant located in the northern basin, to the water masses circulation and sedimentation regime for the elements (like Arsenic, for instance) entering directly into the marine environment from factory and waste treatment. As a matter of fact, significant amounts of heavy metals have been introduced into the bay, mainly in the northern basin, by authorized releases - and accidents - from the industrial complex. In addition, as important changes in land uses and random meteo events produced additional inputs of suspended particle load (to which particle-reactive contaminants associate), an increased accumulation in the sediments was observed, both in terms of sediment accretion rate (g cm^{-2} y^{-1}) and concentration (g kg^{-1}) of metals.

CONCLUSIONS

The main contribution of this work has been to demonstrate the power of the nuclear techniques in environmental studies. Particularly, the use of the ^{210}Pb and ^{137}Cs in the dating of marine sediments and the possibility of studying the historical contamination of heavy metals in estuaries and coastal areas.

From the results of this study can be concluded that:

1. The sedimentation regime in Cienfuegos bay has changed in the last forty years. Sediment accumulation became faster and irregular. The most important reasons likely are the changes in land uses, including the development of intensive agriculture in late Fifties that resulted in enhanced deforestation in the area drained by the rivers, and in significant increase of the suspended load entering into the bay; and the period of heavy rain occurred in 1988, as well as during the hurricanes transits, that also led to enhanced supply of particulate material transported by rivers.
2. In the bay of Cienfuegos, the pollutants introduced in the atmosphere (i.e. vanadium and nickel) are homogeneously distributed all over the two basins, on a time-scale of decades. The highest surface concentrations are found close to their point source.
3. Arsenic, introduced directly into the sea by authorized releases of a fertilizer complex, sedimented in the northern basin, close to the point source. The vertical distribution in the northern sediment core reveals a sharp increase in strata corresponding to the late-Seventies, when a first major accident occurred with the sudden release into the bay of liquid wastes with elevated arsenic concentration.
4. The metals tend to remain in the bay environment for a long period: decades, at least.
5. Results from this study gave a first insight to support adequate strategies for the management of the bay ecosystem and the surrounding area.

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