

XRF analysis of sediments from Nuevitas Bay (Cuba): assessment of current heavy metal contamination

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Abstract

Concentrations of chromium, nickel, copper, zinc and lead in surface sediments from six stations located in Nuevitas Bay (Cuba) were estimated by X-ray fluorescence analysis. The Cr content in sediments shows a strong variation across the studied stations (89-513 mg.kg⁻¹), in contrast with the other elements studied. The application of modified degree of contamination (mC_d) classifies as moderate the contamination of Nuevitas Bay. The comparison with Sediment Quality Guidelines and toxicity mean quotients shows that 100 % of the Sediments are associated with the occasional presence of possible adverse effects to human health.

Key words: sediments, Cuba, pollution control, X-ray fluorescence analysis, heavy metals

Análisis por FRX de sedimentos de la Bahía de Nuevitas (Cuba): evaluación de la contaminación actual por metales pesados

Resumen

Se determinan, mediante el análisis por fluorescencia de rayos X, las concentraciones de cromo, níquel, cobre, zinc y plomo en sedimentos superficiales de seis estaciones de la Bahía de Nuevitas en Cuba. El contenido de cromo se determinó con un intervalo de gran variación (89-513 mg.kg⁻¹) en las estaciones estudiadas. La aplicación del grado de contaminación modificado (mC_d) clasificó la contaminación de los sedimentos de la Bahía de Nuevitas como de "grado moderado". La comparación con las Guías de Calidad de Sedimentos y del cociente promedio de toxicidad, mostró que el 100 % de los sedimentos estudiados están asociados a la presencia ocasional de posibles efectos adversos a la salud humana.

Palabras clave: sedimentos, Cuba, control de la contaminación, análisis por fluorescencia de rayos x, metales pesados

Introduction

Anthropogenic activities and natural sources can discharge different metals to marine water in both dissolved and suspended solid forms. Normally, such metals tend to accumulate in the sediments by superficial adsorption or precipitation. These sedimentation processes of metals (and other pollutants) initially can be considered beneficial as potentially toxic compounds are relatively passivated (and concentrated) in the sediments. Nevertheless, this can also cause long-term problems as they may interact and alter the benthic population. More importantly, it has been recently shown that toxic metals

play an important role modifying the biochemical parameters of bottom water in coastal marine areas with a strong impact on benthic foraminifera [1].

From the analytical point of view, concentration patterns in sediments differ from concentration patterns in water [2], and for this reason, sediments can be considered, in contrast with water, a much more consistent pollution tracer and valuable indicators of the impact of the different human activities on the marine environment. In this sense, information on trends and periodicity can be obtained using time series analysis techniques [3]. In addition, sediment analysis can also inform on mechanisms of transport, as well as sites of preferred accu-

mulation [4]. Consequently, sediment analysis plays an important role in the assessment of pollution status of the marine environment, and moreover, sediments can also be used to differentiate sources of pollution because of their accumulation rates (high concentration of metals can accumulate in sediments within a relatively short time) and preservation [5].

Nuevitas is a 185 years old city (57 662 inhabitants [6]), located in the Camaguey province northern coast. Besides being one of the main Cuban harbours (160 km², with 49 m of maximal depth), several industries are located in Nuevitas, including some considered as potential pollution sources, such as power plants, cement, food and fertilizers. Most of the generated wastes (domestic and industrial) are frequently discharged directly into the sea coast, or indirectly through some rivers with waters flowing into the bay. For this reason, the Engineering Center for Environmental Management of Bays and Coasts (CIMAB) carried out systematic studies on the heavy metal pollution levels in Nuevitas Bay. The last CIMAB study was performed in 2003, considering Nuevitas Bay as unpolluted [7]. Taking into account the reactivation of the previously mentioned industries in the last decade, and the current plan to develop a marine cultivation area of marine species of high relevance in the Fishery Industry, a new study is necessary, in order to assess the current sediment environmental quality in terms of metal contamination and possible risk to the area's biota and consequently, to human health.

Materials and Methods

Surface sediments from the same six stations studied in Nuevitas Bay in 2003 [7] (Figure 1) were collected during the same journey using a Van Veen snapper. All samples were dried at 60 °C. Large rock debris, mollusc skeletons and organic debris were removed before sieving. The fine fraction (< 63 µm) was extracted by sieving and newly dried at 60 °C until obtaining a constant weight.

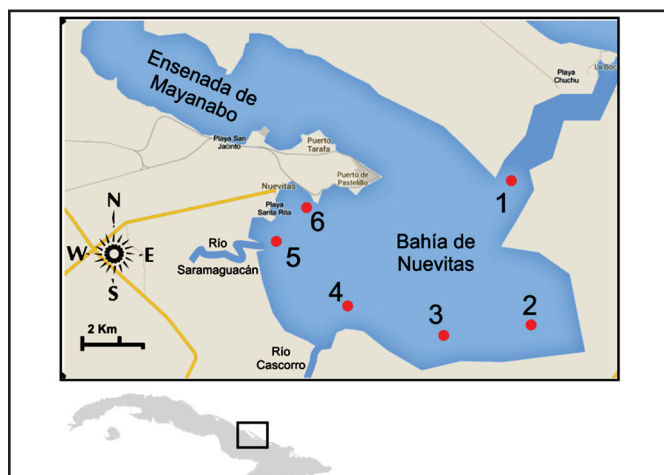


Figure 1. Location of the studied stations in Nuevitas Bay

Metal concentrations were determined by external standard method of X-ray fluorescence analysis (XRF)

using the Certified Reference Materials (CRM) IAEA-356, IAEA-Soil-5, IAEA Soil-7, BCR-2 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 5 grams pellets of 25 mm in diameter and 4-5 mm in 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 238Pu (1.1 GBq) excitation source with ring geometry was used. All spectra were processed with WinAxil code [8]. Detection Limits were determined according to Padilla et al. [9] (in concentration units) as $L_D = 3 \sigma / m$, 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. [10]:

$$SR = \frac{|C_x - C_w| + 2\sigma_x}{C_w} \cdot 100\%$$

where C_x – experimental value, C_w – certified value and σ_x 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: $SR \leq 25\%$ = excellent; $25 < SR \leq 50\%$ = acceptable, $SR > 50\%$ = unacceptable. The analysis of five replica of the CRM IAEA-SL-1 is presented in Table 1. All heavy metals determined by XRF analysis are "excellent" ($SR \leq 25\%$) and the obtained results show a very good correlation ($R = 0.9999$) between certified and measured values.

Table 1. XRF analysis of CRM IAEA-SL-1 (mean $\pm$ SD, $n = 5$, in mg.kg⁻¹ DW), SR values and Detection Limits

Metal	Measured value	Certified value	SR (%)	LD (mg.kg ⁻¹)
Cr	110 $\pm$ 7	104	19	8
Ni	44.5 $\pm$ 2.3	44.9	11	10
Cu	32 $\pm$ 2	30	18	14
Zn	220 $\pm$ 11	223	11	5
Pb	36.2 $\pm$ 1.7	37.7	13	3

The level of contamination was expressed using the modified degree of contamination (mC_d), defined as [11]:

$$mC_d = \frac{\sum_{i=1}^n C_f^i}{n}$$

where n is the number of analysed elements, i the element and C_f the contamination factor, determined as

$$C_f^i = \frac{C_x^i}{C_b^i}$$

where C_x and C_b are the metal content in studied sample and baseline, respectively. The classification of the sediments according to the modified degree of contamination (mC_d) is the following: $mC_d < 1.5$ – very low degree of contamination; $1.5 < mC_d < 2$ – low degree of contamination; $2 < mC_d < 4$ – moderate degree of contamination; $4 < mC_d < 8$ – high degree of contamination; $8 < mC_d < 16$ – very high degree of contamination; $16 < mC_d < 32$ – extremely high degree of contamination; $mC_d \geq 32$ – ultra-high degree of contamination.

In order to assess the possible risk to human health, numerical Sediment Quality Guidelines (SQGs) were used. SQGs have been developed for many potentially toxic substances, i.e., trace elements, chlorinated organics, and polynuclear aromatic hydrocarbons [12]. Sediments are thus classified as non-polluted, moderately polluted and heavily polluted, based on the SQG of US EPA with the threshold effect level (TEL) and probable effect level (PEL) values [13,14]. In order to obtain a more realistic measure of the sediments toxicity, mean quotients were introduced according to the following equation:

$$PEL-Q = \frac{\sum_{i=1}^n C_i / PEL_i}{n}$$

where C_i is the concentration of element i in sediments, PEL_i the guideline value for the element i and n the number of metals. These mean quotients can be used in case of existence of multiple contaminants in the sediment where the adverse effects caused by each chemical are additive and not antagonistic [15]. The classification of sediments according to PEL-Q is as follows: PEL-Q values of < 0.1 , $0.11-1.5$, $1.51-2.3$ and > 2.3 coincide with 10, 25, 50 and 76 %, of toxicity, respectively [16]. Consequently, four relative levels of contamination have been created (*high, medium high, medium low and low*).

Results and Discussion

Mean concentrations, standard deviations, range and average baseline values of the studied heavy metals in sediments from Nuevitas bay are presented in Table 2. Mean concentrations in the studied sediments decreased following this order: $Cr > Zn = Ni > Cu > Pb$. Furthermore, they were all comparable to the baseline values with the exception of Cr and Pb, which mean contents were 3.7 and 1.9 fold higher than their corresponding baseline values, respectively. The concentration of Cr considerably varied while concentrations of the remaining metals were quite homogeneous across the bay.

Tabla 2. Minimum and maximum values of total metal concentrations (in $mg.kg^{-1}$ DW) in sediments from Nuevitas Bay and average baseline values

	Cr	Ni	Cu	Zn	Pb
Mean	237	65	30	65	13
SD	160	10	4	19	3
Min	89	57	26	43	8
Max	513	85	36	95	16
Baseline [7]	65	72	26	65	7

The comparison with SQGs (Table 3) shows those Cr concentrations in sediments from stations 4-6 are potentially toxic, exceeding the Cr-PEL value in 1.45-3.20 folds. The highest Cr content (Table 3) was determined in station 6, located close to Nuevitas city, indicating that important Cr pollution sources must be located in its vicinity. Moreover, other possible Cr pollution sources must be located upstream of the Cascorro and Saramaguacan Rivers, considering the high Cr contents determined in stations 4 and 5, respectively (see Figure 1).

On the other hand, sediments from all studied stations are heavily polluted with Ni and moderately polluted with Cu, independently of the similarity with baseline values. Ni content exceed the Ni-PEL value in 1.3-2.0 fold, which is not surprising given that it is well known the natural high Ni content present in Cuban soils and

Tabla 3. Metal concentrations (in $mg.kg^{-1}$ DW) determined in sediments from studied stations. Comparison with its baseline contents [7] and SQGs [12]

Stations		Cr		Ni		Cu		Zn		Pb	
		2003	2013	2003	2013	2003	2013	2003	2013	2003	2013
1		81	133	87	61	18	32	55	43	5	8
2		86	129	90	57	22	28	56	50	5	14
3		46	89	53	61	14	30	37	61	3	11
4		46	325	53	63	17	26	39	95	4	16
5		60	233	69	65	20	27	59	64	9	11
6		75	513	81	85	67	36	151	76	16	15
TEL		52.3		15.9		18.7		124		30.2	
PEL		160.4		42.8		108.2		271		112.2	
SQb	NP*	< 25		< 20		< 25		< 90		< 40	
	MP*	25-75		20-50		25-50		90-200		40-60	
	HP*	> 75		> 50		> 50		> 200		> 60	
* NP- non-polluted, MP – moderately polluted and HP – heavily polluted.											

* NP- non-polluted, MP – moderately polluted and HP – heavily polluted.

coastal sediments, especially those located in the eastern part of the country [17-19].

The contamination factors (C_f), modified degree of contamination (mCd) and probable effect level quotient (PEL-Q) values are shown in Table 4. The estimated mCd values indicate that sediments from stations 3-4 are moderately contaminated with Pb (stations 3-4) and Cr (station 4), while sediments from stations 5 and 6 are lowly contaminated with Cr due to obtained contamination factors. Independently of the results for mCd , the estimated PEL-Q values show a *medium low* contamination for the sediments collected from all studied stations in Nuevitas Bay, i.e., the 100 % of the sediments are associated with occasional observation of possible adverse effects.

Table 4. Contamination factors (C_f), modified degree of contamination (mCd) and PEL-Q values for sediments from Nuevitas Bay

Station	C_f					mCd	PELQ
	Cr	Ni	Cu	Zn	Pb		
1	1.6	0.7	1.8	0.8	1.6	1.30	0.56
2	1.5	0.6	1.3	0.9	2.8	1.42	0.54
3	1.9	1.2	2.1	1.6	3.7	2.11	0.52
4	7.1	1.2	1.5	2.4	4.0	3.24	0.85
5	3.9	0.9	1.4	1.1	1.2	1.70	0.71
6	6.8	1.0	0.5	0.5	0.9	1.97	1.19

Domestic and industrial sewages are rich in Cr [20], especially those from fertilizer industries and food processing plants, both industries being present in Nuevitas surroundings. Moreover, the study of Cr bioavailability is difficult given its speciation and redox behavior. Chromium exists mainly in two major valency states: as the particle reactive form Cr (III), and as the more soluble hexavalent form Cr (VI). Chromates [Cr (VI)] are more toxic than Cr (III) species, which are relatively non-toxic to organisms and is an essential micronutrient [21]. Due to this fact, in order to evaluate the sediment Cr real impact to Nuevitas fishery plans, a sediment Cr speciation is recommended.

Conclusions

In conclusion, the sediments collected from Nuevitas Bay have shown higher Cr and Pb contents compared to those collected in the same stations in 2003. In particular, Cr is the predominant element in sediments collected from the western area of the bay, whereas Ni is abundant in all of the studied sediments. The application of mCd index classifies as moderate the contamination of Nuevitas Bay, with chromium and lead as main contributors. The application of SQGs and toxicity mean quotients show that 100 % of the sediments are associated with occasional observation of possible adverse effects, especially for Cr, Ni and Cu (based on the TEL/PEL ratios). Taking into account that, by XRF analysis, only the total metal content is estimated, a sediment Cr speciation is recommended.

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Recibido: 8 de abril de 2014

Aceptado: 8 de mayo de 2014