Assessment of heavy metal pollution in sediments from the mampostón sub-watershed (mayabeque, cuba) using X-ray fluorescence analysis

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Abstract
Concentrations of nickel, copper, zinc and lead in surface sediments from 16 stations located in Mampostón sub-watershed (Mayabeque, Cuba) were estimated by X-ray fluorescence analysis. The Cu, Zn and Pb contents in sediments shows a different level of contamination across the studied stations. The application of modified degree of contamination (mC_d) allowed to classify the metal pollution in Ganuza and Mampostón rivers and in Predoso reservoir. 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: *metales pesados; cuba; analisis por fluorescencia de rayos x; sedimentos; contaminacion; agricultura; acuacultura; cuencas sedimentarias*

Estudio por fluorescencia de rayos x de la polucion por metales pesados en sedimentos de la subcuenca Mamposton (Mayabeque, Cuba)

Resumen
Se determinan, por Fluorescencia de Rayos X, las concentraciones de Níquel, Cobre, Zinc y Plomo en los sedimentos superficiales de 16 estaciones en la subcuenca Mampostón (Mayabeque, Cuba). Los contenidos de Cu, Zn y Pb en los sedimentos muestran diferentes niveles de contaminación en las estaciones estudiadas. La aplicación del grado de contaminación modificado (mC_d) permitió clasificar como alta o baja la contaminación de los ríos Ganuza y Mampostón, así como del embalse Pedroso. 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: *heavy metals; cuba; x-ray fluorescence analysis; sediments; pollution; agriculture; aquaculture; sedimentary basins*

Introduction

Mampostón sub-watershed is the smallest hydrological and hydrographic system of Mayabeque River basin in the center of Mayabeque province, Cuba. This hydrographic unit was remodeled in 1970 with the construction of two artificial reservoirs: Pedroso (with a capacity of 4 Mm^3) and Mampostón (150 Mm^3) (see figure 1). Both Mampostón and its tributary Ganuza rivers flow their waters (as well as their potential contaminant charge) into Pedroso reservoir. This water is pumped toward the Mampostón reservoir, which has no direct contaminant source, and it is subsequently sent to irrigate the crops in the South-West region of the most important agricultural zone of the western Cuban provinces, via the artificial channel Mampostón-Güira de Melena. Furthermore, the Pedroso reservoir has an overflow channel into the Mayabeque River and its waters are used to irrigate the sugar cane fields located on the eastside of the Mayabeque province. Additionally, an important aquaculture center is located on the Mampostón reservoir, focused in tilapia (*Oreochromis spp*), tench (*Tinca tinca*) and catfish (*Clarias gariepinus*) farming.

The presence of numerous and potential contamination sources in the area (for example, dairy, rum, paint and asphalt factories), whose residual waters are put into the basin tributaries, indicates a real possibility to contaminate the different pluvial ecological systems of the watershed. It is well know that sediments are the main repository of the pollutants in aquatic ecosystems.

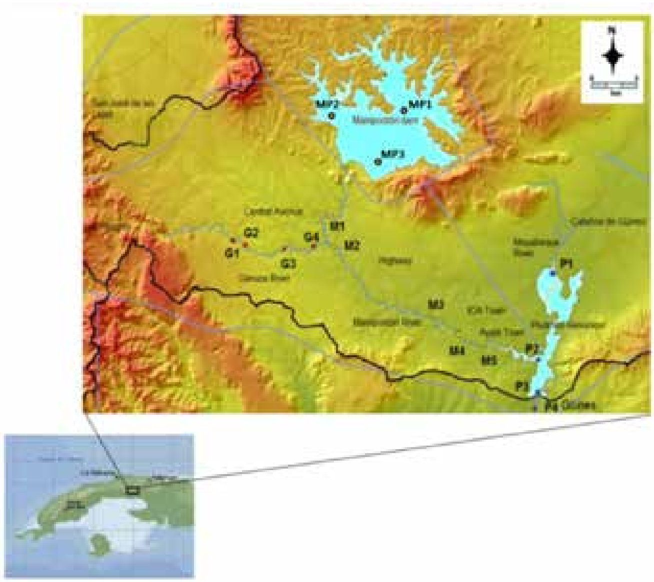

Figure 1. Location of the studied stations in the Ganuza (G) and Mampostón rivers (M) and Pedroso (P) and Mampostón (MP) reservoirs.

In this sense, the main goal of the present research is to study the heavy metal content in sediments of the Mampostón-Pedroso hydrographic system, in order to evaluated its ecological status.

Materials and methods

Sediment samples were collected at the beginning of the rainy season in 16 stations, and are located near the previously considered potential contamination sources (see figure 1): four stations in Ganuza river (G1 – 100 m north of a dairy factory, G2 – 50 m south of dairy factory , G3 – 100 m south of rum factory and G4 – 50 m south of paint factory); five stations in Mampostón river (M1 – 100 m south of aluminum factory and 50 m north of asphalt factory, M2 – 50 m south of asphalt factory, M3 – in the national highway bridge, M4 – free zone and M5 – 100 m south of a research center), four stations in Pedroso reservoir (P1 – Americano River flow into reservoir, P2 – Mampostón River flow into reservoir, P3 – south border of reservoir and P4 – overflow channel of Pedroso reservoir), and additionally, in three stations in Mampostón reservoir (PM1 - PM3). In all cases, sediment samples were collected in the middle of the rivers or five meters offshore in the reservoirs.

All samples were dried at 60oC. Large rock debris, mollusk skeletons and organic debris were removed before sieving. The fine fraction (< 63 mm) was extracted by sieving and newly dried at 60oC until obtaining a constant weight.

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 mm) coupled to a multichannel analyzer. A ^{238}Pu (1.1 GBq) excitation source with ring geometry was used. All spectra were processed with WinAxil code [1]. Detection Limits were determined according to Padilla et al. [2] (in concentration units) as LD = 3 σ/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. [3]:

$$SR = \frac{|C_{exp} - C_{rep}| + 2\sigma}{C_{rep}} \cdot 100\%$$

where: C_{exp} – experimental value, C_{rep} – reported certified value and σ is the standard deviation of C_{exp}. Based on 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-SL-1 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^2 = 0.9996) between certified and measured values.

Tabla 1. XRF analysis of CRM IAEA-SL-^{1} (mean ± SD, n = 5, in mg.kg^{-1}), SR values and Detection Limits.

Metal	Measured values	Certified value	SR(%)	DL (mg.kg^{-1})
Ni	44.5 ± 2.3	44.9	19	10
Cu	32 ± 2	30	11	14
Zn	220 ± 11	223	18	5
Pb	36.2 ± 1.7	37.7	11	3

The level of contamination was expressed using the modified degree of contamination (mCd), defined as [4]:

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

where: *n* is the number of analyzed 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 organic, and polynuclear aromatic hydrocarbons [5]. Sediments are thus classified as non-contaminated, moderately contaminated and heavily contaminated, based on the SQG of USEPA with the threshold effect level (TEL) and probable effect level (PEL) values [6, 7] In order to obtain a more realistic measure of the sediments toxicity, mean quotients were introduced according to the following equation:

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

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. PEL-*Q* is the probable effect level quotient. 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 [8]. 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 [9]. Consequently, four relative levels of contamination have been created (*low, medium low, medium high and high*).

Results and Discussion

Average concentrations and standard deviations of the studied heavy metal contents in sediments from the rivers and reservoirs from Mampostón sub-watershed are presented in table 2. In general, the metal content in Mampostón river, when compared to contents reported for other Cuban rivers, shows two patterns: it is lower than content reported for the contaminated urban rivers from Havana and Camaguey cities, and similar to those reported for rural rivers from Pinar del Río and Santiago de Cuba. The exception are the Cu and Zn contents in Ganuza river. On the other hand, the heavy metal content in Mampostón and Pedroso reservoirs are in the same order than those reported for other Cuban reservoirs.

The behavior of the Ni content in the studied stations (Fig. 2) show an irregular pattern, oscillating the Ni-PEL value. It is has been shown that a high Ni-content in Cuban soils and sediments is common. For example, in un-urbanized soils from Havana city was reported a Ni-content of 58 ± 13 $mg.kg^{-1}$ [16], and the average natural Ni-content in Cuban agricultural soils was fixed in 294.2 $mg.kg^{-1}$ [17]. For this reason, the origin of the Ni content determined in sediments from the Mampostón sub-watershed must be considered as natural.

On the other hand, Cu, Zn and Pb contents show a similar pattern: a maximum value in sediments from the station G2, and practically the same value in sediments from the rest of the studied stations. The comparison with SQGs (Fig. 2) shows those Cu concentrations in sediments from station G2 are potentially toxic, exceeding the Cu-PEL value in more than 10 folds, while Cu-content exceed the Cu-TEL level in the rest of the studied sediments. Moreover, the highest Zn and Pb contents were measured also in sediments from the station G2, exceeding the corresponding Zn-TEL and Pb-TEL values.

The contamination factors, modified degree of contamination (mC_d) and probable effect level quotient (PEL-Q) values are shown in table 3. Taking into account that Mampostón reservoir is not directly impacted by the different possible pollution sources of the studied area, its average metal contents (see table 2) were taken as baseline to estimated the contamination factors.

Tabla 2. Heavy metal content (Mean σ SD, in $mg.kg^{-1}$) determined in sediments from Mampostón sub-watershed and its comparison with contents reported for other Cuban rivers and reservoirs.

	Province	Ni	Cu	Zn	Pb	References
Rivers						
Ganuza	Mayabeque	76 ± 13	211 ± 219	114 ± 102	35 ± 26	-
Mampostón	Mayabeque	26 ± 10	59 ± 17	44 ± 6	16 ± 2	-
San Diego	Pinar del Río	62 ± 8	52 ± 2	72 ± 4	28 ± 2	[10]
Almendares	Havana	nr	176 ± 132	305 ± 183	111 ± 47	[11]
San Francisco	Havana	nr	312,8	398,7	116,7	[11]
Tínima	Camagüey	171 ± 101	105 ± 73	149 ± 37	201 ± 192	[12]
Hatibonico	Camagüey	701 ± 566	219 ± 131	147 ± 24	70 ± 56	[12]
San Juan	Santiago de Cuba	nr	33-59	57-83	9 -18	[13]
Reservoirs						
Pedroso	Mayabeque	55 ± 36	69 ± 14	57 ± 18	16 ± 4	-
Mampostón	Mayabeque	33 ± 11	63 ± 4	40 ± 4	12 ± 1	-
Palmarito	Havana	nr	35 ± 6	59 ± 7	9 ± 2	[14]
Niña Bonita	Havana	nr	35 ± 13	80 ± 34	38 ± 12	[14]
Hanabanilla	Villa Clara	nr	34 ± 28	87 ± 44	23 ± 5	[15]

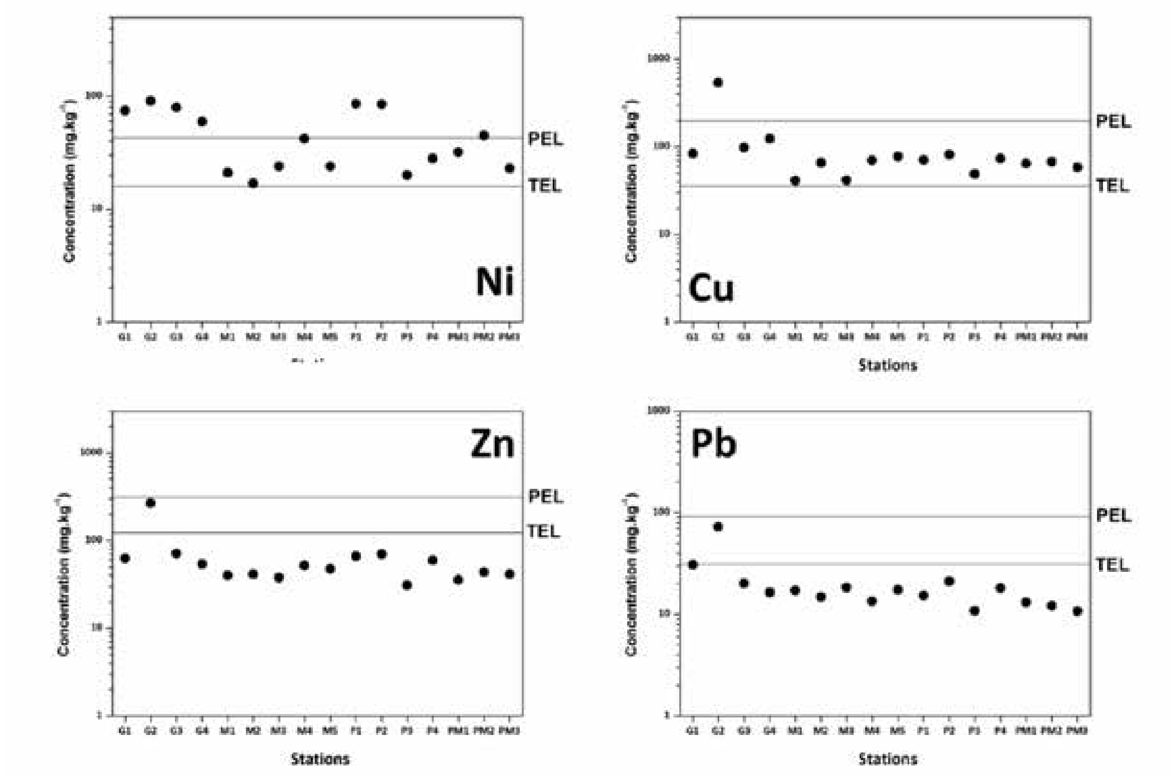

Figure 2. Distributions of Ni, Cu, Zn and Pb determined in the studied stations Dashed lines represent the corresponding TEL and PEL values for each metal.

Table 3. Contamination factors, modified degree of contamination (mCd) and PEL-Q values for sediments from Ganuza and Mampostón rivers and Pedroso reservoir.

Station	Contamination factors				mC_d	*PEL-Q*
	Ni	Cu	Zn			
G1	2.3	1.3	1.6	2.6	1.9	0.8
G2	2.8	8.6	6.7	6.1	6.0	1.7
G3	2.4	1.5	1.8	1.7	1.9	0.8
G4	1.8	2.0	1.4	1.4	1.6	0.7
M1	0.6	0.7	1.0	1.4	0.9	0.3
M2	0.5	1.0	1.0	1.2	1.0	0.3
M3	0.7	0.7	1.0	1.5	1.0	0.3
M4	1.3	1.1	1.3	1.1	1.2	0.5
M5	0.7	1.2	1.2	1.4	1.2	0.4
P1	2.6	1.1	1.7	1.3	1.7	0.8
P2	2.6	1.3	1.8	1.8	1.8	0.8
P3	0.6	0.8	0.8	0.9	0.8	0.3
P4	0.8	1.2	1.5	1.5	1.2	0.4

The estimated mC_d values indicate that sediments from station G2 are highly contaminated with Cu, Zn and Pb, while sediments from the stations G1, G3, G4, P1 and P2 are lowly contaminated with the same metals. Independently of the results for mC_d, the estimated PEL-Q values (Fig. 3) show a high degree of contamination for the sediments from the station 2 in Ganuza river, and medium low contamination for the sediments collected in the rest studied stations in Ganuza and Mampostón rivers and Pedroso reservoir, i.e. the 100 % of the sediments from Ganuza-Mampostón rivers and Pedroso

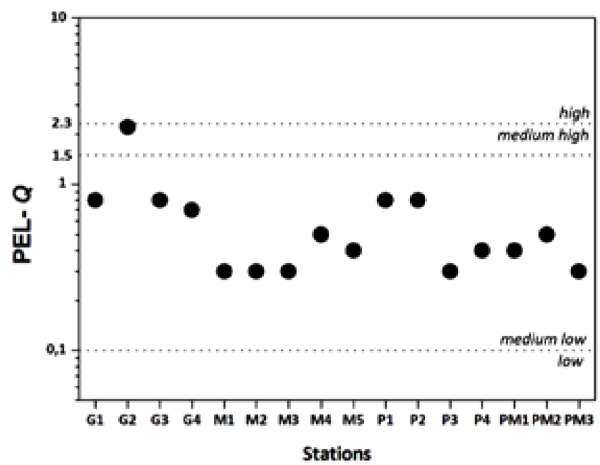

Figure 3. Behavior of the Probable Effect Level Quotient (PEL - Q) of the studied stations in Mampostón sub-watershed.

reservoir are associated with occasional observation of possible adverse effects.

Conclusions

The sediments collected in Ganuza and Mampostón rivers and in Pedroso reservoir (Mampostón sub-watershed (Mayabeque, Cuba) have shown higher Cu, Zn and Pb contents compared to those collected in Mampostón reservoir. The application of mC_d index classifies as highly or lowly contaminated sediments from Ganuza river and from two of the studied stations in Pedroso reservoir. 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 Cu, Zn and Pb. Taking into account the obtained results, the study of heavy metal content in edible muscle from fish species cultivated in Mampostón reservoir and fishes from Pedroso reservoir is recommended.

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Recibido: 24 de julio de 2019
Aceptado: 23 de julio de 2020