MULTIELEMENTAL ANALYSIS OF SEDIMENTS FROM HAVANA BAY BY NUCLEAR ANALYTICAL TECHNIQUES

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ABSTRACT

Instrumental Neutron Activation Analysis (INAA) and Gamma Activation Analysis (GAA) were employed to analyze the surface sediments and in ^{210}Pb-dated profiles sediments from several sites on the Havana Bay, Cuba. INAA was performed in the IEA-R1 research reactor at IPEN, Sao, Brazil. GAA was performed in the MT-25 Microtron at Nuclear Reaction Laboratory at JINR, Dubna, Russia. Measurements of 34 heavy and Rare Earth Elements in the sediments are reported. The results show that the concentration of the elements is site dependent. The data suggest that an anthropogenic input into the bay from domestic sewage and industries occurred.

INTRODUCTION

The analysis of marine sediments has a big importance in the solution of many problems, both scientific and economic. This is why in the last years a special interest has been taken in the investigations focused on determining the regularities of the marine environment's elemental composition in its different phases. This carries out an outstanding role in the knowledge of the dynamics of the ecosystem's biogeochemical processes and of its own state.

From all points of view and fundamentally for the ecology and the geochemistry, the determination of the majority and trace composition, especially of heavy metals and lanthanide

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elements- better known as Rare Earth Elements (REE)- is of great importance for the environment [1]. The importance of the heavy metals is based on the fact that it is essential for them to appear in small concentration in the organisms because of their toxicity in great concentrations. On the other hand, the REE are considered as hydrolyzing elements, for which the migration is characteristic, especially in suspension form in coastal waters, reservoirs and rivers. It is for this reason that the REE and other hydrolyzing elements are taken as indicators of the earthling influence on the marine and coastal sediments.

On the other hand, the study core has shown to an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments. Over the last few decades, sediment profiles from depositional areas were used to trace human activity, witnessed by anthropogenic contaminants like phosphorus [2], mercury [3-4] and trace and heavy metals [5-8]. In addition, the dating of sediment cores using radioactive traces like ^{210}Pb [9] permitted the precise quantification of the history of the inputs in a system.

The Cuban marine sediments' study by nuclear techniques began at the end of the 80's with studies concerning the habitats of important national fauna's marine species and of their pollution in areas such as Batabano [10] and Ana María [11] Gulfs. At the same time, studies of merely geochemical interest were carried out such as the one accomplished at the northwestern coastal zone of our country [12].

The Havana Bay is the most important Cuban port. As bag-type bay, a narrow Bay channel, a central part and three coves (Atarés, Guasabacoa and Marimelena) characterize it. It is has a total area of 5.2 km^2 and 18 km of internal coasts, an average depth of 9 m and a maximum depth of 15m. Its sedimentation is influenced by tide streams and by currents of rivers and brooks. The most important currents are those of the Luyano and the Martin Perez rivers in the Guasabacoa cove [13].

The analytical technique of Instrumental Neutron Activation Analysis (INAA) was chosen for the determination of trace and heavy element pollution in the ^{210}Pb dated sediments from the Havana bay. The aim was to determine the concentration and history of a wide range of elements in sediment samples taken from different sites of the bay, especially of heavy metals and the Rare Earth Elements.

Besides in the present work, the Rare Earth Elements' determination results are shown, as well as results of several heavy metals in superficial sediments of the Havana Bay using the NAA technique in its instrumental variant in a nuclear reactor.

The Gamma Activation Analysis (GAA) is used as a complementary analytical technique to the studies of sediments pollutions. The GAA is a powerful technique that induce artificial radioactivity in the samples through photonuclear reactions as the (γ,n) reactions [14-15].It has been applied successfully in several countries. A preliminary study in superficial sediments of Havana Bay is shown using Gamma Activation Analysis.

ANALYSIS OF ^{210}Pb DATED SEDIMENT PROFILES

Material and Methods

Three sampling points were established: one in each cove and the other in the Bay Center (Fig. 1). Unfortunately, the Atares Cove sample collection could not be carried out because the sediment was too liquid. Sampling was carried out with 1 m long PVC tubes, which was buried in spots that had not been dredged before. All samples were frozen and afterwards were sliced in the Engineering Center for Environmental Management of Bays and Coasts (CIMAB) with a thickness ranging from 1 cm up to 5 cm according to the obtained mass. For irradiation, only ^{210}Pb-dated sediments [16] corresponding to 5, 30 and 60 years were selected. All samples were lyophilized, powered in an agate mortar and sieved at 2 mm.

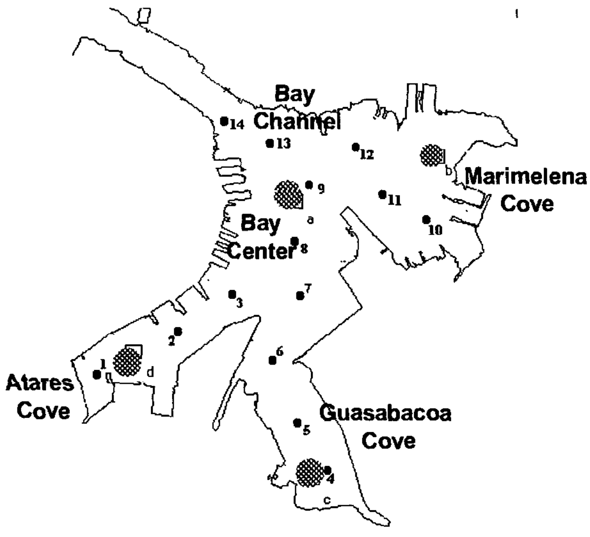

Fig. 1 Map of Havana Bay and sampling sites

The samples were analyzed by Instrumental Neutron Activation Analysis, using the reference certified samples GS-N y BE-N as standards. Nearly 100 mg of each sample (in duplicate) and standards were irradiated during 8 hours in the thermal neutron flux (Φ_{th} = 8,3 .10^{13} n.cm^{-2}.s^{-1}) of the IEA-R1 reactor at the Institute of Nuclear and Energetic Inquiries (IPEN) of Sao Paulo, Brazil.

The measurement of the irradiated samples and standards was carried out by Gamma Spectrometry, using a hyperpure Germanium detector (CANBERRA GMX20190, FWHM = 1.90 keV for the 1332 keV line of ^{60}Co). In order to guarantee the determination of the largest quantity of the REE, two series of measurements were carried out: one after 5 days, the other after 15 days of cooling. The measurement times oscillated between 1 and 2.5 hours. The gamma radiation spectra were processed using the VISPECT system, developed at the IPEN for this purpose. The exactness and precision of the results were verified by the analysis of the reference material IAEA-SL-1 *"Lake Sediment"*.

Results and Discussion

The average concentrations of the 24 elements determined by INAA in the ^{210}Pb-dated sediments from Havana bay are shown in Table 1. The accuracy of the obtained results for all the elements is below 10%, with the exception of Zn for which some of the sampled points' error increases to 13-15%. The main reason for this increase should lie in the high detection limit (3σ) determined for the analytical line of 1115 keV corresponding to ^{65}Zn.

In order to be able to carry out a more detailed discussion, the determined elements are assembled in 2 groups: the first group corresponds to the metals and the rest of the determined elements (excepting the REE), the second one to the REE. In both groups the elemental

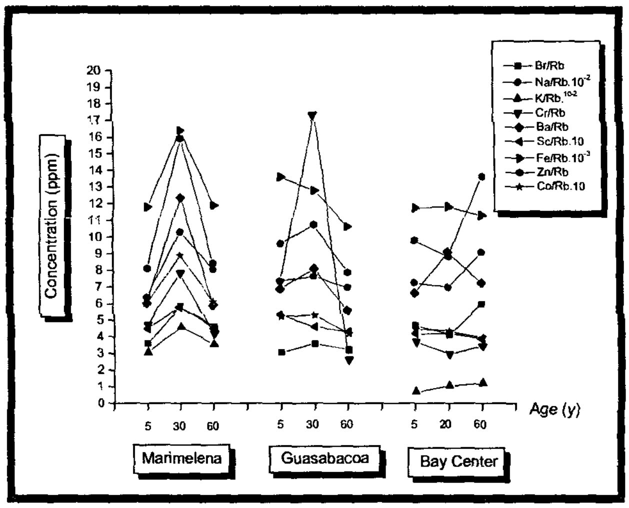

Fig. 2 Major and minor elemental concentrations normalized to Rb in the sediments profiles

concentrations appear normalized in relation to the concentration of Rb, in order to reduce the induced effect due to the variation of the grain's size distribution among the samples [17].

<u>Heavy Metals and others:</u> The Fig. 2 and 3 show the behavior of major, minor and trace heavy metals respect to the sediment age. A considerable increment of metallic pollutants in the entire bay (especially in Marimelena Cove) is observed in the 30 years old sediments, in comparison with the 5 and 60 years old sediments. The industrial development happened in the surroundings of the bay, as well as the increment of its commercial exploitation regime in the 70-80´s, in comparison with the existed situation in the 50's, can be the reason of that remarkable increment in the bay pollution. The pollution diminution observed for the more recent sediments, is an evidence of the efficiency and efficacy of the environmental policy taken by Havana City authorities in the 90´s. That policy considers more strong penalties (including the total closing) to all legal persons classified as several pollutant source of the Havana bay.

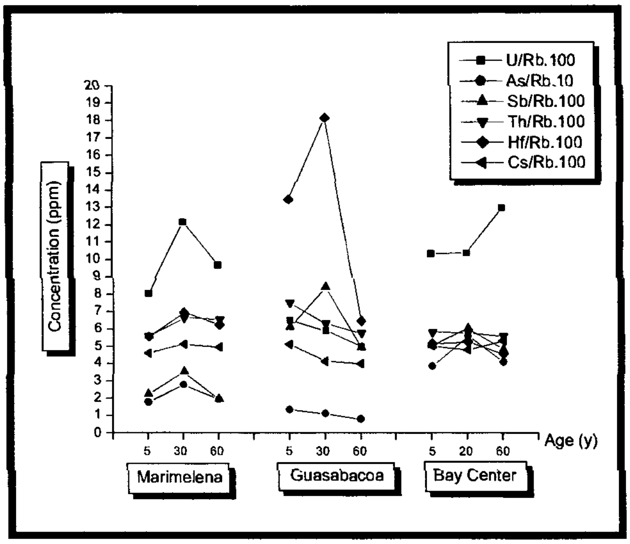

Fig. 3 Behavior of the trace element's concentration normalized to Rb in the sediment profiles, Havana bay.

<u>Rare-earth elements:</u> An important group of REE was determined (La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu) in all studied samples. Their time dependence (Fig. 4) shows the same previously analyzed behavior (in minor degree in Guasabacoa Cove, where the domestic wastes are more influent).

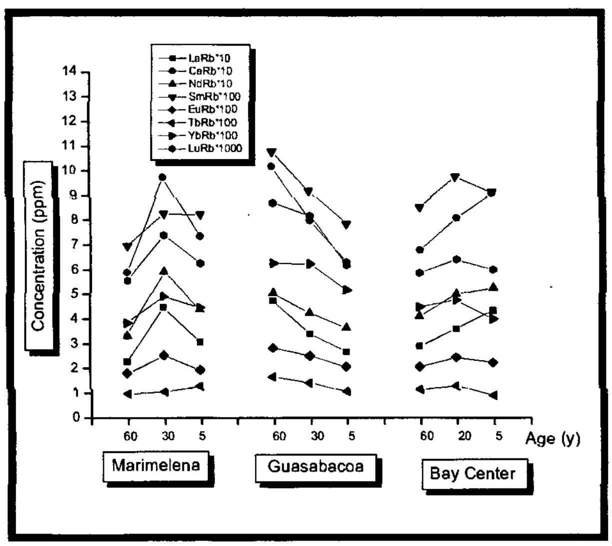

Fig. 4 Behavior of REE concentration normalized to Rb in the sediment profiles, Havana bay.

On the other hand, the REE behavior in the Havana bay recent sediments (Table 2) show an interesting singularity in comparison with the values obtained in sediments from other Cuban regions. The light (Ce/La ratio) and intermediate (La/Sm ratio) lanthanides practically have the same behavior that the sediments from the Pinar del Río Northwestern coast [12] and Batabano Gulf [10]. A great difference in heavy lanthanides (La/Yb ratio) behavior is observed in the sediments from Mariamelena and Guasabacoa coves. It's indicating the possible presence of soil, urban or other non-marine particles, dragged by the rivers toward the bay coves sediments.

Table 1 Average concentrations of elements determined in ^{210}Pb-dated sediments from Havana Bay by INAA (all values in $mg.kg^{-1}$ unless indicated otherwise).

	Mariamelena			Guasabacoa			Bay Center		
Element	**60 y**	**30 y**	**5 y**	**60 y**	**30 y**	**5 y**	**60 y**	**30 y**	**5 y**
La	8,2 ± 0,6	10,3±0,8	9,8±0,8	10,9±0,8	7,5 ± 0,6	9,1±0,7	8,4 ± 0,6	9,0 ± 0,7	13 ± 1
Ce	21,2 ± 0,1	22,4±0,1	23,5±0,1	23,4±0,1	17,56 ±0,08	21,4±0,1	19,7 ± 0,1	20,2 ± 0,1	27,3 ± 0,1
Nd	12,0 ± 0,5	13,6 ± 0,5	14,0 ± 0,5	11,6 ± 0,5	9,3 ± 0,4	12,4 ± 0,5	11,9 ± 0,5	12,5 ± 0,5	15,8 ± 0.6
Sm	2,51±0,03	1,96±0,03	2,63±0,04	2,48±0,03	2,02±0,03	2,67±0,04	2,47 ± 0,03	2,44 ± 0,03	2,74 ± 0,04
Eu	0,65±0,01	0,58±0,01	0,62±0,01	0,65±0,01	0,55±0,01	0,70±0,01	0,60±0,01	0,61±0,01	0,67±0,01
Tb	0,35±0,04	0,24±0,03	0,41±0,05	0,38±0,04	0,31±0,03	0,36±0,04	0,33±0,04	0,32±0,04	0,27±0,03
Yb	1,38±0,05	1,13±0,04	1,43±0,04	1,44±0,05	1,37±0,04	1,76±0,05	1,30±0,04	1,19±0,04	1,20±0,04
Lu	0,20±0,01	0,17±0,01	0,20±0,01	0,20±0,01	0,18±0,01	0,21±0,01	0,17±0,01	0,16±0,01	0,18±0,01
U	2,9±0,3	2,8 ± 0,3	3,1 ± 0,3	1,5±0,2	1,3±0,1	1,7 ± 0,2	3,0 ± 0,3	2,6 ± 0,3	3,9 ± 0,4
Br	131 ± 4	135 ± 4	148 ± 4	71 ± 2	79 ± 2	110 ± 3	137 ± 4	104 ± 3	180 ± 5
As	6,4 ± 0,1	6,4 ± 0,1	6,2 ± 0,1	3,10 ± 0,07	2,47 ± 0,05	2,76 ± 0,06	11,2 ± 0,2	14,0 ± 0,3	12,3 ± 0,3
Sb	0,80 ± 0,03	0,81 ± 0,03	0,62 ± 0,02	1,41 ± 0,04	1,85 ± 0,06	1,68 ± 0,05	1,47 ± 0,05	1,51± 0,05	1,45 ± 0,05
Na (%)	2,31 ± 0,21	2,38 ± 0,22	2,59 ± 0,24	1,70 ± 0,15	1,69 ± 0,15	2,38 ± 0,22	2,11± 0,19	1,75 ± 0,16	2,72± 0,25
K	11137± 582	10658±557	11469±600	< 3020-	< 3200	3722 ± 195	2000±105	2743 ± 143	< 1850
Th	2,01±0,09	1,53±0,07	2,1±0,1	1,73±0,08	1,39±0,06	1,96 ± 0,09	1,69±0,08	1,45±0,07	1,68±0,08
Cr	172 ± 32	181 ± 34	135 ± 25	169 ± 31	382 ± 71	90 ± 17	108 ± 20	75 ± 14	104 ± 19
Hf	2,0±0,1	1,6±0,1	2,0±0,1	3,1± 0,2	4,0±0,3	2,2 ± 0,2	1,5 ± 0,1	1,32 ± 0,09	1,37 ± 0,09
Ba	218±14	285±15	190±13	159 ± 12	179 ± 10	191 ± 13	193 ± 12	228 ± 13	217 ± 13
Cs	1,66±0,04	1,18±0,03	1,59±0,03	1,18 ± 0,03	0,91±0,02	1,37 ± 0,03	1,46 ± 0,03	1,20 ± 0,03	1,60 ± 0,03
Sc	16,3±0,1	13,4±0,1	14,4±0,1	12,3 ± 0,1	10,17±0,08	14,7±0,1	12,2±0,1	10,52 ±0,08	11,71±0,09
Rb	36±2	23±1	32±2	23 ± 1	22 ± 1	34 ± 2	29±2	25 ± 1	30±2
Fe (%)	4,25±0,09	3,78±0,08	3,82±0,08	3,14 ± 0,07	2,82±0,06	3,63 ± 0,08	3,41±0,07	2,96 ± 0,06	3,39±0,07
Zn	294±38	367 ± 48	271 ± 35	222 ± 29	237±31	269 ± 35	285±37	221 ± 29	409±54
Co	21,8±0,6	20,5±0,6	19,6±0,6	12,1 ± 0,4	11,7±0,3	14,3 ± 0,4	13,0±0,4	10,9 ± 0,3	11,9±0,3

This behavior is seen at Guasabacoa (4, 5 and 6), Marimelena (10, 11 and 12) and at the Bay Channel (13 and 14), this last zone standing out for being the one with the highest concentration of REE. Por otro lado, el incremento observó a los puntos 1 y 9, mientras correspondiendo respectivamente a Atarés y al Centro de la Bahía la atención atrae. For the point 1, the cause could lie in the influence of the pouring that is carried out in that zone, whereas for point 9, located in an intermediate zone between Marimelena's exit and the Bay Channel, places in which there is a higher concentration of REE.
Moreover the distribution of the light, intermediate and heavy REE (Fig. 6) shows an interesting singularity in comparison with the obtained values for sediments from other regions of our country (Table 2). The light lanthanides (Ce/La relation) have a very similar behavior to those observed for coastal sediments from other regions of the country as well as to those reported for the continental crust [18].

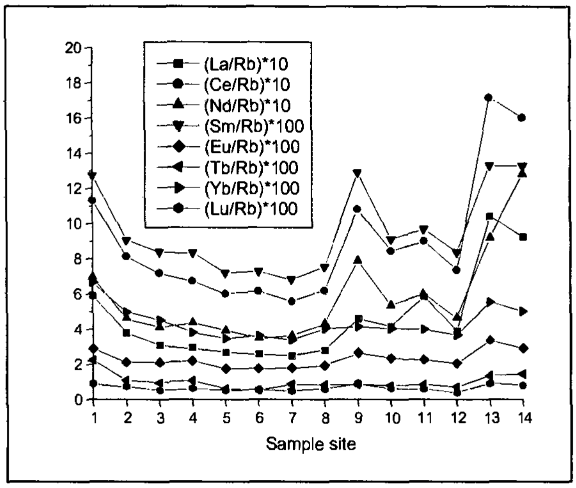

Fig. 5 Behavior of REE concentration normalized to Rb in the superficial sediments, Havana bay.

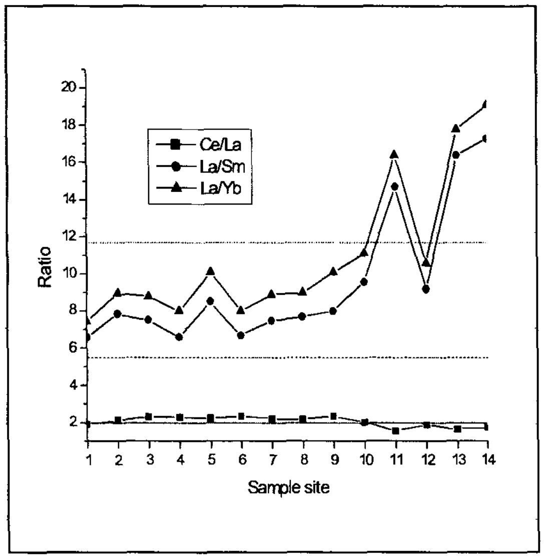

Fig. 6 Ce/La, La/Sm y La/Yb Ratios in the Bay sediments and the continental values (*)

Concerning the intermediate lanthanides (La/Sm) one observes that the behavior of their concentration at the Atares and Guasabacoa coves and at the Bay Center is similar to the one observed at Pinar del Río's northwestern coast. On the other hand there is a considerable decrease of their concentration at Marimelena cove and at the Bay Channel.
Concerning the heavy lanthanides (La/Yb relation), it is obvious that their concentration is very important at the Atares and Guasabacoa coves, showing a very inferior behavior when compared with the rest of the country's studied zones. On the other hand, there is a sudden decrease of their concentration at the Bay Channel. At Marimelena its value is almost normal. This allows us to infer that the pollution of the superficial sediments present at the Atares and Guasabacoa coves has its origin, mainly, in the pouring of domestic and industrial waste in them.

Metals and other elements: At all studied positions, Na and Fe appear in majority concentrations (superior to 1%), while Ba, Cr, Zn and Br appear in concentrations that oscillate between 70 and 1500 ppm. 9 other elements (in addition to the REE) appear in trace concentrations: Rb, Co, Sc, As, Sb, Hf, Cs, Th and U.

The behavior of the majority and minority elements in the studied zones (Fig. 7) allows us to observe that the highest concentrations can be found at the points 1, 9 and also at those belonging to the Marimelena cove and to the Bay Channel. This would allow inferring that the main pollution of the Marimelena sediments has its origin in the pouring of industrial waste. On the other side, at Atares (given the position of point 1 and because of the behavior seen in the points 2 and 3), there is a certain pouring of industrial waste at the bottom of the cove. This agrees with presence of the major industry concentration (including the "Ñico Lopez" refinery) at the outskirts of Marimelena. The increase observed at the point 9 could be explained as follows: the superficial sediments of that zone could have their main origin in the dragging of the sediments resulting from Marimelena cove.

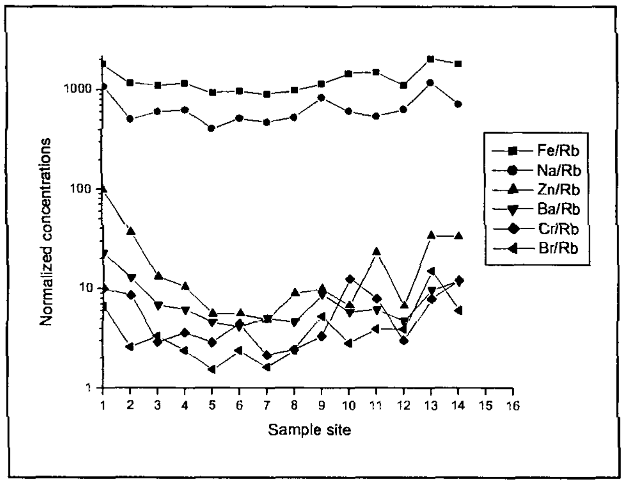

Fig. 7 Major and minor elemental concentrations normalized to Rb in the superficial sediments.

The Bay Channel deserves a different analysis. There seems to be an important presence of sediments resulting from Marimelena. On the other hand, the behavior of its REE shows the possibility of a mainly marine origin. This would allow inferring that its sediments seem to be the result of the re-circulation of marine sediments towards the bay's interior and of sediments, mainly originated at Marimelena cove, towards the bay's exterior. To be more conclusive on this hypothesis, it would be necessary to study the sediments' elemental composition at the outskirts of the Entry of Havana Bay as well as at other points of its own Bay Channel.

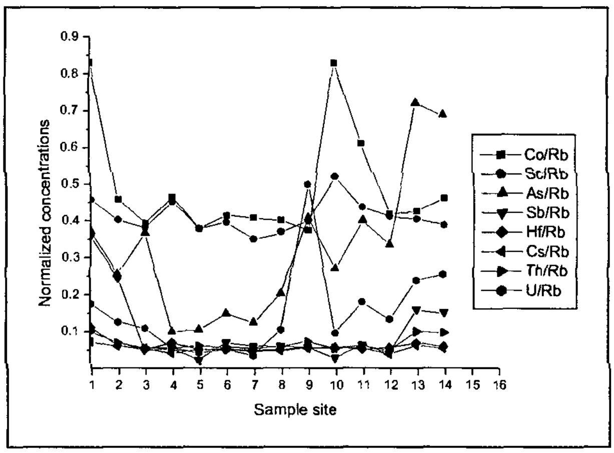

Fig. 8 Behavior of the trace element's concentration normalized to Rb in the sediment profiles, Havana bay.

Concerning the behavior of the trace elements (Fig. 8), the increases observed for elements such as Co and Sc at the points 1 and 10, allow reinforcing the analysis carried out previously concerning the presence of industrial waste in the sediments collected from those points. On the other hand, the concentrations of highly toxic elements (As, Th, and U) are below the limit values allowed and show no pollution of this kind in the whole bay's surface. The behavior observed at the Bay Channel's studied points agrees with the typical marine originated sediments' behavior. There is a surprising increase of the Uranium concentration observed at point 9.

Table 4 Average concentrations of elements determined in superficial sediments from Havana Bay by INAA (all values in $mg.kg^{-1}$ unless indicated otherwise).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
La	8,4 ± 0,6	10,3 ± 0,8	10,3±0,8	9,2 ± 0,4	11,6 ± 0,5	9,3 ± 0,4	10,3 ± 0,4	10,5±0,4	11,1 ±0,4	12,3±0,5	17,6 ± 0,7	11,7±0,5	18,8 ± 0,7	20,2 ± 0,8
Ce	16,1 ± 0,1	22,0 ± 0,1	23,8±0,1	21 ± 1	26 ± 1	22 ± 1	23 ± 1	23±1	26±1	25±1	27 ±1	22±1	31 ± 2	35 ± 2
Nd	9,9 ± 0,5	12,5 ± 0,4	13,6 ± 0,5	13,6 ± 0,7	17 ± 1	12,5 ± 0,8	15 ± 1	16 ± 1	19 ± 1	15,9 ± 0,7	18 ± 1	13,9 ± 0,8	16,6 ± 0,9	28 ± 2
Sm	1,81± 0,03	2,45 ± 0,03	2,77±0,04	2,6 ± 0,1	3,1 ± 0,2	2,6 ± 0,1	2,8 ± 0,2	2,8±0,2	3,1±0,2	2,7±0,1	2,9±0,2	2,5±0,1	2,4 ± 0,1	2,9 ± 0,2
Eu	0,41 ± 0,01	0,58 ± 0,01	0,70±0,01	0,69 ± 0,01	0,77 ± 0,01	0,63 ± 0,01	0,74±0,01	0,72±0,01	0,64±0,01	0,70±0,01	0,68±0,01	0,62±0,01	0,61±0,01	0,64±0,01
Tb	0,32 ± 0,04	0,30 ± 0,03	0,32±0,04	0,34 ± 0,05	0,27 ± 0,05	0,20 ± 0,04	0,36±0,05	0,32±0,05	0,21±0,04	0,24±0,04	0,26±0,04	0,22±0,04	0,25±0,04	0,32±0,04
Yb	0,95 ± 0,04	1,35 ± 0,04	1,50±0,04	1,2 ± 0,1	1,5 ± 0,2	1,3 ± 0,2	1,4 ± 0,1	1,5±0,2	1,0±0,1	1,2±0,1	1,2±0,1	1,1±0,1	1,0±0,1	1,1±0,1
Lu	0,13 ± 0,01	0,20 ± 0,01	0,18±0,01	0,20 ± 0,01	0,23 ± 0,01	0,20±0,01	0,20±0,01	0,23±0,01	0,22±0,01	0,19±0,01	0,18±0,01	0,12±0,01	0,17±0,01	0,18±0,01
U	2,5 ± 0,2	3,4 ± 0,3	3,6 ± 0,2	1,7 ± 0,1	1,8 ± 0,2	1,85 ± 0,05	1,46 ± 0,04	3,9 ± 0,1	12± 1	2,86±0,08	5,4±0,2	4,0 ± 0,1	4,3 ± 0,1	5,6 ± 0,2
Br	94 ± 2	70 ± 2	110 ± 3	75 ± 3	66 ± 3	85 ± 4	67 ± 3	90 ± 4	127 ± 5	84 ± 4	118 ± 5	117 ± 5	271 ± 12	132 ± 36
As	5,3 ± 0,1	6,9 ± 0,1	12,1 ± 0,2	3,1 ± 0,3	4,5 ± 0,5	5,3 ± 0,3	5,1 ± 0,3	7,5 ± 0,9	9,8 ± 1,2	8± 1	12 ± 1	10 ± 1	13 ± 2	15 ± 2
Sb	5,1 ± 0,2	6,6 ± 0,2	1,64 ± 0,05	1,7 ± 0,1	0,97 ± 0,07	2,5 ± 0,2	2,5 ± 0,2	2,2 ± 0,2	1,4± 0,1	0,86 ± 0,06	1,9 ± 0,1	1,25 ± 0,09	2,9 ± 0,2	3,3± 0,2
Na (%)	1,53 ± 0,14	1,36 ± 0,12	1,99 ± 0,18	1,85 ± 0,14	1,75 ± 0,13	1,84 ± 0,14	1,95 ± 0,14	1,95 ± 0,15	2,00 ± 0,15	1,80 ± 0,13	1,61 ± 0,12	1,89± 0,14	2,12± 0,16	1,56 ± 0,12
Th	1,45 ± 0,07	1,88 ± 0,09	1,85±0,08	1,74 ± 0,03	2,63 ± 0,04	2,05±0,03	2,28 ± 0,03	2,19±0,03	1,77±0,03	1,63±0,02	1,88±0,03	1,47 ± 0,02	1,81±0,03	2,13±0,03
Cr	142 ± 26	230 ± 43	96±18	112 ± 12	124 ± 14	158±17	88± 10	90 ± 10	80 ± 9	369 ± 41	236 ± 26	90 ± 10	142 ± 16	264 ± 29
Hf	1,59 ± 0,10	1,66 ± 0,11	1,7±0,1	2,19 ± 0,03	2,24 ± 0,03	1,80±0,03	2,07±0,03	1,91±0,03	1,36±0,02	1,72± 0,03	1,57±0,02	1,69 ± 0,03	1,26 ± 0,02	1,30 ± 0,02
Ba	320 ± 15	346 ± 16	224±13	192 ± 16	198 ± 14	148 ±15	207±15	171±12	210±15	172 ± 12	183 ± 13	142 ± 10	175 ± 13	256 ± 18
Cs	1,03 ± 0,02	1,61 ± 0,03	1,85±0,04	1,29 ± 0,06	2,2 ± 0,1	1,92±0,08	1,92±0,08	1,80±0,08	1,33±0,06	1,65 ± 0,07	1,67±0,07	1,16 ± 0,05	1,13 ± 0,05	1,20 ± 0,05
Sc	6,52 ± 0,05	10,88±0,09	12,6±0,1	14,1 ± 0,6	16,3 ± 0,7	14,1±0,6	14,4±0,6	13,7±0,6	9,6±0,4	15,4 ± 0,7	13,1±0,6	12,3±0,5	7,3±0,3	8,5 ±0,4
Rb	14,2 ± 0,9	27 ± 2	33±2	31,1 ± 0,8	43 ± 1	35,6 ± 0,9	41±1	37±1	24,0±0,6	29,5 ± 0,8	29,9 ± 0,8	29,8 ± 0,8	18,0±0,5	21,8 ± 0,6
Fe (%)	2,56 ± 0,06	3,16±0,07	3,65±0,08	3,62 ± 0,07	3,98 ± 0,08	3,45±0,07	3,71±0,08	3,67±0,07	2,73±0,06	4,26 ± 0,09	4,47±0,09	3,32 ± 0,07	2,66±0,05	2,96 ± 0,06
Zn	1417 ± 186	986 ± 129	434 ± 57	323 ± 10	240 ± 8	< 220	< 208	331 ± 11	237 ± 8	< 202	688±22	< 221	611±20	723 ± 23
Co	11,8 ± 0,4	12,4 ± 0,4	13,0±0,4	14,5 ± 0,1	16,3 ± 0,2	14,8±0,2	16,8±0,2	14,9±0,2	9,01±0,09	24,5 ± 0,2	18,3±0,2	12,5 ± 0,1	7,68±0,08	10,1 ± 0,1

GAMMA ACTIVATION ANALYSIS

Materials and Methods

Sediments samples from 22 points of Havana were collected, 14 were lyophilized and the rest dried at 50 °C of temperature. All samples were grinding by an agate mortar, powered and dried at the same temperature to a constant weight. The samples were mixed in order to achieve an optimal mass (5g) to make GAA, according to five Havana Bay zones: Atares, Guasabacoa and Marimelena coves, Center and Bay Channel (Fig. 1)

The samples were irradiated with the bremsstrahlung radiation in the electron accelerator Microtron MT-25 at the Flerov Laboratory of Nuclear Reactions JINR (Russia) during 4 hours, with average electrons energy of 25 MeV and average current ≈14 μA. Among the samples and standards three cupper monitors were placed in order to measure the bremsstrahlung flux variation along the sample containers.

The gamma rays from the irradiated samples, standards and cupper monitors were counted by using a Ge(Li) and HPGe detectors, with 3.0 and 1.2 keV of FWHM at the 1.33 MeV peak of ^{60}Co respectively. Each detector was connected to a standard amplifier and an 8192 channel pulse height analyzer. It was guaranteed a dead time smaller than 10% for every sample. Three measurement series were made to identify isotopes of different decay times and to obtain interference free photopeaks (cooling time: 4h, 24h and 6 days; counting time 15, 30 and 60 minutes). Recorded spectra were evaluated with the Genie PC software [19].

Results and Discussion

The element average concentrations determined by GAA in the sediment samples from Havana Bay are shown in Table 5. The accuracy of the obtained results for the majority of the elements was below 10%. For some elements the errors were worst due to theirs low concentrations in the samples or standards. The table shows to Fe, Na, Mg, Ca as major; Cr, Ni, Zn, Rb, Sr, Pb, Ti as minor; and Th, Sb, Sm ,As, Y, Nb as trace elements.

The element concentrations were normalized to the Rb concentration reducing the induced effect due to the grain size distribution variation of the samples [5]. In order to be able to carry out a more detailed discussion, the normalized concentrations were plotted, and the elements with similar trends along the bay were grouped as shown the Fig. 9, 10, 11,

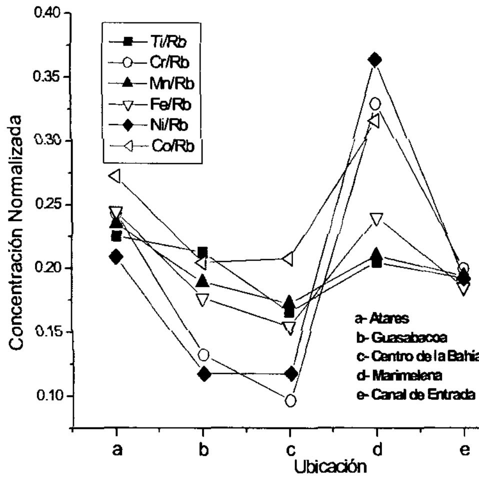

Fig. 9 Ti, Cr, Mn, Fe, Ni and Co concentrations normalized to Rb at Havana Bay.

and 12. The graphics illustrate a close relation between the pollution sources and the concentration levels of various elements.

The Fig. 2 shows a similar behavior of the heavy metals Ti, Fe, Ni, Cr, Mn. There are maximum values for Marimelena and Atares Cove. These zones are precisely of the most pollution ones and are related with an oil refinery and drainage-sewage systems respectively [20-21].

In the Fig. 3, 4, and 5 there are maximums in the Atares Cove and the Bay Channel. The elements showed in these graphics seem to be pollution sources of industrial and urban origins [20].

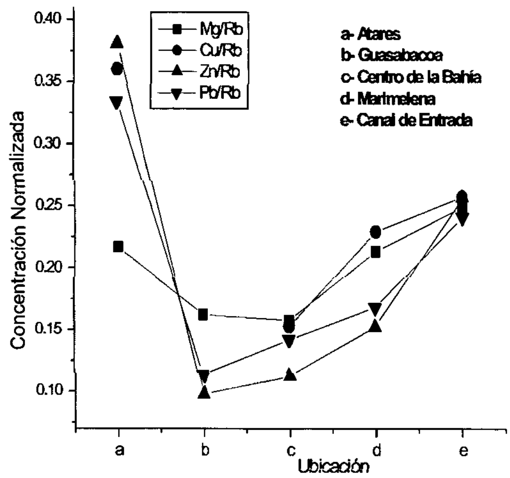

Fig. 10 Cu, Zn, Mg and Pb concentrations normalized to Rb at Havana Bay.

Table 5 Average Concentrations of the elements in the superficial sediments at the Havana Bay (Units: mg kg^{-1}, except Ca, Mg, Na, Fe: %).

Element	Guasabacoa	Marimelena	Bay Center	Atares	Bay Channel
Ti	4191 ± 11	3188 ± 128	4947 ± 289	2977 ± 114	3394 ± 186
Sc	4.4 ± 1.1	5.7 ± 1.3	3.5 ± 1.0	-	2.6 ± 0.9
Ca (%)	11.09 ± 0.23	12.8 ± 0.2	20.9 ± 4.3	15.8 ± 0.3	23.5 ± 0.3
Mg(%)	2.1 ± 0.1	2.2 ± 0.1	3.1 ± 0.2	1.9 ± 0.1	2.9 ± 0.2
Na(%)	3.9 ± 0.3	2.9 ± 0.2	5.8 ± 0.5	3.4 ± 0.2	5.3 ± 0.4
Cr	27 ± 12	52± 23	29 ± 13	33 ± 15	36 ± 17
Mn	737 ± 43	646 ± 42	1017 ± 68	614 ± 42	679 ± 68
Fe(%)	1.3 ± 0.1	1.46 ± 0.08	1.6 ± 0.2	1.21 ± 0.08	1.19 ± 0.07
Cu	-	182 ± 70	327 ± 106	240 ± 70	230 ± 94
Ni	78.5 ± 6.4	190.6 ± 7.4	116 ± 6	92 ± 7	121 ± 10
Co	16.0 ± 0.7	19.5 ± 0.8	24.6 ± 1.2	14.3 ± 0.8	-
Zn	493 ± 57	604 ± 65	855 ± 100	1281 ± 107	1158 ± 120
As	5.0 ± 0.2	12.4 ± 0.3	16.6 ± 0.4	9.2 ± 0.3	18.6 ± 0.5
Rb	78 ± 6	61 ± 5	118 ± 9	52 ± 4	70 ± 5
Sr	266 ± 11	907 ± 4	840 ± 251	522 ± 162	1335 ± 350
Y	2.2 ± 0.2	2.0 ± 0.2	3.1 ± 0.3	1.6 ± 0.2	2.4 ± 0.3
Nb	1.5 ± 0.2	1.1 ± 0.2	2.5 ± 0.4	1.4 ± 0.3	1.0 ± 0.3
Mo	30 ± 2	12.7 ± 0.5	13.7 ± 0.8	19 ± 1	19 ± 1
Zr	102 ± 1	77 ± 1	142 ± 2	79 ± 2	91 ± 2
Sb	6.4 ± 1.1	4.4 ± 1.1	9.3 ± 1.6	10.5 ± 1.4	8.9 ± 2.1
Ba	95 ± 4	71 ± 5	142± 7	104 ± 5	117± 8
Ce	23.6±2.3	28.6±1.3	40.1 ± 3.8	34.8 ± 10.2	75.2 ± 5.0
Sm	8.7 ± 0.7	21.1 ± 1.2	12.8 ± 1.0	7.1 ± 0.7	13.1 ± 1.0
Pb	181 ± 6	210 ± 9	341 ± 12	355 ± 12	343 ± 19
Th	4.2 ± 0.3	3.2 ± 0.3	6.6 ± 0.5	2.8 ± 0.3	4.6 ± 0.4
U	1.2 ± 0.2	2.3 ± 0.3	4.0 ± 0.5	2.4 ± 0.3	3.4 ± 0.5

There is an influence from Marimelena pollution sources over the Bay Channel. The increment of pollution levels in the Bay Channel indicate that the sediments from Marimelena are dragged by the water currents of the drainages toward to the Bay Channel, besides the maritime activity. On the other hand the figures demonstrate that industries around Guasabacoa have a low effect in the pollution of this cove; which is due to the closure of some industries, and to the environmental policy taken by Havana City authorities

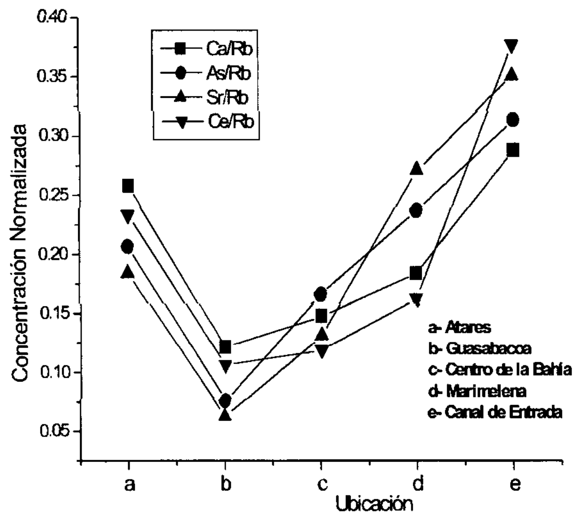

Fig. 11 Ca, As, Sr and Ce concentrations normalized to Rb at Havana Bay.

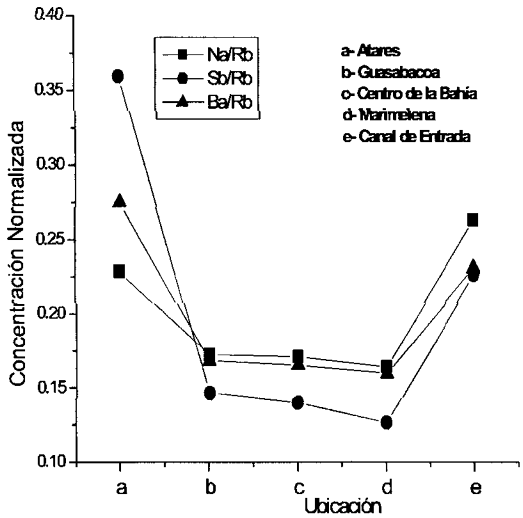

Fig. 12. Na, Sb, and Ba concentrations normalized to Rb at Havana Bay.

CONCLUSIONS

Instrumental Neutron Activation Analysis (INAA) and Gamma Activation Analysis (GAA) were employed to analyze the surface sediments and in ^{210}Pb-dated profiles sediments from several sites on the Havana Bay, Cuba.

Measurements of 23 and 26 elements were reported using INAA and GAA respectively. The obtained results show a close relationship between the element concentration levels, the sedimentation rates and the pollution sources.

Several elements (As, Ba, Ni, Pb, Cu, Zn, Fe, Cr, Mn) show a high concentration levels if the above data is compared with other studies of marine sediments. This could be an additional hazard for the aquatic system, in fact already affected drastically by the great pollution of the bay.

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