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Gamma activation analysis of marine sediments at Havana Bay, Cuba

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Twenty six elements was studied preliminary in the superficial sediments of Havana Bay using gamma activation analysis by the electron accelerator microtron MT-25 at the Flerov Laboratory of Nuclear Reactions, JINR. Samples from five zones of Havana Bay including the three coves were analyzed. The obtained results show a close relation between the concentration levels of the studied elements and the pollution sources. Some elements (As, Ba, Ni, Pb, Cu, Zn, Fe, Cr, Mn) have high concentration levels compared to the values for other environmental marine sediments reported in the literature.

Introduction

Havana Bay (Cuba) is a typical enclosed bay located at the North Coast of west Cuba. It is the main harbor of Cuba and has three coves: Atares, Marimelena and Guasabacoa. Different rivers, several industries, drainage and sewage systems, with high levels of organic material spill wastes to this ecosystem. There is also a intense activity of maritime harbor. Heavy metals and hydrocarbons, which cannot neither be eliminated nor be transferred into less hazardous forms, are inorganic or organic contaminants that cause pollution and can be found in the bay sediments.

The Engineering Center for Environmental Management of Bays and Coasts (CIMAB) has carried out systematic studies on the heavy metal pollution levels in Havana Bay using atomic absorption spectroscopy. These works have been a part of a project for the study and analysis of Havana Bay sediments, supported by the United Nations Organization. Different sampling points have been selected, with superficial sediments as witness samples, showing appreciable levels of chronic contamination of the waters and sediments in this ecosystem.[1–3]

Gamma activation analysis (GAA) could be used as a complementary analytical technique to study the sediment pollution, because it has some advantages, i.e., low detection limits and wide range of detectable elements. GAA is a powerful technique and has been applied successfully in several countries.[4,5]

The present study is part of a geochemical and isotopic analysis project on Havana Bay sediments using nuclear and conventional techniques. Particularly GAA was employed to determine the pollution levels in surface sediments from five zones of Havana Bay.

Experimental

Sediment samples from 22 points of Havana Bay were collected, 14 of them in the year 2000, the rest in the year 2001. Samples collected in the year 2000 were lyophilized, the others were dried at 50 °C in an oven. All samples were ground in an agate mortar, powdered and dried at the same temperature to constant weight. Afterward, samples collected from the same geographical point were mixed and homogenized conveniently in order to achieve an optimal mass (5 g) for performing GAA. As a result, the Havana Bay was divided in five zones: Atares, Guasabacoa and Marimelena Coves, Bay Center and Bay Channel[1–3] as it is shown in 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 an average electron energy of 25 MeV and an average current of about 14 μA. Among the samples and standards three copper 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 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 spectroscopic amplifier (Model 2026 Canberra) and an 8192-channel pulse-height analyzer.

The dead time for every sample was kept smaller than 10%. Three measurement series were made to identify isotopes of different decay times and to obtain interference free photopeaks (cooling time: 4 hours, 24 hours and 6 days, counting time 15, 30 and 60 minutes). Recorded spectra were evaluated with the Genie PC software.[6]

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Table 1 shows the photonuclear reactions and gamma-energies[7] associated with the isotope identification. The element concentrations were calculated using the Russian Standards СТ. 6298-52б and СИ-2.[8,9]

Results and discussion

The element average concentrations determined by GAA in the sediment samples from Havana Bay are shown in Table 2. The uncertainty obtained from counting statistics were below 10% for the majority of the elements. For some elements the uncertainties were worse due to their low concentrations in the samples or standards. The table shows the values of 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 variation of grain size distribution of the samples.[10] 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 in Figs 2, 3, 4, and 5. Remaining elements (Zr, Sm, Y, Nb, Th, U, Mo and Sc) were not included because each one showed a particular behavior.

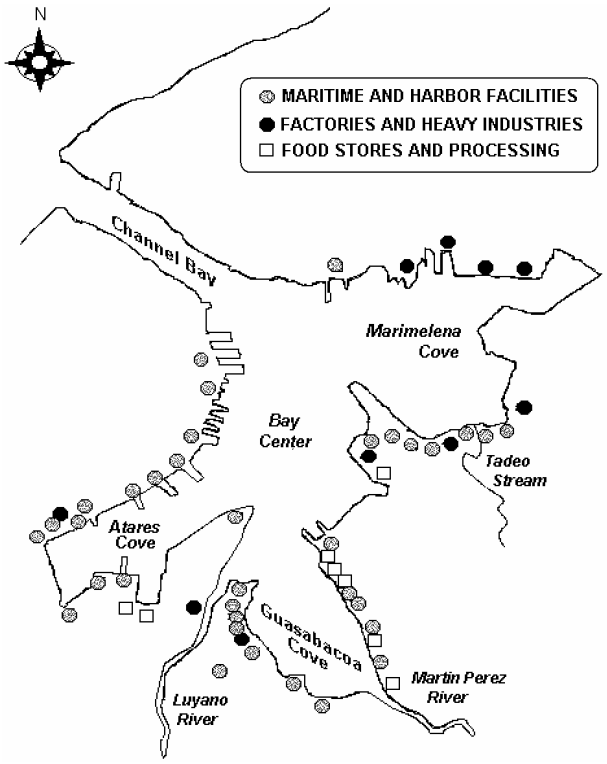

Fig. 1. Locations of main pollution sources in Havana Bay

Table 1. Photonuclear reactions and gamma-ray energies used to detect the elements

Element	Reaction	E_γ, keV	I_γ	$T_{1/2}$
Ti	^{49}Ti(γ,p)^{48}Sc	984.5	1.00	43.7 h
		1037.5	0.98	
		1312.1	1.00	
		159.3	0.68	
	^{48}Ti(γ,p)^{47}Sc	889.3	0.99	3.42 d
	^{47}Ti(γ,p)^{46}Sc	1120.5	0.99	83.8 d
		1297.1	0.75	
		220.6	0.04	
Ca	^{48}Ca(γ,n)^{47}Ca	372.7	0.87	4.5 d
	^{44}Ca(γ,p)^{43}K	396.9	0.11	22.6 h
		593.4	0.11	
		617.5	0.81	
Mg	^{25}Mg(γ,p)^{24}Na	1368.5	0.99	15.0 h
		2754.1	0.99	
Na	^{23}Na(γ,n)^{22}Na	1274.5	0.99	2.6 a
Cr	^{52}Cr(γ,n)^{51}Cr	320.1	0.10	27.7 d
Mn	^{55}Mn(γ,n)^{54}Mn	834.8	0.99	312.7d
Fe	^{57}Fe(γ,p)^{56}Mn	846.8	0.99	2.6 h
		1810.7	0.27	
Cu	^{65}Cu(γ,n)^{64}Cu	1345.7	0.473 (%)	12.7 h
Ni		127.2	0.167	
	^{58}Ni(γ,n)^{57}Ni	1377.6	0.82	36.1 h
		1919.4	0.122	
Co	^{59}Co (γ,n)^{58}Co	810.7	0.994	70.8 d
Y	^{89}Y (γ,n)^{88}Y	1836.0	0.994	106.6 d
		898.0	0.934	
Zn	^{68}Zn(γ,p)^{67}Cu	184.6	0.49	61.8 d
Nb	^{93}Nb(γ,n)^{92m}Nb	934.5	0.99	10.15 d
As	^{75}As(γ,n)^{74}As	595.9	0.60	17.8 d
		634.8	0.15	
Rb	^{85}Rb(γ,n)^{84}Rb	881.5	0.68	32.9 d
Sr	^{84}Sr(γ,n)^{83}Sr	762.6	0.30	32.4 h
	^{86}Sr(γ,n)^{85m}Sr	231.7	0.85	67.7 m
	^{88}Sr(γ,n)^{87m}Sr	388.4	0.82	2.8 h
Mo	^{100}Mo(γ,n)^{99}Mo	140.5*	0.89*	6.0 h*
Zr	^{90}Zr(γ,n)^{89}Zr	909.1	0.99	78.4 h
Sb	^{123}Sb(γ,n)^{122}Sb	563.9	0.71	2.7 d
Ba	^{136}Ba(γ,n)^{135m}Ba	268.2	0.16	28.7 h
	^{134}Ba(γ,n)^{133m}Ba	276.1	0.18	38.9 h
Ce	^{142}Ce(γ,n)^{141}Ce	145.4	0.48	32.5 d
	^{140}Ce(γ,n)^{139}Ce	165.8	0.80	137.6 d
Sm	^{154}Sm(γ,n)^{153}Sm	103.2	0.28	46.7 h
Th	^{232}Th(γ,n)^{231}Th	84.21	0.066	25.5 h
Sc	^{45}Sc(γ,n)^{44}Sc	1157	0.999	3.927 h
U	^{238}U(γ,n)^{237}U	208	0.21	6.75 d
Pb	^{204}Pb(γ,n)^{203}Pb	279.1	0.77	51.9 h

*E_γ, *I_γ, *$T_{1/2}$ of ^{99m}Tc from ^{99}Mo.

The figures illustrate a close relation between the pollution sources and the concentration levels of various elements in the bay sediments. Figure 2 shows a similar behavior of the heavy metals Cr, Ni, Co, Ti, Fe and Mn. These elements show maximum concentrations for Marimelena and Atares Coves, closely followed by Bay Channel. Precisely these coves are the more polluted zones in Havana Bay.

The majority of the heavy industries are located around the Marimelena Cove, between them the greatest pollutants of hydrocarbons and heavy metals: an oil refinery and a power plant (Fig. 1). At the other side the more polluted drainage systems are discharged to the Atares Cove, its spills contains the wastes of a soap factory and a power plant, among others.[2,11] In the case of Bay Channel it is the deepest region and besides it is affected by strong currents of water.[1] Then, sediment movements from the coves increase pollutant concentrations (Fig. 1).

According to Fig. 3, Atares Cove showed the highest concentrations for Cu, Pb, Zn, followed by Channel Bay and Marimelena Cove. Again the influence of sediment movement to Channel Bay is observed. These elements are indicators of urban and industrial pollution, above all of urban origin.[2] Several sewage systems flow into the Atares Coves, they cause high levels of these metals in the sediments.

There are maximum values for Ca, Ce, Mg, As and Sr (Fig. 4) in the Atares and Marimelena Coves, such as in the Bay Channel. These elements seem to be pollution sources of industrial and urban origins[2] discharged in the coves.

Figure 5 shows the maximums for Atares Cove and Bay Channel. Signals for the influence of the Atares sewage systems are the high levels of Na, Sb and Ba in the Bay Channel sediments.

Finally all figures demonstrate that the industries around Guasabacoa have a low effect on the pollution of this cove. The environmental policy applied by the Havana City authorities and the closing of several industries have contributed to this results.[2,12]

Table 2. Average concentrations of the elements in the superficial sediments at the Havana Bay (in $mg \cdot kg^{-1}$, 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	3.1 ± 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

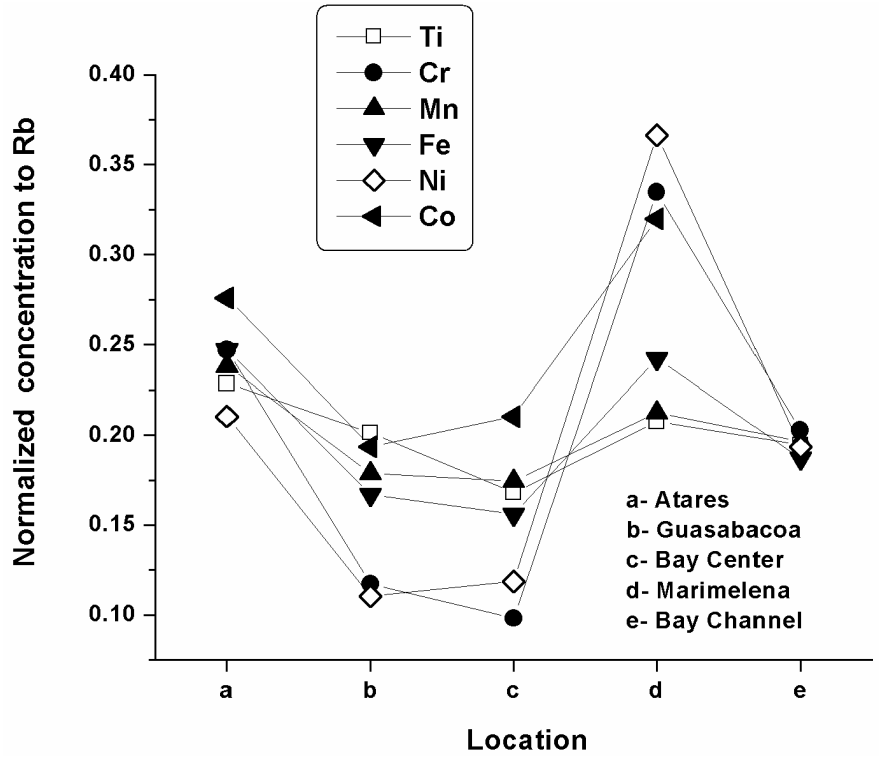

Fig. 2. Ti, Mn, Cr, Ni, Co and Fe concentrations normalized to Rb at Havana Bay

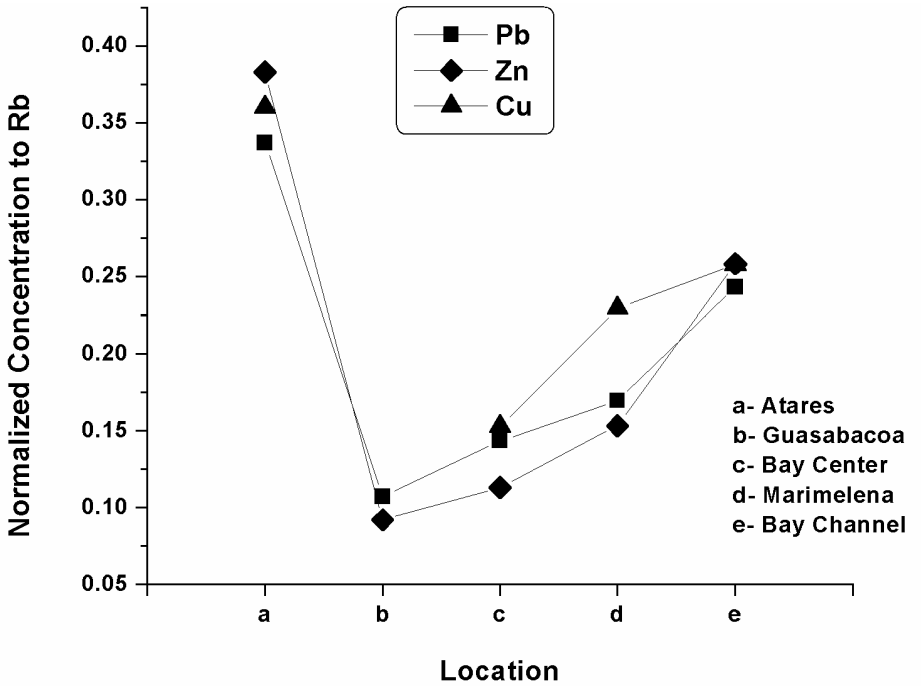

Fig. 3. Zn, Cu and Pb concentrations normalized to Rb at Havana Bay

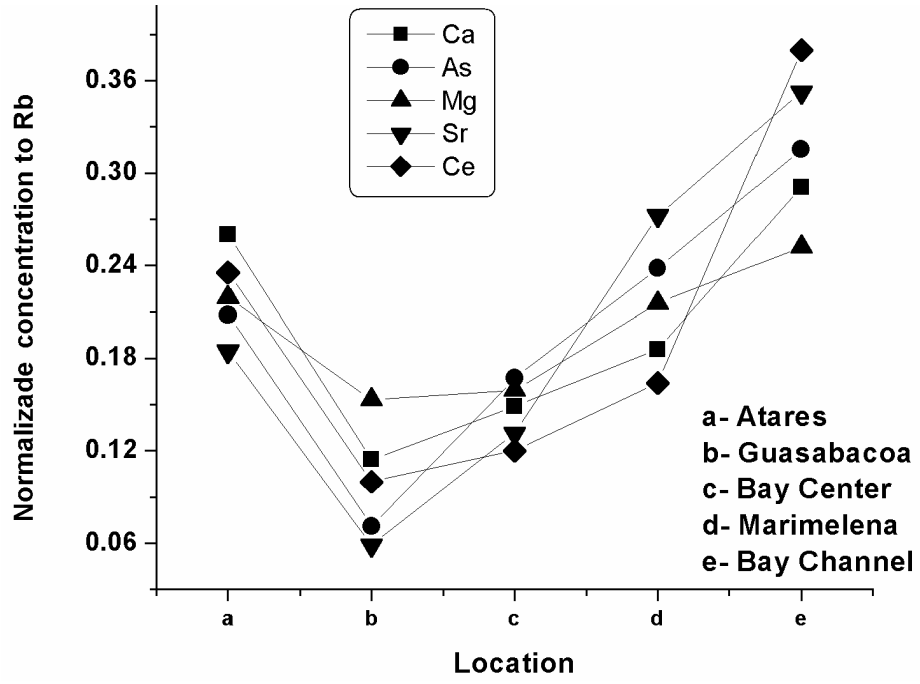

Fig. 4. Ca, Ce, Mg, As and Sr concentrations normalized to Rb at Havana Bay

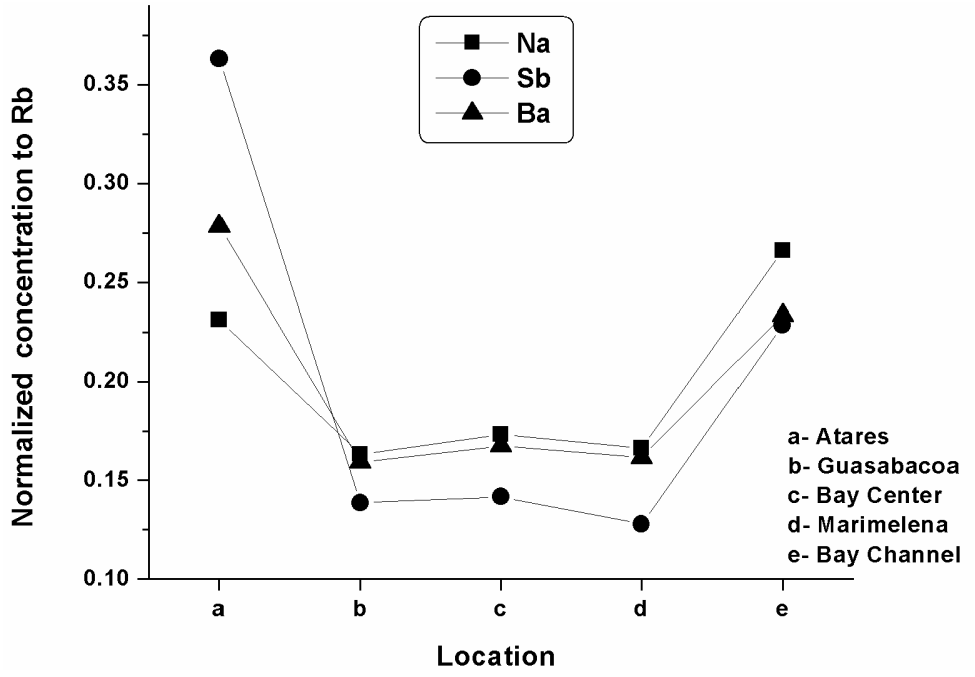

Fig. 5. Na, Sb, and Ba concentrations normalized to Rb at Havana Bay

Conclusions

Using GAA, 26 elements were detected in superficial sediments from Havana Bay. The uncertainties of the concentrations reported for the majority of the elements were below 10%. The results show that several elements (As, Ba, Ni, Pb, Cu, Zn, Fe, Cr, Mn) have high concentration levels compared to the results of other studies of marine sediments.[13-15]

The obtained results confirm the presence of pollutant elements in all the Havana Bay sediments, showing a close interrelation between the concentration levels of the studied elements and the pollution sources.

Atares and Marimelena sediments were found as the more polluted. Both coves showed high heavy metal concentrations, of industrial (Ti, Mn, Cr, Ni, Co, Fe) and urban (Zn, Cu, Pb) origin. Bay Channel results show the influence of cove sediments in this zone. They are indicators of sediments movement from the cove to the channel.

A complementary and more detailed work must be carried out in order to arrive at final conclusions.

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