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Chapter 10

Marine Sediments as Fundamental Repository of Radioactive Contaminants in Aquatic Ecosystems

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.72053

Abstract

In the last three decades, the studies of artificial radionuclides concentration have attracted attention, bringing in the most significant long-term threat to the biosphere. In aquatic ecosystems, the main indicators of pollution are contaminated sediments, which are the primary repository of radionuclides and chemical elements in the marine environment. Radioactive contamination factor (RCF) has been proposed as a suitable unit to measure the magnitude of radioactive contamination at global scale, caused mainly by more than 2000 nuclear explosion tests performed during the 1945–1965 period. It is obtained as percentage of contaminant radioactivity (^{137}Cs) compared to natural radioactivity (^{40}K), both expressed in Bq/g of marine sediments conditioned in Marinelli containers and detected in both NaI(Tl) and HPGe detectors. So, in this paper, samples of marine sediments were taken up along the occidental Cuban coasts and analyzed by gamma spectrometry for the determination of gamma-emitting radioisotopes with energies between 60 and 2000 keV. The results proved that the proposed method is simple and suitable to evaluate radioactive contamination. Also, the RCF values provide an appropriate indicator to predict which will be the future pollution levels and if the rate will go down when only have passed 2,4 half-lives of ^{137}Cs.

Keywords: Cuba, gamma spectrometry, marine sediments, radioactive pollution

1. Introduction

Marine sediments constitute radionuclides and toxic elements repository in aquatic ecosystems. For many years, sediment composition has been studied with the purpose of identifying the contamination zones and to research the anthropogenic causing sources. In addition, sediments studies help to predict the pollutant effects on the ecosystem and the possible risks that can bring for human health.

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The geochemical cycle of these pollutants from urban areas is largely determined by how they interact or are trapped in the sediments. Sediments act as integrators and amplifiers of the chemical elements concentrations in waters and play an important role in estuary areas and shallow waters. So, this subject becomes an interesting and important factor to diagnose the environmental quality of marine ecosystems [1]. The isotope variation concentrations in sediments happens according to the deposition rate, particle sedimentation rate, nature and particle size, as well as the presence or absence of organic matter [2, 3]. However, it is important to mention that the sediments are considered contaminated when the concentration levels are above the established limits according to the region and the type of sediment. This chapter shows how radioactive contamination can be measured by radioactive detection of marine sediments. In this type of samples, an appreciable concentration of natural radioactive isotopes such as ^{40}K can be observed. Therefore, by comparing the fission product radioactivity of ^{137}Cs with natural radioactivity from ^{40}K, this magnitude can be evaluated, and the percentage of radioactive contamination in marine sediments can be obtained (*where* $\boldsymbol{R_1}$ *and* $\boldsymbol{R_2}$ *are the disintegrations per second of Cs-137 and K-40, respectively*) [4].

$$RCF = \frac{R_1(Cs-137)\times 100}{R_2(K-40)} \tag{1}$$

In Cuba, from the 1990s, research starts to take place in coastal ecosystems. Dating studies of ^{210}Pb in sediments were made in the bays of Havana and Cienfuegos and in the Sagua la Grande estuary. But in contrast to the international situation, studies of radionuclide contamination in marine sediments in Cuba are very few, because research has been conducted to the study of atmospheric artificial flows of radionuclides, as reports flow of ^{137}Cs in Cienfuegos between 1994 and 2002 [5, 6].

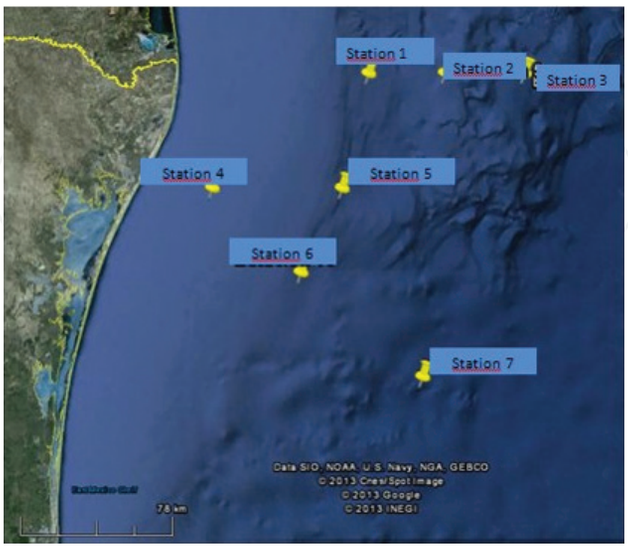


Figure 1. RCF values obtained by Navarrete et al. [4] (left). Location of the sampling sites in Mexico Gulf (right).

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In 2014, minimal values of ^{137}Cs compared to natural radioactivity were found in Mexican sea waters. The researchers used Eq. (1) and estimated values of about 1% of contamination with ^{137}Cs. They also stated that the variations were due to the characteristics of the sample area, the sea currents and the depth of sampling. **Figure 1** shows the location of the study in Mexico Gulf [4]. So, by taking up samples of marine sediments along the occidental Cuban coasts and analyzing gamma spectrometry for the determination of gamma-emitting radioisotopes with energies between 60 and 2000 keV, it is possible to evaluate the radioactive contamination of this area.

2. Experimental

A fundamental question to be solved in sediment sampling is related to the choice of the sampling point. Logically, it is necessary that a point represents the zone conditions; however, given the unstable and seasonal character of the sedimentary deposit, especially in the case of shore sediments, this choice is not always simple and sometimes a point considered as representative for certain time, may cease to be so [7, 8].

To mitigate the possible lack of representativeness from given sample, it has been considered to take up one composite sample, being a topic of discussion the number of subsamples that must conform it. Sampling points are generally defined by their coordinates and depth, in this case, four key points were selected, two on the North coast and two on the South coast, both located in the Western part of the Cuban island.

Guanabo beach: a populated place that belongs to East Havana municipality in Havana province, located at 23.171° North latitude and −82.127° West longitude (in decimal degrees) (**Figure 2**).

Nautico beach: a populated place that belongs to Revolution square municipality, in Havana province, located at 23,097° North latitude and −82,451° West longitude (**Figure 3**).

Bibijagua beach: a populated place that belongs to Youth Island municipality, located at 21.889° North latitude and −82.727° West longitude (**Figure 4**).

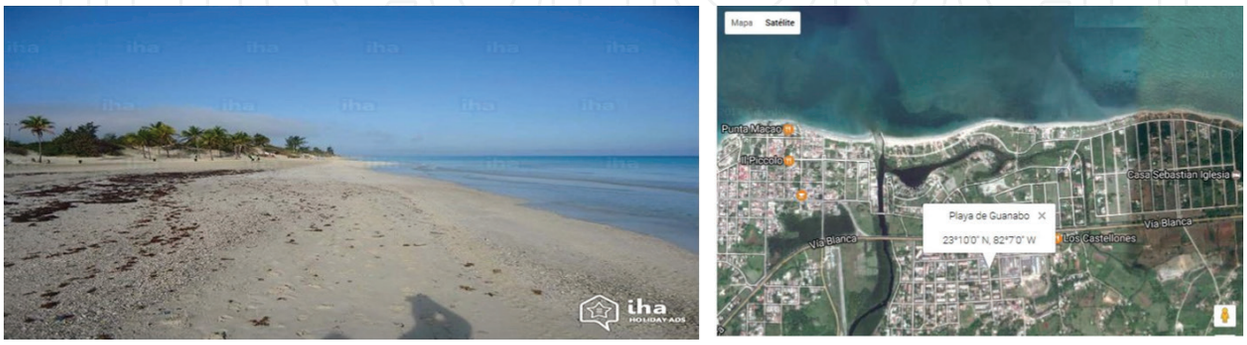


Figure 2. North western coast location of Guanabo beach.

Batabano Gulf: a populated place located to the West south of the island capital, which belongs to Batabano municipality in Mayabeque province, located at 22.698° latitude and −82.293° longitude. It is the main coastal and fishing port on the southern coast of the Mayabeque province (**Figure 5**).

At sampling time, and for our purposes, it is sometimes best to analyze mixtures samples taken simultaneously, at different points, or as close as possible. This allows to evaluate the composition



Figure 3. North western coast location of Nautico beach.



Figure 4. South western coast location of Bibijagua beach.



Figure 5. South western coast location of Batabano gulf.

average of the marine sediments using a mixture of samples that represent several points. Sampling was carried out following one-star design; this method allows to obtain representative fractions of the place. Another important point is the instrument, which must be in accordance with the study that is to be carried out [8]. In this instance, the sampling was carried out at an approximately distance of 100 m from the coast and 1–1.5 m deep. Since this procedure allows the sediment surface layer sampling, the instruments are the simplest on the market. Therefore, the most appropriate would be the "picker type," which is the most affordable [8]. Samples were collected and stored in previously labeled flasks washed with distilled water.

2.1. Drying and sifting samples

For the samples drying, a conventional LAB-LINE Inc. oven was used. The sediments were dried for 3 days at 40°C until total dryness.

Subsequently, the samples were sieved in a 2000-μm sieve, to remove some remains of shells and stones that do not allow the correct Marinelli filling. Then, they were transferred to the containers and proceeded with the gamma measurement (**Figure 6**).

2.2. Gamma spectrometry analysis

The radioactive contaminants analysis of environmental samples has shown interesting results obtained both by the radiometric study of marine sediments samples from western Cuban coasts performed by Gamma Spectrometry with low background scintillation detector [NaI (Tl) crystal] as well as those obtained with one Hyperpure Germanium detector (HPGe).

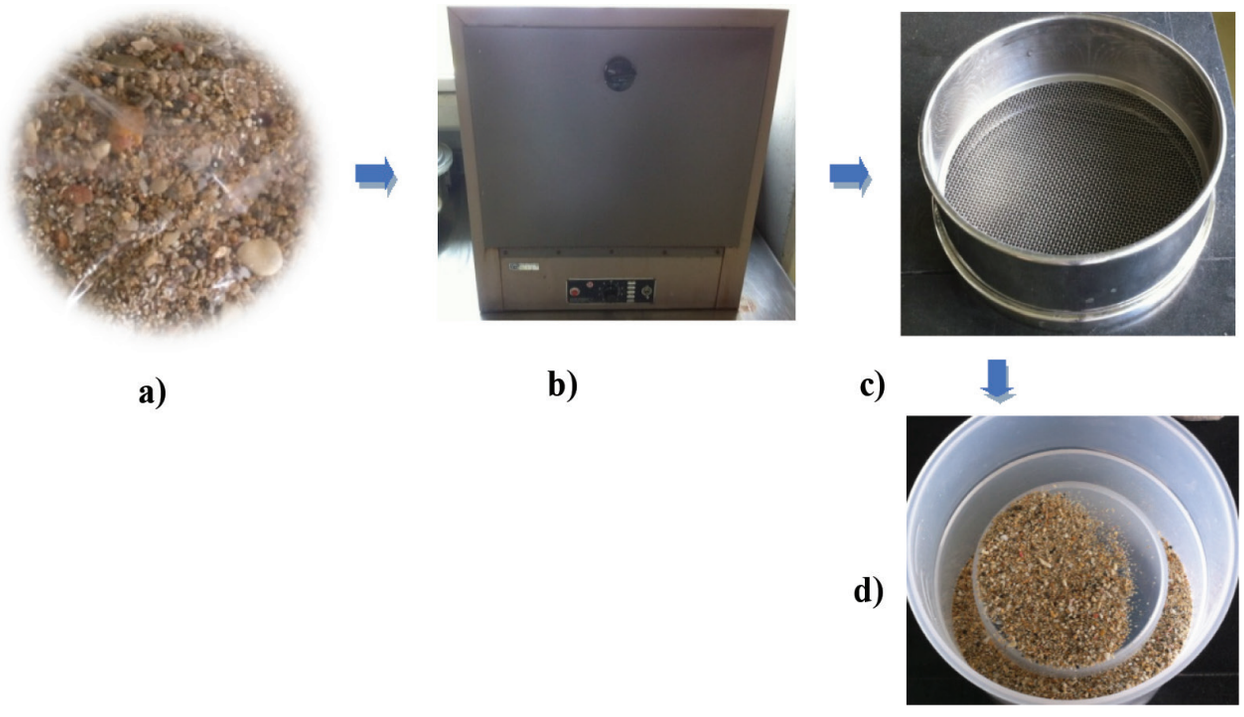


Figure 6. (a) Marine sediments, (b) drying oven, (c) 2000-μm sieve, and (d) Marinelli container.

2.2.1. Gamma spectrometry with low background scintillation detector NaI (Tl)

For scintillation system measurement, a sodium iodide scintillation equipment, Bicron 3 × 3 well Labtech brand with shielding lead distributed by Industrial and Medical Physicians S.A, was used. The results processing was done in the radioactive detection program *Maestro-32 Software Version 6.0 A65-B32 1997* distributed by ORTEC company.

A radionuclide homogeneous mixture also known as a standard certified sample (EG-ML 733-99 Isotope Products Laboratories, Burbank, CA, USA, 91504) was used for the equipment energies calibration. That is to say, an active sample containing a series of photon emitting nuclei with known activity and energy has been used. The positions (channel number) of each energy peak are determined accurately, and the efficiency is plotted as a function of the γ rays energy.

Besides, a known activity of KCl (Potassium Chloride Sigma P9541-500 g) prepared in the laboratory was used. The efficiency value for ^{40}K was 2.9% and for ^{137}Cs of 5.6%. It is important to note that the efficiency value depends on the sample geometry, size, density, and detector distance. For both detectors used in the gamma analysis, the efficiency varies significantly depending on these parameters. Therefore, each counting geometry requires an efficiency calibration, using a known standard sample, with the same geometry.

For the measurement, the samples must be dried, sieved, and weighed. They should be transferred to Marinelli containers (made of polypropylene with a cylindrical shape and an annular space to hold the sample), taking care not to exceed the filling mark and avoiding any areas with empty spaces that may affect the measurement. The detection time was 24 h.

In **Figure 7**, the system described to obtain the gamma spectra of a sample by scintillation is shown.

The spectrum allows to calculate the area under curve of the peak and therefore the net accounts value in 24 h (accounts/24 h). To obtain the counts per second (counts/seconds or cps), the obtained value in the spectrum corresponding to each selected peak area must be divided by the detection time, which in this case was 24 h (86,400 s).



Figure 7. Low background scintillation detector NaI (Tl), 325 Lab, D building, Faculty of Chemistry, UNAM.

Sample	Marinelli weight (g)	Sample weight (g)
Guanabo beach	135	561.1
Nautico beach	135	551.1
Bibijagua beach	136	558.2
Batabano gulf	138	552

Table 1. Each sample weights in the Marinelli container.

Finally, to obtain the disintegrations per second (dps = Bq), the obtained counts per second value must be divided by the detection efficiency determined for each radionuclide. That was previously determined with the certified references samples.

The activity in Bq/g, for each sample, is obtained by dividing the activity in Bq, between the weights of each sample in the Marinelli container. In **Table 1**, each sample weights are reported.

2.2.2. Gamma spectrometry with hyperpure germanium detector (HPGe)

The measurement procedure is similar. In this type of detector, there is a cryostat system that contains a double wall and a vacuum that guarantees thermal insulation. It also has an extension at the top where the detector is cooled with a liquefied gas, generally liquid nitrogen. Before performing the measurement, the liquid nitrogen system must be filled to ensure that it is at the proper working temperature.

For the HPGe detector, the energy calibration is performed using *Gamma Vision program* with radioactive sources of ^{241}Am (60 keV), ^{137}Cs (662 keV), ^{60}Co (1173, 1332 keV), and ^{40}K (1460 keV)) for 900 s (**Figure 11**).

The efficiency calibration is performed with a known specific activity of KCl standard sample (Potassium Chloride Sigma P9541-500 g). The detection efficiency for ^{40}K was 0.25% and for ^{137}Cs was 0.47%. These values are sensibly lower than those obtained with the scintillation

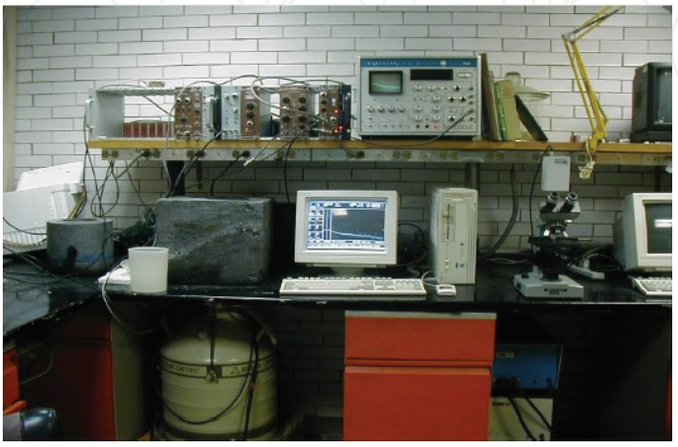


Figure 8. Hyperpure germanium detector (HPGe), ORTEC company. A-23 Lab, Physics Institute, UNAM.

detector. The spectra processing is performed in the Maestro-32 Software Version 6.0 program A65-B32 1997 distributed by the ORTEC company.

In this detector, each peak is better solved, which allows a better energy separation and makes it possible to analyze more complex samples, with more radionuclides and nearby energy values, which cannot be solved in scintillation detectors.

The system used can be seen in **Figure 8**. It has a high-voltage power supply, cryostat, preamplifier, amplifier, multi-channel analyzer (MCA), lead shield, and a computer (PC).

3. Results

The RCF values were calculated from the obtained counts in both detectors using the Eq. (1), and considering that the detection time was 24 h = 86,400 s. In **Tables 2** and **3**, the RCF values are reported with their respective experimental error and standard deviation. It is important to note that the considering activity for the calculation of the RCF must be in Bq/g, the sample grams were reported in **Table 1**.

The statistical percentages errors are reported in **Tables 2** and **3** and were calculated according to Eq. (2), also call, the standard deviation of the activity ratio of two radioactive sources [9, 10]:

$$\frac{a}{b} \pm \frac{x}{y}\left(\frac{1}{x}+\frac{1}{y}\right)^{1/2} \tag{2}$$

Sample	Disintegration per second ^{40}K	Disintegration per second ^{137}Cs	RCF %
Guanabo beach	14.1503	1.6110	11.4 ± 0.09
Nautico beach	8.3413	0.9403	11.3 ± 0.12
Bibijagua beach	11.5162	0.6097	5.3 ± 0.07
Batabano gulf	14.2130	0.7671	5.4 ± 0.06

Table 2. RCF values obtained with the NaI(Tl) detector from the North and South coast of Cuba.

Sample	Disintegration per second ^{40}K	Disintegration per second ^{137}Cs	RCF %
Guanabo beach	0.6091	0.0590	9.7 ± 0.42
Nautico beach	2.5806	0.2805	10.9 ± 0.22
Bibijagua beach	2.8206	0.1715	6.1 ± 0.15
Batabano gulf	3.0632	0.1785	5.8 ± 0.14

Table 3. RCF values obtained with the HPGe detector from the North and South coast of Cuba.

http://dx.doi.org/10.5772/intechopen.72053

where ***a/b*** is the RCF value (%) in each case, ***x*** is the disintegration per second Cs-137, and ***y*** is the disintegration per second K-40.

If, in addition, the obtained RCF values for each sample in each detector are compared, several variations can be observed between them:

- For the North coast, the standard deviation is 3–15% between the two detectors. The standard deviation between both detectors of 15% in Guanabo beach and of 4% for Nautico Beach.
- In the South coast, the standard deviation is 6–13% between both detectors. The standard deviation between the two detectors was 13% in Bibijagua beach and 6% de Batabano Gulf.

These differences are expected because both detectors have several differences:

1. The detection efficiency is higher in the scintillation detector.
2. The radioactive backgrounds are different; the background is higher in the HPGe detector.
3. The peaks resolution is sensibly higher in the HPGe detector, each peak is better resolved.

Another interesting aspect that can be noticed is how the RCF values of the southern coast of the island differ from those obtained on the north coast. In all cases, the southern coast has lower RCF values than the north coast. This anomaly can be due to numerous events that they can go from the geological area characteristics and the sediment type, to the winds direction and the proximity to anthropogenic sources. **Figure 9** shows the spectrum obtained with the scintillation detector for Guanabo beach.

In *Maestro program*, it is possible to extract the information about the peaks: the FWHM (Full Width at Half Maximum), the Net and the Gross Area, the Real, Live and Dead Time with the "Peak Info" function, as shown in **Figure 10**.

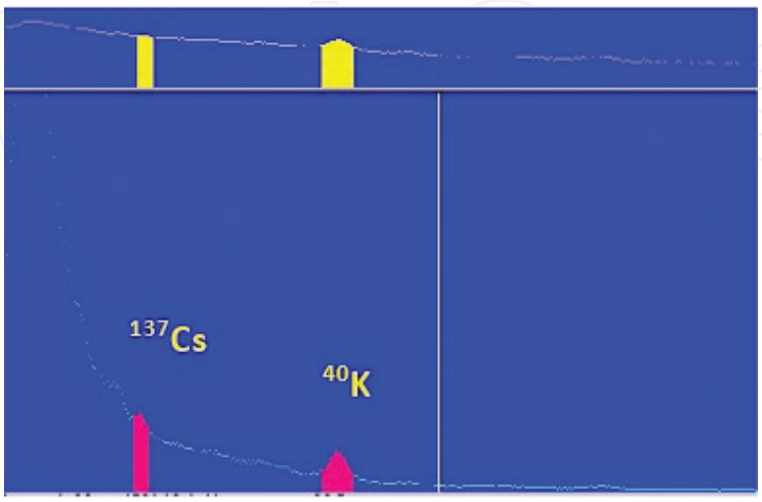


Figure 9. Spectrum obtained with the scintillation detector for Guanabo beach.

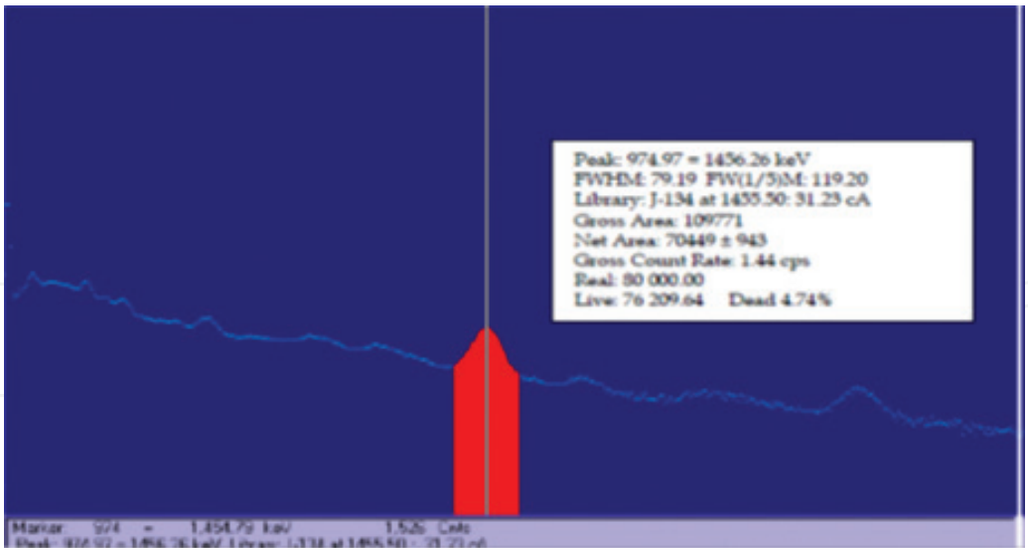


Figure 10. Spectrum displays the peak information in Maestro program.

It is also interesting to compare the obtained RCF values in Cuba with those obtained in 2011 by Navarrete et al. in marine sediments sampling stations in the Gulf of Mexico. It can be noted that in Mexico, the highest value of RCF was 1.21%; while in Cuba, we found values up to 11% on the North coast [11–13]. **Figures 12** and **13** show the spectra obtained with the Hyperpure Germanium detector (HPGe).

Even though, these last values are not alarming because they constitute a minimum percentage of the natural radioactivity. Nevertheless, it is very interesting and exhorts us to extend this study to other geographical points to establish a global indicator of contamination of the Mexico Gulf and the Caribbean zone.

Now, the spectra obtained in the HPGe detector are shown for two marine sediment samples: one from the North (Guanabo beach) and one from the South coast (Batabano Gulf). The different peak resolutions can be noticed.

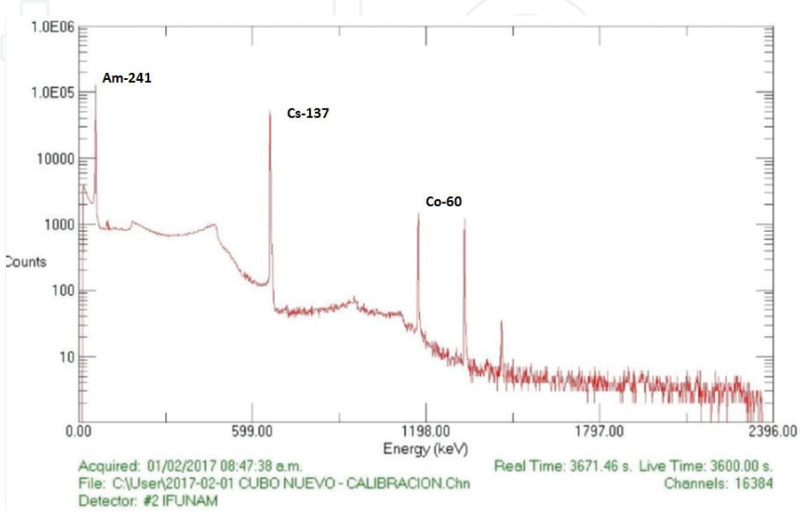


Figure 11. Energy calibration spectra for the HPGe detector.

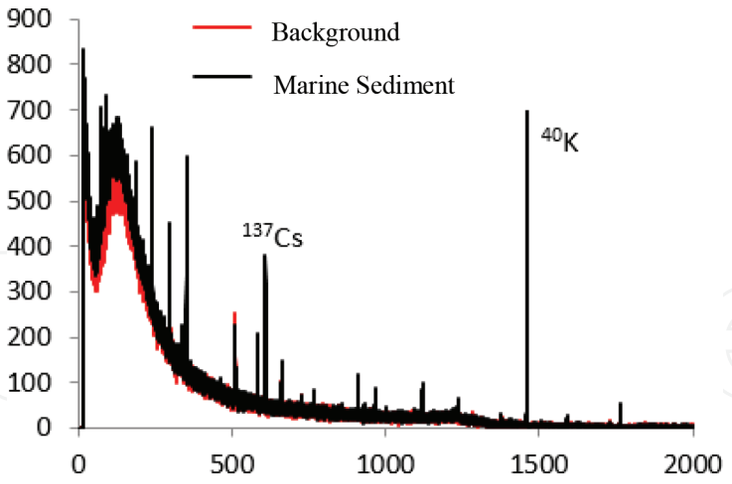


Figure 12. Obtained spectra from the North coast (Guanabo beach) in the HPGe detector.

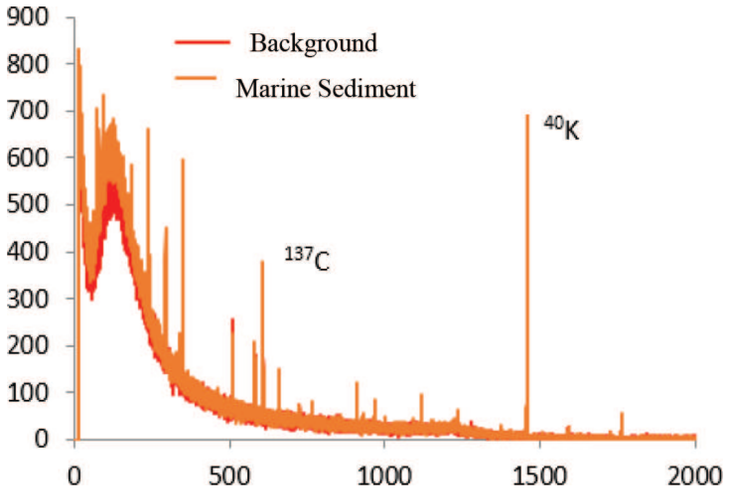


Figure 13. Obtained spectra from the South coast (Batabano gulf) in the HPGe detector.

Until now, it has been found that marine sediments are the fundamental repository of contaminants in aquatic ecosystems. The study of these materials is still necessary because if levels above sediment quality international standards are found [14], the quality of water, soils, and crops can be affected. The basic premise used to reduce the contaminants presence in waters, soils, and sediments is the constant monitoring of contaminated areas. This approach should include the long-term pollutants behavior, which is determined by the physic, chemical, and biochemical reactions in the system [15].

The obtained results for each Cuban sediment samples did not show alarming values or higher than those established, which make required remediation measures of the zone. It should be noted that for a better understanding of the radioisotopes concentrations metals in the sediments a deeper mineralogical and geochemical characterization of the sediments should be carried out.

For example, mass spectrometry methods are generally used to know the isotopic composition of an element, taking into account this premise it can be said that they could also be used

for the determination of radionuclides in a precise way, since it is possible to measure the atomic mass directly from each element (radioactive isotopes of the element).

In recent years, different articles have reported the use of mass spectrometry for the study of radionuclides with a long period of disintegration, obtaining satisfactory results [16, 17]. It is known that due to the nature of the radioactive decay, radiometric methods have a greater statistical variation in the results than those obtained by mass spectrometry. Therefore, a more precise study could be done with this attractive tool.

Finally, it is important to say that a study that allows the establishment of pollutants levels in sediments should be done frequently to regulate these levels, and thus to ensure the quality of the marine ecosystem.

4. Conclusions

1. Marine sediments are the main repository of radioactive contamination. In the Cuban sediments studied, the contents of ^{137}Cs and ^{40}K could be adequately calculated, showing that sediments are much more receptive and representative than the atmosphere and soils in the anthropogenic pollutants study.

2. The measurement of the ratio between the anthropogenic pollutant ^{137}Cs compared to the natural radionuclide ^{40}K in marine sediments (RCF) remains a suitable method for environmental radioactive contamination measuring.

3. The radioactive contamination factor (RCF) values obtained in each gamma detector, showed a 3–15% statistical variation between them.

4. It was found that there are remarkable differences in RCF values between marine sediments form the North coast and those on the South coast. The RCF values for the northern coast are higher than those obtained in samples taken on the southern coast of Cuba.

5. Comparing the RCF values of the Cuban marine sediments samples with the RCF values of the study carried out in 2011 Mexico Gulf, superior results were obtained in all cases, being approximately ten times higher the RCF values of the Cuban sediments.

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