

## Low-level gamma spectrometry for pollution assessment in San Simón Bay (Vigo, Spain)\*

B Quintana<sup>1</sup> P Álvarez-Iglesias<sup>2</sup>, R Santamaría<sup>1</sup>, B Rubio<sup>2</sup> and M Pérez-Arlucea<sup>2</sup>

<sup>1</sup> Group of Experimental Nuclear Physics, University of Salamanca, Spain

<sup>2</sup> Department of Marine Geosciences, University of Vigo, Spain

E-mail: quintana@usal.es

**Abstract.** A gamma spectrometer with HPGe detector of 50% relative efficiency and 1 cps total background has been dedicated to the measurement of an intertidal sediment core from a coastal environment at the Ría de Vigo (Spain). The area is affected by lead pollution and the source identification needs of a precise dating of the sediment core. Such a precise dating requires the measurement not only of the radionuclides directly involved in time calculation, as  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$ , but also of ancillary radionuclides which inform about the dating model to apply and about the validity of its time estimation. Gamma spectrometry with Ge detectors performs a simultaneous measurement of the full content in  $\gamma$ -emitters of the sample. However, its use is limited by its high spectral background. We present the characteristics of our low-level background gamma spectrometer and also of Galea, the computing tool for the expert analysis of natural radionuclides. Both make possible to get the proper experimental results to reach a suitable dating. The results allowed us to detect a change in the sedimentation dynamics in the area under study, to verify the impact of lead pollution in the  $^{210}\text{Pb}$  level, to obtain a sedimentation rate by using the CF:CS model with a suitable correction factor and, finally, to validate the sediment dating.

### 1. Introduction

The use of radionuclides in the characterization of sediment systems has become the main technique in geochronology in order to obtain an absolute temporal scale which allows correlating sediment proxies with their external cause [1]. Sediments are archives of changes in the ecosystem they belong to, therefore a precise sediment dating provides the chronology of the ecosystem history.

When dating recent sediments one can resort to the natural radionuclide  $^{210}\text{Pb}$  ( $T_{1/2} = 22.6$  a) which has a double origin in the sediments because it is a daughter of  $^{222}\text{Rn}$ . There is a  $^{210}\text{Pb}$  fraction supported by the  $^{226}\text{Ra}$  content in the sediment grain structure and another fraction unsupported. This unsupported fraction is due to the fact that  $^{222}\text{Rn}$  partially escapes to the atmosphere once is generated by  $^{226}\text{Ra}$  disintegration. As a consequence,  $^{210}\text{Pb}$  is also produced in air and deposited into sediments isolated from its progenies. Sediments will contain an excess of  $^{210}\text{Pb}$  with respect to that produced in the own sediment by  $^{226}\text{Ra}$ . It is the unsupported fraction that is useful for dating because it diminishes with depth independently to  $^{226}\text{Ra}$  according to the time elapsed between the sediment formation and its measurement. The determination of the in-excess  $^{210}\text{Pb}$  requires the previous knowledge of the supported fraction. This can be achieved by determining the  $^{226}\text{Ra}$  content on the samples and assuming secular equilibrium between  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  supported.

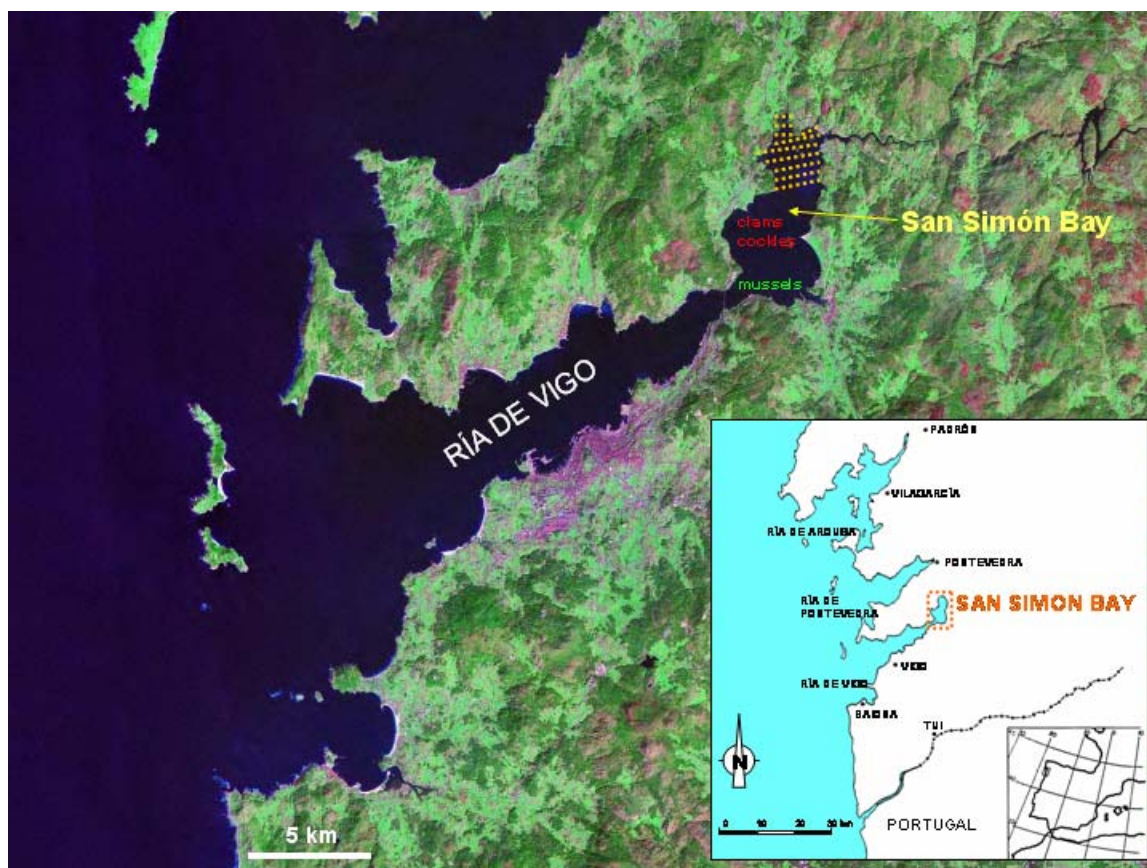


Figure 1. Map of the study area.

However, there is still a challenge related to the application of dating models because they are based on several very simple assumptions whose fulfillment one has to check. In this task, the change in concentration of the other natural radionuclides along the core becomes very useful. Radionuclides such as  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and, even,  $^{40}\text{K}$  are proxies of the conditions in which sediments were formed. Therefore, its measurement provides us a way to test the strong hypotheses of the dating models. Furthermore,  $\gamma$  emitters like  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  give us a validation of the time estimation resulting from the application of the model to the experimental unsupported  $^{210}\text{Pb}$  profile.

Gamma spectrometry with HPGe detectors can constitute a very useful technique in sediment dating because it provides, in just one measurement, with the full content of  $\gamma$  emitters in the sediments. However, to enlarge the application range of the technique, we need to reduce the effects of its high background, which has repercussions, first, on the detection limit and, afterwards, on the technique accuracy. This can be accomplished by acting in two directions: on the one hand selecting suitable detector and shielding configurations, on the other hand optimising the spectral analysis to reduce uncertainties.

In this work, we present the results obtained in the dating of sediments from a Pb polluted area [2] by gamma spectrometry with HPGe detector. The area is of great economical and ecological interest. On the subtidal area close to the Rande Strait, there are mussel platforms which contribute to the bay infilling with the subsequent damage to the native clam and cockle colonies (figure 1). The fact that the area shows Pb pollution makes double interesting its dating: first, it provides the identification of pollution sources and second, it requires the development of a method that enables a variable  $^{210}\text{Pb}$  input to the sediments. In the following section, we start describing the sampling procedure and the characteristics of the studied sediments. Next, we describe the low-level background gamma spectrometer employed in the radionuclide measurements and the main characteristics of Galea, the gamma-line expert analyzer in development at the Salamanca research group, applied to analyze the

spectra. Results are given in section 3. The in-excess  $^{210}\text{Pb}$  profile, which corresponds to the input of the dating method, is obtained. We briefly justify the application of a corrected CF:CS method [3] and, therefore, of the sedimentation rate obtained. We finish with some conclusions that can be extracted from these results.

## 2. Material and methods

Two sediment cores were obtained along August 2003 in the intertidal area of San Simón Bay, between the Oitavén-Verdugo and Ulló Rivers mouths, in an area relatively far from both river mouths and also far from mariculture areas (figure 2). Both cores were carefully collected using a hand-driven PVC coring pipe of 12 mm inner diameter in the intertidal flat. Sediment compaction caused by the coring procedure was measured and was found to be negligible. Recovery varied between 42 (SSMPA) and 50 cm (core replicate, SSMPB). Core pipes were sliced at 1 cm depth intervals. Sediment samples were dried at 60°C until constant weight and water content was determined. SSMPA bulk samples were finely powdered in a ball-mill for geochemical and radionuclide analysis. Textural analyses were performed on the core replicate, SSMPB.



Figure 2. View of the sampling zone towards the sea.

Sediment samples were characterized by grain size [4], organic and inorganic carbon content (TOC and TIC), pH and major and trace element content. Accuracy and precision in total metal content determination were checked by analysing reference material. Elemental analysis and X-ray fluorescence analyses were performed in the C.A.C.T.I. (Universidad de Vigo). For gamma analysis, sources were prepared introducing 20 g dried sediment in plastic cylindrical boxes of 3 cm diameter and 2 cm height (figure 3).

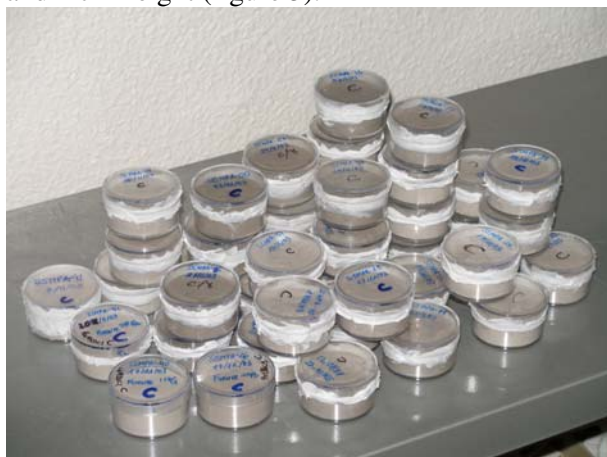


Figure 3. Sediment sources for gamma spectrometry.

Sources were counted in a p-type HPGe detector, model BE5030, manufactured by CANBERRA, with an active volume of 117 cm<sup>3</sup>, which is mounted in an impurity-free cryostat (7915-30-ULB model). Associated electronics is made up of a 3106 model HV Power Supply, a 2002CP model pre-amplifier, a 2026 model spectrometry amplifier and an ACCUSPEC/B multichannel analyzer, all manufactured also by CANBERRA. In order to reduce the laboratory background, the detector is shielded with *sweet* (before Second World War) iron 10 cm thick, very old lead 5 cm thick and internally lined with 2 mm thick electrolytic Cu (figure 4). The detector chamber is ventilated with nitrogen gas to avoid Rn accumulation inside the shielding.



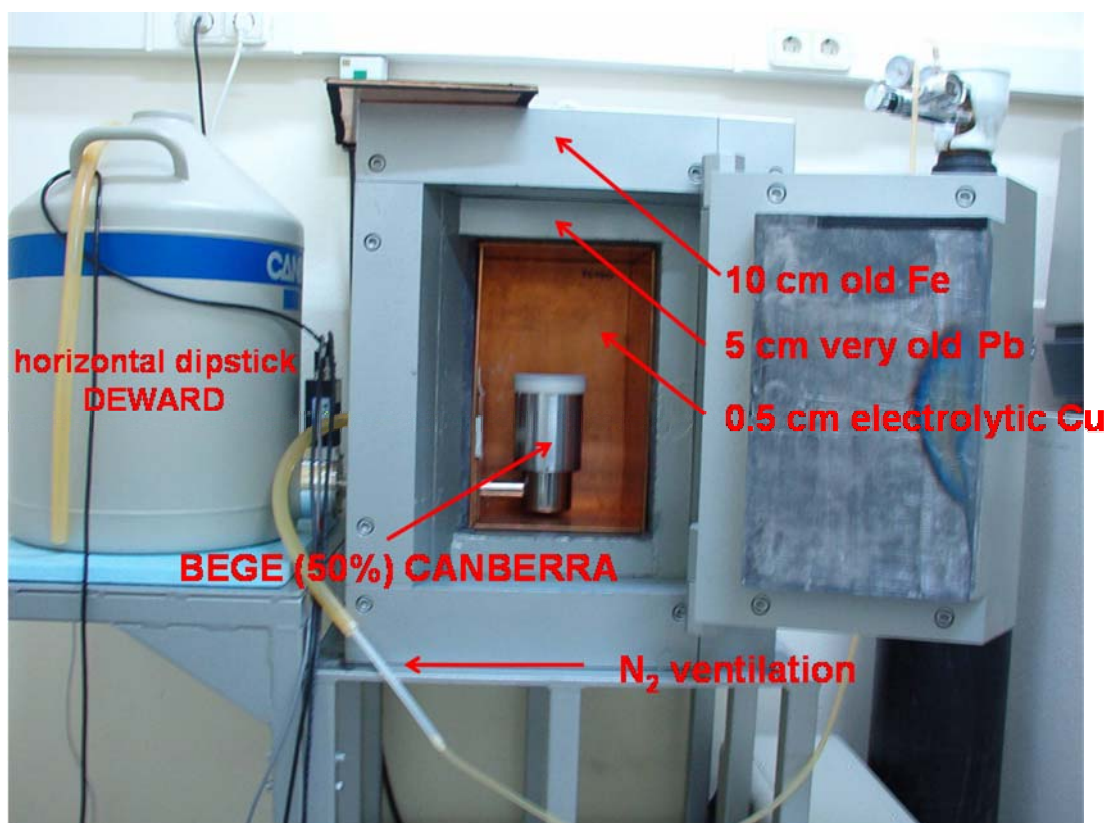


Figure 4. HPGc detector, cryostat and shielding

With this configuration, the main remaining lines in the detector background spectrum are located at 1460.83 keV ( $^{40}\text{K}$ ) with  $1.07(13) \cdot 10^{-3}$  cps, at 66.70 keV ( $^{72}\text{Ge}(n,\gamma)^{73\text{m}}\text{Ge}$ ) with  $0.27(4) \cdot 10^{-3}$  cps, at 351.93 keV ( $^{214}\text{Pb}$ ) with  $0.26(4) \cdot 10^{-3}$  cps and at 609.32 ( $^{214}\text{Bi}$ ) with  $0.22(3) \cdot 10^{-3}$  cps. Quality control is achieved by analysing certified samples, checking the tracer activities, measuring periodically the detector background and controlling the electronic performance. We also carry out external controls by participating annually in blind sample and intercomparison exercises which enable us to validate the methodology employed in the gamma spectrometry measurements.

For this work, absolute peak efficiencies were obtained in the same measuring set up as sediment sources. Spiked sources with the same sediment matrix were prepared using small quantities of three certified standard solutions each one containing  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$ , respectively. Efficiencies obtained are 0,1793 (42), 0,0557(13) and 0,0353(3) at 46.54 keV ( $^{210}\text{Pb}$ ), 351.9 keV ( $^{226}\text{Ra}$ ) and 661.66 keV ( $^{137}\text{Cs}$ ), respectively.

The spectrum analysis has been performed with Galea (figure 5), the gamma-line analyzer optimized for natural radionuclides analysis. Spectra from natural radionuclides are characterized by low intensity peaks highly overlapped at low energy where the continuum background is also higher. A precise analysis of these spectra requires a method capable to extract, confidently, the areas of all emissions in every spectrum. Galea achieved this task in several steps: the whole fit of spectral continuum according to Quintana and Fernández [5], the emission identification with a genetic algorithm and simultaneous area calculation with restrictions based on tabulated intensities, isotopic relations and detector efficiencies [6]. The benefits in using Galea are manifest in  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$  and  $^{238}\text{U}$  results.  $^{210}\text{Pb}$  has one emission at 46.54 keV whose precise quantification requires a reliable base line determination. Otherwise, for the precise  $^{226}\text{Ra}$  determination, emissions from its daughter are used being necessary, previously to area restriction calculations, to check the secular equilibrium assumption. For estimation of  $^{238}\text{U}$  activity, peak area restrictions are also needed because of high overlapping of its emissions at 92.35 and 92.73 keV.

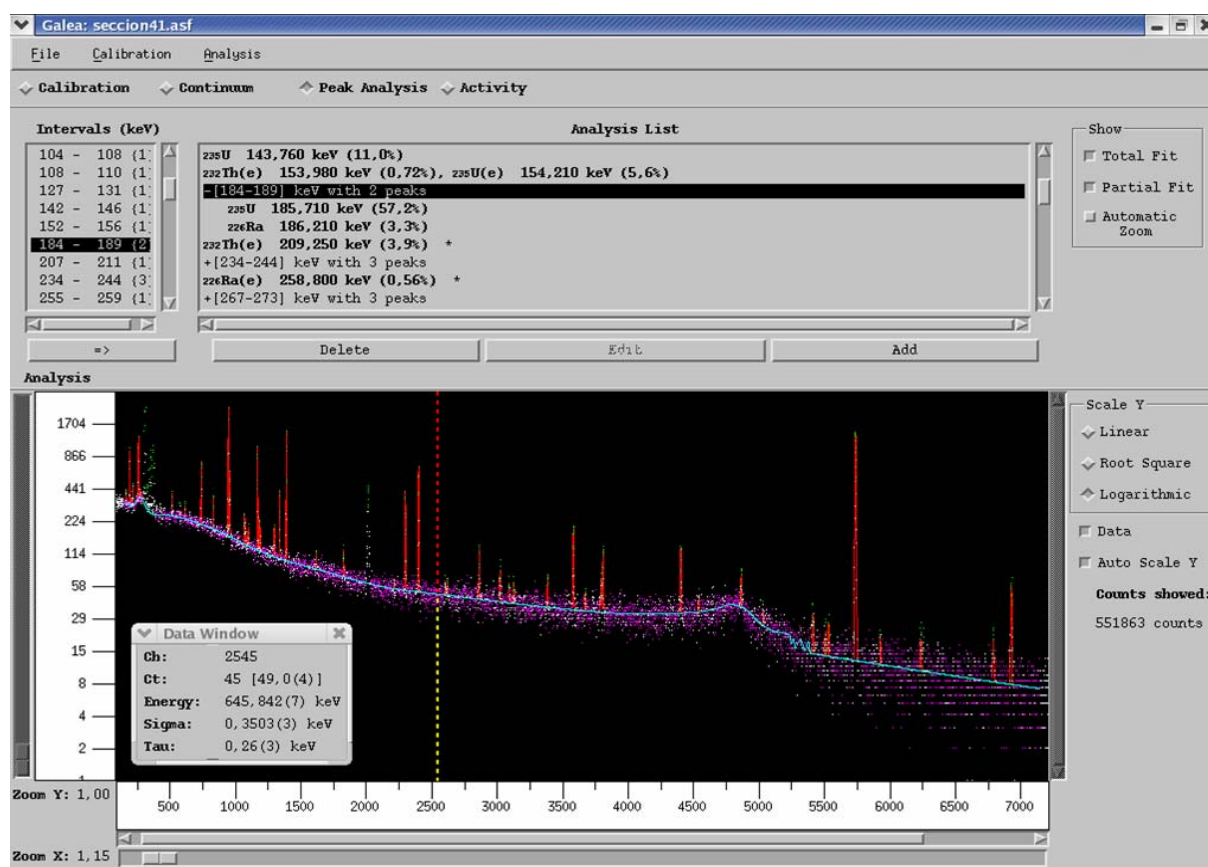


Figure 5. Galea analysis window showing the continuum fit (blue line) and peak fits (red line).

### 3. Results

$^{210}\text{Pb}$  and  $^{226}\text{Ra}$  activity profiles have been obtained (figure 6) where the excess of  $^{210}\text{Pb}$  with respect to  $^{226}\text{Ra}$ , and, therefore, to the supported  $^{210}\text{Pb}$  fraction, can be observed. Visual inspection of  $^{226}\text{Ra}$  activities allows profile splitting into two zones with different sediment characteristics: from sediment surface to around 15 cm, and from 15 cm to bottom. This implies that the sedimentation rate has changed along the time in which the sediment column is formed and prevents the application of the CF:CS model because it assumes constant supply of sediments.

The measurement of  $^{238}\text{U}$  corroborates such a result, as shown in figure 7. If one checks the grain size profiles corresponding to the sediment column, a change in the grain size composition is observed at 15 cm indicating a change in the sediment velocity (figure 7). Otherwise, the Pb-metal concentration

profile, also depicted in figure 8, reveals a peaked behaviour with a maximum of about  $2000\text{ }\mu\text{g/g}$  at 7 cm. The Pb-metal background level in the bay is  $25\text{ }\mu\text{g/g}$  [7]. A variable Pb input in the sediments raises a new difficulty in applying the CF:CS model because this model also assumes a  $^{210}\text{Pb}$  constant flux to the sediments. To solve it, we have corrected the in-excess  $^{210}\text{Pb}$  profile according to Pb metal profile for all values to be referred to the same initial  $^{210}\text{Pb}$  value. The result is shown in figure 8 where we can see that the unsupported  $^{210}\text{Pb}$  profile behaves exponentially, just as CF:CS model predicts.

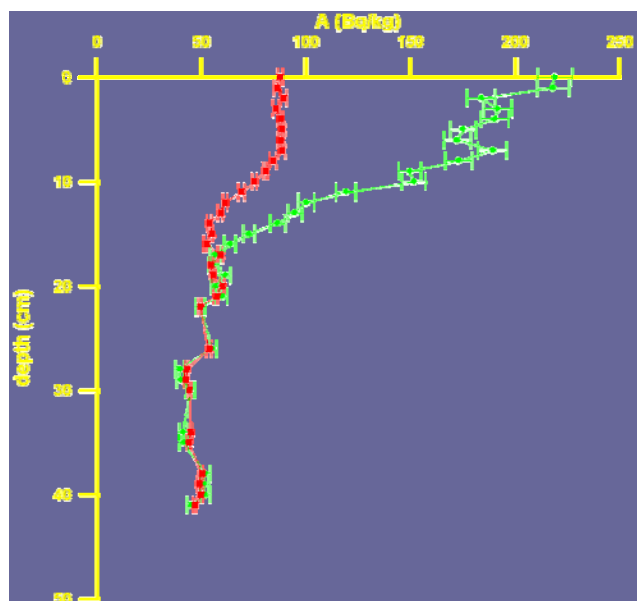


Figure 6.  $^{210}\text{Pb}$  (green dots) and  $^{226}\text{Ra}$  (red dots) activities versus depth.

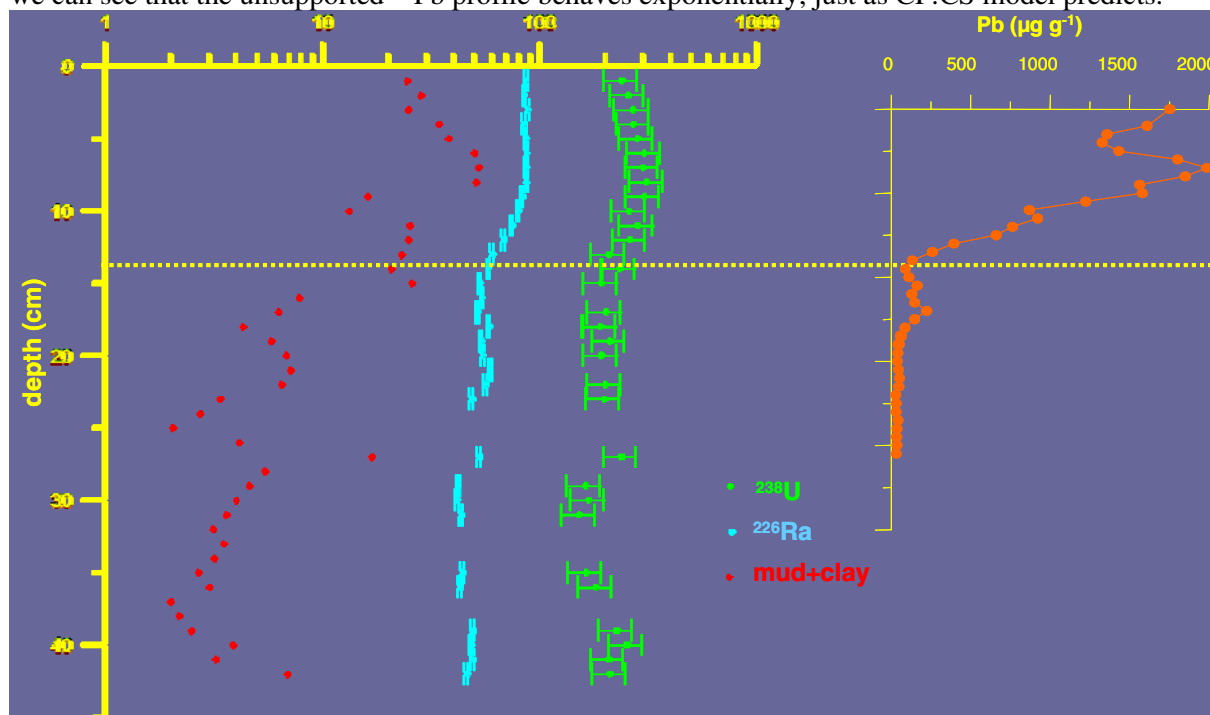


Figure 7.  $^{238}\text{U}$ ,  $^{226}\text{Ra}$ , fine-grain-proportion and Pb-metal profiles.

By using a Minimum-Square-based fitting method, a sedimentation velocity is calculated between top and 17 cm to give  $0.56 \pm 0.05$  cm per year.  $^{137}\text{Cs}$  profile (figure 9) shows an activity peak at 7 cm which, using the sedimentation rate previously obtained and corresponds to the year 1987, one year after Chernobyl accident. Taking into account that one year is the mean  $^{137}\text{Cs}$  residence time in the atmosphere, this estimation match with the maximum  $^{137}\text{Cs}$  fallout after the accident validating the  $^{210}\text{Pb}$  dating.

#### 4. Conclusions

We have obtained a precise  $^{210}\text{Pb}$  dating of a sediment core from San Simón Bay with a low-level gamma spectrometer with HPGe detector together with the natural radionuclide spectrum analysis tool Galea. The dating reliability has been guaranteed by the simultaneous measurement of  $^{226}\text{Ra}$  and  $^{238}\text{U}$  radionuclides which provide the data interval in which to apply the method. The dating method chosen was CF:CS because it provides better precision when assumptions are fulfilled. We have shown that the calculation of a corrected  $^{210}\text{Pb}$  profile allows the use of this method that, in our particular case, gives a sedimentation rate corroborating the  $^{137}\text{Cs}$  activity profile.

The measurement of all radionuclides employed in the whole dating process does not imply longer measuring times nor more sample processing work which points to the utility of gamma spectrometry with HPGe detector in this field of research.

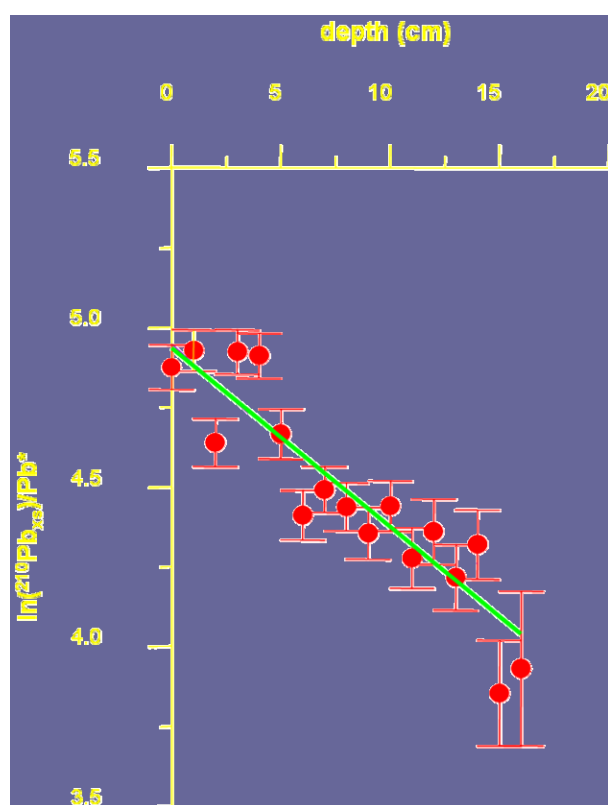


Figure 8. In-excess  $^{210}\text{Pb}$  activity profile corrected with total Pb content.

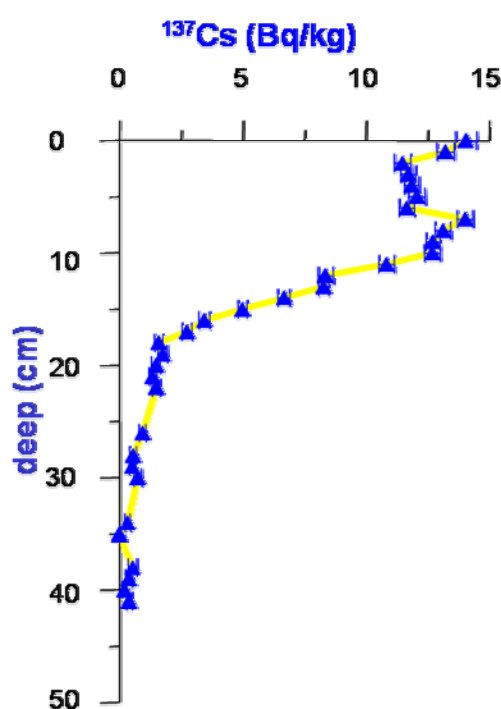


Figure 9.  $^{137}\text{Cs}$  activity profile.

#### References

- [1] Cochran J K and Masqué P 2004 *Marine Radioactivity* ed. H D Livingston (Amsterdam:

- Elsevier) p 1
- [2] Álvarez-Iglesias P, Rubio B and Vilas F 2003 *Mar. Pollut. Bull.* **46** p 491
  - [3] Applebey P G and Oldfield F 1978 *Caten*, **5** p 1
  - [4] Folk R L 1974 *Petrology of sedimentary rocks* (Austin Texas: Hemphill Publishing) p182
  - [5] Quintana B and Fernández F 1998 *Nucl. Instr. and Meth. in Phys. Res. A* **411** p 475
  - [6] Santamaría R and Quintana B 2005 Galea: the Gamma Line Expert Analyzer for natural radionuclide spectra *Preprint*
  - [7] Álvarez-Iglesias P, Rubio B and Pérez-Arlucea M 2004 *Geotemas* **6 (1)** p 315

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<sup>3</sup> To whom any correspondence should be addressed.