Comparison and application of three $^{210}$Pb dating models on a lagoon sediment core in Moulay Bousselham in Morocco

Ait Bouh H. 1*, F. Rokne 2, N. Ziad 3, A. Benkdad 1, A. Laisaoui 1, M. Bounakhla 1

1Division of Earth and Environment Science, Centre National de l’Energie, des Sciences et des Techniques Nucléaires (CENESTEN), B.P.1382 R.P., 10001 Rabat, Morocco.
2Faculté des Sciences, Université Ibn Tofail, Kenitra, Morocco.
3Ecole Nationale des Sciences Appliquées, Université Ibn Tofail, Kenitra, Morocco.

* Email: of corresponding author: aitbouh@gmail.com

Abstract

Radiometric dating of sediment columns is considered as a powerful tool in integrated management of coastal areas. It allows reconstructions of historical input of pollutants, prediction of future concentrations and establishing the functioning of aquatic ecosystems.

In this work, we present a study of a sediment core from the Moulay Bousselham lagoon in Morocco. This core was cut to several subsamples of the same thickness and after appropriate preparations, were subjected to radioisotopic analyzes by Gamma Spectrometry (HPGe), particularly $^{210}$Pb and $^{137}$Cs. In order to establish the recent chronological history of the sediment core, we have relied on vertical distributions of $^{210}$Pb and $^{137}$Cs activity concentrations in this core.

Three dating models based on changes of activity concentrations of unsupported lead or in excess ($^{210}$Pb$_{ex}$) were used: CF-CRS (Constant Flux - Constant Sedimentation Rate), CIC (Initial Constant Concentration) and CRS (Constant Rate of Supply). $^{137}$Cs has been applied as a time marker.

The different results show that the three models are comparable for the superficial layers. With an advantage for CRS, especially for deep layers, which appears to be the best applicable model to be used in in this study site.

Keywords: $^{210}$Pb, $^{137}$Cs, sediment core, Datating models (CF-CRS, CRS, CIC), Moulay Bousselham lagoon.

1. Introduction

Sediment cores can be dated to determine historical inputs to aquatic systems, however, it needs to be emphasized there are limitations to the methods. Disturbance of the sediment cores in any way by biological, physical or chemical factors [1] can preclude accurate dating of the cores or require adjustments in interpretation [2]. This chronology is based on three mathematical models: The Constant Flux - Constant Sedimentation Rate (CF-CS), Constant Rate of Supply (CRS) and the Constant Initial Concentration (CIC).

These three models predict the distribution of $^{210}$Pb in depth. The total signal of $^{210}$Pb in recent sediment profile consists of: supported $^{210}$Pb, which is present due to antigenic material of the sediment and unsupported (excess) $^{210}$Pb, which originates from the atmospheric deposition. $^{210}$Pb$_{sup}$ is usually assumed to be in radioactive equilibrium with its parent nuclide $^{226}$Ra. $^{210}$Pb$_{ex}$ permits the reconstruction of geochronology through the estimation of ages and sediment accumulation rates deposited during the last 150 years. The chronology obtained by the $^{210}$Pb must be validated by an independent tracer. In our case, we chose $^{137}$Cs as a temporal marker [3], which is an artificial radionuclide resulting from atmospheric deposition between (1963-1964 and 1986) [4].

The purpose of this study is to present the chronology of the sediment core collected in 2009 from the Moulay Bousselham Lagoon in Morocco, by applying of the three $^{210}$Pb dating models and comparing them to determine potentials and limitations of each which one and which model is the most appropriate for our case.

2. Materials and methods

2.1. Description of the sampling site

Moulay Bousselham Lagoon is located on the Atlantic Ocean. Its length is 9 km and its width is about 5 km. It exchanges water with the ocean through a main entrance estimated at 357 meters. The lagoon system is drained mainly by the Drader River to the east and by the Nador Canal to the south. The Moulay Bousselham Lagoon provides an important coastal environment for a variety of bird species, fish, plants and wildlife. The Moulay Bousselham Lagoon has been declared a biosphere reserve of international importance.
for wildlife. The population of the Moulay Bousselham lagoon is approximately 154,000 people. The main activities are livestock farming and land cultivation where agricultural chemicals are used excessively, affecting biodiversity and ecology. There are also other less important activities, namely fishing and tourism [5, 6].

In this study, sampling was carried out in 2009 at the Moulay Bousselham lagoon as shown in Figure 1 at latitude and longitude of 34°51’43.498” N; 06°16’1.131” W.

2.2. Sampling, preparation and analysis

The sampling of the sediment core was done manually using a cylindrical plastic corer with a thickness of 2 mm, a diameter of 8.6 cm and a height of 60 cm. The height retained for our study is 37.5 cm. The core was immediately sectioned at 2 cm intervals and stored in labeled plastic bags. Once in the laboratory, the subsamples were measured, dried in an oven until the weight was constant and then measured again. After, the subsamples were finely ground before being packaged in 30 ml flasks for three to four weeks to reach the secular equilibrium between 226Ra and its descendants.

The activity concentrations of gamma emitting radio-isotopes of the homogenized samples were estimated using HPGe detector Gamma-Ray Spectrometer at CNESTEN in Morocco. It is characterized by high energy resolution, excellent symmetry of the peaks and a relative efficiency of 30 to 50%. More details have been reported in the scientific literature [7, 8, 9].

Using this technique, and in order to establish age-depth relationship, we determined the activity concentrations of these three radionuclides $^{210}$Pb$_{total}$, $^{137}$Cs and $^{226}$Ra. These activity concentrations are counted for 24 hours each one and expressed in Bq.kg$^{-1}$.

2.3. $^{210}$Pb dating models

2.3.1. Principle

In the case of sedimentary column dating, the $^{210}$Pb$_{ex}$ is used by the application of conventional dating models, to determine the age-depth relationship in the sediment. The method is based on the fact that a layer which is at a moment ($t_0=0$) at the water-sediment interface (Figure 2) and having an activity $A_0$, after a certain time at ($t$) will have to be buried at a certain depth $z$ in the sediment and with $A$ activity. Overall, an exponential decay of $^{210}$Pb activity in excess with depth is expected according to the following formula:

$$A = A_0 e^{-\lambda t}, \quad (\text{Eq.1})$$

The application of equation (Eq.1) is subject to two conditions:
- The excess $^{210}$Pb flux is constant;
- There must be no redistribution of the particles after their deposition.

2.3.2. Constant Flux–Constant Sedimentation model (CF–CS)

This model, developed by Goldberg in 1963 and Krishna Swami et al. in 1971 [10], is a model that assumes that the $^{210}$Pb flux and the sedimentation rate are constant [11, 12] which implies that the initial activity is constant. This model is basic, and whose profile of $^{210}$Pb ($^{210}$Pb$_{ex}$ activity as a function of the $z$ depth of the sedimentary core), in logarithmic representation, is a slope line ($-\lambda/w$). Indeed, according to the equation (Eq.1), and replacing
the time \( t \) (year) by the sedimentation rate \( w \) (cm.year\(^{-1}\)) and the depth \( z \) (cm), we will have the following equations [13, 14]:

\[
A = A_0 e^{-\frac{z}{w}}, \quad (\text{Eq. 2})
\]

with

\[
t = \frac{z}{w}. \quad (\text{Eq. 3})
\]

2.3.3. Constant Rate of Supply model (CRS)

CRS is the most used model. It is based on the hypothesis of Goldberg in 1963, completed and defined later by Appleby and Oldfield in 1978 and then by Robbins also in 1978 [10]. CRS assumes that changes in \(^{210}\)Pb fallout are negligible regardless of any variation that may have occurred in the sedimentation or sediment accumulation rate.

This model defines the accumulated activity \( A(t) \) for a certain time \( t \) corresponding to a depth \( z \) by the following equation [15]:

\[
A(t) = \int_0^t F(t) \, dt \quad (\text{Eq. 4})
\]

Taking into account the decay of the excess of \(^{210}\)Pb over time, we can deduce \( I \) (the inventory) of \(^{210}\)Pb ex over the entire sedimentary column thanks to the following formula:

\[
I = \int_0^\infty e^{-\lambda t} \, dt = \int_0^\infty (A_z) \, m_z = \sum_{z=0}^{\infty} (A_z) \, m_z \quad (\text{Eq. 5})
\]

\( A_z \) represents the activity of the integrated \(^{210}\)Pb ex over the entire sedimentary column, and \( m_z \) the weight of the dry sediment deposited per unit area to the considered thickness \( z \).

We can also define the inventory of \(^{210}\)Pb ex accumulated below the depth \( z \) by:

\[
I_z = \int_0^z e^{-\lambda t} \, dt = \sum_{z=Z}^{\infty} (A_z) \, M_z \quad (\text{Eq. 6})
\]

The age \( t_z \) of the sediment at the depth \( Z \leq z \) is obtained by the following formula:

\[
\frac{1}{t_z} = e^{\lambda t} \quad (\text{Eq. 7})
\]

From which:

\[
t_z = \frac{1}{\lambda} \ln \left[ \sum_{Z=0}^{\infty} (A_z) \, m_z \right] \quad (\text{Eq. 8})
\]

2.3.4. Constant Initial Concentration model (CIC)

This model has been described by Pennington & al. in 1976 [10]. It is based on the assumption that if the \(^{210}\)Pb flux or sedimentation rate varies, these variations are opposite, so that the initial activity in the surface sediment remains constant [14]. So from equation (Eq.1), and since \( A_0 \) is constant, the age \( t_z \) of a layer is deduced directly from this equation [10, 11]:

\[
t_z = \frac{1}{\lambda} \ln \left[ \frac{A_0}{A_z} \right] \quad (\text{Eq. 9})
\]

3. Results and discussion

3.1. \(^{210}\)Pb activities

Table 1 represents the density, the cumulative dry mass below the sediment-water interface (Mb), the activities and the errors of the considered radionuclides (\(^{210}\)Pb ex, \(^{226}\)Ra, \(^{210}\)Pb ex and \(^{137}\)Cs) for each subsample of the sediment core.

Table 1: Specific activities errors of \(^{210}\)Pb ex, \(^{226}\)Ra, \(^{210}\)Pb ex and \(^{137}\)Cs in the sediment core from Moulay Bousseleham Lagoon (Core sampled 2009) as well as the density, the cumulative dry mass below the sediment-water interface (Mb)

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Bulk Density (g/cm^3)</th>
<th>Cumulative Mass Below Interface (Mb)</th>
<th>(^{210})Pb ex (Bq/kg)</th>
<th>(^{226})Ra (Bq/kg)</th>
<th>(^{210})Pb ex (Bq/kg)</th>
<th>(^{137})Cs (Bq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-1.5</td>
<td>0.40</td>
<td>6.03</td>
<td>4.94</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>1.5-3</td>
<td>0.51</td>
<td>1.44</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>3-4.5</td>
<td>0.70</td>
<td>1.27</td>
<td>0.53</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>4.5-6</td>
<td>0.71</td>
<td>0.83</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>6-7.5</td>
<td>0.78</td>
<td>0.69</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>7.5-9</td>
<td>0.81</td>
<td>0.55</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>9-10.5</td>
<td>0.85</td>
<td>0.44</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>10.5-12</td>
<td>0.88</td>
<td>0.37</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>12-13.5</td>
<td>0.90</td>
<td>0.30</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>13.5-15</td>
<td>0.92</td>
<td>0.23</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>15-16.5</td>
<td>0.94</td>
<td>0.17</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>16.5-18</td>
<td>0.99</td>
<td>0.14</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>18-19.5</td>
<td>1.08</td>
<td>0.10</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>19.5-21</td>
<td>1.17</td>
<td>0.08</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>21-22.5</td>
<td>1.24</td>
<td>0.06</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>22.5-24</td>
<td>1.30</td>
<td>0.05</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>24-25.5</td>
<td>1.36</td>
<td>0.03</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>25.5-27</td>
<td>1.42</td>
<td>0.02</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>27-28.5</td>
<td>1.49</td>
<td>0.01</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>28.5-30</td>
<td>1.54</td>
<td>0.00</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>30-31.5</td>
<td>1.60</td>
<td>0.00</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>31.5-33</td>
<td>1.65</td>
<td>0.00</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>33-34.5</td>
<td>1.70</td>
<td>0.00</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>34.5-36</td>
<td>1.75</td>
<td>0.00</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>36-37.5</td>
<td>1.80</td>
<td>0.00</td>
<td>0.49</td>
<td>0.32</td>
<td>0.32</td>
<td>0.00</td>
</tr>
</tbody>
</table>
(\(^{210}\)Pb\(_{ex}\)) activity concentrations were determined by subtracting the activity concentrations of supported \(^{210}\)Pb (\(^{226}\)Ra) from the total \(^{210}\)Pb activity concentrations (\(^{210}\)Pb\(_{tot}\)). From this Table, we observe that the maximum activity is observed at the water-sediment interface, it is 440.2 ± 37.1 Bq.kg\(^{-1}\) and the minimum activity is 9.7 ± 8.3 Bq.kg\(^{-1}\) obtained before the last layer. The activities have the same order of magnitude as those recently obtained in Moroccan coastal areas [16, 17, 18]. On the other hand, \(^{137}\)Cs presents activities similar to those reported in the literature [19] with localized maximum values for the 18 and 21 cm layers (6.35 and 6.38 Bq.kg\(^{-1}\) respectively). The last five layers have values below the detection limits (LOD).

In addition, Figure 3 represents the profile of the decay of \(^{210}\)Pb\(_{ex}\) activity as a function of cumulative dry mass below the sediment-water interface (Mb).

\[ Y = P_1 \exp(-P_2 X) = 440.76 \exp(-0.08129 x) \]

**Figure 3**: Decay curve of \(^{210}\)Pb\(_{ex}\) activity as a function of cumulative mass below the sediment-water interface (Mb).

We can see that the \(^{210}\)Pb\(_{ex}\) decreases exponentially depending on the depth which qualifies the datable profile obtained. Also, the sediment core shows an extremely regular profile with a slight inflection in depth. The continue line represents the best numerical fit of the experimental data (the blue squares) to an exponential decay expression of the following form:

For CF-CS, the first layer is formed in 2007, while the last in 1920, that is to say, the sediment core needed 88 years to form. For CRS, age is growing from the first layer (1.031 years) to the deepest layer (187.450 years); it can be estimated that the sediment core was formed for almost 187 years, between 2008 (date of the first layer) and 1822 (date of the deepest layer). While for CIC, the age of the formation of the sediment core is 115 that ranges from 2009 (the surface) to 1894 (the last layer).

\( R^2 = 0.98332 \) is the correlation between theoretical and experimental data; and \( Chi^2 = \chi^2 = 282.91009 \) is the chi-square test.

### 3.2. Dating models application for sediment chronologies

In order to quantify the results obtained by applying the three models (CF–CS, CRS and CIC), in what follows, we will present the date and age of the considered subsample with respect to the depth of the sediment core (Table 2). The date is obtained by subtracting the age, of the corresponding layer from the sampling date (2009). The ages are calculated for CF–CS, CRS and CIC respectively by the equations Eq.3, Eq.8 and Eq.9.

**Table 2**: The date and age of each model with respect to the depth of the sediment core.
We also note that the difference between the dates obtained by the three models does not exceed 4 years, with the exception of CIC and CRS for layer 18-19.5. After the 19.5-21 layer, this difference especially between CRS and the other two models becomes clearer, the difference exceeds 7 years and even 20 years and reaches more than 100 years for the last layer. While, CIC and CF-CS continue their superposition until 31.5-33 layer, where the difference in dates exceeds 20 years.

For a better visualization and in order to decide on the exact age of the sediment core, we represent the same date as a function of cumulative dry mass below the sediment-water interface (Mb) by confronting them with $^{137}$Cs activities, Fig.4.

As we indicated above from the table, for the superficial layers, from the surface of the sediment core to the depth 21-22.5 cm, there is a slight difference between the calculated dates for the three models. Thereafter, the dates calculated by CRS experience a significant divergence from those calculated by both CF-CS and CIC models. The other two models continue their superposition to deeper layers, until the depth 30-31.5 cm.

To confirm the $^{210}$Pb chronology and basing on the vertical profiles of $^{137}$Cs concentration detected in sediments. We observe that the evolution profile of $^{137}$Cs is characterized by a single peak observed for the depth (18 – 21 cm) (6.38 Bq.kg$^{-1}$) that corresponds to the dates 1965, 1968, and 1969 respectively for CRS, CIC and CF–CS. It should be noted that the peak of maximum activity in the $^{137}$Cs profile coincides nearly with the years 1963-1964 (the years of intensification of nuclear tests).

In addition, the quality of the results provided by the CF–CS model greatly depends on the quality of the adjustment of the $^{210}$Pb$_{es}$’s activities to the exponential decay of the first order. In our case, even if the correlation between the experimental and theoretical data is quite good, $R^2 = 0.9833$ (Figure 3), the high value of the coefficient $\chi^2 = 283$, indicates a lack of agreement between the activities of $^{210}$Pb$_{es}$ and the expected exponential trend. Therefore, the results of the CF–CS model should be considered with caution. On the other hand, and since the profile of activities does not follow an exponential decay with the radioactive constant of $^{210}$Pb, the application of the CIC model must certainly lead to results whose reliability is not established. In contrast, the results of the CRS model appear to be the most reliable since the calculations made are based on the inventories regardless of the decline in $^{210}$Pb$_{es}$ activities. This represents a validation of the chronologies obtained, especially for the CRS model the most widely used for establishing sedimentary geochronology. Especially for the deepest layers, exception made for the two last layers where this model predicted some values above 150 years mostly. For superficial layers the age difference between the three models is small.

![Figure 4](image_url)

**Figure 4:** The different dates obtained by the three models (CF–CS, CRS and CIC) in comparison with the $^{137}$Cs profile.

### 4. Conclusion

In this work, we investigated the three conventional $^{210}$Pb$_{es}$ radiometric dating models on sediment columns (CF–CS, CRS and CIC) to establish age-depth relation and deduce, by comparing the three models, the most suitable model. This work consists of a theoretical development of these models and their applications to a concrete example, in our case the sediment core sampled in 2009 from Moulay Bousselham Lagoon in Morocco.

The application of each model allowed us to conclude that the Constant Rate of Supply model (CRS) was the best model for our case. Especially for the deepest layers, exception made for the two last layers where this model predicted some values above 150 years mostly. For superficial layers the age difference between the three models is small.
Acknowledgements
This project would not have been possible without the generous support of the International Atomic Energy Agency IAEA.

References


