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Sedimentation Rate and ^{210}Pb Sediment Dating at Apipucos Reservoir, Recife, Brazil

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Abstract: The Apipucos Reservoir is located in Pernambuco-Brazil. Several districts of the metropolitan area use this reservoir to dispose of rubbish, waste and sewage. Dating sediments uses the ^{210}Pb from the atmosphere. ^{210}Pb is a daughter of the ^{222}Rn, which emanates from the soil but is different from that contained in the sediment, which is in balance with the ^{226}Ra. The chosen model for dating sediments depends on certain conditions: in environments where the amount of sediment can vary, the Constant Rate of Supply (CRS) model is adopted. In environments where the sediments can be considered to be constant, a Constant Initial Concentration (CIC) model is applied. A 70 cm long and 5 cm internal-diameter wide core was used for sediment sampling. Samples were dried at 105 °C, and about 5 g dry material was dissolved with acids. The ^{210}Pb and ^{226}Ra content was determined by their radioactive descendants' concentrations. For the second sampling point, both models could be used. The results showed an increase in sedimentation rate over the last 50–60 years. We could conclude that the top sediment interval had been there 30 years ago. We could decide that the CRS was the best applicable model.

Keywords: sedimentation rate; dating sediments with ^{210}Pb; CRS and CIC models

1. Introduction

The Apipucos Reservoir is a sub-basin of the Capibaribe River, located in Apipucos, in the western area of the city of Recife, State of Pernambuco, built in order to control the Capibaribe River flooding. However, several districts of the metropolitan area of Recife, such as Casa Amarela, Nova Descoberta, Macaxeira, among others, make this dam a waste and sewage dumping area.

The ^{210}Pb has two natural origins: one source is the ^{210}Pb, originally formed in the atmosphere due to the decay of the ^{222}Rn, usually named "unsupported ^{210}Pb", while the other, named "supported ^{210}Pb" has its origin in the continuous production of ^{222}Rn arising from the natural ^{226}Ra contained in the sediments [1]. The third source of ^{210}Pb could be due to an anthropogenic origin, coming from wastes enriched in this radionuclide. The basis for the ^{210}Pb dating technique applicable to sediment records is based on the determination of the ^{210}Pb excess activities ("unsupported ^{210}Pb" activities) in the layers of the cores in sediments uncontaminated with ^{210}Pb [1]. These excess ^{210}Pb values are calculated by subtracting the estimated "supported ^{210}Pb" value from the ^{210}Pb activities determined in every layer. In this model, it is assumed that the incorporation of unsupported ^{210}Pb to the sediment is produced at a constant flow and that the sedimentation rate is also constant [2,3]. It is the so-called Constant Initial Concentration (CIC) model. According to this hypothesis, the ^{210}Pb excess activity in a layer z (cm) deep, A (z) (Bq/kg), is expressed as:

$$A\ (z) = A_o \times e^{\ -\lambda\ \times\ (z/\omega)\ t} \tag{1}$$

where A_o (Bq/kg) is the ^{210}Pb excess activity in the top layer of the sediment core, λ is the ^{210}Pb decay constant (0.031 year^{-1}), and ω is the sedimentation rate (cm.year^{-1}). There is another model for calculating this flux and the sedimentation rate is the Constant Rate of Supply model (CRS), which assumes a constant unsupported lead-210 flux to the sediment, but permits the sediment supply to vary [4–6]. According to this model (Figure 1):

$$t = \lambda^{-1} \times \ln(A_\infty/A_x) \tag{2}$$

where A_∞ is the integrated activity from the surface to A_o, and A_x is the integrated activity from x to A_o.

Figure 1. Constant Rate of Supply (CRS) model for dating by ^{210}Pb.
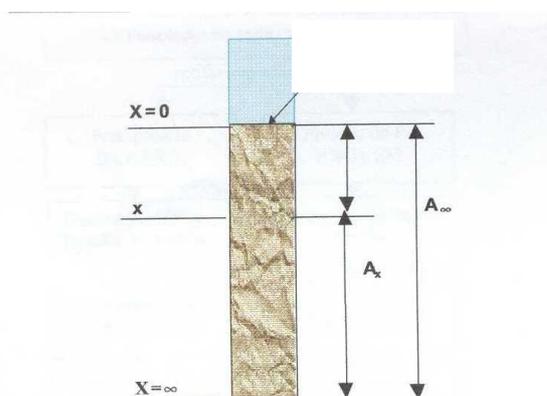
2. Methods

Normally, it is not recommended to use direct methods for measuring alpha and beta radiation for the determination of ^{210}Pb in environmental samples. However, the method becomes accurate when the sample is subjected to a radiochemical separation, stored for 15–30 days (to allow for ^{210}Bi ingrowth) and then counted in a gas flow proportional detector. The efficiency and self-absorption curves are obtained for specific radionuclide and standards.

The sampling locations are shown in Table 1. A 70-cm long 5-cm internal-diameter wide core was used for sediment sampling. Each core was sectioned into 3 cm intervals from the top (an estimated value, determined *in loco*, "theoretical").

Samples were dried at 105 °C to determine their water content. About 5 g dry material from each sample was dissolved with HNO_3 and HF. The ^{210}Pb and ^{226}Ra contents were separated by the method described in Moreira's studies [7]. The samples were placed in a 2 L beaker and the volume was made up to 1 L with water. To the same beaker, we added 1.0 mL (as a spike) of Pb^{2+} (20 mg/mL) and Ba^{2+} (20 mg/mL) with 5.0 mL of citric acid and 6 drops of methyl red indicator. The solution was stirred in a magnetic stirrer while adding concentrated NH_4OH until the turning of the indicator from pink to yellow (pH = 4.5 − 5.0) and heated in a heating plate. After that, 50 mL of 3M H_2SO_4 was added so that all ions precipitate as sulphates. Then the solution was decanted for 24 h. After that, the supernatant was separated and discarded, and the precipitate was transferred to centrifuge tubes with deionized water. After the centrifugation, the supernatant was discarded. To the precipitate was added 15 mL of tritriplex and heated in heating plate to dissolve all the precipitate. Four drops of methyl red and 1 mL of 1.8N H_2SO_4 were added, as well as glacial acid for pH adjustment. After being centrifuged, the supernatant was taken for the analysis of lead and the precipitate was kept for radio analysis. The supernatant containing the ^{210}Pb was heated in a water bath, then, 2.0 mL of 1M Na_2S was added to precipitate the ^{210}Pb as lead sulfide. The solution was centrifuged, the supernatant discarded and 5 mL of nitric acid (1:2) was added to the precipitate. The precipitate was heated in a water bath, where the elemental sulfur is formed while lead remains in solution. The solution was filtered through Whatman filter paper (blue ribbon) with the addition of 10 mL 40% ammonium acetate. The solution was heater in a heating plate and 2.0 mL of 30% Na_2CrO_4 was added to precipitate the lead as $PbCrO_4$. The samples were measured after 15 days of precipitation. To the precipitates previously obtained, 2.0 g EDTA and 40 mL of deionized water, 5.0 mL NH_4OH concentrated and three drops of methyl red were added and the solution was heated again in a heating plate to dissolve any precipitate. After total dissolution 5.0 mL $(NH_4)_2SO_4$ (25 mg/mL) was added and the radio was precipitated with glacial acetic acid. In the next day, the precipitate was filtered. Samples were measured after 21 days of precipitation. The chemical yield was determined by gravimetry and the contents of ^{210}Pb and ^{226}Ra were determined by alpha-beta counting from their daughters with a system Canberra® (model S5-XLB). The measurement time for each sample was standardized at 50 minutes, cover with a plastic thin layer for ^{210}Pb analysis.

Table 1 shows the geographical coordinates of the sampling points. And Figure 2 shows the localization of the sampling points.

Table 1. Sediment sampling points in the Apipucos Reservoir.

| Sampling Point	Latitude (S)	Longitude (W)
1	8°01230'	34°56019'
2	8°01251'	34°55985'
3	8°01265'	34°55930'
4	8°01273'	34°55907'

Figure 2. Points of sediment core sampling.
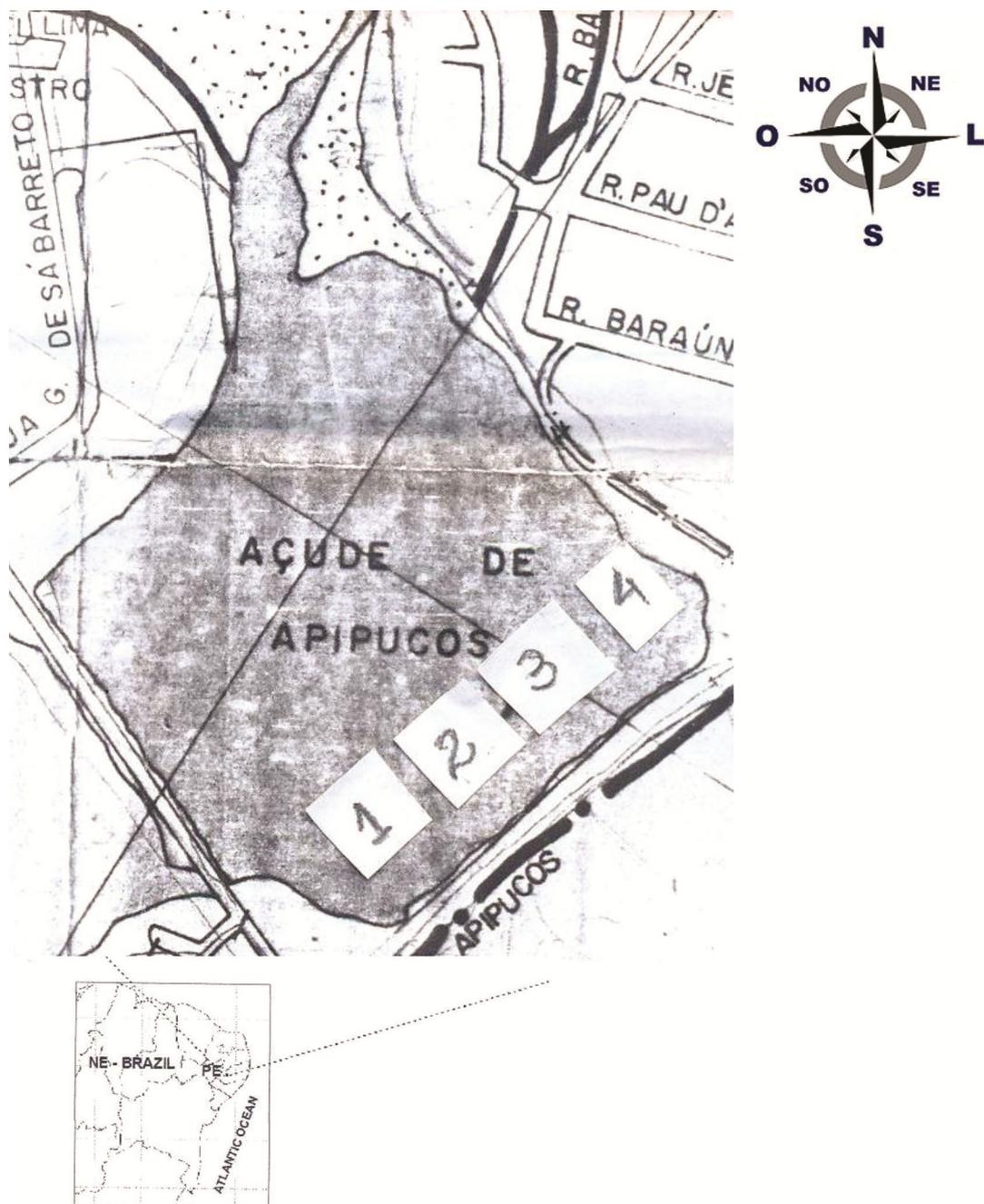
3. Results and Discussions

Figure 3 shows the results for grain size analysis for a section from one of the cores. All core sections analyzed showed a predominance of medium sand in their structure [8].

Figure 3. Grain size analysis.
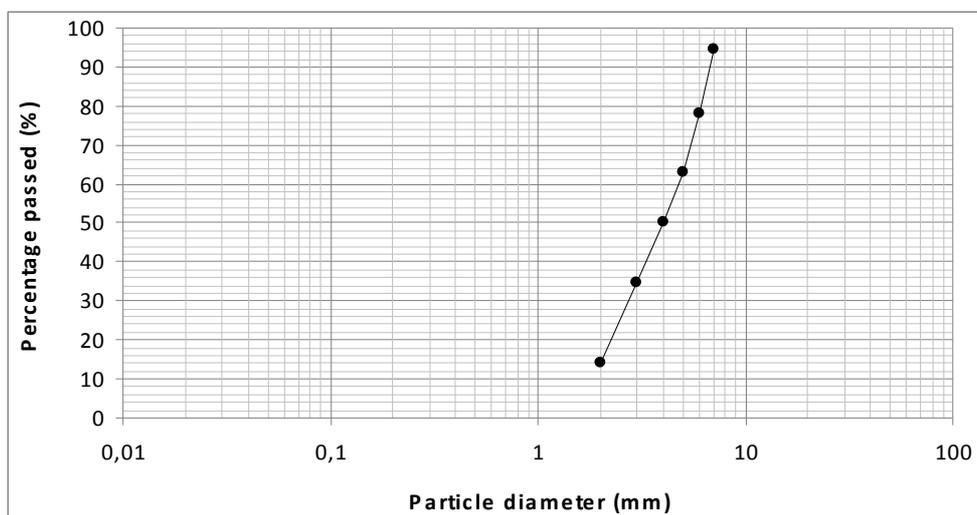
Sedimentation rates in the Apipucos Reservoir were determined by applying the ^{210}Pb CIC model (Figures 4–7) and the CRS model (Figures 10 and 11) to sediment cores collected at different stations. Sedimentation rate refers to the amount of materials (organic and inorganic) deposited by the action of rain water and water over a given time interval. The transport and deposition of sediments in a lake or river can cause degradation of the body of water, causing changes in the physical and chemical characteristics of water.

There is no standard for the optimum thickness for core sectioning, and the literature shows that thickness between 2 and 7 cm have been used. However, a thickness of 1 cm does not show very accurate results. In this work, we intended to maintain an average value of 3 cm for the thickness of each core section. However, when the values are corrected for compaction thicknesses ranging from 5 to 25 cm were found, considering all the collection points. Therefore, the corrected depth values will be used in the graphs for the sediment age calculation. Some researchers do not consider the top part of the core (first sedimentary layers) for calculating the ages because they consider that a lot of mixture can take place in these layers. A difference from 10 years is admissible for this dating method.

For the first collection point, it was possible to fill the entire length of the sampler with sediment. However, for the other collection points it was only possible to fill only half of the sampler length with sediment, due to the influence of the water column. Given the limited number of data points per core the uncertainty on the sedimentation rates are high. There is no information about the water depth.

The presence of anthropogenic inputs of ^{210}Pb (from the atmosphere) in the uppermost layers of the sediment cores is the hypothesis on which the lead-210 method is based. In this way, this technique is used to obtain a confident chronology covering the last 100 years. The depth for sediment analysis at each point, however, depends on how long it takes for the equilibrium between ^{210}Pb and ^{226}Ra concentrations to be reached (Figures 8 and 9).
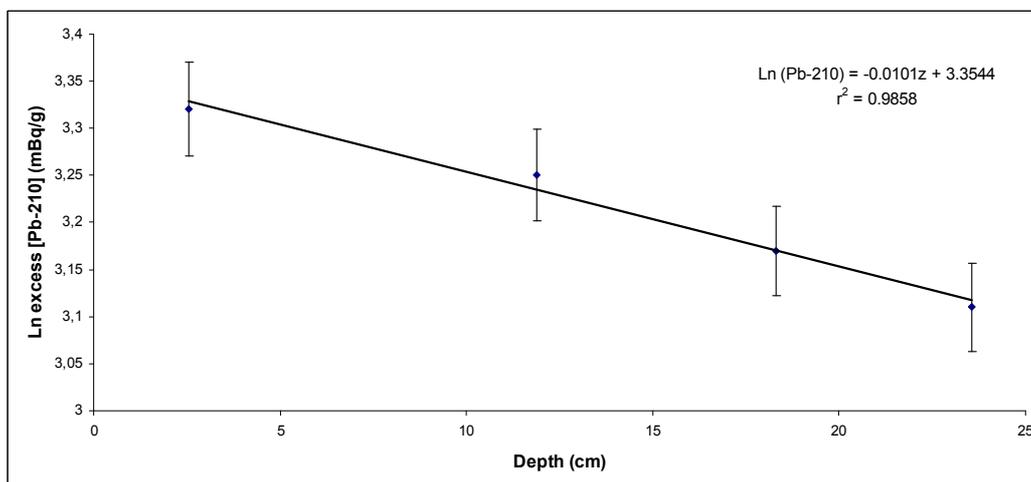
Figure 4. Unsupported ^{210}Pb activity concentration *versus* layer depth from the first sampling point (sedimentation rate: 1.05 cm/y).
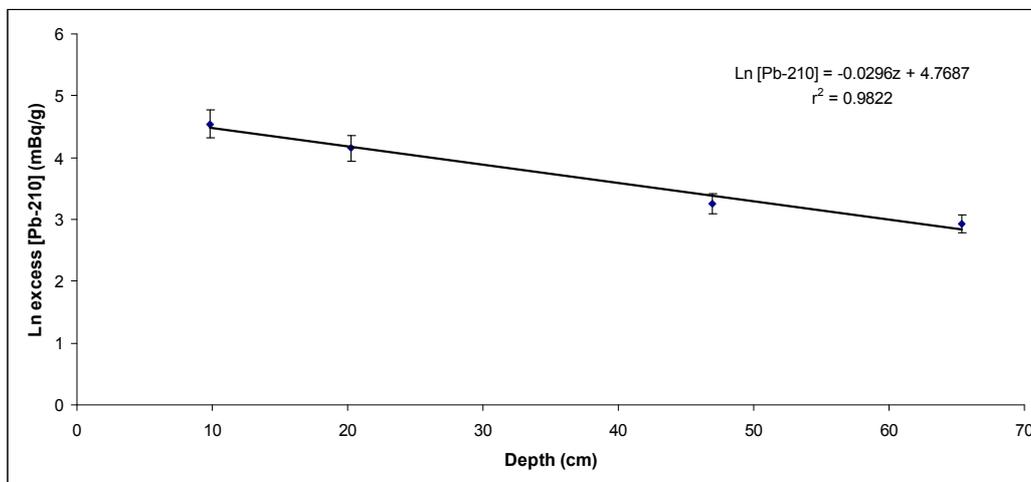

Figure 5. Unsupported ^{210}Pb activity concentration *versus* layer depth from the second sampling point (sedimentation rate: 0.33 cm/y).
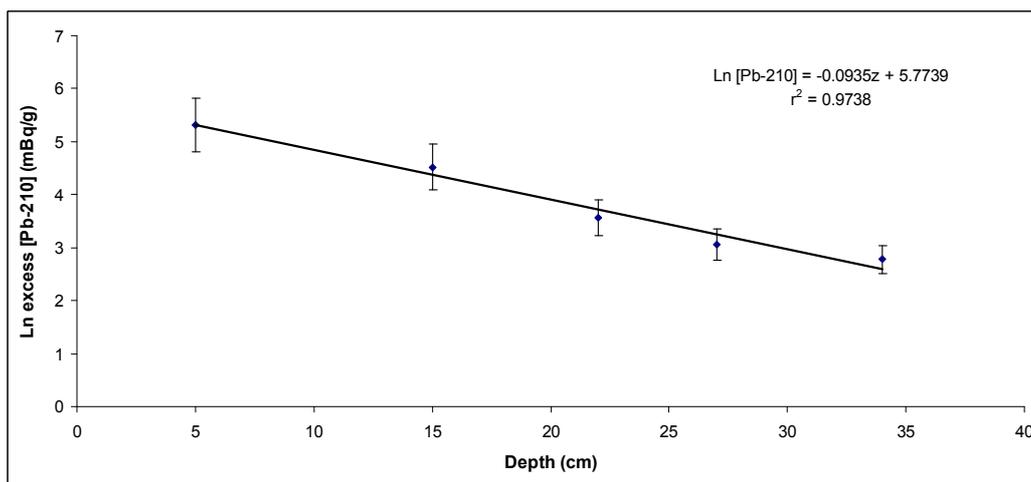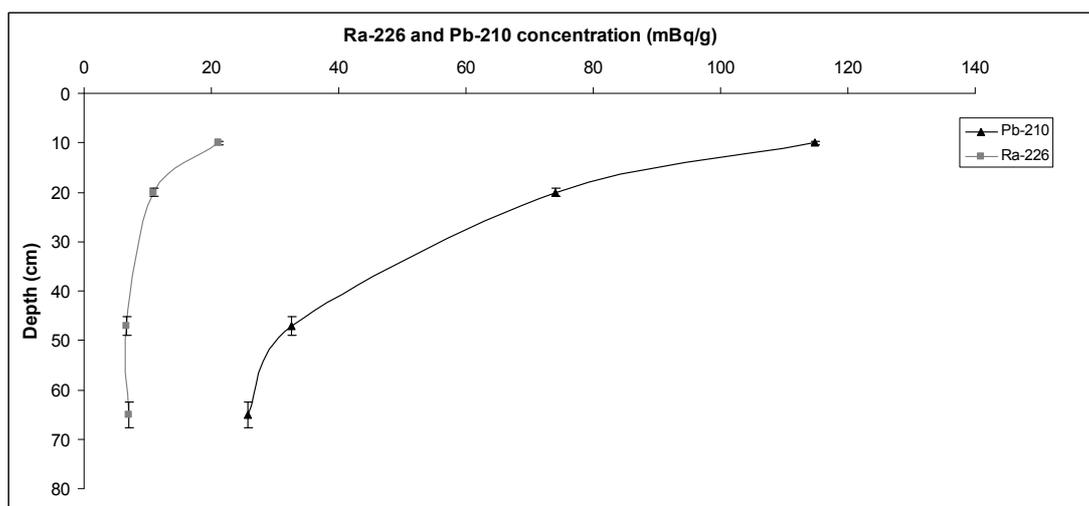

Figure 6. Unsupported ^{210}Pb activity concentration *versus* layer depth from the third sampling point (sedimentation rate: 3.1 cm/y).
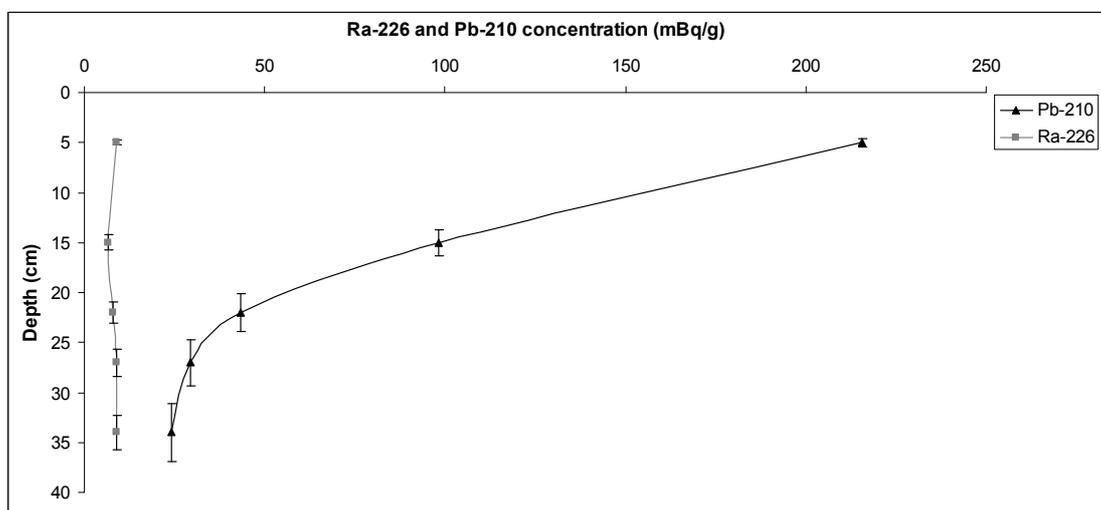
Figure 7. Unsupported ^{210}Pb activity concentration *versus* layer depth from the fourth sampling point (sedimentation rate: 0.69 cm/y).
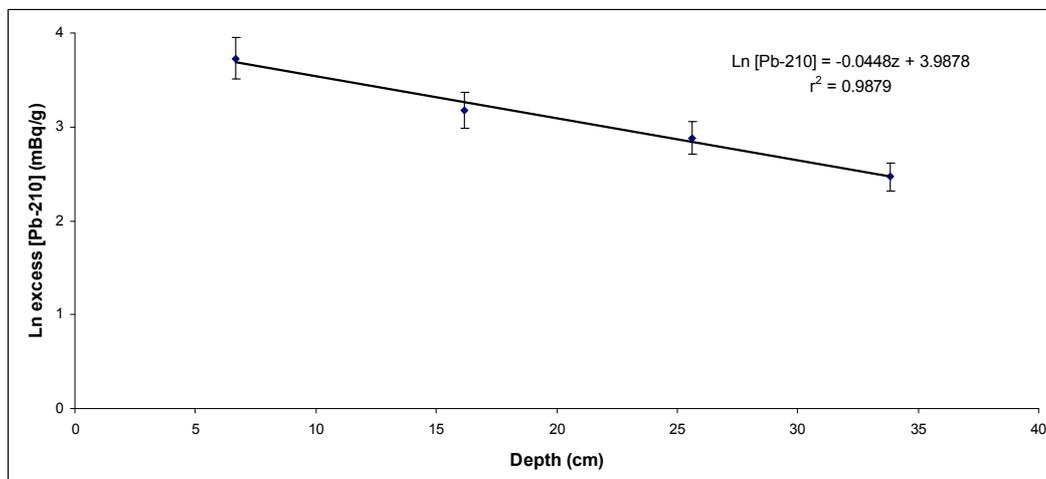
Figure 8. ^{210}Pb and ^{226}Ra concentration from the first sampling point.

Figure 9. ^{210}Pb and ^{226}Ra concentration from the second sampling point.

In order to calculate the ages of the sediments by the CRS model it is necessary to calculate both the porosity and density for the sediment samples. The porosity and the particle density were calculated according to equations 3 and 4, respectively.

$$\phi = [(m_{H20}/(m_{H20} + (m_s/\rho_s)))] \tag{3}$$

where, m_{H20} = mass of water present in the sediment (g) (wet weight of sediment (mt)—mass of dry sediment); ms = mass of dry sediment (g) (considered as the specific mass of medium sand = 2.5 g/cm^3); ρ_s = density of dry sediment. The wet density of the sediment can be calculated by the expression:

$$\rho_u = \rho_s - 1.422 \times \phi \tag{4}$$

The density of the particles is important to calculate the corrected thickness (x_i) by compaction of the sediment (Equation 5) which in turn will be necessary for calculating the integrated activities through the CRS model, evaluated according to Equation 6.

$$x_i = (m_T/\pi r^2 \times \rho_u) \tag{5}$$

$$\text{Integrated activity} = [^{210}Pb] - [^{226}Ra] \times (1\text{-porosity}) \times 2.5 \times \text{corrected thickness} \tag{6}$$

were, $[^{210}Pb]$ = ^{210}Pb concentration and, $[^{226}Ra]$ = ^{226}Ra concentration.

Tables 2 to 5 show the results of the ages of the sediments when calculated by both models (CRS and CIC), from the first to the fourth sampling points.

Table 2. Sediment ages calculated by the Constant Initial Concentration (CIC) model and the CRS model for the first sampling point.

Depth (theoretical) (cm)	Depth corrected by sediment compaction (cm)	Ages (y) of the sediments (CIC model)	Ages (y) of the sediments (CRS model)	Corresponding year (CRS model)
3	10	10	29	1980
6	20	20	75	1934
9	47	40	103	1906
12	65	60	-	-

Table 3. Sediment ages calculated by the CIC model and the CRS models for the second sampling point.

| Depth (theoretical) (cm)	Depth corrected by sediment compaction (cm)	Ages (y) of the sediments (CIC model)	Ages (y) of the sediments (CRS)	Corresponding year (CRS model)
3	5	14	27	1982
6	15	46	50	1959
9	22	65	62	1947
12	27	82	73	1936
15	34	104	99	1910

Table 4. Sediment ages calculated by the CIC model and the CRS models for the third sampling point.

| Depth (theoretical) (cm)	Depth corrected by sediment compaction (cm)	Ages (y) of the sediments (CIC model)	Ages (y) of the sediments (CRS model)	Corresponding year (CRS model)
3	2.5	1	12	1997
6	12	4	32	1977
9	18	6	74	1935
12	24	8	-	-

Table 5. Sediment ages calculated by the CIC model and the CRS models for the fourth sampling point.

Depth (theoretical) (cm)	Depth corrected by sediment compaction (cm)	Ages (y) of the sediments (CIC model)	Ages (y) of the sediments (CRS model)	Corresponding year (CRS model)
3	7	10	37	1972
6	16	23	48	1961
9	26	37	86	1923
12	34	52	-	-

Figures 10 and 11 show the results of mass fluxes and sedimentation rates for the first and second sampling points.

Figure 10. Mass fluxes and sedimentation rates calculated by the CRS model for the first sampling point.
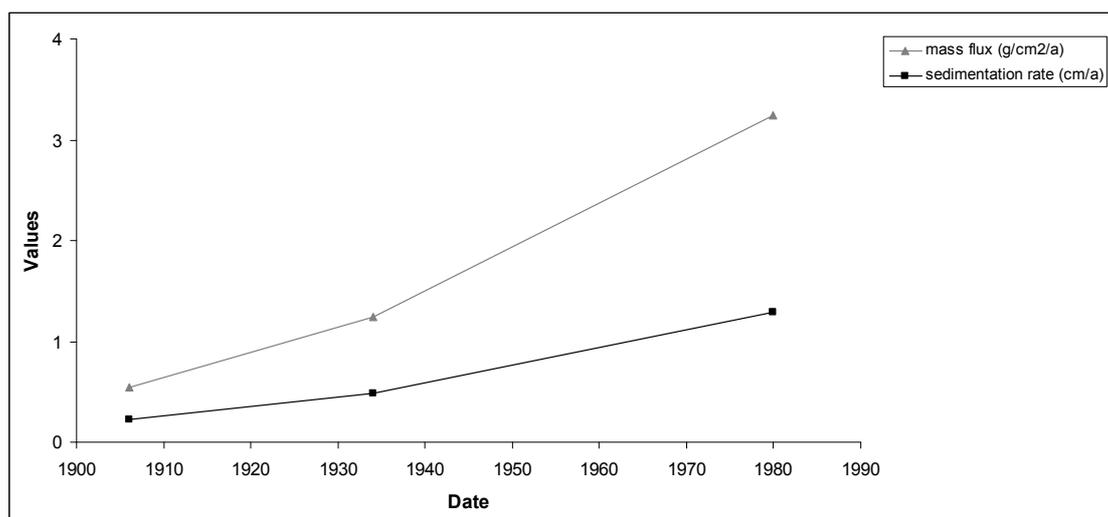
Figure 11. Mass fluxes and sedimentation rates calculated by the CRS model for the second sampling point.
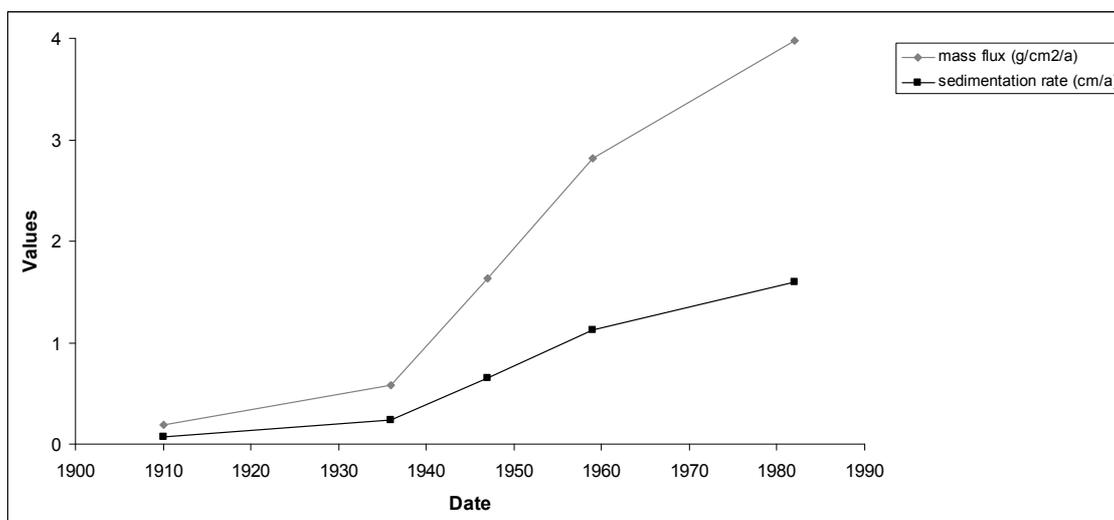
This period (1970–1980) corresponds to the most intensive industrial and population growth in the region around the Reservoir and coincide with the history of the area. Sediment ages calculated by the two models showed some discrepancy between the first and third sampling points. This is because the ages obtained from Constant Initial Concentration model (CIC) were not appropriated. Therefore, only for the second sampling point could both models be used without any problem.

4. Conclusion

The results showed an increase in the sedimentation rate over the last 50–60 years. The chronology shows that the first sedimentary layers are about 30 years old. We can also conclude that the ^{210}Pb Constant Rate of Supply model (CRS) was the best applicable model to be used in this area.

Conflict of Interest

The authors declare no conflict of interest.

References

1. Cazotti, R.I.; Silverio, P.F.; Nascimento, M.R.L.; Mozeto, A.A. *Datação de Sedimentos do Reservatório de Barra Bonita, Rio Tietê, SP com Pb-210: Distribuição Histórica de Metais Pesados*; Report; INAC: Rio de Janeiro, Brazil, 2002.
2. San-Miguel, E.G.; Bolívar, J.P.; Garcia-Tenório, R.; Martìn, J.E. ^{230}Th/^{232}Th activity ratios as a chronological marker complementing ^{210}Pb dating in a estuarine system affected by industrial releases. *Environ. Pollut.* **2001**, 361–368.
3. San-Miguel, E.G.; Bolìvar, J.P.; Garcìa-Tenorio. Vertical distribution of Th-isotope ratios, ^{210}Pb, ^{226}Ra and ^{137}Cs in sediment cores from an estuary affected by anthropogenic releases. *Sci. Total Environ.* **2004,** 143–157.

4.   Ravichandran, M.; Baskaran, M.; Santschi, P.M.; Bianchi, T.S. Geochronology of sediments in the Sabine-Neches estuary, Texas, U.S.A. *Chem. Geol.* **1995**, *125*, 291–306.

5.   Appleby, P.G.; Oldfield, F. The calculation of dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *CATENA* **1978**, *5*, 1–8.

6.   Silva, C.M.; Amaral, R.S.; Tabosa, J.N.; Santos, J.A., Jr.; Menezes, R.S.C.; Farias, E.E.G.; Bezerra, J.D.; Silvestre, R.G.; Oliveira, G.F. Pb-210 in rock and soils of the semi-arid agrest region of Pernambuco, Brazil. *Bull. Environ. Contam. Toxicol.* **2009**, *82*, 647–649.

7.   Moreira, S.R.D.; Fávaro, D.I.T.; Campagnoli, F.; Mazzilli, B.P. Sedimentation Rates and Metals in Sediments from the Reservoir Rio Grande—São Paulo/Brazil. In *Environmental Radiochemical Analysis II*; Warwick, P., Ed.; The Royal Society of Chemistry: London, UK, 2003; pp. 383–390.

8.   Abrams, D.A. *Design of Concrete Mixtures, Bulletin 1*; Structural Materials Research Laboratory, Lewis Institute: Chicago, IL, USA, 1918.