Title
14C-AMS as a tool for the investigation of mercury deposition at a remote Amazon location

Authors
Barbosa, J.A
Cordeiro, R.C
Silva, E.V
et al.

Publication Date
2004-08-01

DOI
10.1016/j.nimb.2004.04.099

Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Nuclear Instruments and Methods in Physics Research B 223–224 (2004) 528–534
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

^{14}C-AMS as a tool for the investigation of mercury deposition at a remote Amazon location

J.A. Barbosa [a], R.C. Cordeiro [a,1], E.V. Silva [a], B. Turcq [b], P.R.S. Gomes [c,*], G.M. Santos [d,2], A. Sifedinne [a], A.L.S. Albuquerque [a], L.D. Lacerda [a], P.A. Hausladen [d], S.G. Tims [d], V.A. Levchenko [d], L.K. Fifield [d]

[a] Departamento de Geoquímica, Universidade Federal Fluminense, Outeiro São João Batista, Valongunho, Niterói, Rio de Janeiro, Brazil
[b] Institute de Recherche pour le Développement, Bondy, France
[c] Insituto de Física, Universidade Federal Fluminense, Av.Litoranea s/n, Niterói, Rio de Janeiro 24210-340, Brazil
[d] Department of Nuclear Physics, Australian National University, Canberra 0200, Australia

Abstract

We present results of the atmospheric mercury deposition rate in the Amazon region during the last 43 000 years. Lake sediment samples were collected from the Lagoa da Pata, a small and remote lake in northern Brazilian Amazon. The samples were divided in sub-samples, for C, Hg, N and ^{14}C-AMS analyses. Three main paleoclimatic events could be identified. The mercury accumulation rates were found to be larger during the periods of the Holocene and Pleistocene associated with high temperatures and frequency of forest fires.

PACS: 07.75.+h; 89.60.+x; 92.70.Gt; 92.70.Cp
Keywords: Amazon; Climate; Mercury; AMS dating

1. Introduction: ^{14}C and Hg as tools for the study of paleoclimatic phenomena

Atmospheric mercury can be related with the frequency and intensity of natural fires. An increase in the Hg flux is a strong indicator of disturbance in a forest ecosystem related to abrupt changes in the water balance [1], and its changes reflect changes in the ocean [2] and average regional temperatures [3]. The overall mercury deposition contains contributions from mining and industrial activities, natural emissions due to volcanic activity and Hg-ore deposits. In regions where the geological background of mercury is negligible, as at remote lakes of the Amazon region, the Hg accumulation rate archived in sediment cores may be a powerful tool for the interpretation of the paleoclimatology and paleoecology of the region. Due to the slow oxidation

* Corresponding author. Tel.: +55-21-2629-5853; fax: +55-21-2629-5887.
E-mail address: paulogom@if.uff.br (P.R.S. Gomes).
[1] CNPq, Programa Especial de Fixação de Doutor (PROFIX), proc. 540846/101-5.
[2] Present address: Earth Science Department, Rowland Hall 220, University of California, Irvine (UCI), CA 92697-3100, USA.

0168-583X/$ - see front matter
doi:10.1016/j.nimb.2004.04.099

process of Hg^0 leading to Hg^{2+}, Hg^0 has a long residence time in the atmosphere, of the order of 1 year [4,5]. Therefore, the atmospheric mercury can be transported large distances before it is deposited in lakes, oceans, rivers and soils. As a consequence, mercury has a global range, and, therefore, it can also be a reliable tracer of more general paleoclimatic conditions.

There are few available data on paleoclimatic changes in the Amazon region, and they are not enough to allow strong conclusions to be drawn [6–10]. However, some few studies on atmospheric mercury deposition and its correlation with forest fires have suggested that average background mercury deposition rates over the Amazon were fairly constant in the past, more than doubled after the last glacial maximum (LGM) and became even higher in more recent periods [8,9].

Mercury flux or accumulation rate can be obtained from the product of the sedimentation rate (cm yr^{-1}), bulk density (g cm^{-3}) and mercury concentration (ng g^{-1}). The sedimentation rate can be obtained from the ^{14}C-AMS dating of samples from the sediment cores.

In this paper we present results of the atmospheric mercury deposition rate in the Amazon region during the last 43 000 years, obtained from one sediment core (called LPT3) from a remote lake in northern Amazon. Two other sediments cores from the same lake were also collected. Some results from one of these cores (LPT4) were published recently [9], while for the other core (LPT6) only preliminary results are presently available.

2. The Lagoa da Pata and the sample collection

Lake sediment samples were collected from the Lagoa da Pata at the Morro dos Seis Lagos (Six Lakes Hill), a small headwater lake located inside the Pico da Neblina National Park, São Gabriel da Cachoeira, northern Amazon State (0° 16′ N and 66° 41′ W). Some of the previous studies in the Amazon region were also performed based on data from the same lake [6,8,9,11]. Fig. 1 shows the location of the Lake, that is 400 m long, 5 m deep, surrounded by a dense tropical rain forest and remote from human activities. The relative confinement of the Lagoa da Pata basin, its small size relative to lake area, and the lack of any mercury-bearing geological formation in the lake's basin suggest that atmospheric deposition is the most significant source of mercury into Lagoa da Pata sediments.

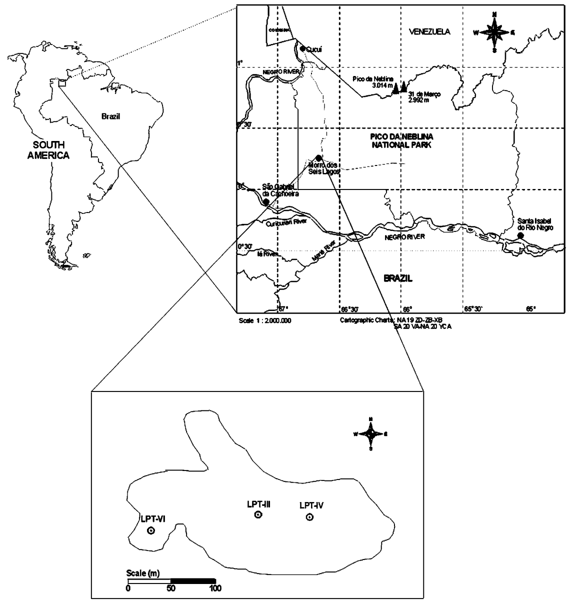

Fig. 1. Location of the Lagoa da Pata and the sediment cores LPT3, LPT4 and LPT6.

Three lake sediment cores were collected with a piston corer in different sub-basins of the lake, as shown in Fig. 1, at water depths of ~5 m. Their lengths were 73 (LPT3), 100 (LPT4) and 68 cm (LPT6). The LPT3 and LPT4 cores, located at the central part of the lake, show three very clear lithologic units. These consist of upper and lower organic rich layers of different colours which are separated by an inorganic sandy layer representing a short period of rapid accumulation. Fig. 3 shows the lithology of the LPT3 core, where the vertical dashed lines represent the limits of the inorganic layer, between ~16 and ~40 cm depth. The LPT6 core consists of only two lithologic units, the upper organic layer and the inorganic layer. As it will be discussed in Section 4, this is due to a higher sedimentation rate for this core.

3. Sample analyses, preparations and measurements

The sediment cores were sliced in 2 cm layers. Samples were stored in acid-cleaned plastic bags and frozen for transport. In the laboratory, the samples were dried. Duplicate sub-samples of about 1.0 g were digested with 50% aqua regia for 1 h at 70 °C in a closed system. Mercury was analysed through CVAAS (cold vapour atomic absorption spectrometry), in a Bacharach MAS-50D mercury analyser system. Simultaneous determination of mercury in reference standards (Community Bureau of Reference – River Sediment BCR, with 60 $ng\,g^{-1}$) was performed, using the same analytical procedure. The detection limit of the method was 0.4 $ng\,g^{-1}$.

The bulk density of each layer was obtained by taking out 8 cm^3 of a wet sediment section and drying it at 60 °C until a constant weight was reached.

The other quantities measured in the present work were water content (% H_2O), total organic carbon (% TOC) and nitrogen (N). Water, carbon and nitrogen contents in the total sediment were measured with a CHN analyser (N2000-Fisons Instruments), with 2.5% reproducibility for carbon and 4.5% for nitrogen, in the Laboratoire des Formations Superficielles – Institute de Recherche pour le Development (IRD, France). C/N ratio and carbon flux were also derived. The % H_2O and % TOC indicate the origin of the material (clastic or organic); low values corresponding to the predominance of clastic material, originating from the edges of the lake, as a consequence of torrential rains; high values indicating that of organic matter (primary production or detritus organic matter from the basin). The C/N ratio indicates the origin of the biogenic organic matter (aloctone or autoctone), and variations of the lacustrine hydric level [12]. The lithology of the different facies of the sediment was logged. For each of the three cores, 30 samples were analysed.

Twenty-two of these samples were selected for the determination of the chronology of the cores. These were pretreated, graphitised and dated by Accelerator Mass Spectrometry (AMS) at the Australian National University (ANU). Most of these samples were from the LPT4 core.

The chemical procedures for the sample preparation, combustion and graphitisation methods for the three cores were identical, and are described elsewhere [9,13]. A conventional acid–base–acid chemical pretreatment was used. Then a bulk combustion of the total organic matter, without microscopic selection, was performed. Sri Lankan graphite and ANU sucrose samples were prepared in the same way and used as a blank correction and primary standard, respectively. Measurements of $\delta^{13}C$ for most of these samples yielded values around −34 ‰, and this average value was used for $\delta^{13}C$ correction in ^{14}C age calculations for all samples. Eventual deviations from this average value lead to ^{14}C age uncertainties much smaller than the error bars dominated by the approximately 2.0%. reproducibility of the ANU system. Conventional radiocarbon ages (yr. BP) were presented, rather than calibrated calendar ages, in order to compare the results with the few other available data for the same period in the Amazon region [1,5–11,14].

4. Results

Fig. 2 shows the radiocarbon chronology of the LPT4 core as a function of depth (black points). This chronology is also used for the derivation of the chronology of the LPT3 core, as it will be

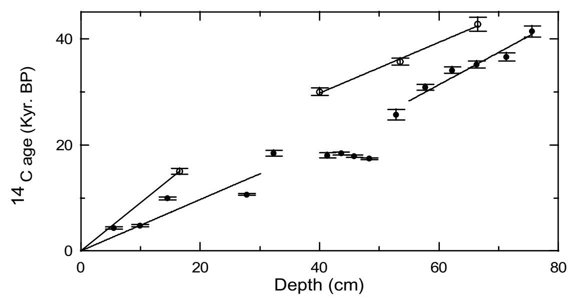

Fig. 2. Radiocarbon chronology, as a function of the depth, for the LPT4 core (black points) and for the LPT3 core (open points). During the period from 30 000 to 15 000 yr BP, corresponding to a sedimentation hiatus, no sedimentation rate could be derived. See details in the text.

Table 1
Characteristics of the three sediment cores

Sediment core	^{14}C age at the base of the core (Kyr BP)	Sedimentation rate before the hiatus (cm Kyr^{-1})	Sedimentation rate after the hiatus (cm Kyr^{-1})	Depth range of the hiatus from 15 to 30 Kyr BP (cm)
LPT3	43.0	1.1	2.0	16–40
LPT4	41.5	2.0	1.6	31–57
LPT6	21.0		3.6	

explained later in this paper. A good correlation can be noticed in the whole range between 41 500 and 4500 yr BP, from the late Pleistocene to the Holocene. Three different sedimentation regimes, representing paleoclimatic processes that influenced the characteristics of the deposited material, are clearly observed from the chronology/sedimentation rate and the other measured physical and chemical properties.

In the first regime, corresponding to the period from ~41 500 to ~26 000 yr BP (Pleistocene), the sedimentation rate is steady at 1.6 cm Kyr^{-1}. This region consists of organic-rich clay.

In the middle of the core there is a sedimentation hiatus between ~30 000 and ~15 000 yr BP, corresponding to a sudden input of ~20 cm of clastic material, represented by a sandy facies which exhibits lower carbon and water contents and higher bulk density than the layers above and below it. Probably this event was due to the occurrence of torrential rains on a very local scale, during the Last Glacial Maximum (LGM) at ~18 000 yr BP. Therefore, from depths ranging from 54 to 31 cm, the sedimentation rate could not be calculated.

Finally, during the Tardiglacial and the Holocene periods, the sedimentation rate has been reasonably constant at 2.0 cm Kyr^{-1}, corresponding to an organic-rich clay region of the core and high total carbon concentration.

The LPT3 core was taken from close to LPT4 at the center of the lake, as shown in Fig. 1. The analyses of the lithology of the different facies of this sediment, the water content, total organic carbon and C/N weight ratio showed strong similarities with the LPT4 core. Therefore, just a few samples were dated, and interpolation and extrapolation of the age versus depth curves were performed, with the aid of additional age data obtained from the LPT4 core corresponding to the well determined lithologic borders of the central sandy facies. The radiocarbon-lithologic chronology for the LPT3 core is also shown in Fig. 2 (open points). The age corresponding to the basis of the core is ~43 000 yr BP.

For the LPT6 core, taken from near the edge of the lake, the lithology shows the presence of only the two most superficial facies of the other cores. From the dating, the sedimentation rate for this core was found to be much higher than for the other two cores, corresponding to a radiocarbon age of ~21 000 yr BP at the base of the core. Consequently, the analysis of this core will be restricted to a more recent period.

Table 1 shows the sedimentation ratios and some characteristics of the three cores. The difference in the sedimentation rates obtained from the three cores are believed to be due to their

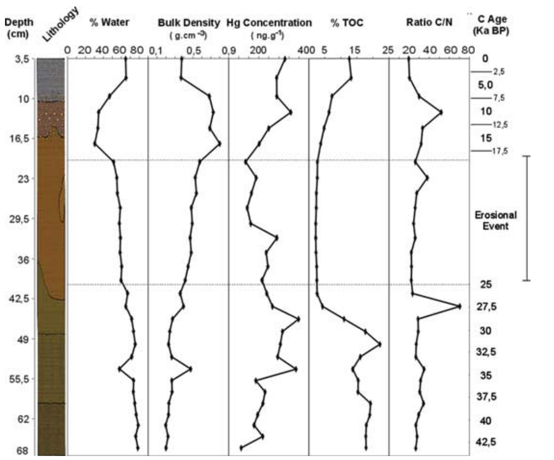

Fig. 3. Results from the LPT3 lake sediment core. The dashed lines are the borders of the sandy layer corresponding to an erosional event. The mercury and carbon fluxes could not be determined during this period. See details in the text.

different locations in the lake, such as the significant drainage of the lake basin at the LPT6 location.

Fig. 3 shows the lithology, % H_2O, bulk density, Hg concentration, % TOC, C/N ratio, mercury and carbon deposition rates (fluxes) as function of the core depth and ^{14}C age for the LPT3 core. The mercury and carbon fluxes were not calculated during the period from ~30 000 yr BP to ~15 000 yr BP, corresponding to depths from 40 to 16 cm associated with the sandy facies produced by the sudden input of clastic material. In Fig. 3 this period is referred as the "erosional event" responsible for this sedimentation hiatus.

5. Discussion

The present results for the LPT3 core are in agreement with previous works, leading to the identification of different climatic events in the region, of which the most significant are discussed below.

In the range from ~43 000 to ~30 000 yr BP (Pleistocene), high carbon fluxes are observed. As the carbon flux is probably associated with the hydric level of the lake [12], our results suggest a decrease in the level of the lake towards the Last Glacial Maximum during this period. The C/N ratio is roughly constant at ~25% during this period, indicating the mixture of aloctone and autoctone organic carbon. Clear peaks of both carbon and mercury fluxes are observed at ~35 000 yr BP, coincident with reported forest fire events occurred in the Brazilian Central Plateaux [15]. It is important to mention that the carbon concentration has a peak at ~33 000 yr BP, but as the bulk density has a peak at ~35 000 yr BP, the carbon flux, obtained from the product of these two quantities and the constant sedimentation ratio, peaks at ~35 000 yr BP.

From the lithology of the clastic facies corresponding to the interval ~30 000 yr BP to ~15 000 yr BP, it is evident that there was high remobilisation of sand and clay from the lake, due to the occurrence of episodic torrential rains during the LGM. This agrees with a study of pollen [14] which suggests that during the LGM there was a decrease of ~6 °C in the temperature of the region and a drier period, with strong local seasonal rains. Other studies, on a more global scale, of surface ocean temperatures [16] and temperature changes, lead to similar conclusions. Our results, showing low values of water content and TOC, strengthen these hypotheses. During this dry period the lake reaches its lowest level.

After the LGM, significant changes in the sediment lithology and in mercury and carbon fluxes have occurred. From ~15 000 to ~10 000 yr BP (Tardiglacial), the mercury and carbon fluxes were small, suggesting a low level of the lake. During this period the rains increase but they are still strong and intermittent [6], as also attested by the changes in the lithology and increase in % TOC and C/N ratio found in the present work. Schoonmaker and Foster [17] suggest an increase of the average temperature during this period.

The Holocene is characterised as a period of high and constant precipitation, with suggestions of occurrence of a dry period in the Amazon region between ~7000 and 4000 yr BP [7,8], favouring forest fires. Our results show increases of Hg and carbon fluxes and C/N ratio in this period, in comparison with the Tardiglacial, indicating the deposition of Hg and aloctone organic carbon, probably due to forest fire events produced either by natural fires or primitive agriculture. The forest fires are important sources of atmospheric Hg in Amazon, where the Hg accumulated in soils is re-emitted [1]. Moreover, the charcoal particles adsorb the Hg and reduce its residence time in the atmosphere, leading to an association of the deposited Hg with carbon flux [18], as observed from our results. The stratigraphy of the three sediment cores studied in the present work show that during this period the hydric level was reduced, exposing the lake sedimentation surface to atmospheric oxidation. Other sources of atmospheric Hg during warm dry periods may be oceanic degassing, due to the increasing ocean temperature (SST) [19] and events similar to El Niño lasting tens or hundred years [20].

From ~5000 yr BP to the present, the carbon flux was constant, whereas the Hg flux

Table 2
Average mercury flux for different periods, for the LPT3 core

Period	^{14}C Age range (Kyr BP)	Mercury flux ($\mu g\, m^2\, yr^{-1}$)
Pleistocene	43.0–30.0	1.3
(dry phase during the Pleistocene)	(36.5–34.5)	(2.5)
Tardiglacial	15.0–10.0	1.1
Early and medium Holocene	10.0–5.0	1.9
Late Holocene	5.0–present	1.1

decreased. These behaviours may be linked with the occurrence of rains during this period, leading to the deposition of organic matter from production in the lake, whereas the Hg flux has its origin from the atmosphere. The increase of the temperature in this last period allowed the breeding of swamps and some kind of palm trees typical of high temperatures at the region, without a significant change in the forest vegetation [14].

Table 2 shows the average mercury flux during the Pleistocene (before 30 000 yr BP), the Tardiglacial (from 15 000 yr BP to 10 000 yr BP), early and medium Holocene (from 10 000 yr BP to 5000 yr BP) and late Holocene (from 5000 yr BP to the present). Although there are significant fluctuations in the mercury flux, it is clear that the average flux during the medium Holocene was much higher than in the other periods. This high value of the mercury deposition rate seems to be linked to drier periods and a higher frequency of forest fires, since revolatilisation of deposited Hg from soils and the ocean was most likely the dominant source of atmospheric Hg in this region. Another period with these characteristics is ~35 000 yr BP, when the mercury flux also shows a peak and significant fire events were identified [15]. Nowadays, the mercury flux in the Amazon region is hundred times larger than in the Holocene [1,5,10], due to gold mining activities.

Acknowledgements

The Brazilian authors would like to thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for their financial support. They also thank IBAMA and Força Aérea Brasileira (CAN) for logistical support and transport during the field work at Morro dos Seis Lagos.

References

[1] L.D. Lacerda, Nature 374 (1995) 20.
[2] G.M. Vandal, W.F. Fitzgerald, C.F. Boutron, J.P. Candelone, Nature 362 (1993) 621.
[3] A. Marínez-Cortizas, X. Pontevedra-Pombal, E. Garcia-Rodeja, J.C. Nóvoa-Muñoz, W. Shotyk, Science 284 (1999) 939.
[4] J.O. Nriagu, Science 272 (1996) 223.
[5] M.M. Veiga, J. Hinton, C. Lilly, in: Proceedings of the National Institute for Minamata Desease – Forum 99, Minamata, Japan, 1999, p. 19.
[6] P.A Colinvaux, P.E. de Oliveira, J.E. Moreno, M.C. Miller, M.B. Bush, Science 274 (1996) 85.
[7] B. Turcq, A. Sifeddine, L. Martín, M.L. Absy, F. Soubies, K. Suguio, C. Volkmer-Ribeiro, Ambio 27 (1998) 139.
[8] L.D. Lacerda, M.G. Ribeiro, R.C. Cordeiro, A. Sifeddine, B. Turcq, Ciência e Cultura 51 (1999) 363.
[9] G.M. Santos, R.C. Cordeiro, E.V. Silva Filho, B. Turcq, L.D. Lacerda, P.A. Hausladen, L.K. Fifield, A. Sifeddine, P.R.S. Gomes, Radiocarbon 43 (2001) 801.
[10] R.C. Cordeiro, B. Turcq, M.G. Ribeiro, L.D. Lacerda, J. Capitaneo, A. Oliveira da Silva, A. Sifedinne, P.M. Turcq, Sci. Total Environ. 293 (2002) 247.
[11] M.P. Ledru, J. Bertaux, A. Sifeddine, Quaternary Res. 49 (1998) 233.
[12] P.A. Meyers, Chem. Geol. 114 (1994) 289.
[13] G.M. Santos, P.R.S. Gomes, R.M. Anjos, R.C. Cordeiro, B. Turcq, A. Sifeddine, M.L. di Tada, R.G. Cresswell, L.K. Fifield, Rev. Físi. Apl. Instrum. 14 (1999) 1.
[14] P. A Colinvaux, P.E. de Oliveira, M.B. Bush, Quaternary Sci. Rev. 19 (2000) 141.
[15] M.L. Salgado-Laboriau, K. Ferraz-Vicentini, L. Martin, F. Soubies, K. Suguio, B. Turcq, Palaeoclimatol. Palaeoecol. 128 (1997) 215.

[16] W.J. Beck, J. Récy, F. Taylor, R.L. Edwards, G. Cabioch, Nature 385 (1997) 705.
[17] P.K. Schoonmaker, D. Foster, The Botanic Rev. 57 (1991) 204.
[18] P.E. Rasmunssen, Environ. Geol. 33 (1998) 96.
[19] M. Servant, J. Maley, B. Turcq, M.L. Absy, P. Brenac, M. Fournier, M.P. Ledru, Glob. Planet. Change 7 (1993) 25.
[20] L. Martin, M. Fournier, P. Mourguiart, A. Sifeddine, B. Turcq, Quaternary Res. 39 (1993) 338.