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Title

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Permalink

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Journal

Brazilian Journal of Physics, 34(3a)

ISSN

0103-9733

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Publication Date

2004-09-01

DOI

10.1590/s0103-97332004000500007

Peer reviewed

Use of ^{14}C - AMS in the Study of Biological Production in Coastal Upwelling Areas

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Received on 6 September, 2003

We describe the use of the ^{14}C -AMS technique to study the influence of upwelling waters to the local biological production, at Arraial do Cabo, Brazil. Results on $\Delta^{14}\text{C}$ from seaweed tissues incubated into three different types of water mass show the association of primary production with the upwelling waters. We also discuss the importance of high-precision ^{14}C - AMS measurements for this kind of study, and the proper application of isotopic fractionation corrections on radiocarbon results.

1 The ^{14}C - AMS technique and its application on oceanographic studies

Radioactive ^{14}C isotopes are produced in the upper regions of the atmosphere by the reaction $^{14}\text{N}(n,p)^{14}\text{C}$ induced by neutrons yielded by spallation processes resulting from the interaction of proton cosmic radiation with atomic nuclei. The accurate measurement of small variations of the $^{14}\text{C}/^{12}\text{C}$ ratios allow the study of geomagnetic effects, circulation of the water masses of the oceans and has important applications in environmental studies, climatology, oceanography, hydrology and geology, among other research fields[1].

Comparing with other kinds of mass spectrometry techniques, Accelerator Mass Spectrometry (AMS) is performed by converting the atoms in the sample (e.g., graphite) into a beam of fast moving ions. The masses of these ions are then selected by the application of magnetic and electric fields. The Tandem accelerator is used to help to remove molecules and ions that might be mixed with ^{14}C particles before the final detection[2].

The 8UD Pelletron Accelerator, at the Universidade de São Paulo, will be used by the AMS-Brazilian research community when the implementation of the AMS technique is completed and the required modifications to reach reliable measurements of ^{14}C are performed. The IF-UFF group, at the Universidade Federal Fluminense, has been mainly responsible to establish collaborative work with AMS facilities overseas. It is also involved on radiocarbon sample preparation, a very important step in the dating process. A broad of collaborative work between the AMS-Brazilian re-

searchers, the Australian National University (ANU), Purdue University (PRIMELAB) and University of California, Irvine (KCCAMS-Facility) has been done and can be found in the literature [3-16].

Measurements of ^{14}C in ocean waters have been used in the study of the turnover and the mean residence times of deep ocean water, mixing between basins, transfer of heat from low to high latitudes, surface ocean circulation and atmosphere-ocean exchange processes. The difference in the $\Delta^{14}\text{C}$ concentration values of the measured samples can be of the order of ≤ 4 ppm and, therefore, measurements with such small differences require a high-precision on AMS results[17]. The AMS technique has the characteristics required for such kind of tracing studies, since it allows the determination of concentrations down to one atom of rare isotope in 10^{15} stable atoms, from samples of a few milligrams. For oceanographic studies, 0.5 liters of water are sufficient for a sample preparation and measurement.

In the field of biological oceanography, particularly in the marine ecology domain, C and N are the most frequently used stable isotopes, since they are the essential nutrients and have high mobility in the trophic chains. The stable isotopes have been used as tracers of matter transfer in trophic chains, of organic matter in estuarine and fresh water and marine environments, and for determining the trophic position of marine consumers and fish migrations. Also, the differentiation of the isotopic signature in waters from upwelling environments has been reported. However, very often the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ results are not enough to elucidate

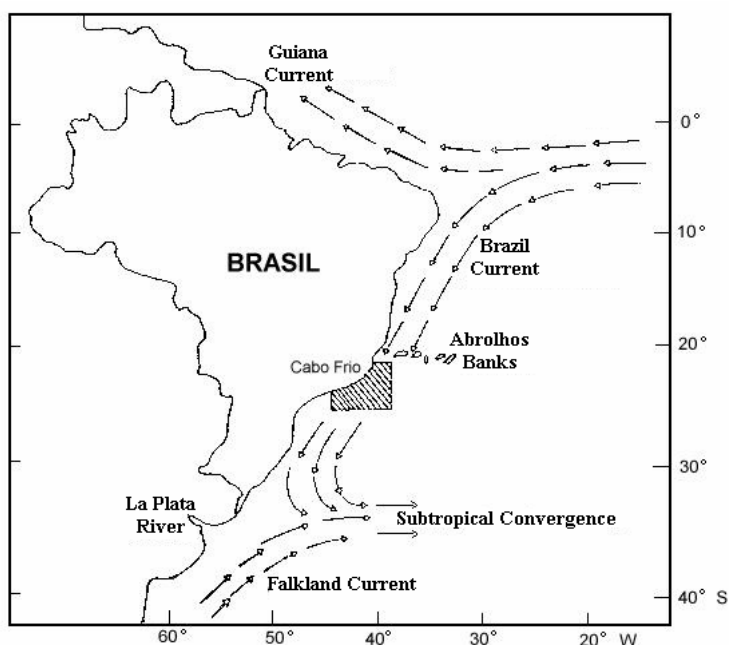


Figure 1. The South Atlantic ocean water mass currents in the Brazilian coast (From Ref. 20).

these important issues, due to the similarities between isotopical ratios of different sources. The additional information from ^{14}C measurement has allowed their relative contributions to be evaluated. It has been shown that $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ are powerful tools in elucidating the source and cycling process of the organic matter in the oceans [18].

In this paper we report an original experiment concerning the isotopic signature of the local waters of an important Brazilian coastal upwelling, located in Arraial do Cabo, R.J., with applications in the fields of Oceanography and Marine Ecology. We assess the contribution of the wind-driven coastal upwelling of Arraial do Cabo to the local biological production, within a more general study dealing with relevant economical and ecological questions such as the dependence of commercial fish species of economical interest on this source of allochthonous material. The ^{14}C concentrations of three different types of water mass were measured in seaweed tissues.

2 The Brazilian coastal waters and the Arraial do Cabo Upwelling

The Brazilian surface waters are called Tropical Water (TW) and are usually poor in nutrient concentrations and productivity, with high temperature and salinity. This oligotrophic water originates from the South Equatorial Current, at $\sim 8^\circ\text{S}$, and it is transported by the Brazil Current (BC) along the continental shelf, reaching depths down to 200m. Fig. 1 [19] shows the South Atlantic water mass currents in the Brazilian coast. Below the TW and above the Antarctic Intermediate Water (AIW), between depths of 200 and 600

m, a high nutrient, cold and less saline water circulates in an opposite direction, compared with the TW. This water is known as the South Atlantic Central Water (SACW), and it originates at the Sub-Tropical Convergence, at $\sim 30^\circ\text{S}$, as can be seen in Fig. 1. In the continental shelf, down to the 50 m isobath, there is a predominance of oligotrophic warm waters, with low salinity, and influenced by the continental flux, the TW and the SACW. This is called Coastal Water (CW).

In the Arraial do Cabo region, Rio de Janeiro State, Brazil, due to climatic and topographic aspects of the local coast (sudden change in the coastal direction, position of the axis of the BC and a strong wind regime), there is the upwelling of the SACW to the surface, mainly during the summer season. This upwelling is responsible for a high biological productivity in this region, with important direct regional economical consequences, since this coastal region is one of the main sardine production centres in Brazil.

3 Experimental procedure and results for dissolved inorganic nutrients and net primary production

The variation of the carbon isotopic compositions was investigated in a population of benthonic seaweed called *Ulva* sp. Upwelling events were simulated in the laboratory, in order to study three regimes: total upwelling (SACW), partial upwelling (SACW:TW 1:1 mixed water) and no-upwelling (TW).

Water samples were collected at the Arraial do Cabo coast, near the Ponta do Focinho, in an area 85 m deep,

corresponding to the main location of upwelling in the region. 125 liters of each type of water were collected, at 70 m depth (SACW) and at 10 m (TW). The seaweed *Ulva* sp. samples, used in the laboratory simulations, were collected in the intertidal region of an adjacent coastal area subject to the influence of the three kinds of water. In the IEAPM Laboratory, the seaweed was submitted to acclimation during 48 hours. The seaweed was cultivated during seven days, in controlled conditions, into the three mentioned types of water. The following parameters were measured in the seaweed tissue during the experiment: net primary production (NPP), respiration (R), carbon concentrations and carbon isotopes ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$). The dissolved inorganic nutrients - DIN (N-NO_3^- , N-NH_4^+ , P-PO_4^{3-}) in the waters were also determined.

In the first day of the experiment, the DIN concentrations were different in the three incubations, being one order of magnitude higher for the SACW than for the TW. A fast absorption by the seaweed was observed during the first 24 hours. In the following days, there were strong indications

of the presence of remineralization process of the organic material. The experiment as a whole was characterized by the predominance of photosynthetic processes, more intense during the first 24 hours. After that, a respiratory process was observed in the seaweed. Similarly to the DIN, the net primary production (NPP) in the *Ulva* sp. was more intense in the first day, for the three incubations. The total production during the whole experiment was highest for the SACW and lowest for the TW, indicating the importance of the upwelling events for the biological production.

A more detailed analysis of these quantities will be published.

4 General definitions for the ^{14}C and ^{13}C measurements

The ^{14}C concentration is usually expressed, in oceanographic studies, as [17, 18, 20]

$$\Delta^{14}\text{C} = [(FMc/100)\exp(-\lambda(c - 1950)) - 1]X1000, \quad (1)$$

where λ is the decay constant, c is the year of the sample collection and FMc is Fraction Modern carbon corrected by the corresponding $\delta^{13}\text{C}$ values, and defined as

$$FMc = FM[(1 + (\delta^{13}\text{C}_{standard}/1000))/(1 + (\delta^{13}\text{C}_{sample}/1000))]^2, \quad (2)$$

where $\delta^{13}\text{C}_{standard}$ and $\delta^{13}\text{C}_{sample}$ are the isotopic fractionation of a standard normalization and the unknown samples, respectively, and the Fraction Modern value is defined as

$$FM = [(^{14}\text{C}/^{13}\text{C})_{sample}/(^{14}\text{C}/^{13}\text{C})_{standard1950}]X100. \quad (3)$$

A variation in the equilibrium distribution of the ^{12}C , ^{13}C and ^{14}C is known as isotopic fractionation of the carbon ($\delta^{13}\text{C}$). Radiocarbon measurements have to be corrected for isotopic fractionation by measuring the ratio of the isotope ^{13}C related to ^{12}C in the sample being measured. The ratio $^{13}\text{C}/^{12}\text{C}$ can be measured by a conventional mass spectrometer system (stable isotope ratio mass spectrometer (IRMS), for example). The $\delta^{13}\text{C}$ value, in this case, is also an important information regarding the composition of the immediate environment where the sample came from. However, in many cases, the AMS sample preparation process and measurement itself can add some more isotopic fractionation visible at high-precision measurements ($<1\%$ precision). The causes of this fractionation can vary. An incomplete conversion of the sample from one stage to another during combustion or graphitization can lead to a fractionation as well as small accelerator drifts during a conventional AMS run.

AMS systems that are equipped with beam diagnostics (Faraday cups off line and beam scanners) to aid in tuning stable isotope (^{12}C and ^{13}C) are the ideal spectrometers to obtain also the $^{13}\text{C}/^{12}\text{C}$ ratios from the sample being measured by ^{14}C [21, 22]. The FMc values corrected by AMS-

$\delta^{13}\text{C}$ gain in precision, in which any isotopic fractionation, if it occurs, is considered into the normalization.

5 ^{14}C and ^{13}C measurements, performed at ANU and Waterloo

The first ^{14}C -AMS measurements of *Ulva* sp. samples were performed at the ANU 14UD Tandem accelerator, a very large shared facility that lacks the refinements of the high-precision systems. The main source of uncertainty was the 2% reproducibility of this system on a set of modern standard samples (ANU sucrose) spread into a 32 cathode wheel McSNICS ion-source. Radiocarbon results of the standards and unknown samples were obtained by one run of a maximum of three cycles of sequential measurements of ^{14}C (minutes) and ^{13}C (seconds). The system does not support to inject ^{12}C beams without creating some instability at the terminal voltage. The $^{14}\text{C}/^{12}\text{C}$ ratios are calculated assuming the percent of ^{12}C (98.7%) and ^{13}C (1.1%) on nature. The statistical errors were of the order of 1%. Reproducibility of 2% is acceptable for several AMS studies, when high-

precision ($<0.5\%$) is not an issue and dating results with

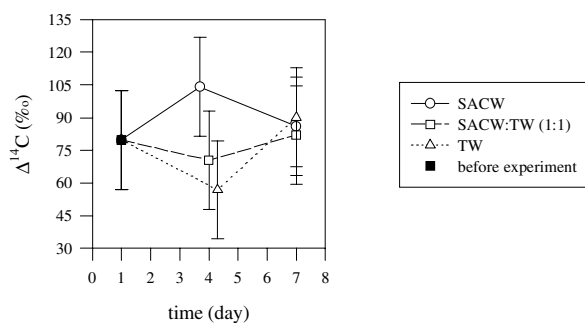


Figure 2. Variation of the $\Delta^{14}\text{C}$ values in the *Ulva sp.* seaweed tissue, during the laboratory experiment. The measurements were performed at ANU. The time displacement around the 4th day was artificially made, to allow the visualization of the error bars.

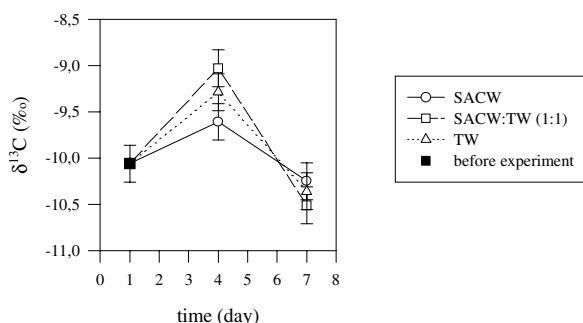


Figure 3. Variation of the $\delta^{13}\text{C}$ values in the *Ulva sp.* seaweed tissue, during the laboratory experiment. The measurements were performed by IRMS, at Waterloo.

errors bars larger than 160 years old (radiocarbon dating of modern samples) can still be a valuable information.

Since that the $^{13}\text{C}/^{12}\text{C}$ ratios could not be obtained directly from the AMS-ANU system, the ^{13}C values to normalize the ^{14}C results were determined using IRMS, at the Environmental Isotope Laboratory of the University of Waterloo, Canada. The precision of these measurements were 0.2 ppm.

The carbon isotope concentrations in the seaweed were determined in the 1st, 4th and 7th days of the experiment. The results are shown in Figs. 2 and 3, with the corresponding uncertainties. The $\Delta^{14}\text{C}$ value in the seaweed tissue before the experiment (with its original water) was 80 ± 23 ppm. By the fourth day of the experiment there was a significant difference between the ^{14}C values of the seaweed grown in the SACW (104 ± 23 ppm) and TW (57 ± 22 ppm) waters. Although the error bars are large, there is a clear indication of difference in the isotopic signature of the two water sources. Furthermore, the mixture water is intermediate between the two components (70 ± 23 ppm). The $\Delta^{14}\text{C}$ values in the seventh day of the experiment are similar for the three types of water and similar to its original value (before the incubations). As the experiments were performed with closed systems, without water renovation, this behavior is attributed to the re-incorporation of remineralized ^{14}C

in the systems after one week of the seaweed incubation. The derived values of $\Delta^{14}\text{C}$ in the seaweed tissues after the fourth day reflect the isotope signature of each type of water.

This result allows one to infer the differences of the water sources. On the other hand, no important difference was observed for the $\delta^{13}\text{C}$ values in the seaweed, submitted to similar conditions, as can be seen in Fig. 3.

It is also very interesting to notice that the largest $\Delta^{14}\text{C}$ values were observed for the upwelling water SACW, that is deeper than the TW. This result is consistent with the measured values of $\Delta^{14}\text{C}$ in surface waters, as compiled by Nydal[23]. The $\Delta^{14}\text{C}$ values of the SACW and TW are the ones found at the latitudes where they were formed, thousand miles way from Arraial do Cabo, and were maintained in the waters during their long trajectories along the Brazilian coast.

We believe that the present results contribute to opening new perspectives for the use of ^{14}C as a tracer of the biological production in upwelling areas all over the world. However, this kind of experiment should be performed with better precision than the present one.

In the next section we describe preliminary results of such experiments.

6 High precision ^{14}C and ^{13}C measurements, performed at UC-Irvine

In order to perform high-precision AMS measurements, seaweed samples were sent to the recently installed compact AMS system (0.5MV 1.5SDH-1) from NEC at the Keck Carbon Cycle AMS facility (KCCAMS) of the University of California, Irvine (UCI). This compact model can measure isotopes of carbon, including ^{14}C and the stable isotopes ^{13}C and ^{12}C , simultaneously. Each sample, unknowns and standards, are measured at least 7 times (run) each. Each run corresponds to at least 500 cycles of ^{12}C (micro seconds), ^{13}C (micro seconds) and ^{14}C (seconds) injected beams. The analytical precision of the system is achieved on repeated analyses of primary radiocarbon standard (Oxalic acid I, OX-I) and accepted secondary standards, as Oxalic acid II (OX-II) and ANU sucrose. Precision of ^{14}C measurements is in the range of 0.3% to 0.5%.

The KCCAMS-facility also possesses an IRMS (Delta Plus - Finegan) with combustion/GC (gas chromatography) interface capabilities. This device determinates $\delta^{13}\text{C}$ values with precision from 0.05 to 0.2 ppm, depending on sample size, carbon concentration and methods applied. This precision is far higher than the precision provided by the AMS system for $\delta^{13}\text{C}$ measurements (~ 1 ppm). IRMS- $\delta^{13}\text{C}$ values can be very important to provide information on the natural carbon sources and pathways taken through terrestrial and ocean reservoirs. However, for the ^{14}C correction it is preferable to use the AMS- $\delta^{13}\text{C}$ values rather than the IRMS- $\delta^{13}\text{C}$ ones, because this procedure allows to normalize any undesirable fractionation that might happened during sample preparation or ^{14}C measurement.

The seaweed samples measured at KCCAMS were two years old. Despite of the careful storage of the samples, they passed through remineralization processes and they could still aggregate bacteria that might disturb the truly results. Even so, we decided to perform the measurements. The derived $\Delta^{14}\text{C}$ values were around 80-90 ppm for the three water incubations along the whole experiment. These values are similar to the ones obtained previously at ANU for the samples corresponding to the first (before the incubation) and last (7th) days of the experiment. The high precision UCI-KCCAMS results are, therefore, in agreement with the previous low-precision ANU results. However, due to the remineralization processes and aggregation of bacteria during nearly two years of sample storage, the possible distinct $\Delta^{14}\text{C}$ values of the three incubations along the experiment (2nd to 6th day) were lost, in a similar way as the ANU measurements showed that they were lost at the last day of the experiment. Therefore, we concluded that we have to perform a new similar experiment, with seaweed collection and incubation processes, and then send the samples to be analyzed at UCI-KCCAMS for AMS measurements.

Although the new measurements were not conclusive, we believe that it is worth to show their results, in order to realize the importance of the appropriate normalization ($\delta^{13}\text{C}$ correction) that has to be applied in high-precision AMS measurements. Fig. 4 shows, as example, the ^{14}C results for the SACW water mass, corrected by AMS- $\delta^{13}\text{C}$ and IRMS- $\delta^{13}\text{C}$ values. The differences in the results of ^{14}C for each method of $\delta^{13}\text{C}$ determination are impressive, considering the small error bars. Such differences could not be noticed from the ^{14}C values obtained at ANU, but in high-precision AMS measurements, the AMS- $\delta^{13}\text{C}$ correction should be used.

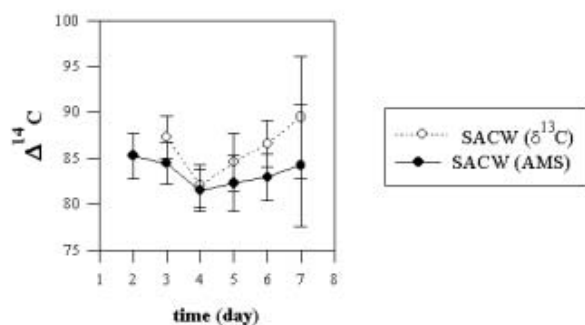


Figure 4. Variation of the $\Delta^{14}\text{C}$ values in the *Ulva sp.* seaweed tissue, during the laboratory experiment, for the SACW water mass. The $\Delta^{14}\text{C}$ measurements were performed at UCI-KCCAMS facility and the $\delta^{13}\text{C}$ values were obtained by IRMS and by AMS.

Acknowledgements

The authors would like to thank the Fundação de Amparo à Pesquisa do Rio de Janeiro (FAPERJ) for their financial support, the CAPES (K.C.F.) and CNPq (G.M.S. and P.R.S.G.) councils for their grants and the IEAPM for the support during the experiment period.

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