Organic Carbon-14 in the Amazon River System

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Thu Apr 22 12:21:13 2004
Organic Carbon-14 in the Amazon River System


Coarse and fine suspended particulate organic materials and dissolved humic and fulvic acids transported by the Amazon River all contain bomb-produced carbon-14, indicating relatively rapid turnover of the parent carbon pools. However, the carbon-14 contents of these coexisting carbon forms are measurably different and may reflect varying degrees of retention by soils in the drainage basin.

Dissolved and particulate organic materials transported by rivers provide a continuous record of physical and biological processes at work within the drainage basin (1, 2). Rivers also contribute a potentially important quantity of organic matter to the ocean (3), where the dissolved component may exhibit an appreciable residence time (4, 5). Although the magnitude of the global river contribution is known (2), the dynamics of organic materials within terrestrial ecosystems and their effects on the composition of the corresponding marine reservoirs are poorly understood (3). This is particularly true for rivers draining tropical rain forests; these account for at least 40 percent of the total riverine organic carbon discharged into the ocean (3).

We report an analysis of the 14C contents of dissolved humic substances and coarse (65 to 3000 μm) and fine (0.5 to 65 μm) suspended particulate organic material (SPOM) from the Amazon River system (Fig. 1). These results, obtained from accelerator mass spectrometry (AMS) of carbon samples a few milligrams in mass, have enabled us to make the first comparative determinations of 14C levels in dissolved and particulate organic materials from a large tropical river.

All dissolved and particulate organic materials were obtained from depth and cross-channel integrated composite water samples that reflect the average compositions of the substances in transit (6). Vertically integrated water samples were collected with a collapsible-bag sampler at a minimum of nine equally spaced points across each mainstream section and five equally spaced points across the Rio Negro (6). The coarse and fine SPOM samples (7) were combined on a flux-weighted basis from materials collected at Santo Antônio do Içá (Fig. 1) approximately every 4 months on CAMREX (8) cruises 1 to 8 (1982–84) (6, 9).

Dissolved humic substances were collected on CAMREX cruise 7 (February to March 1984) in the mainstream at Itapéua and Óbidos and from the lower Rio Negro (Fig. 1). Humic substances, isolated by adsorption at pH 2 on macroporous resin (10), constituted an average of 60 weight percent of the total dissolved organic carbon (11). The remaining dissolved organic material was too hydrophilic to be isolated on resin (10) and thus could not be characterized. Total humic substances collected at Óbidos and from the Rio Negro were separated into acid-insoluble (humic acid) and acid-soluble (fulvic acid) fractions. The total carbon blanks for the humic acid and fulvic acid fractions were less than 1 and 0.2 percent, respectively (11). Radiocarbon levels were directly measured on all samples by AMS at the University of Washington Nuclear Physics Laboratory and are reported as Δ14C (per mil) (12).

In the central mainstream, coarse and fine SPOM and dissolved humic and fulvic acid accounted for an average of 7, 35, 5, and 30 percent, respectively, of the total organic carbon in transit (7, 11). Almost all the organic material in the Rio Negro was dissolved with humic and fulvic acids, accounting for about 30 and 45 percent of the total carbon, respectively (11). The elemental and chemical compositions of the mainstream coarse and fine SPOM fractions were relatively constant both seasonally and with distance downstream between Santo Antônio do Içá and Óbidos (7). In addition, the outstanding compositional differences among the humic substances collected on CAMREX cruise 7 were between the samples from the Rio Negro and the other 15 samples; the latter, compositionally uniform group included samples from a wide variety of other tributaries at various hydrographic stages (11). Thus, in spite of the limited geographic and temporal (for humic substances) coverage afforded by these samples (Fig. 1 and Table 1), there is good reason to expect that the 14C patterns reported here are representative of the Brazilian Amazon as a whole.

All riverine organic carbon fractions had positive Δ14C values (Table 1) and thus must contain "bomb" carbon derived from atmospheric testing of thermonuclear devices after 1954 (13, 14). Therefore, atmospheric CO2 apparently has been incorporated over the last 30 years by the carbon

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Fig. 1. Study area. CAMREX sampling sections are indicated by solid dots. Section identification abbreviations: S, Santo Antônio do Içá; I, Itapéua; N, Rio Negro; O, Óbidos.

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<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta^{14}C$ (per mil)</th>
<th>Modern carbon* (%)</th>
<th>Minimum bomb carbon† (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse SPOM</td>
<td>+227 ± 14</td>
<td>123</td>
<td>32</td>
</tr>
<tr>
<td>Fine SPOM</td>
<td>+19 ± 19</td>
<td>102</td>
<td>5</td>
</tr>
<tr>
<td>Total humics</td>
<td>+283 ± 13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Humic acid</td>
<td>+141 ± 18</td>
<td>114</td>
<td>21</td>
</tr>
<tr>
<td>Fulvic acid</td>
<td>+344 ± 20</td>
<td>134</td>
<td>47</td>
</tr>
<tr>
<td>Total humics‡</td>
<td>+264 ± 15</td>
<td>126</td>
<td>37</td>
</tr>
<tr>
<td>Humic acid</td>
<td>+180 ± 12</td>
<td>118</td>
<td>26</td>
</tr>
<tr>
<td>Fulvic acid</td>
<td>+290 ± 14</td>
<td>129</td>
<td>40</td>
</tr>
<tr>
<td>Total humics‡</td>
<td>+265 ± 12</td>
<td>127</td>
<td>37</td>
</tr>
</tbody>
</table>

*Santo Antônio do Içá*  
*Itapecuru*  
*Rio Negro*  
*Obidos*  

*Percentage of the $^{14}C$ concentration of modern (1950) atmospheric CO$_2$. † A minimum value calculated from 

$$\Delta^{14}C_{\text{atom}} = \frac{[750(x/100) + (-20)(1 - x/100)]}{x/100}$$

where $x$ is the percentage of bomb carbon, +750 represents the maximum $\Delta^{14}C$ for CO$_2$ in the equatorial atmosphere after atmospheric testing of nuclear weapons [estimated from (13)], and $-20$ corresponds to the $\Delta^{14}C$ of atmospheric CO$_2$ just before testing (20). Calculated from the weight percent of organic carbon and the $\Delta^{14}C$ of the component humic and fulvic acids. Ratios of fulvic acid to humic acid fraction for the Rio Negro and Obidos samples are 1.55 and 3.42, respectively (11).  

reservoirs from which these organic forms derive. For all carbon forms except fine SPOM, the minimum percentage of bomb carbon exceeded 20 percent (Table 1), corresponding to maximum average residence times in the drainage basin of less than 150 years before riverine export (15).  

The four coexisting carbon forms, however, had measurably different $\Delta^{14}C$ values (Table 1) and thus different dynamics within the drainage basin. Coarse SPOM had a $\Delta^{14}C$ of $+227 ± 14$ per mil, similar to the 1983 value of $+234 ± 3$ per mil for atmospheric CO$_2$ in the Northern Hemisphere (14), which we take to be globally representative by that time (13). This fraction was primarily composed of undegraded tree leaf remains as indicated by lignin and elemental and stable carbon isotope analyses (7). Because leaf material is rapidly formed and remineralized in the Amazon jungle (16), the measured $\Delta^{14}C$ probably reflects essentially present-day carbon as opposed to a fortuitous mixture of fossil and bomb carbon.  

The dissolved fulvic acid fractions from the Amazon River at Obidos and the Rio Negro had $\Delta^{14}C$ values of $+290 ± 14$ and $+344 ± 20$ per mil, respectively; these values significantly exceed the $\Delta^{14}C$ (+234 ± 3 per mil) of atmospheric CO$_2$ in 1983 (14). These fulvic acids contained at least 40 percent bomb carbon (Table 1), a significant portion of which must have been photosynthetically fixed between 1963 and 1979, when the $\Delta^{14}C$ of atmospheric CO$_2$ in the tropics exceeded $+300$ per mil (13). In contrast, the Obidos and Rio Negro humic acid fractions had $\Delta^{14}C$ values of $+180 ± 12$ and $+141 ± 18$ per mil, respectively; these values are distinctively lower than both the coarse SPOM and corresponding fulvic acids. Thus, humic and fulvic acid fractions from the same water samples had consistently different retention times within the Amazon drainage system. In spite of these internal differences, dissolved total humic substances from the Itapecuru, Obidos, and Rio Negro sites all had similar radiocarbon contents (Table 1), indicating a uniform $^{14}C$ enrichment in this major organic matter fraction at this time over the lower Amazon system.  

Organic carbon in the fine SPOM fraction ($\Delta^{14}C = +19 ± 19$ per mil) contained the largest component of "prehemoglobin" carbon (Table 1). Fine SPOM from the Amazon mainstem was characterized by uniformly high organic nitrogen levels (atomic C:N, 11) and low concentrations of highly oxidized lignin, all of which are typical of soil organic matter (7). Although organic matter in surface soils typically reflects the influence of bomb carbon, $\Delta^{14}C$ values for subsols and many topsoils are $±50$ per mil and less (17). Thus, both the chemical and $^{14}C$ compositions of the fine SPOM indicate a predominant soil organic matter source. Although the geographic sources and mobilization mechanisms of the fine SPOM are not necessarily the same as those of the coexisting dissolved humic substances (7, 11), the lower $\Delta^{14}C$ of the fine particulate component nevertheless indicates a longer average retention time within the basin as a whole.  

One important aspect of these results is their implication concerning organic matter processing in tropical drainage basins. Because production and decay of organic matter and riverine transport are relatively rapid processes (6, 16), measurable aging within the different organic carbon reservoirs must occur primarily in the soil. The relative residence times of the humic and fine SPOM fractions correspond well with their expected behavior during chromatographic transport within the soil. For example, dissolved fulvic acids from the Amazon River system are less hydrophobic and more nitrogen-poor (atomic C:N, 40 to 85) than the corresponding humic acids (C:N, 15 to 60) (11). Laboratory and field studies of organic matter adsorption by soil minerals indicate that uptake can be extensive and highly selective for hydrophobic and nitrogen-containing constituents (11, 18). Thus, fulvic acids should be adsorbed less strongly and pass more rapidly through the soil than humic acids of the same source. This model suggests that the hydrophilic fraction of the total dissolved organic material (which cannot be isolated on resin) may have an even shorter residence time in the Amazon basin than the coexisting fulvic acid. Dissolved nitrogen-rich degradation products may be strongly adsorbed by fine grained minerals that they ultimately are exported largely in particulate form by soil erosion, as opposed to redissolution.  

The $^{14}C$ results also are significant in terms of the dynamics of dissolved organic carbon (DOC) within the ocean, the second largest active organic carbon reservoir on earth (3). The $^{14}C$ content of DOC from the deep northern Pacific corresponds to an age of about 3400 years (4). The global annual discharge of DOC by rivers alone is nearly sufficient to support the ocean DOC pool at this residence time, and a significant terrestrial-derived component in the marine DOC pool cannot be ruled out at present (5). However, if the Amazon is considered typical of tropical rivers, and perhaps of rivers in general (19), it is evident (Table 1) that appreciable aging of exported DOC does not occur within the drainage basins. Therefore, the low radiocarbon content of marine DOC probably results primarily either from an "old" marine source, such as sediment pore water, or from aging within the ocean itself (4).  

REFERENCES AND NOTES
Sea-Air Partitioning of Mercury in the Equatorial Pacific Ocean

JONATHAN P. KIM AND WILLIAM F. FITZGERALD

The partitioning of gaseous mercury between the atmosphere and surface waters was determined in the equatorial Pacific Ocean. The highest concentrations of dissolved gaseous mercury occurred in cooler, nutrient-rich waters that characterize equatorial upwelling and increased biological productivity at the sea surface. The surface waters were supersaturated with respect to elemental mercury; a significant flux of elemental mercury to the atmosphere is predicted for the equatorial Pacific. When normalized to primary production on a global basis, the ocean effluxes of mercury may rival anthropogenic emissions of mercury to the atmosphere.

Recently we presented preliminary evidence for the evasion of mercury from the surface waters of the equatorial Pacific Ocean. This evidence supported model predictions of a low-latitude ocean source of mercury and suggested that the volatilization process may be mediated by marine biota (J). Here we report results confirming that biologically productive regions of the equatorial Pacific are a source of atmospheric mercury. Moreover, the principal species appears to be elemental mercury (Hg\textsubscript{0}). The largest dissolved quantities of Hg\textsubscript{0} were associated with cooler temperatures and higher nutrient and chlorophyll a levels, suggesting that Hg\textsubscript{0} efflux is tied to equatorial upwelling and phytoplankton activity.

Evidence for an atmospheric source of mercury in the equatorial Pacific was obtained on a research cruise of the O.S.S. Researcher from 8 June to 3 July 1984. The equatorial cruise track from 155\degree S to 93\degree W and the track at 85\degree W from 4\degree 30'S to 4\degree 30'N are shown in Fig. 1. Seawater for measurement of dissolved gaseous mercury (DGM) was collected in the surface mixed layer at every 5\degree of longitude along the equator and at closer intervals (<2') along the track at 85\degree W. Water samples were also obtained for determination of temperature, total mercury (2), nitrate plus nitrite, and chlorophyll a. Total gaseous mercury (TGM) and organic gaseous mercury (OGM) in the air were sampled at bow level (10 m above the surface) on both cruise legs while the ship was underway. The broad coverage of these two cruise tracks allowed quantification of the horizontal extent and range of DGM in surface water and TGM and OGM in the overlying air in the equatorial Pacific.

Samples of DGM in surface seawater were collected in acid-cleaned, Teflon-lined, 30-liter Go-Flo bottles suspended on Kevlar line and anchored with a plastic-bagged concrete weight. The seawater was then purged with mercury-free air in a 4-liter flow-through glass bubbler that had been scrupulously acid-cleaned (3). The sparging efficiency for Hg\textsubscript{0} was 90 to 95 percent, as determined with dissolved oxygen as a tracer and a volatilization rate ratio of Hg\textsubscript{0} to dissolved oxygen of 0.94 (4). Total DGM was purified from 30 to 60-liter aliquots, trapped on gilded quartz sand columns, and analyzed by cold vapor atomic absorption spectrophotometry (5). Another 30- to 60-liter aliquot was used to separate the total DGM into an organic and an inorganic fraction with a silver-gold stack method (6). In this arrangement the silver column collects Hg\textsubscript{0} while passing volatile organic mercury species such as (CH\textsubscript{3})\textsubscript{2}Hg to be trapped on the gold column. Subsequent measurements are made with a two-stage gold amalgamation technique (5).

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