Carbon cycling in the Amazon River: Implications from the $^{13}$C compositions of particles and solutes

Abstract—The $^{13}$C: $^{12}$C of suspended particulate organic C (POC), dissolved organic C (DOC), and dissolved inorganic C (DIC) were measured during 1982–1984 at 11 main-channel and 7 tributary stations over an 1,800 km reach of the Amazon River between Vargem Grande and Obidos, Brazil. The measured $\delta^{13}$C range vs. marine carbonate (PDB) was $-32$ to $-26\%$ for suspended POC, $-30$ to $-28\%$ for DOC, and $-26$ to $-12\%$ for DIC. The $\delta^{13}$C of the fine particulate organic C (FPPOC) decreased downriver from Vargem Grande, with values lowest during the falling-water portion of the runoff cycle; these trends were the result primarily of input of $^{13}$C-depleted FPPOC from tributaries draining the lowland regions of the Amazon basin and floodplain soils. The $\delta^{13}$C of the FPPOC at Obidos implies that at least 35% of the POC exported by the Amazon River is derived from the lowland portion of the Amazon basin. The $\delta^{13}$C of DIC decreased downriver with the lowest values measured during falling water; these trends were due primarily to within-river respiration and tributary input. The $\delta^{13}$C of the DIC suggests that $\sim 40\%$ of the organic matter being respired in the river is $C_4$ plant material derived from floodplain grasses.

Within its basin, the discharge of chemically diverse tributaries is blended by the Amazon River, resulting in main-channel concentrations of chemical species and sediment that are close to the world average for rivers (Stallard and Edmond 1983). In the main channel of the river, we found that $\sim 20\%$ of the total C was particulate organic C (POC), $30\%$ was dissolved organic C (DOC), and $50\%$ was dissolved inorganic C (DIC) (Richey et al. 1990). The lignin composition of the POC and DOC suggests that most of the organic C in the main channel is refractory, with a degradation trend that increases from coarse particulate C ($>63$ $\mu$m) to fine particulate C ($<63$ $\mu$m) to the humic component of the DOC (Hedges et al. 1986; Ertel et al. 1986). Yet high respiration rates were measured throughout the year (Devol et al. 1987; Richey et al. 1990). The apparently unreactive nature of the bulk of organic C in the river combined with respiration rates that equal $\sim 50\%$ of the total organic C (TOC) flux requires a major, and as yet unidentified, source of organic C (Richey et al. 1990). Identifying the organic substrate that is fueling within-river respiration is crucial to understanding the C cycle in the river.

Study of the C cycle of a large river requires accurate measurement of downriver trends in concentrations and fluxes of the major C species. These measurements yield a C mass balance for rivers that provides a first-order estimate of the impact of tributary input on the main-channel C flux. Complementary measurements of the molecular and isotopic composition of organic C can yield important tracers of C source material in rivers (e.g. Hedges et al. 1986). Such tracers are particularly useful in tropical rivers where large drainage basins can encompass a diversity of geologic and climatic zones and large, productive floodplains often border rivers. Tropical rivers are an especially important link between terrestrial C inputs and oceanic export, as these rivers deliver $>60\%$ of the TOC discharged into the ocean (Meybeck 1982).

In this note we analyze the temporal and

Acknowledgments

We thank the Instituto de Pesquisas da Amazonia for cooperation and logistical support. Samples were collected with assistance from Bruce Forsberg, Bob Meade, and the crew of the research vessel L. M. Amanai. Fayla Swartz helped with the $^{13}$C sample preparation and Minze Stuiver provided mass spectrometer time. Luiz Martinelli provided comments. Support was provided by NSF grant DEB 81-07522. Contribution 49 of CAMREX and 1896 of the School of Oceanography, University of Washington.
downriver trends in the $^{13}$C composition of particulate and dissolved C in the Amazon River. We demonstrate that the $^{13}$C composition provides a means to identify and quantify input of organic C from the lowland and floodplain portion of the Amazon drainage basin. Although measurements of stable C isotope have been used to study C cycling in the ocean and lakes (e.g. Kroopnick 1985; Quay et al. 1986), there have been few studies of the riverine C cycle utilizing this isotopic tracer. Most $^{13}$C:$^{12}$C measurements of riverine C have been used to distinguish between terrestrial and marine organic C sources in estuaries (e.g. Spik er and Schemel 1979; Cai et al. 1988). In the Amazon River, $\delta^{13}$C measurements made previously on suspended POC range from $-33$ to $-25\%$ (Cai et al. 1988) and on DIC range from $-22$ to $-14\%$ (Longinelli and Edmond 1983).

We use $^{13}$C data obtained during the CAMREX study to address two questions. Is the POC exported by the river derived predominantly ($>85\%$) from the upland (i.e. Andean) drainage region as is the case for the bulk suspended sediment? Are the large areas of rapidly growing grasses in the floodplain (e.g. the floating meadows) significant sources of the labile organic material maintaining high rates of within-river respiration?

The Amazon drainage basin ($\sim 6 \times 10^6$ km$^2$) encompasses the Andean Cordillera, lowland Amazon basin or trough, Precordillera, and a large floodplain (i.e. varzea) that covers $\sim 100,000$ km$^2$. This geomorphological diversity of drainage regions results in rivers that have a large range of chemical characteristics (Gibbs 1967; Stallard and Edmond 1983). Rivers within the Amazon drainage basin have been classified previously by color (Sioli 1968). Whitewater rivers have high suspended and dissolved loads; clearwater rivers are depleted in suspended and dissolved material; blackwater rivers have low suspended sediments and dissolved inorganic material but high concentrations of dissolved organic materials. Rivers within the Amazon basin were further classified according to the geomorphological characteristics of their drainage regions (Stallard and Edmond 1983). Whitewater rivers are characteristic of all rivers with substantial drainage in the Andes or sub-Andean trough, with the main channel of the Amazon River and the Rio Madeira being good examples; clearwater rivers are widely distributed and typically drain clay-rich soils in the shield; blackwater rivers are found in the lowland basin draining nutrient-poor soils (Stallard and Edmond 1983). During CAMREX we sampled eight rivers in the basin (Fig. 1), six were categorized as white, two were black, and none were clearwater rivers.

Descriptions of the procedures used during CAMREX to measure discharge, suspended sediments, and particulate and dissolved chemistry have been presented previously (Richey et al. 1986, 1990; Hedges et al. 1986; Devol et al. 1987). The sampling and analytic procedures will therefore be described only briefly.

Between April 1982 and June 1984, eight cruises between Vargem Grande and Obidos, Brazil, a distance of $\sim 1,800$ km, were made on the Amazon River (Fig. 1). Water discharge, suspended sediment, and particulate and dissolved chemistry measurements were made at 11 main-channel and 7 tributary stations (Richey et al. 1986). The eight cruises occurred over two annual run-off cycles (Fig. 2), with five rising-water (cruise numbers 1, 3, 4, 6, and 7) and three falling-water (cruise numbers 2, 5, and 8) sampling times. Data from cruise 1, because it did not cover the entire reach between Vargem Grande and Obidos, are not presented.

Depth-integrated, discharge-weighted composite water samples (20–40 liters) were collected at each river section (Richey et al. 1986). Coarse and fine suspended sediments were separated by a 63-$\mu$m sieve; fine sediments were concentrated by continuous flow centrifugation (Hedges et al. 1986). Weight percentages of organic C were measured (Carlo Erba model 1106 elemental analyzer) with a precision of $\pm 1.5\%$ for fine and $\pm 3\%$ for coarse sediments. Fine particulate organic C (FPOC) concentrations were then calculated as the product of the wt% measurements and fine sediment concentrations (Richey et al. 1986) for the fraction $<63 \mu$m, and coarse particulate organic
C (CPOC) concentrations were determined similarly for the size fraction >63 μm. The concentration of DIC (DIC = HCO$_3^-$ + CO$_3^{2-}$ + CO$_2$ aq) was determined from pH and alkalinity titration measurements with a precision of ±3% assuming that titration alkalinity equals carbonate alkalinity, as discussed by Devol et al. (1987).

Suspended sediment samples were prepared for $^{13}$C analysis by acidifying with HCl overnight at 50°C, drying and then combusting with a sealed-tube combustion pro-
procedure. DIC samples for $^{13}$C analysis were collected by overfilling a glass bottle from a Niskin bottle, poisoning with HgCl$_2$, capping with a polyseal screwcap, and storing at ambient temperatures. The CO$_2$ gas was extracted from the DIC samples with the stripping procedure described by Kroopnick (1974).

$^{13}$C composition of the DOC was determined on water samples collected during cruises 1–5 that had been previously analyzed for the $^{13}$C composition of DIC. DOC sample preparation utilized a potassium persulfate oxidation procedure to convert DOC to CO$_2$ gas (Goulden and Anthony 1978), which was then stripped out of the water with the same procedure described for DIC analysis. We observed a large range in DOC yields using wet oxidation, i.e. 60–100% relative to DOC concentration measurements made by a Dohrmann model DC-80 carbon analyzer. There was no significant trend between $^{13}$C and yield for the DOC samples.

During the study, $^{13}$C:$^{12}$C measurements were made with two mass spectrometers, a Nuclide 6-60 and Finnigan MAT 251, which were intercalibrated. The precisions (±1 SD) of the $^{13}$C measurements of the POC, DIC, and DOC were ±0.1, 0.1, and 0.2%, based on replicate analyses ($n = 3$) of the same sample. Because of the variability in DOC yields, reported $^{13}$C values for DOC (i.e. $[^{13}$C]DOC) likely represent an incomplete portion of the DOC and were not as accurate as the $^{13}$C values for POC (i.e. $[^{13}$C]POC) and DIC (i.e. $[^{13}$C]DIC), where yields were 100±2%. Yields for the $[^{13}$C]POC and $[^{13}$C]DIC procedures were determined by comparison to the organic C content measured by a Dohrmann carbon analyzer and to gravimetrically prepared Na$_2$CO$_3$ solutions, respectively.

The $^{13}$C values are reported vs. marine carbonate (PDB) with the following notation: $^{13}$C($\%$) = $[(^{13}$C: $^{12}$C)$_{\text{sample}}/(^{13}$C: $^{12}$C)$_{\text{PDB}} - 1] \times 1,000$. Intervals given about arithmetic sample means are ±1 SD. A two-tailed parametric t-test was used to determine significance of differences between group means, and the Spearman rank correlation procedure was used to determine the significance of downriver trends in a parameter (Zar 1974).

The $^{13}$C of the FPOC (i.e. $[^{13}$C]FPOC) in the Amazon main channel ranged from −28.2 to −26.4% (Fig. 3) with a mean value ($\pm$1 SD) of $-27.2 \pm 0.5\%$ ($n = 70$). Lower $[^{13}$C]FPOC values were measured during falling-water than rising-water cruises (Fig. 3). The mean falling-water value of $-27.6 \pm 0.4\%$ was significantly ($P < 0.01$) lower than the mean rising-water value of $-26.9 \pm 0.3\%$. During falling water there was a significant ($P = 0.01$) down-river decrease in $[^{13}$C]FPOC to Sao Jose do Amatari (1,200 km downriver from Vargem Grande). During rising water, a significant ($P < 0.01$) downriver decrease only occurred until Jutica (500 km downriver from Vargem Grande). On all cruises, except low-water cruise 6, $[^{13}$C]FPOC increased downriver from Sao Jose do Amatari.

The $^{13}$C of CPOC (i.e. $[^{13}$C]CPOC) in the main channel ranged from −29.0 to $-27.3\%$, with the mean value of $-27.9 \pm 0.4\%$ ($n = 73$) being significantly ($P < 0.01$) lower than the mean $[^{13}$C]FPOC value. Downriver trends in $[^{13}$C]CPOC differed during rising- and falling-water cruises (Fig. 3). During rising water there was a significant ($P < 0.01$) downriver decrease to Sao Jose do Amatari, except for low-water cruise 6. Contrarily, during falling water there was a significant ($P < 0.01$) downriver increase, with the greatest increase occurring in the reach between Jutica and Anorí (874 km downriver).

$[^{13}$C]DIC ranged from $-17.7$ to $-11.5\%$ with a mean value of $-14.0 \pm 1.6\%$ ($n = 76$); $[^{13}$C]DIC always showed a significant ($P < 0.01$) downriver decrease (Fig. 3). The greatest downriver decrease and lowest values were measured during falling water, with the mean falling-water, main-channel value of $-15.0 \pm 1.4\%$ being significantly ($P < 0.01$) lower than the mean rising-water value of $-13.3 \pm 1.3\%$.

The mean $[^{13}$C]DOC for all cruises was $-28.7 \pm 0.6\%$ ($n = 26$). Although $[^{13}$C]DOC measurements were made only on cruises 1–5, because of the inconsistency in our yields during oxidation (as discussed above), the available data indicate no significant
downriver or rising- vs. falling-water trends (Fig. 4).

The eight rivers sampled were categorized into predominantly lowland- or upland-, i.e. Andean, draining rivers (Table 1) using the geomorphologically based classification scheme of Stallard and Edmond (1983). The Rio Madeira and the main channel at Vargem Grande have predominantly upland drainage regions; the other rivers have large or exclusive lowland drainage regions (Table 1). The Amazon River at Vargem Grande and the Rio Madeira have the highest δ13C and concentrations of FPOC, CPOC, and DIC (Table 1). In contrast, the Rio Jutai and Rio Negro (blackwater rivers with ex-
clusive lowland drainage) have the lowest \( \delta^{13}C \) and concentrations of FPOC, CPOC, and DIC. The tributaries with significant upland and lowland drainage regions have \( \delta^{13}C \) and concentrations of FPOC, CPOC, and DIC intermediate between the Andean whitewater and lowland blackwater rivers (Table 1). Tributaries with significant lowland drainages, i.e. all tributaries excluding the Rio Madeira, had mean values for \([^{13}C]\)FPOC, \([^{13}C]\)CPOC, and \([^{13}C]\)DIC of \(-28.5 \pm 1.2\), \(-28.8 \pm 0.7\), and \(-19.9 \pm 3.5\%\). For each C species the mean lowland river \( \delta^{13}C \) was significantly \((P < 0.01)\) lower than the mean main-channel (Vargem Grande-Obidos) values of \(-27.2 \pm 0.5\), \(-27.9 \pm 0.4\), and \(-14.0 \pm 1.6\%\), respectively. Cai et al. (1988) found a similar \([^{13}C]\)POC trend for rivers in the Amazon basin, with the highest values (up to \(-24.5\%\)) for rivers in the Peruvian Andes and the lowest values (down to \(-33\%\)) for lowland rivers.

We made only six individual \([^{13}C]\)DOC measurements on four tributaries. These few \([^{13}C]\)DOC results agree with the trend in \([^{13}C]\)POC, i.e. the Rio Madeira had the highest and the lowland blackwater rivers had the lowest \([^{13}C]\)DOC values.

Table 1. The \( \delta^{13}C \) and concentration of POC and DIC for rivers in the Amazon basin. Data represent mean \pm 1 SD for cruises 2–8 (not determined—ND).

<table>
<thead>
<tr>
<th>Category*</th>
<th>River</th>
<th>([^{13}C])FPOC (%)</th>
<th>FPOC (mg liter(^{-1}))</th>
<th>([^{13}C])CPOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andean whitewater</td>
<td>Amazon†</td>
<td>(-26.8 \pm 0.3)</td>
<td>3.65 \pm 1.1</td>
<td>(-27.8 \pm 0.4)</td>
</tr>
<tr>
<td></td>
<td>Madeira</td>
<td>(-26.8 \pm 0.5)</td>
<td>2.75 \pm 2.2</td>
<td>(-27.4 \pm 0.4)</td>
</tr>
<tr>
<td>Andean whitewater with</td>
<td>Ica</td>
<td>(-28.3 \pm 0.7)</td>
<td>1.39 \pm 0.37</td>
<td>(-28.6 \pm 0.7)</td>
</tr>
<tr>
<td>large lowland drainage</td>
<td>Japura</td>
<td>(-28.2 \pm 1.1)</td>
<td>1.34 \pm 0.36</td>
<td>(-28.8 \pm 0.1)</td>
</tr>
<tr>
<td>Lowland whitewater</td>
<td>Jurua</td>
<td>(-28.9 \pm 0.8)</td>
<td>1.66 \pm 0.63</td>
<td>(-29.3 \pm 1.8)</td>
</tr>
<tr>
<td></td>
<td>Purus</td>
<td>(-28.8 \pm 0.9)</td>
<td>1.03 \pm 0.54</td>
<td>(-29.9 \pm 1.7)</td>
</tr>
<tr>
<td>Lowland blackwater</td>
<td>Negro</td>
<td>(-28.2 \pm 0.9)</td>
<td>0.46 \pm 0.21</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>Jutai</td>
<td>(-30.1 \pm 2.6)</td>
<td>0.92 \pm 0.25</td>
<td>(-29.1 \pm 1.1)</td>
</tr>
</tbody>
</table>

* Based on Stafford and Edmond (1983).
† Main channel at Vargem Grande.
The lower δ¹³C values measured on POC carried by lowland- vs. upland-draining rivers provide a means to identify the source region for POC input to the Amazon River. The difference between the [¹³C]POC in lowland- and Andean-draining rivers likely reflects differences in the sources of plant material from these regions. A global trend toward ¹³C-enriched leaf material at high altitudes was observed by Korner et al. (1988) who found that plants growing at 2,500–6,500 m had a mean leaf δ¹³C of −26.5‰ vs. a mean leaf δ¹³C of −28.8‰ for lowland plants; the δ¹³C range they observed overlaps with the −30 to −26.8‰ range measured on FPOC in lowland- vs. upland-draining rivers in the Amazon basin (Table 1). The mean [¹³C]FPOC and [¹³C]CPOC values of −28.5±1.2 and −28.8±0.7‰ for lowland rivers is similar to the mean δ¹³C values of −28±1 and −30±1‰ measured on wood and leaf material from 15 of the most abundant tree species in the igapo, varzea, and terra firme forests of the lowland Amazon basin (Hedges et al. 1986). Diagenetic alteration of organic material is a less likely explanation of the [¹³C]POC trend observed in Amazon basin rivers because there is typically <1‰ difference between the δ¹³C values for FPOC and CPOC in each river (Table 1), despite the significant difference in the diagenetic state of these organic C pools (Hedges et al. 1986). In comparison, there is a >3‰ range in [¹³C]FPOC for rivers in the Amazon basin (Table 1).

The ¹³C composition of the FPOC in the Amazon River provides a quantitative measure of the proportion of lowland- vs. upland-derived POC exported at Obidos; FPOC composes 90% of the total suspended POC in the main channel (Richey et al. 1990). The flux-weighted annual mean [¹³C]FPOC of −27.4‰ measured at Obidos implies that ~35% of the FPOC was derived from the lowland Amazon basin, if one uses a simple mixing ratio and assumes the mean [¹³C]FPOC values of −28.5‰ measured on lowland rivers and −26.8‰ measured at Vargem Grande and for the Rio Madeira (Table 1) represent lowland and upland source material, respectively. More likely, the lowland FPOC input was significantly greater than 35% because the upland end-member [¹³C]FPOC value of −26.8‰ probably included some lowland FPOC material. If the high δ¹³C values, up to −24.5‰, measured on suspended POC for headwater rivers in the Peruvian Amazon by Cai et al. (1988) were more representative of the pure upland end-member, a much higher lowland FPOC contribution would result. Thus FPOC derived from the lowland Amazon basin contributed a significant portion (>35%) of the FPOC exported by the Amazon River, in contrast to the bulk suspended sediment of which <15% is derived from the lowland basin (Gibbs 1967; Meade et al. 1985).

Lowland tributary input of FPOC, CPOC, and DIC should yield downriver main-channel decreases in δ¹³C until the confluence of the Rio Madeira at 1,220 km. The expected downriver decreases in [¹³C]FPOC, [¹³C]CPOC, and [¹³C]DIC are observed, with the notable exception of [¹³C]CPOC during falling water (Fig. 3), suggesting that tributary inflow dominates the ¹³C composition of POC and DIC in the Amazon River. To quantify the contribution that tributary inflow makes to the ¹³C composition of POC and DIC in the Amazon River, we compare the δ¹³C values measured at Obidos with the values expected based on upriver inputs at Vargem Grande—the sum of all the tributary inputs and input from the floodplain; this approach is similar to that taken by Richey et al. (1990) to calculate flux imbalances for the major C species in the main channel. The expected δ¹³C at Obidos is calculated from a ¹³C flux balance as follows:

Table 1. Extended.

<table>
<thead>
<tr>
<th>CPOC (mg liter⁻¹)</th>
<th>[¹³C]DIC (%)</th>
<th>DIC (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.74±0.17</td>
<td>−12.4±0.6</td>
<td>1,042±122</td>
</tr>
<tr>
<td>0.52±0.45</td>
<td>−14.5±1.7</td>
<td>535±42</td>
</tr>
<tr>
<td>0.25±0.13</td>
<td>−19.7±0.9</td>
<td>251±77</td>
</tr>
<tr>
<td>0.19±0.09</td>
<td>−17.7±2.7</td>
<td>313±60</td>
</tr>
<tr>
<td>0.18±0.08</td>
<td>−16.6±2.6</td>
<td>933±172</td>
</tr>
<tr>
<td>0.16±0.07</td>
<td>−17.9±2.3</td>
<td>599±98</td>
</tr>
<tr>
<td>ND</td>
<td>−24.2±2.3</td>
<td>118±58</td>
</tr>
<tr>
<td>ND</td>
<td>−22.5±2.8</td>
<td>340±148</td>
</tr>
</tbody>
</table>
\[ ^{13}C_{ob} = \frac{[(Q_{vg} \cdot C_{vg} \cdot ^{13}C_{vg}) + (Q_{t} \cdot C_{t} \cdot ^{13}C_{t})]}{(Q_{vg} \cdot C_{vg}) + (Q_{t} \cdot C_{t}) + (Q_{r} \cdot C_{r})} \]  

where \(^{13}C\) is the \(\delta^{13}C\) of the POC or DIC (\%), \(Q\) the discharge (m\(^3\) s\(^{-1}\)), \(C\) the POC or DIC concentration (mol m\(^{-3}\)), \(ob\) is Obidos, \(vg\) is Vargem Grande, \(t\) the sum of all measured tributaries, and \(f\) the floodplain. We made a comparison between expected and observed POC and DIC concentrations at Obidos using a similar flux balance:

\[ C_{ob} = \frac{Q_{vg} \cdot C_{vg}}{Q_{vg} + Q_{t} + Q_{r}}. \]

The discharge onto or out of the floodplain is calculated from the discharge imbalance measured between Vargem Grande and Obidos, i.e. \(Q_{f} = Q_{ob} - Q_{vg} - Q_{t}\). The concentration of POC in the water returning from the varzea is assumed zero and a mean value for the DIC concentration and \(^{13}C\)-DIC in the varzea waters is determined from measurements typically of ~25 varzea samples collected on each cruise.

The uncertainty in the predicted \(\delta^{13}C\) values and concentrations was calculated with a bootstrap method (Efron 1981) from the \(\pm 1\) SD error in the FPOC, CPOC, and DIC flux measurements that have been estimated at \(\pm 8\), \(\pm 10\), and \(\pm 5\%\) (Richey et al. 1990) and the error (\(\pm 1\) SD) in the \(\delta^{13}C\) measurement (e.g. \(\pm 0.1\) to \(0.2\%\)). The comparison of predicted vs. measured values (Fig. 5) uses a seasonal time sequence of cruise results (i.e. cruises 6, 3, 7, 4, 5, 2, and 8) that follow a typical annual hydrograph starting at the low-water cruise (cruise 6) in November and progressing through rising (December–June) and then falling water (June–October); this approach facilitates comparison of rising- vs. falling-water trends.

During falling water the predicted FPOC concentrations at Obidos are always less than the measured values (Fig. 5), indicating a nontributary falling-water FPOC source, as concluded by Richey et al. (1990). During rising water the situation is not as clear; for two cruises the predictions equal the measured values and on the other two cruises the predicted values exceed the measurements (Fig. 5). The falling- vs. rising-water trends in FPOC are similar to those observed in fine suspended sediment measurements made during CAMREX (Meade et al. 1985). Whether the falling-water source of fine particles is derived from within-channel sediment resuspension (Meade et al. 1985) or from the floodplain (Richey et al. 1990) is less certain.

During rising water predicted \(^{13}C\)-FPOC values generally were more enriched than the measurements (Fig. 5). We gain insight into the cause of the predicted vs. measured \(^{13}C\)-FPOC trends at Obidos by dividing the Vargem Grande–Obidos section into three reaches (Vargem Grande–Jutica, Jutica–São José do Amatari, and São José do Amatari–Obidos) and examining the flux and isotope balances over each reach; this approach was used by Richey et al. (1990). The concentrations and \(\delta^{13}C\) values were predicted at the downriver end of each reach using the same procedure described by Eq. 1 and 2 and compared to measured values (Fig. 6).

The predicted \(^{13}C\)-FPOC values in reach 1 (Vargem Grande–Jutica) generally were higher than measured even though the predicted FPOC concentrations show no consistent difference from measurements. The predicted \(^{13}C\)-FPOC and concentration trends in reach 1 imply that main-channel FPOC material often was replaced with \(^{13}C\)-depleted FPOC. The source region for \(^{13}C\)-depleted FPOC must be the lowland portion of the basin, as discussed above and seen in the data presented in Table 1. One possible replacement mechanism is the concurrent deposition of fine suspended sediment and erosion of bank soils containing lowland-derived, \(^{13}C\)-depleted (relative to the main channel) FPOC. Although deposition and erosion likely occur throughout the Vargem Grande–Obidos section, the effect on main-channel \(^{13}C\)-FPOC would be strongest in reach 1 where the main-channel \(^{13}C\)-FPOC is most enriched relative to the lowland \(^{13}C\)-FPOC, i.e. there is a downriver drop in the rate of \(^{13}C\)-FPOC decrease (Fig. 3) as the cumulative lowland FPOC contribution increases.

The constant downriver \(^{13}C\)-FPOC mea-
Fig. 5. Concentrations and $\delta^{13}$C values of FPOC, CPOC, and DIC measured at Obidos (▲) compared to values predicted (□) with Eq. 1 and 2 for cruises 2–8, as discussed in text. The ±1 SD uncertainty in the predicted values, averaged over all cruises, is represented by the error bars. The time sequence follows a typical hydrograph starting at low water (November), progressing through rising water (December–June), and then falling water (June–October). The sequence of cruises is 6, 3, 7, 4, 5, 2, and 8.

measured between Jutica and Sao Jose do Amatari (reach 2) during both rising and falling water (Fig. 3) suggests that lowland FPOC input was small in this reach. The proportion of tributary-derived FPOC is smallest in reach 2 (i.e. tributaries contribute 9% of upriver input vs. 23 and 36% for reaches 1 and 3). Insignificant nontributary lowland FPOC input in reach 2 is indicated by the good agreement between predicted and observed $[^{13}]$C-FPOC (Fig. 6).

A substantial nontributary FPOC source exists between Sao Jose do Amatari and Obidos (reach 3) during falling water based
Fig. 6. Concentrations and δ13C values of FPOC, CPOC, and DIC measured at Jutica, São José do Amatari, and Obidos (△) compared to values predicted (□) from the three-reach model for cruises 2–8. Predicted values are calculated with Eq. 1 and 2, as discussed in the text. The cruise sequence is the same as in Fig. 5. Error bars represent ±1 SD for the predicted values.
on the underestimated predictions of FPOC concentrations at Obidos (Fig. 6); a similar observation was made by Richey et al. (1990). Meade et al. (1985) also identified the Sao Jose do Amatari–Obidos reach as a site of fine suspended sediment input during falling water based on suspended sediment balance calculations. The predicted falling-water $^{13}$C-FPOC values in reach 3 are lower than observed for two of the falling-water cruises (Fig. 6), implying that the FPOC source likely is $^{13}$C enriched. The only source of $^{13}$C-FPOC material that is enriched in $^{13}$C, vs. the main-channel $^{13}$C-FPOC in this reach, is derived from the Rio Madeira (Table 1). Thus resuspension of previously deposited fine sediments carried by the Rio Madeira during falling water is a possible mechanism to explain the predicted vs. observed trends in FPOC and $^{13}$C-FPOC between Sao Jose do Amatari and Obidos.

In summary, two processes likely are occurring over the Vargem Grande to Obidos section that contribute substantially to the amount of FPOC exported at Obidos: remobilization of lowland floodplain fine sediments (e.g. via bank erosion) and resuspension during falling water of previously deposited Rio Madeira fine sediments in the Sao Jose do Amatari–Obidos reach. $^{13}$C-FPOC distinguishes between these two FPOC sources because the $\delta^{13}$C of the FPOC derived from the lowland basin is significantly depleted vs. the Rio Madeira. Overall the lower $^{13}$C-FPOC values measured in the main channel during falling vs. rising water (Fig. 3) imply that input of lowland-derived FPOC was greatest during falling water. The increased input of lowland-derived FPOC during falling waters does not seem restricted to the section between Vargem Grande and Obidos as the lowest $^{13}$C-FPOC values at Vargem Grande were measured during falling water.

The predicted CPOC concentrations and $^{13}$C-CPOC values at Obidos are higher than observed during rising water (Fig. 5), indicating a loss of $^{13}$C-enriched CPOC. The middle reach between Jutica and Sao Jose do Amatari is the likely site of the CPOC loss (Fig. 6). A possible CPOC loss mechanism has been identified by Richey et al. (1990), who observed a substantial increase ($>2\times$) in the wt% C of the CPOC immediately upstream of the confluence of the Rio Madeira (at $\sim 1,220$ km) during rising water. They attributed this observation to the preferential deposition of heavier coarse sand grains vs. lighter coarse plant debris during the period when the main channel is dammed by the Rio Madeira. $^{13}$C-CPOC showed a consistent downriver decrease at this same location in the main channel (1,000–1,200 km) during rising water (Fig. 3) which implies that the preferentially deposited coarse sediment was enriched in $^{13}$C relative to the bulk suspended CPOC.

During falling water the predicted CPOC concentrations and $^{13}$C-CPOC values at Obidos were lower than observed (Fig. 5), implying a CPOC source enriched in $^{13}$C relative to main-channel CPOC. The reach between Jutica and Sao Jose do Amatari was the primary site of the $^{13}$C-enriched CPOC input (Fig. 6). This midreach CPOC source shows up in the downriver $^{13}$C-CPOC trends, i.e. there was a sharp $^{13}$C-CPOC increase between Jutica and Anori (500–874 km) during each falling-water cruise (Fig. 3). Since there is no tributary inflow within the 500–874-km reach, the $^{13}$C-CPOC increase must result from a non-tributary source. One explanation of the increase is remobilization of the $^{13}$C-enriched CPOC deposited in reach 2 during a previous rising-water period, as discussed above. The measured falling-water $^{13}$C-CPOC increase occurred between 500 and 874 km, however, well upriver from the site of the percent C increase (Richey et al. 1990) and $^{13}$C-CPOC decrease (Fig. 3) that occurred at $\sim 1,200$ km, just above the Rio Madeira confluence, during rising water.

Alternatively the falling-water, downriver $^{13}$C-CPOC increase between Jutica and Sao Jose do Amatari could result from input of varzea soil. Victoria et al. (in press) found that the coarse fraction of varzea soils preferentially accumulates organic matter derived from varzea grasses, predominantly Paspalum repens and Echinocloa polystachya, which are C$_4$ plants with a $\delta^{13}$C = $-13\%$ (Hedges et al. 1986). A mean $\delta^{13}$C value of $-25\pm3\%$ ($n = 11$) was measured on the coarse fraction (>50 $\mu$m) of varzea soil sam-
amples collected between Itapeua (680 km) and Obidos (Victoria et al. in press). The main-channel \(^{14}C\)CPOC is very sensitive to varzea grass input; if CPOC input from C\(_4\) varzea grasses contributed only 5\% of the CPOC input from tributaries, the predicted falling-water \(^{14}C\)CPOC values would match the measurements at Obidos. Previously, Hedges et al. (1986) estimated that up to 10\% of the main-channel CPOC could be composed of C\(_4\) grass material, based on the lignin and \(^{13}C\) compositions of the CPOC and its primary source material (i.e. leaf and wood tissue).

Lowland tributary input of \(^{13}C\)-depleted DIC would be expected to decrease the \(^{13}C\)DIC downriver from Vargem Grande to the confluence of the upland-draining Rio Madeira, as observed (Fig. 3). Although CO\(_2\) gas exchange and within-river respiration affect downriver DIC concentrations (Richey et al. 1990), we can examine the tributary effects on the downriver DIC trends by making the same comparison made for FPOC and CPOC. Thus we use Eq. 1 and 2 to calculate expected \(^{13}C\)DIC values and DIC concentrations, respectively, assuming that water discharge from the varzea carries with it a mean DIC concentration and \(^{13}C\)DIC value determined from varzea samples measured on each cruise. The effect of including the varzea DIC flux is small, i.e. the average difference between DIC concentrations predicted with or without the varzea DIC flux term is 4\%, within the \(\pm 5\%\) error (\(\pm 1 \text{ SD}\)) of the DIC flux calculation (Richey et al. 1990).

The predicted rising- and falling-water trends in DIC concentration and \(^{13}C\)DIC at Obidos agree well with the measurements (Fig. 5), suggesting that tributary inflow exerts a major control on DIC in the main channel. Apparent dominance of DIC by tributary input in the main channel is surprising in light of the high rates of respiration measured in the river (Devol et al. 1987; Richey et al. 1990). This apparent contradiction is resolved if one considers that the dissolved CO\(_2\) concentration in the main channel was in dynamic equilibrium (i.e. CO\(_2\) input from respiration was approximately offset by CO\(_2\) gas evasion as discussed by Devol et al. 1987).

Applying the concept of dynamic equilibrium to the \(^{13}C\) composition of the dissolved CO\(_2\), one would conclude that the \(^{13}C\):\(^{12}C\) of the CO\(_2\) produced during respiration was equal to the \(^{13}C\):\(^{12}C\) of the CO\(_2\) lost during evasion. We can estimate the \(\delta^{13}C\) of the CO\(_2\) lost during evasion based on the \(\delta^{13}C\) of the DIC and the equilibrium isotopic fractionation that exists between dissolved CO\(_2\) and HCO\(_3^-\). The mean main-channel \(^{13}C\)DIC was \(-14.0\%\) and typically the DIC was composed of \(84\%\) HCO\(_3^-\) and \(16\%\) dissolved CO\(_2\); CO\(_3^{2-}\) concentrations were essentially zero for all rivers sampled during CAMREX. Given an equilibrium fractionation of \(8.7\%\) between HCO\(_3^-\) and dissolved CO\(_2\) at 27\(^\circ\)C (Mook et al. 1974), with the CO\(_2\) being more depleted in \(^{13}C\), the mean \(\delta^{13}C\) of the dissolved CO\(_2\) should have been \(-21.3\%\) after accounting for the relative concentrations of HCO\(_3^-\) and CO\(_2\).

During CO\(_2\) gas transfer from water to air there is a \(\sim 1\%\) depletion in the \(\delta^{13}C\) of the CO\(_2\) (Seigenthaler and Munnich 1981). Thus the \(\delta^{13}C\) of the CO\(_2\) evading from the Amazon River should have been about \(-22\%\). Independently we determined the \(\delta^{13}C\) of the CO\(_2\) lost from the river to be \(-22\%\) by measuring the diurnal change in the \(\delta^{13}C\) of CO\(_2\) in air above the river (Quay et al. 1989).

If a dynamic equilibrium existed for dissolved CO\(_2\), then the \(\delta^{13}C\) of the CO\(_2\) produced during respiration was \(-22\%\).

The \(\delta^{13}C\) of the CO\(_2\) produced during respiration was determined independently with bottle incubations of river water collected near Jutica during a CAMREX cruise in November 1988. In this experiment the DIC concentration and \(^{13}C\)DIC in a 20-liter carboy was measured initially and after 5 d. DIC concentration increased from 496 to 630 \(\mu\)M with a corresponding decrease in \(^{13}C\)DIC from \(-11.9\) to \(-14.1\%\). A value of \(-22\pm3\%\) (\(\pm 1 \text{ SD}\)) was calculated for the \(\delta^{13}C\) of the CO\(_2\) added during the bottle incubation, in good agreement with the \(-22\%\) value determined by assuming that \(^{13}C\)DIC was in dynamic equilibrium.

Main-channel \(^{13}C\)DIC was controlled by the \(^{13}C\):\(^{12}C\) of the CO\(_2\) produced during respiration and the relative concentrations of dissolved HCO\(_3^-\) and CO\(_2\). The \(\delta^{13}C\) of the dissolved CO\(_2\) was about equal to the \(\delta^{13}C\) of the respired CO\(_2\), assuming that dynamic equilibrium existed. Because the \(\delta^{13}C\) of the
dissolved HCO$_3$ is 8.7% enriched relative to the dissolved CO$_2$ (Mook et al. 1974), the lower the ratio of HCO$_3$ to dissolved CO$_2$, the lower the [${}^{13}$C]DIC. The dependence of [${}^{13}$C]DIC on HCO$_3$: CO$_2$ is observed in the strong correlation between [${}^{13}$C]DIC and pH within the main channel ($r^2 = 0.74$, $n = 77$) and for all the rivers ($r^2 = 0.81$, $n = 49$) sampled during CAMREX (Fig. 7). The HCO$_3$: CO$_2$ ratio is directly correlated with pH, and the pH of the lowland rivers is lower than the main channel (Fig. 7). Thus discharge from the acidic lowland tributaries coupled with high within-river respiration rates causes the downriver [${}^{13}$C]DIC decrease; similarly the lower falling- vs. rising-water [${}^{13}$C]DIC values observed in the main channel (Fig. 3) are explained by the higher inputs of acidic lowland tributaries and draining varzea during falling water.

A δ$^{13}$C of about −22‰ for CO$_2$ produced during respiration was ~6‰ enriched vs. the mean δ$^{13}$C of −28‰ for the POC and DOC in the river. The difference between the δ$^{13}$C of the respired CO$_2$ and reduced organic C in the main channel is likely explained by selective respiration of a 13C-enriched component of the organic C pool, because there is little or no measurable 13C fractionation during respiration (e.g. Smith 1971).

We hypothesize that the respired CO$_2$ was 6‰ enriched vs. the organic C in the river because of the preferential oxidation of organic C derived from C$_4$ varzea grasses at about −13‰. A δ$^{13}$C of −22‰ for respired CO$_2$ requires that ~40% of the within-river respiration was supported by varzea grasses, using a simple mixing ratio and assuming that the CO$_2$ produced by oxidation of C$_3$ and C$_4$ plant tissues has δ$^{13}$C values of −28 and −13‰. An annual average respiration rate of 1.6 × 10$^7$ t C yr$^{-1}$ integrated over the main channel between Vargem Grande and Obidos (Richey et al. 1990) implies an annually averaged loss of varzea grass material to within-river respiration of 0.6 × 10$^7$ t C yr$^{-1}$, assuming 40% C$_4$ contribution.

Independently, Junk (1985) estimated a total macrophyte (predominantly the C$_4$ plants $P$. repens and $E$. polystachya) productivity of 8 × 10$^7$ t C yr$^{-1}$ for the entire floodplain of which ~12% (i.e. 1 × 10$^7$ t C yr$^{-1}$) is available for export. Correcting this value for the floodplain area of ~50,000 km$^2$ between Vargem Grande and Obidos yields a floodplain grass export rate of 0.5 × 10$^7$ t C yr$^{-1}$. The rough estimate of floodplain grass export by Junk agrees well with our calculated rate of varzea grass-supported respiration in the river. The estimate by Junk that ~50%, excluding dead wood, of the organic C available for export from the floodplain is macrophyte derived agrees well with our estimate that 40% of the organic material being oxidized in the river is derived from macrophytic C$_4$ plants. The similarity between both the total amount of C$_4$ carbon and the proportion of C$_3$ vs. C$_4$ plant material exported by the floodplain and oxidized in the river suggests that the floodplain is a likely source of the organic C substrate being respired in the Amazon River.

The estimated productivity of 15 × 10$^7$ t C yr$^{-1}$ for the Amazon floodplain (Junk 1985) exceeds by >4× the TOC exported by the Amazon River at Obidos, underscoring the potential of the floodplain as an
important source of C for the river. Junk’s (1985) estimate that ~30% of the total floodplain C production is available for export about equals the TOC flux at Obidos. The downriver trends in $^{13}$C/POC and $^{13}$C/DIC measured during CAMREX suggest that the lowland drainage basin and floodplain are active sources of C for the main channel of the river, especially during falling water. Specifically, $^{13}$C/POC indicates that particulate C derived from the lowland basin contributes at least 35% of the POC exported by the Amazon River. The $^{13}$C/DIC results suggest that organic C derived from varzea grasses contributes ~40% of the substrate for within-river respiration.

Downriver $^{13}$C trends in DIC and CPOC measured during CAMREX provide evidence that the aquatic and terrestrial macrophytes and flooded forests in the floodplain are likely sources of labile organic C input to the main channel. The diffuse nature of the floodplain organic C source and short within-river turnover times make it difficult to detect the labile organic C pool. The water residence time of ~2 weeks between Vargem Grande and Obidos and the apparently low main-channel concentration of labile C imply a short turnover time (i.e., days). The labile C source strength must be large (i.e., equal to ~50% of the TOC exported at Obidos) to sustain the high measured rates of within-river oxidation (Rich ey et al. 1990). In contrast most of the organic C in the main channel (i.e., the humic and fulvic fractions of the DOC and the FPOC which together compose two-thirds of the TOC) is refractory (Ertel et al. 1986). Thus organic C produced on the varzea either is oxidized on the floodplain or in the rivers and has little chance to reach the ocean. The bulk of the organic C that the Amazon River delivers to the ocean is refractory once it passes through the respiratory filter of the river.

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A modified fiber-optic light microprobe to measure spherically integrated photosynthetic photon flux density: Characterization of periphyton photosynthesis–irradiance patterns

Abstract—A fiber-optic light sensor was modified by adding a broadband filter (420–750 nm) to sense photosynthetic photon flux density. A sphere of acrylic paint added to the fiber tip allowed estimation of spherically integrated irradiance. The modified light probe and an O₂ microelectrode allowed 250-μm-resolution photosynthesis–irradiance profiles to be determined. In Ulothrix-dominated periphyton, there was greater ability to utilize low light as depth increased from 0 to 750 μm, and photosynthesis was not saturated up to 1,800 μmol quanta m⁻² s⁻¹. In a benthic diatom assemblage, light attenuation was greater than in the Ulothrix filaments in the top 250 μm, photosynthesis approached saturation at 1,000 μmol quanta m⁻² s⁻¹, and photosynthetic rates were extremely low at the 250- and 500-μm depths.

Periphyton can account for a significant portion of primary production in shallow aquatic environments. Photosynthetic production in periphyton communities is dependent on photon flux rates. Given the complex architecture of many periphyton communities, little is known about variation in ambient spherically integrated light fields and associated photosynthetic responses at relevant spatial scales.

The upper layers of periphyton can attenuate a large portion of incoming light (Howard-Williams and Vincent 1989; Losee and Wetzel 1983; Meulemans 1987). Light microsensors have sensed light gradients in natural periphyton assemblages with 100-μm vertical resolution (Dodds

Submitted: 5 February 1987
Accepted: 22 May 1990
Revised: 4 November 1990