Oxidation and Reduction Rates for Organic Carbon in the Amazon

Mainstream Tributary and Floodplain, Inferred from
Distributions of Dissolved Gases

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(NASA-CR-182943) OXILATION AND REDUCTION BATES FOR OBGANIC CAREON IN THE ALAZON N88-25062 EAINSTREAM TRIETTERY AND FICCIFIAIN, INFERRED FROM DISTRIBUTIONS OF DISSCLUED Unclas GASES (Washington Univ.) 28 p CSCL 13B G3/45 0146699

Abstract. Concentrations of CO<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O in the Amazon River system reflect an oxidation-reduction sequence in combination with physical mixing between the floodplain and the mainstem. Concentrations of CO<sub>2</sub> ranged from 150  $\mu M$  in the Amazon mainstem to 200-300 µM in aerobic waters of the floodplain, and up to 1000 µM in oxygen-depleted environments. Apparent oxygen utilization (AOU) ranged from 80 μM to 250 μM. Methane was highly supersaturated, with concentrations ranging from 0.06 µM in the mainstem to 100 µM on the floodplain. Concentrations of N<sub>2</sub>O were slightly supersaturated in the mainstem, but were undersaturated on the floodplain. Fluxes calculated from these concentrations indicated decomposition of 1600 g C m<sup>-2</sup>y<sup>-1</sup> of organic carbon in Amazon floodplain waters. Analysis of relationships between CH<sub>4</sub>, O<sub>2</sub> and CO<sub>2</sub> concentrations indicated that approximately 50% of carbon mineralization on the floodplain is anaerobic, with 20% lost to the atmosphere as CH<sub>4</sub>. The predominance of anaerobic metabolism leads to consumption of N<sub>2</sub>O on the floodplain. Elevated concentrations of CH<sub>4</sub> in the mainstem probably reflect input from the floodplain, while high levels of CO<sub>2</sub> in the mainstem are derived from a combination of varzea drainage and in situ respiration.

Metabolic processes in rivers change dramatically with increasing river size (Vannote et al., 1980). Much is known of small streams, yet the sequence of metabolic processes operating in very large rivers is essentially unknown. Many large river systems are located in the tropics, have extensive floodplains, and are regions of high primary and secondary production (Welcomme, 1979). Large rivers may be very important to global biogeochemistry. For example, recent studies suggest that tropical river basins may be strong sources of such gases as methane to the troposphere (Mayer et al., 1982; Keller et al., 1983), indicating the potential for global influence by the highly productive, strongly reducing aquatic environments associated with these rivers.

The productivity of large tropical systems and the apportionment of production between flowing waters and floodplain are not well known. There is little evidence detailing linkages between mainstem, floodplain and off-channel processes in these rivers (cf. Welcomme, 1979). Analysis of patterns of organic matter production in such environments is complicated by the large scale and the temporal and spatial heterogeneity of major habitats. Hence it is difficult to extrapolate from traditional, site-intensive studies to determine mesoscale patterns of metabolic processes in large systems.

Distributions of biologically reactive dissolved gases provide useful indices for rates of production and consumption of organic matter (Odum, 1957). We attempt here to use such distributions to integrate the effects of metabolic transformation over large areas and over time in the Amazon River system. We examine the oxidation and reduction of organic carbon in mainstem, tributary, and floodplain waters by analyzing the spatial and

temporal distributions of dissolved carbon dioxide (CO<sub>2</sub>), oxygen (O<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O). The distribution of CO<sub>2</sub> provides a measure of total rates for mineralization of carbon, and the distributions of CH<sub>4</sub>, N<sub>2</sub>O, O<sub>2</sub> and CO<sub>2</sub> help elucidate the relative importance of aerobic oxidation, anaerobic oxidation, and methanogenesis.

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### The Amazon River System

The Amazon River system consists of a 6700 km main channel and floodplain fed by tributaries that drain 6 million km<sup>2</sup> of Andean and lowland basins. The structure of a representative region is represented in Figure 1. The extensive floodplain, or *varzea* represents 100,000 km<sup>2</sup> of lowlands connected to the main channel via a network of channels, or *paranas*. It is periodically inundated by the annual 10-m rise and fall of the river. During high water much of the floodplain is under water and the lakes (isolated oxbows and depressions) are typically 6-8 m deep. Some lakes stratify on a time scale of weeks (Melack and Fisher 1983; Tundisi et al., 1984). As the river falls, land is reexposed and the lakes become isolated from the main channel, with depths decreasing to 1-2 m.

Primary production occurs almost exclusively in and along the extensive floodplain, and not in the main channel (Junk, 1970; Sioli, 1975; Wissmar et al., 1981). In central

Amazon lakes, plankton production is initiated as river water enters the floodplain at rising water, dropping its sediment load (Schmidt 1970, 1973; Junk 1970, 1973; Fisher and Parsley 1979). Rooted macrophyte growth in these lakes and along the river banks starts at low water; by high water, much of this material has been uprooted, and either decays in situ or is carried away (Junk, 1973, 1976, 1985). In the Amazon River mainstem, dissolved CO<sub>2</sub> is supersaturated by a factor of about 10 and in situ O<sub>2</sub> consumption is on the order of several μM O<sub>2</sub>hr<sup>-1</sup> (Richey et al., 1980; Wissmar et al., 1981; Devol et al., in press). As the summation of these processes, Sioli (1975) and Junk (1985) hypothesized that the varzea would be a net exporter of organic matter to the mainstream during falling water.

## Sampling Collection and Analysis

A series of cruises was conducted along a 2000 km reach, from Vargem Grande to Obidos, Brazil, approximately every 4 months at different stages of the hydrograph (Richey et al., 1986). A complete suite of hydrological and chemical measurements were made at eleven mainstem and seven tributary stations. Extensive sampling of the flood-plain took place in the vicinity of these stations. Cruises were numbered 1 (April-May 1982, mid-late rising water), 2 (August-September 1982, falling water), 3 (November-December 1982, early rising water), 4 (March-April 1983, mid-rising water following brief falling period) 5 (June-July 1983, post-high water), 6 (October-November 1983, very early rising water), 7 (February-March 1984, mid-rising water), 8 (July-August 1984, post-high water), and 9 (July-August 1985, high water).

Sampling locations were distributed to represent various habitat types: mainstem, tributaries, paranas, surface of standing waters, and bottom of standing waters. At each station along the mainstem samples for dissolved CO<sub>2</sub> and O<sub>2</sub> were taken at 5 sites and for CH<sub>4</sub> and N<sub>2</sub>O at 2 sites, spaced equally across the river, using a Niskin bottle. Samples from the varzea waters were taken at the surface and at the bottom (with lesser frequency) at locations accessible by small outboard, primarily during daylight. Upriver, these included the small, sheltered oxbow-type lakes of the region, as well as flooded fields and forests, paranas and areas covered by dense growths of macrophytes. Downriver, the varzea was sampled mostly in the characteristic large open lakes.

The Niskin bottle was subsampled for measurement of O<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub> by filling 60-ml glass-stoppered BOD bottles to overflowing. Thirty ml Erlenmeyer flasks were used to collect samples for analysis of dissolved inorganic carbon. Determinations of pH were made immediately after collection, using a closed container and a Corning Model 130 pH meter with Orion Ross electrode. Alkalinity was determined by micro-Gran titration (Edmond, 1970). Free dissolved carbon dioxide (CO<sub>2</sub>) was calculated from pH and alkalinity (Skirrow 1975). Stallard (1980) showed that these calculated parameters agreed with those measured by infrared CO<sub>2</sub> analysis, for a variety of Amazon waters, and we found comparable results using gas chromatography. Oxygen concentrations were determined using a YSI Model 58 or Radiometer oxygen meter and electrode standardized as described by Devol (1978), except that nitrogen-purged water was used as the zero solution.

For Cruises 1-8, samples for CH<sub>4</sub> and N<sub>2</sub>O were preserved with HgCl<sub>2</sub>, returned to the laboratory at Harvard University for measurement using flame ionization (FDS) and electron capture gas chromatography, respectively. On Cruise 9, CH<sub>4</sub> was measured immediately on board the research vessel using FID gas chromatography.

## Conceptual framework for analysis of dissolved gas distributions

The rate of change of the concentration, C, of a gas in a water parcel is determined by exchange with the atmosphere (F), biological reactions (B) within the parcel, net physical transport (advection and diffusion) from adjacent parcels or sediments (T), and ionic equilibrium reactions (I),

$$dC/dt = F/H + B + T + I,$$
(1)

where H is depth of the water column and t is time. The flux of gases between atmosphere and water can be calculated using an empirical boundary layer model for gas exchange (Liss and Slater, 1974), calibrated using measurements by Devol et al. (in press) for the Amazon:

$$F = D(C - C_{eq})/z$$
 (2)

where F is the diffusive flux of gas through the air-water interface, D is the molecular diffusion coefficient, z is the empirical thickness of a hypothetical stagnant boundary layer,  $C_{eq}$  is the concentration at equilibrium with the atmosphere and C is the observed concentration in the water.

The terms in Eq. 1 cannot be evaluated solely from observed distributions. We can, however, obtain useful information about these terms for CO<sub>2</sub> and O<sub>2</sub> by considering the ratio of their respective concentrations. For reference, consider an isolated water parcel

at steady state (dC/dt=0) with transport terms T=0 for both  $O_2$  and  $CO_2$ . At ambient conditions (pH 6-7, alkalinity of 500-1000  $\mu$ Eq), with dissolved  $CO_2$  of 100-150  $\mu$ M or higher, the  $CO_2$  produced through respiration remains primarily as dissolved  $CO_2$ , thus term I may be neglected (I=0) for both gases. The principal terms in Eq. 1 would then be biological production/consumption and exchange with the atmosphere. If oxidation were strictly aerobic, then approximately one mole of  $CO_2$  would be evolved per mole of  $CO_2$  consumed. Likewise, for every mole of  $CO_2$  fixed via photosynthesis,  $O_2$  is increased by one mole. Hence  $B_{CO_2}/B_{O_2} = -1$  and

$$D_{CO_2}([CO_2] - [CO_2]_{eq})/z = -D_{O_2}([O_2] - [O_2]_{eq})/z$$
 (5)

The ratio of excess CO<sub>2</sub> to O<sub>2</sub> depletion, defined as Rq, would be given in this case by

$$Rq = -([CO_2] - [CO_2]_{eq})/([O_2] - [O_2]_{eq}) = \frac{D_{O_2}}{D_{CO_2}} = 1.2,$$
(6)

where  $D_{O_2} = 2.1 \times 10^{-5}$  and  $D_{CO_2} = 2.6 \times 10^{-5}$  (Broecker and Peng, 1974). Systematic deviations of Rq from 1.2 provides an indication of anaerobic metabolism. Essentially, Rq is a "riverine respiratory quotient", normalized for differences in diffusion coefficients.

The concentration of  $O_2$  is generally below equilibrium with the atmosphere and the concentration of  $CO_2$  is generally above atmospheric equilibrium. For comparison with Eq. 6 we define the departure of  $O_2$  from atmospheric equilibrium as the apparent oxygen utilization (AOU),

$$AOU = [O_2]_{eq} - [O_2]$$
 (7a)

and similarly define  $CO_2^*$  as

$$CO_2^* = [CO_2] - [CO_2]_{eq}.$$
 (7b)

Anoxia corresponds approximately to AOU  $\approx 250 \mu M$ .

Results from all sites were converted to the defined quantities in (7a) and (7b), and aggregated for mainstem, tributary, parana (surface), lake surface, and lake bottom waters, respectively. "Lake" in this application refers to still as opposed to flowing waters. Data are presented as means ± one standard deviation, unless otherwise noted.

## Results

The aquatic environments of the Amazon were characterized by positive values for  $CO_2^*$  and AOU (i.e. an excess of respiration over photosynthesis), and by a general association between high levels of AOU and high  $CO_2^*$  (Figure 2). Mainstem values for  $CO_2^*$  exceeded levels expected for atmospheric equilibrim (~10 $\mu$ M) by a factor of 10-20, with mean  $CO_2^*$  of  $131 \pm 70 \,\mu$ M. Mainstem  $O_2$  averaged about 35% undersaturated relative to the atmosphere, with mean AOU of  $84 \pm 22 \,\mu$ M (Fig. 2a). The mean  $CO_2^*$  in tributaries was  $180 \pm 116 \,\mu$ M, while AOU averaged  $94 \pm 51 \,\mu$ M.

Gas concentrations on the *varzea* fell, generally, into two categories: (1) aerobic waters where  $CO_2^*$  was less than about 250  $\mu$ M and AOU less than 200  $\mu$ M, and (2) microaerobic or anaerobic waters where  $CO_2^*$  exceeded 250  $\mu$ M and AOU exceeded 200  $\mu$ M (Fig. 2b). The primary linkages between the mainstem and the *varzea*, the *paranas*, had higher mean  $CO_2^*$  (165  $\pm$  102  $\mu$ M) than did the mainstem, where AOU values were similar. However, when AOU was greater than 200  $\mu$ M, the mean  $CO_2^*$  was much larger, 410  $\pm$  90  $\mu$ M.

Lake surface waters are influenced by input from paranas and by local drainages

(Forsberg et al., in review) and by plankton photosynthesis and respiration. As might be expected, lake surface waters had a broader range of gas concentrations than did the mainstem or the *paranas*, with mean values for  $CO_2^*$  of  $190 \pm 95 \,\mu\text{M}$  in the low AOU environments and  $496 \pm 200 \,\mu\text{M}$  where AOU was high. There was a second group of surface waters, generally black water (see Sioli 1985) lakes of low alkalinity, where a very wide range of values was observed for  $CO_2^*$ ,  $214 \pm 141 \,\mu\text{M}$ . Lake bottom waters were generally much more depleted in oxygen and highly enriched in  $CO_2$  than the mainstem, *paranas* or lake surface waters. When AOU was less than  $200 \,\mu\text{M}$ ,  $CO_2^*$  averaged  $244 \pm 90 \,\mu\text{M}$ , while the average for waters with AOU greater than  $200 \,\mu\text{M}$  was  $500 \pm 146 \,\mu\text{M}$ .

Methane concentrations were supersaturated with respect to atmospheric equilibrium in all surface waters (Fig. 3). Even the turbulent mainstem was supersaturated by a factor of 30, with a mean value of  $0.053 \pm .091$  nM (Fig. 3a). Methane concentrations increased exponentially with increasing  $CO_2^*$  in the *varzea*, (Fig. 3b). Variance about the mean was considerable due to high values in anaerobic environments. When AOU was less than 200  $\mu$ M, the overall mean CH<sub>4</sub> in the *paranas*, lake surface, and bottom waters was  $0.38 \pm .69 \mu$ M. In high AOU environments, mean CH<sub>4</sub> in the *paranas*, surface, and bottom waters was  $17.9 \pm 30.7 \mu$ M,  $58.8 \pm 76.8 \mu$ M, and  $55.0 \pm 67.6 \mu$ M, respectively. The resultant overall mean of lake surface samples was  $11.9 \mu$ M. The maximum CH<sub>4</sub> concentrations observed were close to  $100 \mu$ M, where the fugacity of CH<sub>4</sub> is about 1 atm, i.e. bubbles can form.

Nitrous oxide exhibited a distribution pattern very different from the other dissolved gases (Fig. 4). Mainstem  $N_2O$  averaged  $13.4 \pm 2.5$  nM, or about 1.5 times saturation (Fig. 4a). Tributary values were slightly lower, averaging  $10.8 \pm 3.3$  nM. Nitrous oxide levels on the *varzea* decreased with increasing  $CO_2^*$  and AOU, in contrast with results for  $CH_4$  (Fig. 4b). The overall *varzea* mean was  $8.9 \pm 3.7$  nM in waters with AOU less than  $200 \mu M$ , and  $4.4 \pm 2 n M$  for waters with AOU greater than  $200 \mu M$ . There was essentially no dissolved  $N_2O$  in anoxic waters.

To investigate potential sources of the excess CH<sub>4</sub> in the main channel, cross-channel transects were taken on cruise 9 at 5 locations equally spaced across the main channel. Significant cross-channel gradients were observed at all stations, (Fig. 5). Concentrations of CH<sub>4</sub> at most stations were greatest off one bank (usually the left, or north bank), fell at mid-channel, then either remained low or increased toward the opposite bank.

#### Discussion

The nominal value for Rq in aerobic conditions (=1.2) is compared to the observations in Table 1. All measured values for Rq were larger than 1.2. The highest values, Rq = 1.8 to 2.1, were found in varzea waters where AOU > 200  $\mu$ M. Slightly lower values, Rq = 1.7 to 1.9, were observed in tributaries and in aerobic surface and bottom waters (AOU < 200  $\mu$ M), and the lowest values, about 1.4, were found in mainstem and well oxygenated *parana* waters. The standard error of the mean for Rq in each type of environment was less than 10% of mean value.

Observed Rq values indicate that there is substantial surplus  $CO_2^*$  relative to AOU in all waters. It follows that  $CO_2$  has been produced without  $O_2$  consumption, i.e. anaerobically. The surplus  $CO_2^*$  increases sequentially from the mainstem to paranas and from paranas to anoxic varzea waters. Paranas have Rq values reflecting source waters, with low Rq when mainstem waters are flowing onto the varzea and higher Rq values when water is flowing off the varzea into the mainstem. Tributaries are intermediate.

Devol et al. (in press, 1986) estimated a boundary-layer thickness  $z \approx 50 \, \mu m$ , for air-water exchange on the mainstem, and  $z = 300 \, \mu m$  for the *varzea*, using floating chambers. These experiments may be expected to underestimate water-air exchange in the still waters of the *varzea* (Brutsaert and Jirka, 1984; Wannikopf et al., 1985; Devol et al., in press, 1986), and we therefore adopted an estimate of  $z \approx 150 \, \mu m$  for the *varzea*. Note that, in the discussion which follows, we are most interested in examining ratios between fluxes of  $CO_2$ ,  $O_2$ ,  $CH_4$  and  $N_2O$ , and therefore the particular value chosen for z is relatively unimportant.

Estimates of air-water gas exchange flux F are shown in Table 2. The estimate for the mainstem evasive flux of CO<sub>2</sub> was 2100 gC m<sup>-2</sup>y<sup>-1</sup>, approximately equal to the riverine transport of dissolved inorganic carbon (Stallard and Edmond 1983; Devol et al., in press, 1986). The mean *varzea* flux was somewhat lower, 1300 gC m<sup>-2</sup>y<sup>-1</sup>.

The diffusive flux of  $CH_4$  calculated for the mainstem, 1 gC m<sup>-2</sup>y<sup>-1</sup> is considerably less than the 65 gC m<sup>-2</sup>y<sup>-1</sup> for the *varzea*. The flux calculated from dissolved  $CH_4$  concentrations accounts only for the diffusive component of the total flux. Ebullition

(bubbling) is observed in the *varzea* on many occasions, and could be the main mechanism of transport from the sediments to the overlying waters and subsequently to the atmosphere. Devol et al. (in review) and Crill et al. (in review) made direct measurements of both ebullition and evasion, showing that ebullition accounts for 70 to 90% of the CH<sub>4</sub> flux. Hence, we estimate the total CH<sub>4</sub> flux from the *varzea* to be on the order of 300 gC m<sup>-2</sup>y<sup>-1</sup>. This value is comparable to fluxes observed in freshwater swamps in Louisiana (160 gC m<sup>-2</sup>y<sup>-1</sup>, DeLaune et al., 1983), and is significantly greater than fluxes in most temperate swamps (4 to 40 gC<sup>-2</sup>y<sup>-1</sup> Harriss et al. 1981, 1982). The mean emission rate from the entire central Amazon basin has been estimated to be about 5 gC m<sup>-2</sup>y<sup>-1</sup> (Wofsy, 1985). However, the soils of terra firme forests consume CH<sub>4</sub> from the atmosphere (Keller et al., 1983, 1986). The large floodplain area and high emission rates for CH<sub>4</sub> indicate that Amazon floodplain could provide a major part of the observed regional emissions of CH<sub>4</sub>.

A conceptual model can now be presented to describe the sequences of biological and physical processes which produce the observed dissolved gas concentrations. Total. decomposition of organic carbon is represented by the sum of CO<sub>2</sub> and CH<sub>4</sub> fluxes; thus, from Table 2, biogenic emissions are estimated to be

$$F_{CO_2} + F_{CH_4} = 1300 + 300 \text{ gC m}^{-2}\text{y}^{-1} = 1600 \text{ gC m}^{-2}\text{y}^{-1}$$
.

This value is comparable to estimates of total primary production entrained in the *varzea* waters, as derived from site-specific primary production experiments (1000 - 2000 gC  $m^{-2}y^{-1}$ ; Devol et al., 1983; Bayley in press). The aerobic part of organic carbon decomposition may be calculated from the flux of  $O_2$  into the water (2200  $gO_2$   $m^{-2}y^{-1}$ ),

corresponding to about 825 gC m<sup>-2</sup>y<sup>-1</sup>. A similar value can be calculated from Melack and Fisher's (1983) analysis of eighty diel cycles of dissolved oxygen in Lago Calado. This estimate is probably an upper limit, because  $O_2$  may be consumed in reactions with other reduced elements, such as sulfide and iron.

Aerobic oxidation of organic matter accounts for less than 65% of the total CO<sub>2</sub> emitted (825/1300), and less than 55% of the total mineralization rate for organic carbon (825/1600). The remainder of the CO<sub>2</sub> is presumably produced anaerobically. Approximately one mole of CO<sub>2</sub> is produced for every mole of CH<sub>4</sub> (e.g., during acetate fermentation); hence, most of the anaerobic CO<sub>2</sub> could be derived directly from methanogenesis.

We estimate that nearly 20% of the organic carbon mineralized is released to the atmosphere as CH<sub>4</sub> (300/1600). Conversion of organic C to CH<sub>4</sub> accounts for 5-10% of net production in typical freshwater lakes and marshes (Rudd and Hamilton, 1978; Fallon, 1980; Delaune et al., 1983), and conversion is less efficient in marine environments (Martens and Goldhaber, 1978; King and Wiebe 1980). Methanogenesis becomes the dominant pathway of anaerobic metabolism once nitrate, sulfate and N<sub>2</sub>O are removed. Nitrate and sulfate concentrations in *varzea* waters are low, generally less than 5 μM (Forsberg et al., in review; J. Richey, unpubl. data), and a significant fraction of the ntirate is probably assimilated for primary production. The influx of N<sub>2</sub>O from the atmosphere is very small compared to carbon mineralization rates. Thus, rates of denitrification and sulfate reduction are limited by available oxidized species. The large fraction of organic matter converted to CH<sub>4</sub> may reflect the low ambient levels of ωt

electron acceptors in the Amazon.

Inputs from the *varzea* impact the levels of CH<sub>4</sub> in main channel, as shown by the cross-channel gradients of dissolved CH<sub>4</sub> (Fig. 5). *In situ* sources are probably limited in the mainstem, as the sediments are mobile, sandy and, presumably, oxygenated to a significant depth, precluding significant methanogenesis. Tributaries are only slightly elevated in CH<sub>4</sub>. J. Richey (unpubl. data) has calculated inputs of *varzea* water to the main channel to be on the order of 1 to 10% of the mainstem discharge, depending on the season. Input of waters at these rates with CH<sub>4</sub> levels typical of the *varzea* (>10 µM), appears adequate to supply the CH<sub>4</sub> levels of 0.1-1.0 µM as observed in the mainstem.

#### **Conclusions**

The results presented here indicate that simultaneous measurements of dissolved biogenic gases provide a powerful technique for analyzing mesoscale patterns in the oxidation of organic matter in a large river system. Analysis of results for the Amazon River indicate that:

- (1) Dissolved concentrations of CO<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O in the Amazon are regulated by oxidation-reduction reactions. The redox sequence is controlled by supply of organic matter and by the amount of oxygen available through invasion from atmosphere.
- (2) Net decomposition rates for organic carbon in Amazon varzea waters are approximately 1600 gC m<sup>-2</sup>y<sup>-1</sup>, with about 1300 gC m<sup>-2</sup>y<sup>-1</sup> as CO<sub>2</sub> and 300 gC m<sup>-2</sup>y<sup>-1</sup> as CH<sub>4</sub>. Approximately 40% of the CO<sub>2</sub> is produced by anaerobic processes. Estimates

of the anaerobic  $CO_2$  production rate (475 gC m<sup>-2</sup>y<sup>-1</sup>), derived from the invasion rate for  $O_2$  and from the evasion rate of  $CO_2$ , are in harmony with estimates for  $CH_4$  emission rates if we assume a production ratio of about 1 for  $CO_2/CH_4$  during methanogenesis.

(3) High levels of CO<sub>2</sub> in the mainstem are derived from a combination of varzea drainage waters and in situ respiration. High levels of CH<sub>4</sub> in the mainstem are probably derived from the varzea.

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Table 1. Calculation of the ratio  $Rq = CO_2^*/AOU$  (Eq 4). s.e. = standard error of the mean.

	Rq	s.e.
Mainstem	1.4	.04
Tributaries	1.9	.12
Varzea with AOU<200 μM		
Paranas	1.4	.10
Surface	1.8	.06
Bottom	1.7	.12
·		
Varzea with AOU>200 μM		
Paranas	1.8	.12
Surface	2.1	.22
Bottom	2.1	.10

Table 2. Diffusive flux of gases between the atmosphere and water from Eq. 2. As a first approximation it is probably realistic to consider an effective *varzea* boundary layer of 150 microns (see text). Diffusion coefficients of 2.1 x 10<sup>-5</sup>, 2.6 x 10<sup>-5</sup>, 2.3 x 10<sup>-5</sup> and 2.7 x 10<sup>-5</sup> cm<sup>2</sup>/s for CO<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O respectively (Broecker and Peng, 1974) were used, and mean mainstem and *varzea* surface water (*paranas* and lakes) concentrations C\* (ambient - equilibrium) were used.

Site	C* (μM)	$F(g m^{-2} y^{-1})$
Mainstem		
CO <sub>2</sub>	131	2080
AOU	84	4400
CH <sub>4</sub>	.050	.9
N <sub>2</sub> O	.004	.1
Varzea		
CO <sub>2</sub>	250	1320
AOU	130	2240
CH <sub>4</sub>	12	` 66
$N_2O$	.0004	004

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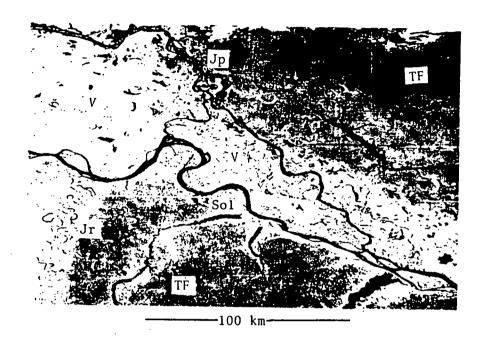


Fig. 1

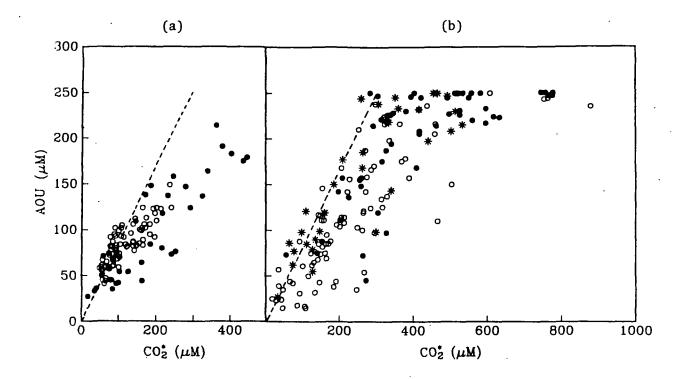


Fig. 2

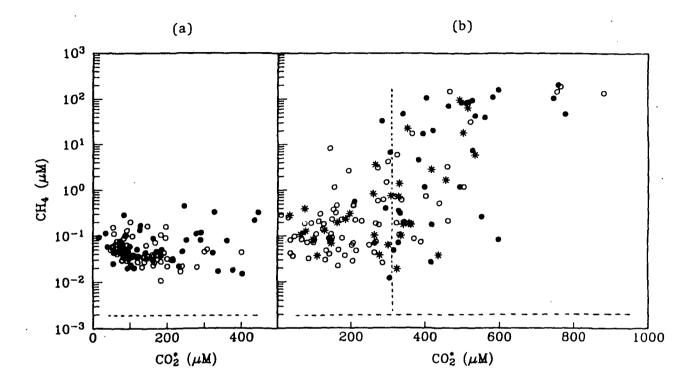


Fig. 3

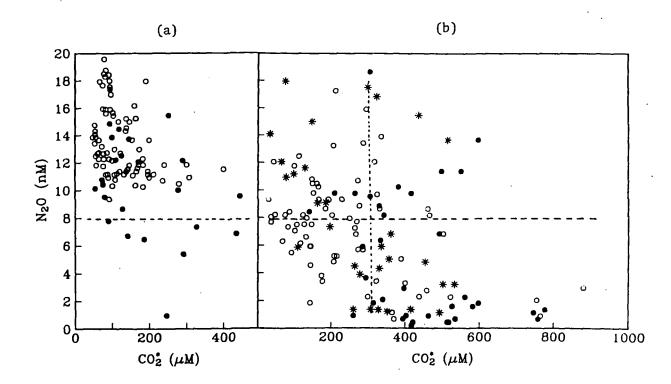


Fig. 4

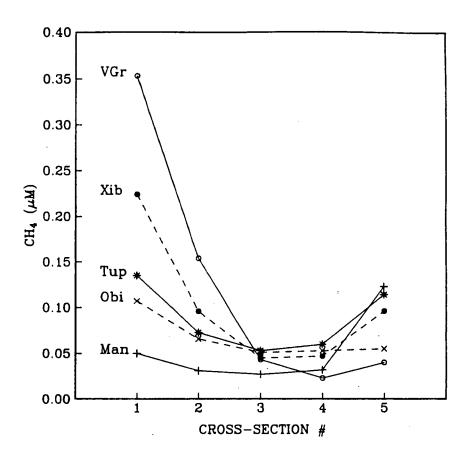


Fig. 5

## Figure Captions

- Fig 1. Landsat multi-spectral scanner image (bands 5,6, and 7) of the Rio Japura (Jp) and Rio Jurua (Jr) confluence with the Rio Solimoes (Amazon) mainstem (Sol). Light areas represent varzea habitat (V), and dark areas represent terra firme (non-flooded) habitat (TF). Image tapes were provided by the Instituto de Pesquisas Espaciais, and were processed by the Laboratory of Remote Sensing, University of Washington.
- Fig. 2.  ${\infty_2}^*$  AOU property-property plots. Dotted line corresponds to the theoretical ratio Rq = 1.2. (a) mainstem (o) and tributaries ( $\bullet$ ); (b) parana (\*), surface (o), and bottom waters ( $\bullet$ ).
- Fig. 3.  ${\rm CO_2}^*$   ${\rm CH_4}$  property-property plots. The horizontal dashed line is the atmospheric equilibrium,  ${\rm C_{eq}}$ . The region to the left of the vertical stippled line represents AOU < 200  $\mu$ M; the region to the right represents AOU > 200  $\mu$ M. (a) mainstem (o) and tributary (e); (b) parana (\*), surface (o), and bottom waters (e).
- Fig. 4.  ${\rm CO_2}^*$  N<sub>2</sub>0 property-property plots. The horizontal dashed line is the atmospheric equilibrium, C<sub>eq</sub>. The region to the left of the vertical stippled line represents AOU < 200  $\mu$ M; the region to the right represents AOU > 200  $\mu$ M. (a) mainstem (b) and tributary (c); (b) parana (\*), surface (c), and bottom waters (c).
- Fig. 5. Cross-channel profiles of  $CH_4$  (# = equidistant cross-sections) on the Amazon mainstem at Vargem Grande (VGr), Xibeco (Xib), Tupe (Tup), Manacapuru (Man), and Obidos (Obi).