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NAC-1-563

P.51

Methane Flux from the Central

Amazonian Floodplain

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Short title: Amazonian Methane Flux

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(NASA-TH-89296) HETHANE FLUX FECH THE CENTRAL AMAZONIAN FLOCUPLAIN Final Report (NASA) 51 p Avail: NIIS HC A04/MF A01 CSCL 04A

N87-27338

Unclas G3/46 0085445

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### **ABSTRACT**

A total of 186 methane measurements from the three primary Amazon floodplain environments of open water lakes, flooded forests, and floating grass mats were made over the period 18 July through 2 September 1985. These data indicate that emissions were lowest over open water lakes, where flux averaged 27 +/- a standard error of 4.7  $mgCH_4/m^2/d$  (n=41). Flux from flooded forests and grass mats was significantly higher. Emissions from flooded forests averaged 192 +/-26.8  $mgCH_4/m^2/d$  (n=90), while those from floating grass mats averaged 230 +/- 72.2 mgCH<sub>4</sub>/m<sup>2</sup>/d (n=55). At least three transport processes contribute to tropospheric emissions: ebullition from sediments, diffusion along the concentration gradient from sediment to overlying water to air, and transport through the roots and stems of aquatic plants. Measurements indicate that the first two of these processes are most significant. Diffusive flux from flooded forests averaged 50.5 +/- 11.0 mgCH<sub>4</sub>/m<sup>2</sup>/d, while that from floating mats averaged 43.7 +/- 11.8  $mgCH_4/m^2/d$ . Diffusive flux from open waters averaged 8.3 +/-1.9  $mgCH_4/m^2/d$ . Emissions through bubbling were 168 +/- 32.2 (flooded forest), 346 +/- 128 mgCH $_4/m^2/d$  (floating grasses), and 17.3 +/- 5.2 (open water). We estimate that on the average bubbling makes up 49% of the flux from open water, 54% of that from flooded forests, and 64% of that from floating mats. If we apply our measurements to the entire Amazonian floodplain, we calculate that the region could supply up to 12% of the estimated global natural sources of methane.

#### INTRODUCTION:

Methane (CH<sub>4</sub>) has an important role in tropospheric and stratospheric chemistry and in radiation transfer [Crutzen, 1973; Logan et al., 1981; Ramanathan et al., 1985]. The majority of atmospheric CH<sub>4</sub> is produced microbially under anaerobic conditions in such diverse environments as the guts of ruminants and termites [Zimmerman et al., 1982; Crutzen et al., in press], agricultural wetlands [Cicerone et al., 1983; Holzapfel-Pschorn and Seiler, 1986], and a variety of natural wetlands [for example, Harriss et al., 1982; Svensson and Rosswall, 1984; Bartlett et al., 1985; Sebacher et al., 1986].

In flooded freshwater anaerobic environments such as those of riverine floodplains, decomposition by methanogenic bacteria is the primary pathway of carbon remineralization and significant emissions of CH<sub>4</sub> to the atmosphere can therefore result [Martens and Goldhaber, 1978]. Extensive wetlands occur along the floodplains of the Amazon River and its tributaries, where high solar radiation and high temperatures throughout the year can result in high rates of primary production [Westlake, 1963; Klinge et al., 1975; Junk, 1985].

Decomposition processes however, both in Amazonian upland forests and floodplains, are also reported to be rapid [Klinge et al., 1975; Howard-Williams and Junk, 1976; Junk, 1983] and little of this production appears to be stored as peat deposits.

The middle reaches of the Amazon in the vicinity of Manaus are characterized by high precipitation (ca. 2000 mm/yr), high temperatures (an annual average of ca. 27°C), and high relative humidity

(monthly means ranging from 74 to 82%) [Junk, 1983]. Rainfall is not distributed evenly thoroughout the year, and the year can be divided into a period of more frequent rain (approximately February through April) and a period of less intense rainfall, with the driest period between July and September. Seasonal differences in precipitation give rise to large water level fluctuations in the Amazon and its tributaries which result in annual water level changes of between 8 and 14 m [Junk, 1983; Meade et al., 1985]. Due to the low relief of the basin, the period of high water causes extensive flooding and the seasonal creation of enormous areas of shallow lakes and flooded forest (igapo) in the floodplain area [Melack, 1984]. Plant species within the floodplain or varzea, show a number of adaptations to these highly variable conditions [Worbes, 1985]. One very successful adaptation lies in adopting a floating habit so that access to solar input is maintained as water levels change [Junk, 1970]. This strategy results in vast areas of floating mats of vegetation (capim) throughout the varzea, some of which are moved about over the water surface by water currents and wind.

Water in the Amazon basin has been classified into three general types, largely on the basis of origin and subsequent chemical characteristics: white, black, and clear [Sioli, 1964; Junk, 1983]. White water such as the Rio Solimões, because of its origin in the Andes, carries a large sediment load, has a pH of near neutrality, and generally has substantial dissolved nutrients [Meade et al., 1985; Fisher and Parsley, 1979]. Black water such as the Rio Negro, drains the highly leached soils of the Amazonian lowlands. These waters are generally of low pH, highly colored by humic materials, and are quite

low in nutrients. Significant growth of floating grass mats seldom occurs in black water systems. Habitats in these varzea regions are largely flooded forest and open water lakes [Junk, 1983]. The third water class, clear water, is distinguished by its clarity and drains Pre-Cambrian Shield areas in central Brazil and the Guianas. Nutrient levels and pH are variable but are higher than those of black water rivers. Varzea vegetation in clear water rivers is reported to be similar to that in white water systems although somewhat less well developed due to the generally lower nutrients [Junk, 1983].

In this paper, we report emissions of  $\mathrm{CH}_4$  from the three dominant environments within the central Amazonian floodplain. Measurements were made during a period of high and falling water (July to September), in a region adjacent to the Rio Solimões in the central Amazon Basin. Our measurements indicate that the Amazon basin could be a globally significant source of atmospheric methane.

This project was part of the Amazon Ground Experiment (AGE) conducted in conjunction with the Global Tropospheric Experiment in the Brazilian Amazon (GTE/ABLE-2A). A companion paper in this volume [Crill et al., this issue] reports in more detail on some of the processes controlling methane emissions.

### MATERIALS AND METHODS:

Methane flux measurements were made in the vicinity of Lago Calado, a varzea lake along the Rio Solimões 60 km upstream and west of Manaus, Brazil at  $3^{\circ}15'$  S,  $60^{\circ}34'$  W. Lago Calado has been a focus

of tropical limnological research and further description of its geographical, physical, and ecological setting can be found in Melack and Fisher [1983], Fisher et al. [1983], MacIntyre and Melack [1984], and Setaro and Melack [1984]. Our measurement sites were generally within 25 km of L. Calado and encompass a variety of floodplain habitats and water depths (Figure 1). Sampling effort was concentrated in the three primary varzea environments of open water, floating grass mats, and flooded forests. Primary measurement sites were within L. Calado and Lago Cabaliana, a much larger lake surrounded by extensive flooded forest and floating grass meadows. Vegetation from mat environments was identified according to herbarium samples in Manaus and includes the dominant species in terms of biomass and numbers for the region. Species are listed in Appendix 1.

Methane emissions were measured by two techniques, both involving a closed recirculating flux chamber set over the air-water or air-soil interface. The GFC technique (Gas Filter Correlation) uses a non-dispersive infra-red absorption analyzer integrated in a recirculating air stream with the chamber. Changes in the enclosed air are continuously monitored and recorded, a capability that permits evaluation of any disturbance during the measurement period. This capability also permits separation of emissions due to CH<sub>4</sub> bubbles from those due to diffusive transport. Bubble fluxes were calculated from the CH<sub>4</sub> concentration increase within the system and the time interval between bubbling episodes. When more than one bubble occurred during a measurement period, individual bubble fluxes were averaged to calculate a mean rate for the period. Details of the GFC system design and calibration can be found in Sebacher and Harriss [1982] and Sebacher

[1985]. The system has a detection limit of approximately 0.1  $mgCH_4/m^2/d$  for a typical 15 minute measurement period. Chamber surface area and volume are 0.41  $m^2$  and 0.14  $m^3$  respectively.

Flux measurements were also made by taking periodic samples by syringe from the same chamber. Comparison of the two techniques indicates that they yield similar results for total flux, although periodic sampling does not allow flux separation into diffusive and bubble components. Samples were taken from the chamber every 5 minutes over a 20 minute measurement period using 60 ml polyethylene syringes equipped with nylon and polyproplylene stopcocks. Samples were analyzed within two hours of collection with a flame ionization detector gas chromatograph (FID-GC). Further detail on syringe sampling techniqes and calibration can be found in Crill et al. [this issue].

In conjunction with flux measurements, water column samples were taken to measure dissolved methane and oxygen, temperature, and conductivity. Dissolved CH<sub>4</sub> samples were collected by van Dorn bottle or through the use of a submersible pump. Sub-samples were collected in syringes similar to those used for air sampling. To prevent possible contamination, syringe pools used for water and air samples were not mixed. Water samples were analyzed by FID-GC after dissolved methane was stripped with ambient air [McAuliffe, 1971]. Water column dissolved oxygen was measured by lowering a Clark polarographic electrode equipped with a submersible stirrer through the water column. Temperature was determined with a thermistor on the oxygen electrode assembly. These measurements allow evaluation of physical and chemical stratification in the water column. Conductivity

measurements, performed on surface water samples from flux measurement sites, can identify water sources since upland drainage and river waters have distinctly different concentrations of dissolved salts [e.g. Howard-Williams and Junk, 1977]. Conductivity measurements were made using a conductivity cell with a cell constant of 1.0 and were corrected to 25°C using a coefficient of 2% per degree.

Vertical depth profiles of dissolved  $\operatorname{CH}_4$  in sediment pore waters and within grass mats were obtained through the use of equilibration samplers similar to those designed by Hesslein [1976]. Samplers were 62 cm long with a sampling interval of 1.6 cm. Sampling wells were filled with surface lake water of known  $\operatorname{CH}_4$  concentration, covered with teflon membrane, and placed for equilibration times ranging from 4 (water column) to 14 days (sediments). Once withdrawn from the sampling site, equilibrated water was removed from the sampler by 10 ml glass syringes equipped with plastic stopcocks. Sample withdrawal was complete in less than 15 minutes and analysis was performed by FID-GC after stripping with ambient air as for water column  $\operatorname{CH}_4$  samples.

## RESULTS AND DISCUSSION:

### Methane Flux

Flux measurements from varzea environments in the central Amazon region are summarized for all sites in Table 1. Fluxes range from -10 to nearly 3000 mgCH $_4/m^2/d$ . In spite of high variability, it is clear

that significant differences between habitats exist. A Student-Newman-Keuls test (SNK) for differences between means [Sokal and Rohlf, 1969] indicates that average fluxes from open water areas are significantly lower than those from floating mats and flooded forests (p < .01).

The range of Amazonian measurement values is quite similar to those from a variety of natural wetland types throughout the world [e.g. DeLaune et al., 1983; Svensson and Rosswall, 1984; Harriss et al., 1985]. It is greater than those reported from salt and brackish water marshes and from some tundra environments [Bartlett et al., 1985; Sebacher et al., 1986]. Although seasonality makes habitat comparison difficult, relatively high fluxes appear to occur more frequently in the Amazon measurements, resulting in high average emissions. Overall, compared with emission rates reported in the literature Amazonian wetland fluxes appear to be relatively high.

We are aware of few other measurements made in tropical wetland ecosystems with which to compare our values. Keller et al. [1983 and 1986] and Goreau and de Mello [1985] report flux data from upland forest sites indicating that these soils are not significant sources of  $CH_4$  and that upland soils may in fact be a sink rather than a source for atmospheric  $CH_4$ . Harriss and Sebacher [1981] report a survey of  $CH_4$  fluxes from forested freshwater swamps in subtropical areas of the southeast United States  $(32^O45'$  to  $26^O15'$  N). Made under a variety of hydrologic regimes at near peak annual temperatures, their measurements range from 4.6 to 265 mg $CH_4/m^2/d$  for natural wetlands. This range is lower than our Amazonian measurements, but is overlapped by them.

Devol et al. [this issue] report a quasi-synoptic survey of  $\mathrm{CH}_4$  emissions from floodplain habitats throughout much of the Amazon River basin made at the same time our measurements were taken. In general, their fluxes are similar to those reported in Table 1. They report average fluxes from lake areas of 120 mgCH $_4/\mathrm{m}^2/\mathrm{d}$ . Emissions from flooded forest and macrophyte environments are 108 and 590 mgCH $_4/\mathrm{m}^2/\mathrm{d}$  respectively. In light of the large variability that is common in methane flux measurements, these emissions may not be significantly different than those reported here.

Frequency distributions of our measurements (Figure 2), indicate that the majority of fluxes from open water areas (64%) fall within a single order of magnitude (10 - 100 mgCH $_4/m^2/d$ ). All but two measurements fall within two orders of magnitude. These unusual samples include the single negative flux (consumption of atmospheric methane) found during our measurements. Crill et al. [this issue] argue that CH4 oxidation is a relatively minor process at this time in L. Calado due to nitrogen limitation in the oxygenated epilimnion. Fluxes from flooded forest and grass mat areas are quite similar to one another and have a much broader distribution than those from open waters. vast majority of fluxes from these environments fall within three orders of magnitude (1 - 1000 mgCH $_4/m^2/d$ ). In both environments, a small number of very high measurements (1000 - 10,000  $mgCH_4/m^2/d$ ) tend to skew average values derived for the data sets. These rare high observations result in large differences between the calculated mean and median values. For floating meadows, the mean flux is 230 and the median is 83  ${\rm mgCH_4/m}^2/{\rm d}$ . For flooded forest, these values are 192 and 93 mgCH<sub>4</sub>/m<sup>2</sup>/d, respectively. Although relatively rare in our measurements, these samples are representative of emissions that occur throughout the floodplain in lush, highly productive shallow-water regions. These high emissions were largely due to the episodic release of bubbles. Including these values in averages should yield emissions figures that are more representative of flux from the region than are median values.

# Methane Loss Mechanisms

Pore water data from L. Calado indicate that the primary source of CH<sub>4</sub> to overlying water is the sediment (Figure 3). Calculated fluxes of methane from sediments into bottom water based on concentration gradients in the pore waters can account for the increase in water column CH<sub>4</sub> concentrations measured over the sampling period of approximately a month and a half [Crill et al., this issue]. Our data suggest that in floodplain habitats, one of the primary reasons for flux differences between habitats lies in the transport processes that transfer methane generated in the sediments into the atmosphere.

Once produced in the sediment, methane can escape into overlying water through two mechanisms - diffusion along the concentration gradient from sediment to water (see Figure 3) and by ebullition. In L. Calado, it appears that the sediment pore waters are saturated with methane within 5 - 10 cm of the sediment surface (Figure 3). These data indicate that methane loss as bubbles from the sediment should be a common and significant loss mechanism. Sediment gas bubbles captured at the air-water interface were between 58 - 72% CH<sub>4</sub>.

Measurements for which we can separate diffusive and ebullient components suggest that non-normal distributions for total flux (Figure 2) arise because the observed fluxes are a combination of emissions through several loss mechanisms. Viewed individually, diffusive and bubble flux distributions have different ranges (Figure 4).

# Losses Through Bubbling:

Flux data for which we can separate diffusive and bubble fluxes demonstrates that bubbling contributes significantly to  ${\tt CH_4}$  losses from the varzea (Table 2). Emissions through ebullition averaged 17.3 +/- 5.2 (SEM)  $mgCH_4/m^2/d$  from open water areas, 168 +/- 32.2  $mgCH_4/m^2/d$  from flooded forests, and 346 +/- 128  $mgCH_4/m^2/d$  from floating mats. These losses account for, on average, between 49 and 64% of total flux. We are not aware of reports from other wetland evironments in which ebullition from sediments plays such an important In agreement with our measurements, Devol et al. [this issue] calculate indirectly that ebullition makes up 70 - 90% of total  $CH_4$ Bubbling events are episodic and it is apparent, given the high average bubble flux, that when bubbling does occur it usually dominates CH, release. During our sampling, bubbling occurred in 39% of our measurements. The variability of bubbling in time and space accounts for much of the scatter in the flux data sets. The processes controlling emissions by diffusive and bubble transport mechanisms are different and data suggest that the relative importance of these mechanisms may change from habitat to habitat. A Student-Newman-Keuls test for differences between mean fluxes indicates that significant

differences exist between bubble emissions from the floodplain habitats at the 95% confidence level.

# Losses Through Diffusion:

In contrast to bubble fluxes, a Student-Newman-Keuls test indicates that diffusional fluxes from the three habitats are not significantly different from one another. The absence of site differences in diffusional flux suggests that methane release through this mechanism is mediated by processes operating similarly in all environments such as water column stratification, turbulent mixing, and the rate of supply of dissolved CH<sub>4</sub> to the water column. The observation of differences in bubble flux between environments suggests that site specific variables such as sediment-associated controls on methane production and consumption regulate bubble emission.

The diffusional loss of methane across a water surface to the atmosphere is a function of the surface water concentration, wind speed across the surface, and methane supply to the surface water [Sebacher et al., 1983; Crill et al., this issue]. The correlation of surface water dissolved methane with concurrent flux measurements confirms that flux is related to surface  $CH_4$  concentrations (r = .858; p < 0.01; n = 44). This relationship, however, is largely dependent upon three samples having  $CH_4$  concentrations greater than 2  $\mu$ M and high diffusive fluxes. The relationship between flux and surface water dissolved  $CH_4$  for concentrations less than 2  $\mu$ M is poor (r = .293; not significant; n = 40). Surface water dissolved  $CH_4$  therefore appears to be a poor predictor of flux in most of the areas we worked.

Surface CH<sub>4</sub> concentrations ranged from 0.14 to 23.7  $\mu$ M. Most surface CH<sub>4</sub> concentrations were between 0.2 and 0.4  $\mu$ M (in flooded forest, 44% were within these values; in floating mats, 36% were; in open water areas, 38% were). Average concentrations in flooded forests (1.43 +/-0.73  $\mu$ M, n = 18) and grass mats (3.22 +/- 2.30  $\mu$ M, n = 11) were higher than those from open water for which we have more samples (0.84 +/-0.20  $\mu$ M, n = 39).

Diffusional flux of methane from overlying water to the atmosphere is indirectly controlled by mixing processes that determine the resupply of CH<sub>4</sub> to surface waters as it is degassed. Water column stability and stratification are therefore important controls on diffusion. Crill et al. [this issue] examine the critical role of stratification and diffusion across the chemo- and thermocline into the surface mixed layer of L. Calado. Incoming solar radiation and wind velocity across the water surface were found to control the intensity of daily stratification within the surface mixed layer of the lake. These diurnal temperature gradients largely controlled the diffusive flux of CH<sub>4</sub> to the atmosphere by regulating the resupply of methane from deeper water to the surface layer [Crill et al., this issue].

Water column measurements of temperature and oxygen in grass mat, flooded forest, and open water areas indicate that the shape of the oxygen profiles and the intensity of thermal stratification vary between environments. Typical profiles (Figure 5) show upper water column temperatures that are generally similar in all three environments. Temperatures under mats of grass, however, appear to be more constant with depth, probably due to shading and the insulating

effect of the thick layer of vegetation. Oxygen profiles under mats frequently show an oxygen minimum between 0.5 and 1.5 m, reflecting decomposition processes within the thick root mat, as noted in Junk [1983]. Although flooded forests also shade the water surface, temperature and dissolved oxygen profiles from these areas were much more variable than those below floating mats. The importance of water column stratification is illustrated by measurements made in two flooded forest sites within L. Cabaliana on 5 August. At a site where oxygen concentrations were below detection limits, water temperatures were constant with depth at 28.8°C and little water column stratification was apparent. Under these conditions, diffusive  ${
m CH}_4$  fluxes of 29, 30, and 34  ${\rm mgCH_4/m}^2/{\rm d}$  were recorded. At a nearby second site in similar water depths of 1.6 m, temperatures decreased from 31.20 at the surface to 30°C and oxygen concentrations dropped from 4.9 to 3.1 mg/l, indicating moderate water column stratification. Over this stratified water column, no measurable diffusive flux was found. Although in some cases such as that above, the relationship between stratification and diffusive flux seems clear, simple correlation of the two for the entire data set is poor. Methane fluxes for which we have concurrent water column limnological information can be found in Appendix 2.

Water column profiles of dissolved  $\operatorname{CH}_4$  and temperature across habitat types illustrate differences in water column structure and demonstrate some of the controls on  $\operatorname{CH}_4$  flux (Figure 6). Depth profiles taken across the basin of L. Calado (Figure 1) from grass mats on the western edge into open water and re-entering mats on the east are shown in Figure 6A. Pools of warmer water in the vicinity of

the grass mats are apparent. Dissolved oxygen samples taken at this time indicate decreased oxygen under the mats as in Figure 5. The warmer surface water temperatures near the east mats suggest movement of surface water into the open water region. Methane concentration profiles indicate diffusion of CH<sub>4</sub> from benthic sediments into bottom waters. Under the floating grass, these bottom waters are isolated by shallow sills approximately 2 m in height. Surface water CH<sub>4</sub> concentrations under the capim mats are somewhat lower than those in the open water.

Figure 6B shows profiles taken down an inundated stream (Igarape Pato) on L. Calado from flooded forest to open, relatively quiet water. High water temperatures and dissolved  $\mathrm{CH_4}$  were found within a small pool vegetated by a submerged macrophyte (Cabomba spp.) near the head of the stream in an opening in the forest. Within the forest, profiles of both variables are essentially constant along the transect. Water column temperatures increase and oxygen concentrations (data not shown) decrease at the edge of the forest. Methane concentrations fall as stream waters enriched in  $\mathrm{CH_4}$  are diluted and mixed within the deeper water column.

Similar trends are seen in Figure 6C, showing sampling down the main axis of L. Calado from flooded forest, through open quiet water, into the main basin of the lake, and out into the R. Solimões. The track of this transect follows water flow at this time, moving from the lake into the river. Water temperatures increase from shaded forest to exposed open water where stratification is quite constant and isothermal lines are flat. Surface temperatures fall upon passage through the channel linking the lake with the R. Solimões and are

essentially constant with depth in the river where the water column is well mixed. Water column  $\mathrm{CH_4}$  concentrations suggest that the most active source of methane along the transect is the sediments of the basin of the lake since pools of  $\mathrm{CH_4}$  are greatest in these deep waters. Mixing and subsequent degassing of  $\mathrm{CH_4}$ - laden lake water appears to be quite rapid upon entrance to the Solimões.

## Losses Through Plants:

Significant methane emissions through the internal air spaces of wetland plants in temperate areas have been reported by a number of authors [e.g. Cicerone et al., 1983; Sebacher et al., 1985]. Preliminary samples in grass mats suggest that plants may also play a role in mediating  $CH_A$  flux in the Amazon. Pore water samplers inserted into capim mats reveal that  $CH_{\Lambda}$  concentrations vary widely in near-surface waters and exhibit large gradients with depth (Figure Profiles are not consistent in shape from site to site, although concentration maxima were found within the root mat at all three sites (at 20 and 50 cm, and in the surface few cm). From the top 50 cm of the profiles, we calculate an integrated methane concentration of 1.82 mmol  $CH_4/m^2$  (Figure 7A, 31 July), 0.76 mmol  $CH_4/m^2$  (Figure 7B, 6 August), and 3.67 mmol  $\mathrm{CH_4/m^2}$  (Figure 7C, 6 August) in these waters. These values are between 2 and 8 times the average amount of  $CH_A$  in the unvegetated surface water of L. Calado (0.46 +/- 0.10 (SEM) mmol  $\mathrm{CH_4/m^2}$ ). Higher concentrations in the root mat could be the result of two processes: in situ methanogenesis in high density mats with restricted flow where water can become oxygen deficient [Junk, 1983], and through the trapping and subsequent dissolution of bubbles coming

from sediments below the mats. Our measurements can not distinguish between these two sources, although the latter seems more likely given the widespread occurrence of sediment bubbling and the observation of only minor oxygen depletion in these mats.

Air samples from gas spaces in stems and leaves of common mat plants indicate elevated CH<sub>4</sub> concentrations over those in ambient air (Table 3). Concentrations in samples taken from plant structures below water surfaces are greater than those found in exposed plant parts, suggesting loss through plant stomata where the plant is in air. Our measurements are preliminary in nature and can not be used to evaluate the relative importance of different plant species as CH<sub>4</sub> conduits. It is interesting to note though, that the highest concentrations are found in a rooted grass and that higher concentrations in the giant waterlily, <u>Victoria regia</u>, are found in older structures as would be expected from previous work on other waterlily species [Dacey, 1981]. Similar pressurized transport processes may be operating in this large tropical species.

Flux measurements made over plants and adjacent open water areas indicate that the presence of plants does cause enhancement of CH<sub>4</sub> flux, although differences between open water and vegetated sites are not great (Table 4). Accurate flux measurements when plants serve as an important transport component are difficult to make without causing changes in plant physiology affecting flux. Emissions through plants would also be expected to have significant diurnal variations tied to environmental changes and alterations in rates of respiration and photosynthesis [Dacey, 1981; Sebacher et al., 1985]. Our Amazonian measurements to date suggest that enhanced emissions through plants

occur and that they are probably worth more study. Although emissions by other transport mechanisms appear to be more significant, the transport of  $\mathrm{CH_4}$  through plants may be of interest for other reasons, for example, changes in  $\mathrm{CH_4}$  isotopic composition induced during transport.

## Methane Emissions from the Amazon Basin

## Spatial Variation:

Assessing the importance of a region as large and complex as the Amazon as a source of  $CH_A$  is fraught with uncertainty. A significant concern in making large scale emissions estimates is the adequate incorporation of variability in source strength since scales at which flux varies and scales required to determine global inputs are so different. A SNK test applied to our flux measurements indicates that there can be significant site-to-site differences within a habitat type in a relatively small area (25 km). Flooded forest habitats at L. Calado have significantly lower fluxes than do those at L. Cabaliana (p < .01) and floating grass areas at Pesqueiro have significantly higher fluxes than either L. Calado (p < .01) or L. Cabaliana (p < .05). Grass mat and flooded forest form a fairly narrow band along the sides of L. Calado. The generally lower fluxes observed at L. Calado may in part be related to topographic differences between relatively steep-sided shorelines and flatter areas such as L. Cabaliana or Pesqueiro. For example there may be differences in the importance of upland run-off as well as groundwater flow and nutrient transport between these types of shores.

In addition to variability on these local scales, we also expect that there should be significant regional differences in flux from river tributaries of different water types. Most of our measurements were made in areas under the influence of the R. Solimões, a white water river. A limited data set from along the R. Negro indicates that emissions from flooded forests in black water are similar in magnitude to those from the R. Solimões region. The absence of grass mat environments and their replacement by open water areas that emit significantly less methane suggests however, that emissions may be lower as a whole from black water systems. We also expect that differences in nutrient level between water types will result in some differences in flux [Harriss and Sebacher, 1981]. Topographic variation resulting in changes in hydrology (ie. floodplain width, lake shape and abundance, water flow and mixing rates) should also create regional within-basin flux variation.

## Temporal Variations:

Accurate flux estimates from Amazonia also require assessment of temporal variation, since these floodplain areas are seasonal in nature. Changes in water level, water column structure, and substrate availability for example, occur on a seasonal basis.

The measurements reported here were made over a single part of the hydrographic cycle when water levels were relatively high but falling, so we have few data on seasonal changes in flux. Emissions during rising water as forests are flooded, when capim mat plants are still rooted in the soil and when water levels are lower, may be significantly different. In addition, emissions from freshly exposed

inundated surfaces as water levels fall may have interesting dynamics. Although preliminary measurements as waters recede suggest that emissions from these surfaces fall sharply within a period of one to two days, these data indicate that higher emissions may occur for a brief time immediately after exposure to the air.

Falling water levels will also result in large changes in water column stratification before sediments are exposed. Once levels fall to the point where persistent stratification can not be maintained, the water column will mix and CH<sub>4</sub> trapped in the anoxic hypolimnion will be released [Melack and Fisher, 1983]. Water column destratification and mixing is also reported to occur upon periodic passage of strong cold fronts, when surface waters are cooled and strong winds occur simultaneously. Brinkmann and Santos [1974] report significant releases of H<sub>2</sub>S from bottom waters under these conditions, resulting in fish kills. We expect that similar large inputs of CH<sub>4</sub> to the atmosphere will occur over these brief periods.

Annual plant senescence in grass mats late in the dry season results in enhanced inputs of nutrient-rich organic material to floodplain ecosystems [Junk, 1970; Howard-Williams and Junk, 1977]. Although some of this material falls on dry and newly exposed sediments, accelerated rates of methanogenesis are possible where nutrients and carbon are added to aquatic areas [Harriss and Sebacher, 1981].

Atmospheric Inputs:

While acknowledging that spatial and temporal uncertainties exist in our knowledge of fluxes, we can however, make a first order assessment of Amazonian methane inputs to the atmosphere from the relatively large data set acquired to date. Flux from a large area is a function of emission rate (mediated by environmental variables such as substrate, temperature, or water level) and emission area. In general, estimates of the area occupied by the Amazonian floodplain are poorly The seasonal nature of the region of inundation contributes defined. to this uncertainty. We estimate methane source areas based on several scenarios: 1) a minimum estimate that the floodplain occupies 1% of the Amazon drainage area of 7 x 10<sup>6</sup> km<sup>2</sup> [Junk, 1983; Setaro and Melack, 1984]; 2) an approximation using Hedges et al. [1986] estimate that the central Amazonian floodplain occupies a band an average of 60 km wide for the mainstem river length of 6500 km; and 3) a maximum estimate that the floodplain is half of the 1 x  $10^6$  km<sup>2</sup> area calculated as lying below the 100 m contour [Junk, 1983]. Using these independent estimates, the area of Amazon floodplain varies by about an order of magnitude and is calculated to be  $7 \times 10^4 \text{ km}^2$  (scenario 1),  $3.9 \times 10^5 \text{ km}^2$  (scenario 2), and  $5 \times 10^5 \text{ km}^2$  (scenario 3).

Obtaining the areas of various floodplain habitats is also difficult. Estimates of Bayley and Moreira [1980] and analysis of Landsat imagery (Melack, unpubl. data) allow calculation of the area of floodplain habitats in the region we were working (along the R. Solimões from the Rio Purus to the Rio Negro). Areas occupied by open water lakes, floating grass mats, and flooded forest are estimated to be 700, 900, and 1700 km<sup>2</sup> respectively. Using these per cent coverage figures (open water lakes 21%, grass mats 27%, and flooded forest 52%) and the area of the entire floodplain, we can then

generate approximate habitat coverage areas for the entire region.

Per cent coverage figures are similar to those estimated roughly by

Junk [1985] for varying water levels; open water between 30 and 60% of
the floodplain, grass mats between 10 and 40%, and forests 30%.

For basin-wide extrapolation, we have elected to include some of the observed site variability in flux by using weighted flux averages rather than simple arithmetic means such as in Table 1. Flux data was divided into two subsets based on flux differences between areas that were found to be significant at the 99% level by a SNK test. subdivisions separated emissions from steep fringing margins like L. Calado from those taken in broad flat floodplain areas (L. Cabaliana and Pesqueiro). Average flux from floating grass mat areas along fringing floodplains was 107  $mgCH_4/m^2/d$  and was 390  $mgCH_4/m^2/d$  from broad open floodplains. Flooded forests along margins had an average flux of 123  $mgCH_4/m^2/d$ . Forests located on flat floodplain had average emissions of 266 mgCH $_{4}/m^{2}/d$ . We estimate that only about 10% of the Amazonian floodplain area occupies fringing margins and that about 90% is found in broad flat areas. Weighting flux subsets by these proportions, flux from floating mats on a basin-wide basis is increased to 362  $mgCH_4/m^2/d$  from a simple mean of 230  $mgCH_4/m^2/d$  for all of the mat data. For flooded forest, weighting emissions by habitat differences increases average flux from 192 to 252  $mgCH_4/m^2/d$ . Emissions from open water areas are unchanged at 27 mgCH<sub>4</sub>/m<sup>2</sup>/d. In an initial attempt to include the seasonal nature of inundation, we have made the conservative assumption that  $\operatorname{CH}_4$  flux occurs for only half of the year at any one site.

Based on these assumptions, estimates of  ${\rm CH_4}$  emissions from the Amazon basin lie between 3.0 x  $10^{12}$  (scenario 1) and 21 x  $10^{12}$  gCH<sub>4</sub>/yr (scenario 3). Total CH<sub>4</sub> flux using the average width assumption is 17 x  $10^{12}$  gCH<sub>4</sub>/yr. Flooded forest habitats contribute the largest amount to basin-wide emissions due to relatively large estimated areal coverage and emissions are calculated to be between 1.7 and 12 x  $10^{12}$  gCH<sub>4</sub>/yr. Flux from open water appears to be relatively insignificant at between 0.08 and 0.6 x  $10^{12}$  gCH<sub>4</sub>/yr, although our figure does not include flux from river waters. Emissions from floating grass meadows are calculated to be between 1.3 and 8.7 x  $10^{12}$  gCH<sub>4</sub>/yr.

Ehhalt and Schmidt [1978] and Khalil and Rasmussen [1983] have estimated biogenic sources of  $\mathrm{CH_4}$  to the global atmosphere; their figures for natural sources of  $\mathrm{CH_4}$  (excluding anthropogenically controlled sources from ruminant animals and rice paddies) range between 185 and 345 x  $10^{12}$  gCH<sub>4</sub>/yr. Based on our preliminary estimates of the Amazon as a  $\mathrm{CH_4}$  source, the region could therefore supply between 1 and 12% of this total.

#### **ACKNOWLEDGEMENTS:**

Without the help and cooperation of L. Smith-Morrill and L. Lesack this work could not have been carried out. A. da Silva provided expert assistance in field operations. Floristic samples were identified by B. Nelson. Sponsorship and support were provided by the Instituto Nacional de Pesquisas da Amazônia (INPA) and Instituto Nacional de Pesquisas Especiais (INPE). Financial support

was provided by NASA co-operative agreement NCC1-82 under the Biospheric Research Program and (in part) by NSF grant BJR 85-0794. During this project, P.M. Crill and J.O. Wilson were National Research Council resident research associates at NASA Langley Research Center.

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TABLE 1: Methane Flux from Amazon Floodplain Habitats.

HABITAT	AVG. FLUX	NUMBER OF	STD ERROR	RANGE	
	$(mgCH_4/m^2/d)$	OBSERVATIONS	OF THE	$(mgCH_4/$	$m^2/d$ )
			MEAN	MIN.	MAX.
OPEN WATER	27	41	4.7	-10.5	111
FLOODED FOR	EST 192	90	26.8	bd*	1224
GRASS MATS	230	55	72.2	bd	2997

<sup>\*</sup>below detection limits, between 0.1 and -0.1  $mgCH_4/m^2/d$ .

TABLE 2: Average Diffusive and Ebullient Methane Fluxes.

HABITAT	AVG. DIFFUSIVE	AVG. BUBBLE	% BUBBLE FLUX
	FLUX	FLUX	OF TOTAL FLUX
	$(mgCH_4/m^2/d)$	$(mgCH_4/m^2/d)$	
OPEN WATER	8.3 +/- 1.9*	17.3 +/- 5.2	48.7 +/- 8.3
	(22)	(22)	(21)
FLOODED FOREST	50.5 +/- 11.0	168 +/- 32.2	54.4 +/- 5.5
	(66)	(69)	(60)
GRASS MATS	43.7 +/- 11.8	346 +/- 128	63.7 +/- 7.3
	(29)	(29)	(27)

\*standard error of the mean; number of observations in parentheses. There are fewer measurements in per cent calculations since observations in which: 1) a diffusive flux could not be determined, and 2) both diffusive and bubble fluxes were below detection limits, are not included. Diffusive flux could not be determined when bubbling (a sharp jump in concentration within the chamber system) occurred frequently, obscuring the more gradual concentration increase due to diffusion. The per cent contribution of bubble flux to total flux was calculated for each single measurement and then averaged.

TABLE 3: Methane Concentrations from Floating Grass Mat

Vegetation

PLANT SPECIES	CH <sub>4</sub> AT/ABOVE	CH <sub>4</sub> BELOW	COMMENT
	WATER SURFACE	WATER SURFACE	
	(ppm)	(ppm)	
Paspalum spp.	90.5	3540	stem
(capim grass)	90.5	-	**
	12.2/42.0	233	"
	12.4	96.3	10
Oryza grandiglumis	101	5084	rooted, stem
(rice)			
Eichornia crassipe	<u>s</u> 8.7	43.3	stem
<u>Victoria regia</u>	72.1	- y	oung leaf stem
(giant water lil	y) 44.5	54.5	11
		741	old leaf vein
		918	old leaf stem

Typical ambient air methane concentrations were between 1.8 and  $2.0\ \text{ppm}$ .

TABLE 4: Flux Measurements over Grass Mat Plants and Adjacent Open Water

SITE/DATE	FLUX OVER  ADJACENT  OPEN WATER  (mgCH <sub>4</sub> /m <sup>2</sup> /d)	FLUX WITH PLANTS IN CHAMBER (mgCH <sub>4</sub> /m <sup>2</sup> /d)	PLANT SPECIES
Marrecao/	5.7	5.7	Eichornia
22 July		11.4	Paspalum spp.
		64.0	<u>Victoria</u> regia
Cabaliana/	13.0	145	Paspalum spp.
22 July			
Pesqueiro/	14.0	26.0	<u>V. regia</u>
2 August			
Pesqueiro/	-	38.0	Y. regia
31 August		331	H

## FIGURE LEGENDS

Figure 1: Flux measurement site map of the central Amazon floodplain (A). Lago Cabaliana, a large lake system, lies to the west of L. Calado, which is labelled to its left (east) and enlarged in (B).

Figure 2: Order of magnitude frequency distributions of methane flux from floodplain habitats. In addition to the fluxes shown, there was a single measurement below our flux detection limits of between -0.1 and 0.1  $mgCH_4/m^2/d$  from open water (making up 2% of total), 2 from floating mats (4%), and 6 from flooded forests (7%).

Figure 3: Dissolved methane water column profile (27 August) and pore water profile (15 - 28 August) from Lago Calado.

Figure 4: Frequency distributions of diffusive flux (solid line) and bubble flux (dashed line) from floodplain habitats. Distributions are based on measurements made with the GFC instrumentation only (120 out of a total of 186 measurements). Distributions do not include measurements below detection limits: for diffusive fluxes in open water, 2 of 22 (9% of all observations); in floating grasses, 2 of 28 (7%); and in flooded forest, 11 of 66 (17%). Bubble fluxes during our 15 - 20 minute measurement periods when no bubbling occurred were calculated to be zero and are also not included. There were 9 out of a total number of 22 measurements (41%) of these cases in open water,

8 out of 29 (28%) in grass mats, and 30 out of 69 (44%) in flooded forests.

Figure 5: Typical temperature ( □ ) and oxygen ( ■ ) profiles from grass mats, flooded forests, and open water.

Figure 6: Temperature and dissolved methane profiles along habitat transects. Solid lines: dissolved  $CH_4$  in  $\mu M$ . Dashed lines: temperature in  $^{O}C$ . A) west to east across Lago Calado, floating mat - open water - floating mat; B) east to west down Igarape Pato on Lago Calado, flooded fost - open water; and C) north to south down Lago Calado, flooded forest - lake - river. Arrows indicate sampling locations. Horizontal scales are compressed and total 1.75 km (A), 3.25 km (B), and 8.12 km (C).

Figure 7: Surface water dissolved methane profiles in Lago Calado floating grass meadows.

## APPENDIX 1

Plant Species (and Family) from Methane Flux Sites

Paspalum repens Berg. (Poaceae)

Echinochloa polystachya (H.B.K.) Hitchc. (Poaceae)

Orzya grandiglumis (Doell.) Prod. (Poaceae)

Salvinia auriculata Aubl. (Salviniaceae)

Azolla ?microphylla Kaulf. (Salviniaceae, Pteridophyta)

Eichornia crassipes (Mart.) Solms. (Pontederiaceae)

Pistia stratioides L. (Araceae)

Ludwigia spp.

Alchornea schomburgkiana Klotz (Euphorbiaceae)

Phyllanthus fluitans Muell. Arg. (Euphorbiaceae)

<u>Utricularia</u> spp. (Utriculariaceae or Lentibulariaceae)

APPENDIX 2
Fluxes and Associated Limnological Conditions

## FLOATING GRASS MATS

LOCATION	DATE	WATER DEPTH (m)	THERMAL	~	g/l)		H <sub>4</sub> FLUX
Marrecao	 22 Jul	 C	strong	2.7	0	decanted	5.7;0 <sup>*</sup>
narrecao	22 041	V	scrong	2.1	U	Solimoes	
						Solimoes	11.4;0
Pesqueiro	24 Jul	1.8	strong	5.7	0.5	decanted	•
- -						Solimoes	•
Pesqueiro	2 Aug	1.1	none	4.1	3.9	decanted	•
						Solimoes	11; 0
							21;331
							14;480
Pesqueiro	31 Aug	3.1	moderate	0.6	0	decanted	167
						Solimoes	126
Cabaliana	22 Jul	4	strong	6.2	0.3	decanted	41;104
						Solimoes	
Cabaliana	1 Aug	3.9	moderate	3.6	0.8	decanted	14;118
						Solimoes	16; 0
							0; 0
						,	0; 0
Cabaliana	5 Aug	3.3	moderate	1.0	1.3	decanted	43;316

					•	Solimoes	32;716
							30;637
Cabaliana	14 Aug	3	weak	1.6	1.7	-	69;163
							14;116
							38;133
Cabaliana	20 Aug	3.7	v. weak	3.9	3.1	decanted	7.9
						Solimoes	30
							29
Cabaliana	30 Aug	3.1	weak	1.0	1.9	decanted	75
						Solimoes	38
							91

<sup>\*</sup> Measurements taken with the GFC instrumentation are noted by two values. The first value indicates diffusive flux; the second, bubble flux. A single measurement denotes total flux, taken with syringe sampling techniques.

## FLOODED FOREST

LOCATION	DATE	WATER DEPTH	THERMAL	_	CONC. $g/1)$	WATER C	H <sub>4</sub> FLUX
		( m )			BOTTOM		$CH_4/m^2/d)$
Cabaliana	22 Jul		strong				103;360*
						Solimoes	6.3;97
							-;656
Cabaliana	1 Aug	2.1	weak	1.5	0.5	decanted	9; 0
						Solimoes	20; 0
							25;468
Cabaliana	5 Aug	1.6	none	0	0	decanted	29;180
						Solimoes	30;163
							34;263
Cabaliana	5 Aug	1.6	moderate	4.9	3.1	decanted	-;916
						Solimoes	0;410
Cabaliana	14 Aug	1.6	moderate	0.5	0	-	46;494
							40;147
							43; 0
Cabaliana	14 Aug	1.8	strong	5.4	1.2	-	5.6;259
							26;181
							9.5;66
Cabaliana	20 Aug	1.8	weak	0.8	0.4	decanted	183
						Solimoes	39
							295
Cabaliana	20 Aug	1.7	weak	3.8	0.6	decanted	251

						Solimoes	1.6
							105
Cabaliana	30 Aug	1.1	none	0.4	0.2	decanted	39
						Solimoes	123
							93
Cabaliana	30 Aug	0.7	moderate	5.0	1.0	decanted	199
						Solimoes	120
							387
Calado	23 Jul	1.7	moderate	7.6	5.1	upland	7.9;0
						runoff	
Calado	23 Jul	4.5	strong	6.3	0.4	upland	4.6;0
		٠				runoff	
Calado	23 Jul	4.6	strong	6.1	0.4	upland	4.6;0
						runoff	
Calado	28 Aug	4	strong	7.8	1.2	upland	2.1
			•			runoff	1.0
							19

<sup>\*</sup> Measurements taken with the GFC instrumentation are noted by two values. The first value indicates diffusive flux; the second, bubble flux. A dash for diffusive flux indicates that this flux could not be calculated due to high rates of bubbling. A single measurement denotes total flux, taken with syringe sampling techniques.



















