Pathways of organic matter mineralization and nitrogen regeneration in the sediment of five tropical lakes.

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ABSTRACT: Pathways of organic matter mineralization and nitrogen regeneration in the sediment of five tropical lakes. Sediment-water fluxes of O_2, CO_2, NH_4^+, NO_3^-, and NO_2^- and rates of denitrification, sulfate reduction and methanogenesis were measured in 3 Amazon floodplain lakes near the confluence of Rio Trombetas and Rio Amazonas and in 2 coastal lakes in the state of Rio de Janeiro, Brazil. The sites represented a wide range of alkalinity (19-912 μEq l^{-1}) and pH (4.2-8.2). Oxygen fluxes varied from 15 mmol m^{-2} d^{-1} in the humic and clear water lakes to 75 mmol m^{-2} d^{-1} in the sewage-impacted lake. Oxygen penetration depth in the sediment varied accordingly from 3.4 to 0.9 mm. Methanogenesis dominated carbon mineralization with rates up to 370 mmol C m^{-2} d^{-1}. Carbon mineralization rates by sulfate reduction and denitrification were below 2 mmol C m^{-2} d^{-1}. Concentrations of DIN in the water column were low (‹1 μM) at all locations, and denitrification was mostly coupled to benthic nitrification. Relatively high rates of denitrification (0.3-0.7 mmol N m^{-2} d^{-1}) were recorded in the white water lakes, where fluxes of NO_3^- and NH_4^+ also showed that the sediment was a net sink for combined inorganic nitrogen (-0.001 – -0.1 mmol N m^{-2} d^{-1}). The much lower rates of nitrification-denitrification in the other lakes (0.05 – 0.06 mmol N m^{-2} d^{-1}) were ascribed to limitation of nitrification by ammonium in the humic lake, phosphate in the clear water lake and oxygen in the sewage impacted lake. The C:N ratio of net organic matter mineralization was high (›25) at all sites.
Keywords: denitrification, nitrification, sulphate reduction, methanogenesis, sediment, tropical lakes.

RESUMO: Trajetória de mineralização da matéria orgânica e regeneração de nitrogênio no sedimento de cinco lagos tropicais. Os fluxos de O_2, CO_2, NH_4^+, NO_3^- e NO_2^- e as taxas de desnitrificação, sulfato redução e metanogênese foram mensuradas no sedimento de 3 lagos Amazônicos próximos aos rios Trombetas e Amazonas e em duas lagoas costeiras no Estado do Rio de Janeiro.Os ecossistemas representavam um amplo espectro de valores de alcalinidade (19-912 μEq l^{-1}) e pH (4.2-8.2). Os fluxos de oxigênio variaram de 15 mmol m^{-2} d^{-1} nos ecossistemas húmicos e de águas claras a 75 mmol m^{-2} d^{-1} no ecossistema impactado por esgoto doméstico. A penetração de oxigênio no sedimento também variou respectivamente de 3.4 a 0.9 mm. O processo de metanogênese foi o processo predominante na mineralização do carbono com taxas de até 370 mmol C m^{-2} d^{-1}. A mineralização do carbono através dos processos de sulfato redução e de desnitrificação foram abaixo de 2 mmol C m^{-2} d^{-1}. As concentrações de nitrogênio inorgânico dissolvido na coluna d'água foram baixas (‹1 μM) em todos os ecossistemas estudados, sendo o processo de desnitrificação notadamente acoplado ao processo de nitrificação. Taxas mais elevadas de desnitrificação (0.3-0.7 mmol N m^{-2} d^{-1}) foram observadas nos lagos amazônicos de águas brancas, onde os fluxos de NO_3^- e NH_4^+ ocorreram da coluna d'água para o sedimento, demonstrando que este compartimento absorve nitrogênio inorgânico (-0.001 – -0.1 mmol N m^{-2} d^{-1}). As reduzidas taxas de nitrificação-desnitrificação nos outros ecossistemas (0.05 – 0.06 mmol N m^{-2} d^{-1}) foram atribuídos a limitação do processo de nitrificação por: amônia na lagoa húmica, fosfato no lago amazônico de águas claras e oxigênio na lagoa impactada por efluentes domésticos. As razões C:N da matéria orgânica mineralizada era elevada (›25) em todos os ecossistemas estudados.

Introduction

In shallow aquatic systems a significant part of the organic matter from primary production and allochtonous sources sinks to the sediment and becomes buried and mineralized by the benthic animals and microorganisms. Due to the limited diffusion of oxygen, aerobic mineralization is restricted to the sediment surface layer, below which fermentation and anaerobic respiration takes over using nitrate, sulfate and metals as electron donors for the oxidation of organic matter (Fenchel & Jørgensen, 1977). Further below all external e-donors are eventually depleted, and methanogenesis in combination with fermentation becomes the only carbon mineralization processes. During coupled fermentation-methanogenesis there is not net oxidation of carbon, and CH_4 and CO_2 are produced in almost equal amounts (Jørgensen, 2000). The benthic processes are completed by the lithotrophic oxidation of sulfides, methane and other reduced products of the anaerobic processes, as they migrate towards the sediment surface (Fenchel et al., 1998). Organic nitrogen is mineralized to ammonium, which can be oxidized to nitrate by ammonium oxidizing and nitrite oxidizing bacteria in the oxic surface layer. Some of the nitrate is in turn reduced to dinitrogen gas by denitrifying bacteria in the anoxic zone. Also ammonium and nitrate from the overlying water may contribute to nitrification and denitrification in the sediment (Seitzinger, 1988). For the aquatic ecosystems the benthic processes have a unique role in regulating both the balance of burial and regeneration of carbon and nutrients, the elimination of combined nitrogen by denitrification, and the emission of potent greenhouse gasses like methane from methanogenesis and nitrous oxide from nitrification and denitrification.

Despite the enormous area occupied by tropical, shallow lakes, hardly any integrated measurements of the benthic biogeochemical processes have been reported, while numerous studies of benthic processes have been conducted in the sediment of temperate, shallow lakes and coastal waters. The aim of this study was to quantify pathways of organic matter mineralization and nitrogen regeneration in the sediment of various shallow, tropical lakes, using methods and experience from temperate studies. For this study we selected two white water lakes and a clear water lake in the Amazon floodplains and an eutrophic and an oligotrophic coastal lakes in Brazil.

Methods

Sampling sites

Five shallow, Brazilian lakes representing different chemical and biological characteristics were selected for this study (Tab. I). Lagoa Comprida and Lagoa Imboassica are two coastal lakes in the State of Rio de Janeiro while Lake Batata, Lake Purus and

Table I: Physicochemical characteristics of the five lakes at the time and place of sampling. nd = not determined

Variables	Unit	Comprida	Imboassica	Batata	Purus	Sapucuá
Area	km^2	0.13	2.15	18.04	ca. 300	ca. 200
Sampling depth	m	2.2	1	5	4	6.5
Salinity	‰	0.1	0.7	0.0	0.0	0.0
Conductivity	$\mu S\ cm^{-1}$	176	1430	8.2	nd	nd
Temperature	^oC	29.4	29.1	29	29	28.8
pH		4.24	8.18	6.06	7.27	7.25
Alkalinity	$\mu Eq\ l^{-1}$	19.2	912.3	74	nd	nd
90% light reduct. depth	m	0.7	0.5	1.7	0.3	0.3
O_2 water surface	% saturation	85	118	72	100	123
O_2 water bottom	% saturation	85	114	62	76	105
O_2 sediment penetration	mm	3.4	0.9	1.3	nd	nd

Lake Sacupuá are floodplain lakes near the confluence of Rio Amazonas and Rio Trombetas in the state of Pará.

L. Comprida (22° 16' S and 41° 39'W) is a humic, low-alkaline and nutrient poor lake draining a surrounding restinga area, an open shrub vegetation on old marine sand deposits. Intrusion of seawater was marginal at the time of sampling (salinity 0.1 ‰) but occasionally more seawater pass through the sand. L. Imboassica receives freshwater from a small river draining cultivated land and some sewage from the surrounding settlements in the vicinity of the city of Macaé. L. Imboassica is occasionally connected to the sea, and salinity was 0.7 ‰ at the time of sampling. Compared to L. Comprida it is more alkaline and rich in nutrients. The two lakes are described in detail by Esteves (1998).

Lake Batata (1° 30'S and 56° 20'W) is classified as a clear-water lake (Sioli, 1950) and receives most of its water from Rio Trombetas. Until 1989 large amounts of bauxite tailing were deposited in the western part of the lake, and the possible impact has been studied intensively (e.g. Ferrão-Filho & Esteves, 1994). For this study, however, sampling was done in the non-impacted eastern part of the lake. Lake Purus (1° 55'S and 55° 45'W) is separated by narrow land barriers from the main stem of Rio Amazonas on one side and a parallel channel of the river on the other side. The contribution of water from local watersheds is therefore marginal, and the water chemistry mostly resembles white river water with relatively high turbidity, alkalinity and nutrient content (Forsberg et al., 1988). Lake Sapucuá (1° 50'S and 56° 00'W) is a black water, humic lake in the low water season, when runoff from the forest dominate, and a white water lake in the high water season when intruding water from Rio Amazonas dominates. Sampling was done in the filling period when the two types of water mixed in the lake. Precipitation and settling reduced the amount of suspended matter and allowed for a significant phytoplankton production, which was observed as a mm thick layer of settled algae on the bottom.

Sampling

Sampling of all lakes was done in March/2000 at depths where the sediment should be permanently inundated and devoid of photosynthetically active plants or algae. Tubes made of acrylic (ID 2.6 and 3.6 cm) were fixed on a long stick and closed at the top with a rubber stopper and a valve. The tubes were forced into the sediment and withdrawn with a column of about 4 cm intact sediment and 8 cm overlying bottom water. At the same time surface and bottom water was collected for chemical analysis and water column profiles of oxygen were measured with an electrode (Unisense Co.). Light attenuation was measured with Secchi disc or a radiometer (Li-Cor LI184B).

The sediment cores were brought to a laboratory within 3-6 hours and immersed in a dark tank with aerated bottom water from the location kept at "in situ" temperature. A set of 5-6 wide cores (3.6 cm ID) were reserved for flux and denitrification measurements while narrow cores (2.6 cm ID) were used for sulfate reduction and methane production assays. An extra wide core was used for determination of oxygen penetration and sediment density and porosity.

Flux measurements

The height of sediment in each core was adjusted to about 3 cm (Comprida) or about 6 cm (all other lakes) leaving a water column inside the cores of about 10 or 7 cm, respectively. Water within the cores was continuously mixed with suspended magnetic bars driven by an external, rotating magnet (60 rpm). For the coastal lakes fluxes of O_2, CO_2, NO_3^- and NH_4^+ were measured by taking initial samples of the water, closing the cores with stoppers, and take final samples from each core after about 1 hour (Imboassica) or 5 hours (Comprida). A tube with water only was incubated parallel with the sediment cores to account for water column processes in Imboassica and Comprida, but not in the Amazon lakes. The optimal incubation time was estimated from previous crude measurements of oxygen consumption in a few cores. Oxygen concentrations were measured immediately with an oxygen sensor, samples for CO_2 analysis were preserved with saturated $ZnCl_2$ and stored in gas tight vials, and samples for NO_3^- and NH_4^+ were

filtered (GF/F glass filters) and frozen. CO_2, NO_3^- and NH_4^+ fluxes in the Amazon lakes were measured with a reduced water column (2-3 cm) and an air headspace to obtain more significant concentration changes without oxygen depletion in the water column. Oxygen consumption in these cores was measured together with denitrification (see below).

Samples of DIC were analyzed on a Shimadzu TOC analyzer within 4 weeks, NO_3^- and NO_2^- was analyzed by high performance liquid chromatography (HPLC). Sediment-water fluxes were calculated from changes in concentration, incubation time, and height of the water column.

Denitrification

Denitrification was measured with the isotope pairing technique (Nielsen, 1992) following the same procedure for all lakes. The water column in the cores was renewed after the flux measurements and specific amounts of $^{15}NO_3^-$ were added to each core from a stock solution to obtain a range of concentrations from zero up to 90 μM. Initial oxygen concentrations were measured before the cores were closed and incubated with stirring for 1-5 hours. The incubation times were designed to ensure that oxygen should not be depleted by more than 30% in the water column. Sediment structure, coloration, and tracks of benthic animals were observed and noted for each core before the end of the incubation. Height of sediment and water column was recorded as well. At the end of the incubation the cores were opened, final oxygen concentrations were measured and about 5 drops of a saturated $ZnCl_2$ solution (1g ml ml^{-1}) was added to stop respiration processes. Sediment and water was mixed up and the slurry was sampled in 12ml exetainers (Labco Co.) for later analysis of $^{15}N_2$. Mixing and sample transfer was done with minimal contact with air to avoid loss of $^{15}N_2$, and the exetainers were pre-filled with a drop of $ZnCl_2$ solution for extra preservation.

Samples of $^{15}N_2$ were analyzed on a mass spectrometer for the determination of excess $^{29}N_2$ and $^{30}N_2$ produced by denitrification. Production of $^{28}N_2$ (P28) was then calculated assuming that $^{29}N_2$ and $^{30}N_2$ had been formed by random pairing of $^{14}NO_3^-$ and $^{15}NO_3^-$ during denitrification:

$$P28 = (P29)x2 / (4xP30) \qquad (1)$$

Denitrification of ^{14}N (D14) and ^{15}N (D15) was finally calculated from P28, P29, and P30 knowing the incubation time, volume of water column, volume of sediment and sediment porosity. More details in Dalsgaard et al. (2000).

Oxygen consumption rates measured during the incubations for sediment-water fluxes and denitrification were all included in the calculation of average rates in Comprida and Imboassica.

Sulfate reduction

Sulfate reduction rates were measured in intact sediment cores from lakes Imboassica, Comprida and Batata using radioactive isotope tracer technique (Jørgensen 1978). Sediment cores (26 mm ID) were drained of overlying water and 5 μl aliquots of $^{35}SO_4^{-2}$ (activity 50 kBq) were injected at 1 cm depth intervals through silicone sealed holes in the acrylic tubes. After an incubation time of 30 minutes the cores were sliced in at 1 cm intervals down to 7 cm. Each slice was preserved in 10 ml $ZnCl_2$ solution (20%) and later the radioactivity of sulfate and reduced sulfur (HS$^-$, FeS, FeS$_2$, and S^0) was measured after distillation with reduced chromium (Fossing & Jørgensen 1989). Sulfate reduction rates were calculated from the turnover rate of the tracer and the porewater concentration of sulfate.

Methane production

Methane production was only measured in lakes Batata, Comprida and Imboassica. For each station 3 sediment cores were sliced at the depth of 1, 2, 6, and 10 cm (Batata)

or at 4, 8, and 12 cm (Comprida and Imboassica). The slices were transferred to 110 ml serum bottles flushed with N_2 and the bottles were closed. Then the sediment was mixed up and the bottles flushed with N_2 twice. At ½ hours intervals gas samples of 3 ml were collected 5 times with syringes and stored in vacuutainers (Terumo Corp.). Concentrations of methane were measured on a gas chromatograph within 3 months. Methane production rates (nmol CH_4 cm^{-3} d^{-1}) were calculated from the increase in concentration with time. Areal rates (mmol CH_4 m^{-2} d^{-1}) were obtained by depth integration.

Porewater profiles of oxygen and sulfate

Profiles of oxygen in the sediment were measured with a microsensor (Unisense Co.) at a depth resolution of 0.1 mm at 3 spots in cores from Comprida, Imboassica, and Batata. The overlying water was kept gently stirred to ensure natural boundary conditions. The average oxygen penetration depth was determined from the profiles.

A sediment core from each location was sliced at 1 cm intervals for the determination of porewater concentrations of sulfate and sediment porosity. Porewater was extracted by centrifugation, filtered, and preserved with $ZnCl_2$. Porosity was determined from wet and dry weight of slices with known volume.

Results

Physicochemical parameters for the five lakes at the time of sampling are presented in Tab. I. All lakes were well mixed with oxygen concentrations near saturation and the temperatures were around 29ºC at all sites. In accordance with the water sources pH and alkalinity were very low in the humic lake Comprida, low in the clear water lake Batata, and moderate in the white water lakes and lake Imboassica. Light penetration was low in all lakes but the dominating cause seemingly varied from dissolved humics in Comprida, phytoplankton in Imboassica and Sacupuá and suspended clay particles in Purus and Batata.

The appearance of the sediment varied among the 5 lakes: In Imboassica it was fine grained mud/sand and the surface layer was inhabited by the dominating macro invertebrate in Imboassica, the little gastropod *Heleobia australis* (Callisto et al., 1998). Methane bubbles were abundant at depths below 6 cm. No invertebrates were observed in the sediment of Comprida which had a distinct lamination with a 1-2 cm top layer of fluffy brown debris, a 1-3 cm layer of coarse sand in between, and solid peat below. In the 3 Amazon lakes the sediments were all characterized by fine clay particles and few invertebrates. In Batata the sediment contained debris of some annual Cyperaceae species, and methane bubbles were observed at sediment depths below 3 cm. In Sapucuá a 1 mm-thick layer of settled phytoplankton was observed on the top.

Measured sediment-water fluxes and processes are presented in Fig. 1 and Fig. 2. Water column processes accounted for up to 30% of the concentration changes in the cores from Comprida and Imboassica, and this was subtracted in the calculation of sediment-water fluxes. None of the analyzed substances were depleted by more than 30% in any of the flux measurements except for ammonium in the cores from Purus and Sacupuá. Here ammonium concentrations dropped from 0.7-1.1 μM to ‹ 0.1 μM indicated significant consumption in the water column, but it was not possible to correct for that.

Sulfate was only detected in the upper 2 cm of the sediments, and sulfate reduction rates were always low (‹1 mmol m^{-2} d^{-1}) compared to oxygen consumption rates. The added $^{35}SO_4^{-2}$ tracer was rapidly reduced at all sediment depths below 2 cm indicating a persistent potential for sulfate reduction.

Methane production was restricted to sediment depths below 2 cm and varied significantly among the 3 investigate lakes (Fig. 3).

Denitrification rates of $^{15}NO_3^-$ were in general proportional to the added concentrations thus confirming that the calculated denitrification rates of $^{14}NO_3^-$ did represent in situ activity (data not shown; Nielsen, 1992). In Batata and Sapucuá D15 leveled off at $^{15}NO_3^-$ concentrations

above 40 μM, but the estimated D14 rates were not significantly affected and therefore included in the calculated average. Where the $^{15}NO_3^-$ concentrations were below 5-10 μM it was sometimes not possible to calculate reliable D14 rates (Eq. 1) because the production of $^{30}N_2$ was close to the detection limit of the mass spectrometer. Calculated D14 rates were also lowered at the low $^{15}NO_3^-$ concentrations indicating some influence of non-uniform mixing of the isotopes (Nielsen, 1992). All measurements at the lowest $^{15}NO_3^-$ concentrations (‹5-10 μM) were therefore discarded in the estimation of in situ denitrification rates. The water column concentration of NO_3^- in Comprida was 2.4 μM and here NO_3^- from the water column supported as much as 40% of the denitrification activity. All other lakes had lower concentrations of nitrate (0 - 1 μM) and nitrification in the sediment was the only significant source of nitrate for denitrification (80-100%).
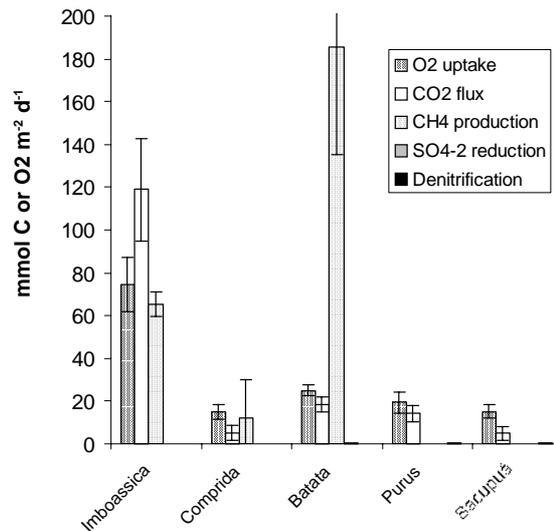

Figure 1: Rates of oxygen uptake, carbon dioxide flux, and mineralization of carbon by methanogenesis, sulfate reduction and denitrification. All rates of sulfate reduction and denitrification were below 1 mmol C m^{-2} d^{-1}. Pins indicate +/- 95% confidence interval of the mean.
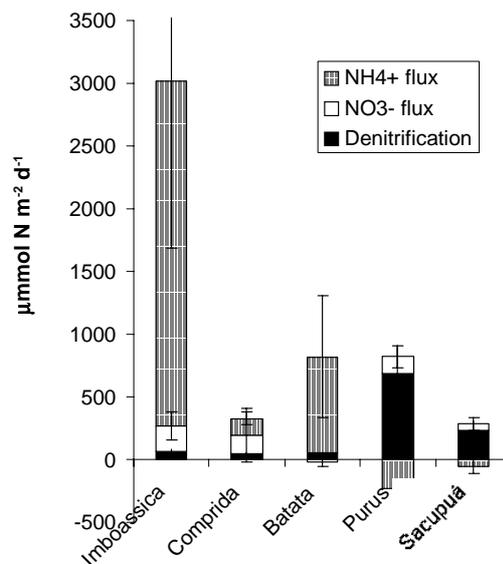

Figure 2: Sediment-water fluxes of ammonium and nitrate and denitrification rates. Negative values indicate uptake by the sediment. Pins indicate +/- 95% confidence interval of the mean.
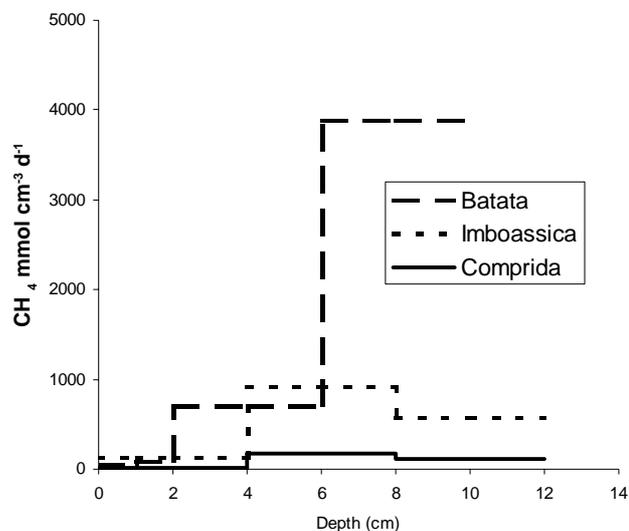
Figure 3: Depth distribution of methane production in lake Imboassica, Comprida, and Batata. Lines represent rates from a certain depth.

Discussion

Oxygen consumption

Benthic oxygen consumption in the eutrophied Lake Imboassica was more than 3 times higher (116 mmol O_2 m^{-2} d^{-1}) compared to any of the four pristine lakes (15 - 31 mmol O_2 m^{-2} d^{-1}). This was also reflected by a thin oxic zone in the sediment of Imboassica (0.9 mm) compared to the other lakes (1.3-3.4 mm). The thin oxic layer indicate that even a minor decrease in bottom water oxygen concentration or increase in oxygen consumption may result in a critical situation where the benthic oxygen demand can no longer be met by diffusional supply from the water column. Then the sediment should turn anoxic to the surface and reduced substances might be released to the water column.

At first glance it seemed strange, that oxygen uptake in the two nutrient rich, white water lakes Purus and Sacupuá was not higher than in lakes Batata and Comprida (Fig. 1). Supersaturated or balanced oxygen concentrations in lakes Purus and Sacupurá (100 and 123%) emphasized the importance of primary production within these systems. In lakes Batata and Comprida the sub-saturation of oxygen in the surface water of (72 and 85% respectively) indicated net heterotrophic systems fueled by terrestial organic matter, which might have compensated for low primary production within the lakes (Roland, 2000; Esteves, 1998). Ultimately the benthic oxygen consumption also depends on how much of the organic carbon input that settled on the bottom and how much of that was oxidized or released as methane.

Anaerobic respiration processes

Reduction of one mole sulfate to sulfide (8 electron equivalents) oxidize 2 moles of organic carbon to CO_2 (4 electron equivalents each), and the highest recorded sulfate reduction rate of 0.5 mmol S m^{-2} d^{-1} in Imboassica thus represents an oxidation of 1 mmol C m^{-2} d^{-1} or about 2% of the measured CO_2 flux (106 mmol m^{-2} d^{-1}). Generally sulfate reduction in lakes is not very important compared to marine systems due to much lower sulfate concentrations (10-500 μM versus 28 mM, Holmer & Storkholm, 2001). We did not measure sulfate reduction in the two lakes influenced by Amazonian white water, but

as sulfate concentrations in the Amazon river mainstem are around 35 μM only (70 μEq l[-1], Furch & Junk, 1997) compared to 500 μM in Lake Imboassica, they probably also have negligible sulfate reduction activity.

Denitrification of one mole NO_3^- to N_2 oxidize 2 moles of organic carbon to CO_2, and in Lake Purus and L. Sacupuá denitrification thus accounted for about 10% of the CO_2 flux. In the other lakes denitrification activity was lower and could not account for more than 1% of the carbon mineralization. The nitrate concentration was very low in all five lakes (‹ 1μM, data not shown) and denitrification was therefore limited by the supply of nitrate from benthic nitrification. In eutrophic streams with much higher NO_3^- concentrations (around 1 mM) denitrification can be the major pathway of carbon oxidation (e.g. Christensen et al., 1989).

Methane production was only measured in Batata, Imboassica, and Comprida and the measurements were based on slurry incubations, opposed to incubations of intact sediment cores for all other processes. The measured methane production rates were very high compared to the measured CO_2 fluxes (60, 80 and 1000% for Imboassica, Comprida and Batata respectively). Methane production in intact cores could be observed from small gas bubbles formed in the sediment cores while standing in the laboratory, and in Imboassica a distinct upper limit of bubble formation was observed at 6 cm depth in the sediment and in L. Batata the upper limit was seen at 3 cm depth. Methane bubbles in the sediment should directly show where the pore water concentration of methane has exceeded saturation (200 μM at 29°C). The importance of ebullition versus diffusive flux of methane to the sediment surface can be estimated roughly from the depth distribution of CH_4 production (Fig. 3). In Comprida, Imboassica, and Batata more than 90% of the methane production (11 and 59 mmol C m^{-2} d^{-1} respectively) was produced below 4 cm depth in the sediment. The maximum possible pore water concentration of methane (C) is given by the saturating concentration of 900 μM CH_4 at 29°C and 1 atm (or 1350 μM at 29°C and 1.5 atm, corresponding to the pressure at 5 m depth). With a diffusion coefficient (D) of methane of 2×10^{-5} cm[2] s^{-1} at 29°C, a porosity (p) of 0.8 v/v, and a methane concentration at the sediment surface of 0 μM (Co) the diffusive flux (J) from 4 cm depth (z) to the sediment surface becomes J = D * p^2 * (C-Co) / z = 0.6 mmol C m^{-2} d^{-1}. Added to the methane production above 4 cm depth the maximal contribution of diffusion to methane flux becomes 15% and 11% in Comprida, Imboassica and Batata, respectively. In Batata this estimated maximal diffusive flux was 15 mmol m^{-2} d^{-1}, well above the diffusive flux of 4 mmol CH_4 m^{-2} d^{-1} that we measured in a parallel study at this location (Enrich-Prast et al, in preparation)

Ebullition of methane may also strip some CO_2 out of the sediment and this could explain the low diffusive CO_2 fluxes relative to CH_4 production rates. As a minimum, the total CO_2 flux from a sediment should equal the CH_4 flux and be higher to the extent that CH_4 oxidation occur in the sediment and organic carbon is mineralized by other pathways. The measured methane production in Lake Batata was 40 times higher than the average methane flux measured by Bartlett et al. (1990) at the air-water interface in the open waters of the Amazon floodplains (74 mg CH_4 m^{-2} d^{-1} = 4.6 mmol C m^{-2} d^{-1}). This discrepancy could be explained by methane oxidation in the water column. Before making any firm conclusions on methane oxidation and benthic methane production, the slurry technique applied here should be more carefully tested and developed to clarify whether methane production could have been stimulated as the sediment slurries were mixed in the glass incubation bottles.

Nitrogen cycling

The higher rates of nitrification-denitrification in the two white water lakes, Purus and Sapucuá were also reflected in the fluxes of NO_3^- and NH_4^+. Both sites had significant release of nitrate from the sediment and a net uptake of ammonium from the water column. In both the sewage impacted L. Imboassica and in the oligotrophic lake Batata the situation was opposite, with the sediment acting as a significant net source of ammonium and with NO_3^- fluxes not significantly different from zero. The results are

readily explained by limitation of nitrification by availability of either phosphorus, ammonium or oxygen in the different lakes. In a parallel nutrient enrichment study we have shown, that in Batata the nitrifying as well as methane oxidizing bacteria most likely are limited by the availability of phosphate (Enrich-Prast et al., in preparation). In the more nutrient rich L. Purus and L. Sacupuá the negative ammonium fluxes implied that nitrification consumed not only the NH_4^+ generated in the sediment, but also some NH_4^+ from the water column. During the flux measurements in L. Purus NH_4^+ was depleted to ‹ 0.1 μM in the overlying water of all cores except one, thus indicating that the nitrification rate might have been even higher in situ where the concentration was around 0.6 μM. It should be noted, however, that nitrification of ammonium from the water column is concentrated in the upper part of the oxic zone and therefore not very closely coupled to denitrification. In L. Imboassica both phosphate and NH_4^+ were available and yet the nitrification-denitrification activity was low. Here an oxic zone of only 0.7 mm most likely induced a severe O_2 limitation of nitrification. Both models and experiments with coastal and limnic sediments have demonstrated how nitrification activity peaks at intermediate levels of benthic metabolism (15 mmol O_2 m^{-2} d^{-1}) while ammonium or O_2 becomes limiting at lower and higher levels, respectively (Blackburn & Blackburn, 1995).

L. Imboassica receives more than 70 kg N d^{-1} with sewage from the surrounding settlements (Lopes-Ferreira & Pasin, 1998). That is equal to a nitrogen load of 2.3 mmol m^{-2} d^{-1} for the whole lake or 35 times more than the measured rate of denitrification in the sediment. Apparently this system has reached a level of eutrophication where oxygen depletion in the sediment stops a natural elimination of nitrogen through nitrification-denitrification.

Previous attempts to measure denitrification in flooded sediments of the Amazon basin have mostly failed to detect any activity with "in situ" levels of nitrate (Melack & Fisher 1988, Enrich-Prast et al., 2001; Kern et al., 1996). Only Kern et al. (1996) detected some activity in the white water lake Camaleão in November and December (29 and 293 μmol N m^{-2} d^{-1} respectively) in association with higher water column concentrations of nitrate. Otherwise denitrification was undetectable in August, September, October, January and February in Lake Camaleão, in September and March in another white water lake, Calado (Melack & Fisher, 1988) and in March in Batata and the neighboring lake Mussurá (Esteves & Enrich-Prast, 1998). Contrary to these studies we detected denitrification rates from 52 to 685 μmol N m^{-2} d^{-1} in all three investigated Amazonian lakes, and the activity was not associated with nitrate in the overlying water. The discrepancy is most likely explained by methodological differences. The previous studies are all based on the acetylene inhibition technique, and as acetylene also inhibits nitrification, coupled nitrification-denitrification has probably been grossly underestimated (Seitzinger et al., 1993). Part of the discrepancy may also be due to different oxygen concentrations in the bottom water as nitrification is dependent on the availability of oxygen. The results indicate that nitrification-denitrification in the white water, flood plain lakes must vary considerably with the season as bottom water oxygen concentrations changes from 100 % saturation during mixing to zero during stratification in the high water period.

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