Nitrous oxide and methane in two tropical estuaries in a peat-dominated region of North-western Borneo

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Abstract. Estuaries are sources of nitrous oxide (N_2O) and methane (CH_4) to the atmosphere. However, our present knowledge of N_2O and CH_4 emissions from estuaries in the tropics is very limited because data is scarce. In this study, we present first measurements of dissolved N_2O and CH_4 from two estuaries in a peat-dominated region of north-western Borneo. Two campaigns (during the dry season in June 2013 and during the wet season in March 2014) were conducted in the estuaries of the rivers Lupar and Saribas. Median N_2O concentrations ranged between 7.2 and 12.3 nmol L^{-1} and were higher in the marine end-member (13.0 ± 7.0 nmol L^{-1}). CH_4 concentrations were low in the coastal ocean (3.6 ± 0.2 nmol L^{-1}) and higher in the estuaries (medians between 10.6 and 64.0 nmol L^{-1}). The respiration of abundant organic matter and presumably anthropogenic input caused a slight eutrophication, which did not lead to hypoxia or enhanced N_2O concentrations, however. Generally, N_2O concentrations were not related to dissolved inorganic nitrogen concentrations. Thus, the use of an emission factor for the calculation of N_2O emissions from the inorganic nitrogen load leads to an overestimation of the flux from the Lupar and Saribas estuaries. N_2O was negatively correlated with salinity during the dry season, which suggests a riverine source. In contrast, N_2O concentrations during the wet season were not correlated with salinity but locally enhanced within the estuaries, implying that there were additional estuarine sources during the wet (i.e. monsoon) season. Estuarine CH_4 distributions were not driven by freshwater input but rather by tidal variations. Both N_2O and CH_4 concentrations were more variable during the wet season. We infer that the wet season dominates the variability of the N_2O and CH_4 concentrations and subsequent emissions from tropical estuaries. Thus, we speculate that any changes in the Southeast Asian monsoon system will lead to changes in the N_2O and CH_4 emissions from these systems. We also suggest that the ongoing cultivation of peat soil in Borneo is likely to increase N_2O emissions from these estuaries, while the effect on CH_4 remains uncertain.

1. Introduction

Nitrous oxide (N_2O) and methane (CH_4) are greenhouse gases whose global warming potentials exceed that of carbon dioxide (CO_2) by far (a factor of 265 for N_2O and 28 for CH_4 on a 100 year time horizon, Myhre et al., 2013). Thus, an assessment of the natural and anthropogenic sources and sinks as well as the formation pathways of N_2O and CH_4 is essential
5 to understand Earth's present climate variability and to predict its future development. The world's oceans, including its coastal zones, are sources of N_2O and CH_4 to the atmosphere and play a major role in the global budget of atmospheric N_2O, but only a minor role in the global budget of atmospheric CH_4 (Ciais et al., 2013). Rivers and estuaries are considered hotspots for the production and emission of both N_2O and CH_4 (Bange, 2006; Bastviken et al., 2011; Borges et al., 2015; Murray et al., 2015; Seitzinger and Kroeze, 1998).

10 In aquatic systems, N_2O is mainly formed as a byproduct during nitrification ($NH_4^+ \rightarrow NO_3^-$) and to minor extent as an intermediate during denitrification ($NO_3^- \rightarrow N_2O \rightarrow N_2$) (Freing et al., 2010). In both processes, the yield of N_2O strongly depends on the concentration of oxygen (O_2) (e.g. Bange, 2008). Both nitrification and denitrification are microbial processes and occur in the water column and in sediments (e.g. Bange, 2008). CH_4 is formed during the decomposition of organic material by microbial methanogenesis (e.g. Reeburgh, 2007; Valentine, 2011; Ferry, 2010). Since CH_4 formation
15 requires strictly anaerobic conditions, CH_4 is produced in anoxic environments found in sediments, in the interior of suspended particles or in zooplankton guts (see e.g. Reeburgh, 2007; Valentine, 2011). Additionally, CH_4 is oxidized under aerobic and anaerobic conditions in the water column and in the sediments, respectively (e.g., Valentine, 2011). On the continental shelf so-called geological CH_4 can be released directly to the water column through mud volcanoes, via groundwater input or seeping at pockmark structures (e.g., Valentine, 2011). Alternative aerobic CH_4 formation pathways in
20 the nutrient poor (oligotrophic) surface ocean have been suggested (see e.g. Karl et al., 2008; Damm et al., 2010; Zindler et al., 2013), but they are negligible in nutrient rich (eutrophic) coastal systems.

In this study, we present first measurements of dissolved N_2O and CH_4 from the estuaries of the rivers Lupar and Saribas, which are located in north-western Borneo (Sarawak, Malaysia, Southeast Asia). These measurements are complemented by dissolved N_2O and CH_4 measurements from a cruise on the adjacent coastal shelf of the South China Sea. The Lupar and
25 Saribas rivers drain catchments which are covered by tropical peatlands, parts of which have been converted to oil palm plantations or other crops. This study aimed at investigating the effect of the carbon-rich peatlands on the N_2O and CH_4 estuarine distributions and emissions and the potential impact of estuarine eutrophication. Two intensive sampling campaigns took place during the dry and wet seasons in June 2013 and March 2014, respectively, and provide a first account of the seasonality in these systems.

2. Materials and Methods

2.1 Study Area

Our study was conducted in Sarawak, the largest Malaysian state, which is located in the north of the island of Borneo (see Fig. 1a). About 12 % of the area of Sarawak is covered by peatlands (Chai, 2005), approximately 41 % of which have been converted to oil palm plantations (SarVision, 2011). Sarawak has a tropical climate with a mean annual air temperature of 26.1°C in the capital Kuching and average (1961-1990) annual rainfall of 4101 mm (DWD, 2007). Between November and February, Sarawak experiences enhanced rainfall due to the Northeast monsoon, while June and July are the driest months (DWD, 2007).

Two macrotidal estuaries which enclose Malaysia's largest peat dome, the Maludam peninsula, are in the focus of this study. The catchment areas of the Lupar and Saribas rivers are 6558 km² and 1943 km², respectively (Lehner et al., 2006), with approximate discharges of 490 $m^3 s^{-1}$ and 160 $m^3 s^{-1}$ (Müller et al., 2016). The Lupar catchment comprises mainly the division of Sri Aman, which has a population of approximately 95,000. The Saribas basin belongs largely to the Betong division, with a population of approximately 110,000 (SPU, 2012). Major settlements along the Lupar River and estuary are Sri Aman, Lingga and Sebuyau (Fig. 1b). Important settlements along the Saribas River and estuary are Betong, Pusa and Beladin. Oil palms are being cultivated in both catchments (Fig. 1b).

In the Lupar and Saribas estuaries, sampling took place during two campaigns in June 2013 and March 2014. Our sampling strategy is described in detail in Müller et al. (2016). In that study, we showed that precipitation during June 2013 and March 2014 did not deviate much from the historical average, so that we considered the measurements in June 2013 representative of the dry season and those in March 2014 representative of the wet season. Therefore, we refer to the two campaigns as "MLD dry" (June 2013) and "MLD wet" (March 2014). Note that the peak of the monsoon season is between December and February, so the monsoon recedes in March, which is why our statements about seasonality are conservative.

We complement this dataset with measurements that were performed during the cruise SO218 – SHIVA with the German research vessel (R/V) *Sonne* (15-29 November 2011) (Quack and Krüger, 2013). The cruise started in Singapore and went along the Sarawakian coastline to end in Manila, Philippines (see Fig. 1a). For this study, we selected those samples that were taken in the coastal ocean off north-western Sarawak (latitude <2.5, 110.5<longitude<111.5) in order to complement our dataset from the Lupar and Saribas estuaries.

2.2 Water chemistry

In the Lupar and Saribas inner and outer estuaries, we sampled 20 stations during the dry season and 23 during the wet season. Water samples were taken from approximately 1 m below the water surface. Samples were taken for dissolved organic carbon (DOC), dissolved inorganic (nitrogenous) nutrients (DIN = NO_3^-, NO_2^-, and NH_4^+), salinity, water temperature and O_2:

1. Samples for DOC were filtered (pore size 0.45 μm) and acidified with 21 % phosphoric acid until the pH had dropped below 2. DOC concentrations were determined by high temperature combustion and subsequent measurement of resultant CO_2 with a non-dispersive infrared detector (NDIR) (EPA method 415.1). Details are given in Müller et al. (2016).

2. Inorganic nutrient samples were filtered through a Whatman glass microfibre filter (pore size 0.7 μm), preserved with a mercuric chloride ($HgCl_2$) solution and frozen until analysis. Concentrations of NO_3^-, NO_2^- and NH_4^+ were determined spectrophotometrically (Hansen and Koroleff, 1999) at a wavelength of 540 nm with a Continuous Flow Analyzer (Alliance, Austria).

3. Salinity and temperature were measured with a CastAway CTD at each station during the MLD cruises. Additionally, we measured conductivity using a TetraCon 925 conductivity sensor (WTW, Germany). We converted conductivity to salinity using the equations from Bennett (1976). During SO218, salinity and temperature were measured continuously with a thermosalinograph on board.

4. Dissolved oxygen (DO) was measured using a Multi3420 with an FDO 925 oxygen sensor (WTW, Germany). A routine function check in water vapor saturated air was conducted prior to the measurements using the check and calibration vessel that was provided with the sensor.

2.3 N_2O and CH_4 measurements

Our setup during the MLD cruises is described in detail in Müller et al. (2016). Surface water was pumped through a Weiss equilibrator (Johnson, 1999) at a rate of approximately 20 L min^{-1}. The headspace air was analyzed using an in-situ Fourier Transform InfraRed (FTIR) trace gas analyzer (University of Wollongong, Australia). This instrument allows for the continuous and simultaneous measurements of several trace gas species, such as N_2O and CH_4 as well as CO_2 and CO (Müller et al., 2016) with high accuracy and precision over a wide range of concentrations (Griffith et al., 2012). Spectra were averaged over 5 min and dry air mole fractions were retrieved using the software MALT5 (Griffith, 1996). The gas dry air mole fractions were corrected for pressure, water and temperature cross-sensitivities (Hammer et al., 2013). The CO_2 and CO data obtained from these measurements have been reported by Müller et al., (2016). Here, we present the N_2O and CH_4 measurements. Calibration was achieved by measuring a suite of gravimetrically prepared gas mixtures (Deuste Steininger) ranging from 324 to 3976 ppb N_2O and 1.8 to 239 ppm CH_4 in synthetic air, which were calibrated against the World Meteorological Organization (WMO) reference scale at the Max-Planck-Institute for Biogeochemistry in Jena, Germany. The error associated with the FTIR retrieval is usually small. In ambient air, the total uncertainties reported by Hammer et al. (2013) are 0.084 nmol mol^{-1} for N_2O and 0.25 nmol mol^{-1} for CH_4, corresponding to approximately 0.01 % and 0.03 %. The larger source of uncertainty is a potentially remaining disequilibrium between water and headspace in the equilibrator, which can cause an error of <0.2 % for N_2O and 2 % for CH_4 (Johnson, 1999).

Water temperature in the equilibrator and in the water as well as ambient air temperature and pressure were monitored as described in Müller et al. (2016). N_2O and CH_4 partial pressures were calculated. Since the sample air was dried before

entering the FTIR analyzer, we corrected for the removal of water vapor (Dickson et al., 2007). N_2O molar concentrations were calculated from N_2O fugacity and solubility (K_0) according to Weiss and Price (1980). CH_4 molar concentrations were calculated from CH_4 partial pressure and solubilities were derived from the equations given by Wiesenburg and Guinasso (1979).

5   During the R/V *Sonne* cruise SO218, surface sea water was continuously supplied from the ship's hydrographic shaft (moon pool) using a submersible pump at about 4 m water depth. N_2O and CH_4 samples were taken in triplicates, preserved with $HgCl_2$ and analyzed in the lab using headspace equilibration and gas chromatography. Details about the analytical procedures can be found in Walter et al. (2006) and Bange et al. (2010). The average of the three samples was calculated and data was discarded if the standard deviation exceeded 30 % of the average value. For N_2O, two additional data points were

10   taken from the surface N_2O concentrations determined in depth profiles.

Atmospheric mixing ratios of N_2O were taken from the Mauna Loa (Hawaii) monitoring station of the NOAA/ESRL halocarbons in situ program (Dutton et al., 2015) which was the nearest atmospheric N_2O monitoring station in the northern hemisphere. Atmospheric N_2O in Mauna Loa averaged 325.15 ppb in November 2011, 326.26 ppb in June 2013 and 327.08 ppb in March 2014. Atmospheric CH_4 was derived from the NOAA/ESRL GMD Carbon Cycle Cooperative Global Air

15   Sampling Network (Dlugokencky et al., 2014). The nearest atmospheric CH_4 monitoring station was Bukit Kototabang, Indonesia. Unfortunately, CH_4 data from NOAA/ ESRL were not available for March 2014, so we estimated the atmospheric CH_4 during that month from the value reported for March 2013 and an annual growth rate of 4 ppb between 2004-2013 at Bukit Kototabang. Atmospheric CH_4 averaged 1841.64 ppb in November 2011, 1798.64 ppb in June 2013 and a value of 1879.35 ppb was derived for March 2014.

20   **2.4 Flux estimation**

In order to calculate N_2O and CH_4 flux densities F (in nmol m^{-2} s^{-1}) across the water-air interface, we used the thin film model, which is expressed by the following equation:

$$F = kK_0(pGas_{water} - pGas_{air})f, \qquad\qquad (1)$$

where k is the gas exchange velocity (m s^{-1}), K_o ist the solubility of N_2O and CH_4 in seawater (mol L^{-1} atm^{-1}, see Sect. 2.3),

25     $pGas_{water}$ is the partial pressure derived from the equilibrator measurements (natm), $pGas_{air}$ is the partial pressure of the gas in air (natm) as measured at the atmospheric monitoring stations (see Sect. 2.3), and f is a conversion factor from L^{-1} to m^{-3}.

For k, we used k600 values that were derived for the Lupar and Saribas estuaries using the floating chamber method (Müller et al., 2016). Floating chamber measurements were conducted at several locations along the estuaries during the wet season campaign and averaged over the spatial extent of the individual estuaries. We argued in Müller et al. (2016) that the k600

30   values determined in this way are more appropriate than commonly used wind speed parameterizations, which neglect the influence of tidal currents and the water flow velocity. In-situ k was calculated based on the Schmidt numbers of N_2O and CH_4, which relates the kinematic viscosity to the diffusivity of the gas in water. Kinematic viscosity was calculated according to Siedler and Peters (1986), the diffusivity of N_2O was computed using Eq. 2 in Bange et al. (2001) and the

diffusivity of CH_4 was calculated with the formula given in Jähne et al. (1987). The annual areal flux density was estimated as the average of the wet and dry season values (for the spatial extent that was covered during the 2013 cruise, see Müller et al., 2016). The total N_2O and CH_4 fluxes (t N yr^{-1} and t C yr^{-1}) were calculated assuming an estuarine surface area of 220 km² for the Lupar and 102 km² for the Saribas estuary (Müller et al., 2016). For N_2O, we compare this estimate to one derived using the DIN export and the emission factor for estuaries suggested in Mosier et al., (1998) (0.0025 kg N_2O-N / kg N leaching and runoff). The DIN export was calculated from river discharge (see Sect. 2.1) and the median DIN concentration.

3. Results

3.1 Water chemistry

In the estuaries of Lupar and Saribas, salinity ranged from 0-30.6 in the dry season and from 0-31.0 in the wet season. N_2O and CH_4 concentration data are available for salinities of 4.3-26.5 (MLD dry) and 6.9-26.4 (MLD wet). For the coastal ocean off north-western Sarawak, N_2O measurements covered salinities between 31.3 and 32.7 and CH_4 measurements between 32.2 and 32.7. DO saturation in the estuaries ranged between 63.6 to 94.6 % (MLD dry) and 79.0-100.4 % (MLD wet) (Müller et al., 2016).

The total DIN concentrations were already published in Müller et al. (2016). Here, we report the concentrations of the different inorganic nitrogen species. Generally, DIN concentrations were quite low, but locally enhanced. NO_3^- ranged between 6.3 µmol L^{-1} and 36.3 µmol L^{-1} in the dry season and between 2.8 and 17.9 µmol L^{-1} in the wet season. A maximum value of 84.0 µmol L^{-1} was observed during MLD dry approximately 20 km offshore in north-western direction from Sebuyau. There, an influence from the Lupar river plume, but possibly also from the close-by Sadong River was detected (salinity = 22.2).

NO_2^- concentrations ranged between 0.1 µmol L^{-1} and 0.6 µmol L^{-1} in the dry season and between <0.1 µmol L^{-1} and 2.3 µmol L^{-1} in the wet season. NH_4^+ ranged between <0.1 µmol L^{-1} and 2.6 µmol L^{-1} in the dry season, whereas a maximum value of 8.0 µmol L^{-1} was observed at one station in the Lupar estuary. In the wet season, NH_4^+ was higher, ranging between 0.2 µmol L^{-1} to 7.8 µmol L^{-1}. However, overall, DIN concentrations were higher in the dry season than in the wet season (Müller et al., 2016, Table 1).

On the Lupar River, we determined average DIN concentrations of 5.1 µmol L^{-1} (2013) and 5.3 µmol L^{-1} (2014) upstream of the town of Sri Aman, which can be considered unpolluted. This value is 2-6 times lower than the DIN concentrations in the Lupar estuary. On the Saribas River, a slightly enhanced value of 18.6 µmol L^{-1} (2013) was measured at salinity 0 outside the town of Betong, so it cannot be considered unpolluted, yet it was lower than the DIN concentrations in the estuary during that season (Table 1). We estimated that together, Lupar and Saribas deliver 6086 t N as DIN to the South China Sea every year (Table 1).

3.2 N$_2$O

Dissolved N$_2$O concentrations in the water ranged from 6.9 nmol L^{-1} to 13.4 nmol L^{-1} during MLD dry in June 2013 (corresponding to saturations of 103 to 184 %) and from 6.6 nmol L^{-1} to 116.8 nmol L^{-1} during MLD wet in March 2014 (102 to 1679 % saturation). Most of the time, N$_2$O was close to atmospheric equilibrium. However, local enhancements were

5   observed: During both the dry and the wet season, the Saribas tributary exhibited markedly higher N$_2$O concentrations than the Saribas main river (Fig. 3a,b, Table 2). During the wet season, N$_2$O concentrations were more variable (higher standard deviation (SD)) and higher maximum concentrations were observed (Table 2). Although the mean N$_2$O concentrations in the Saribas estuary and Saribas tributary were higher in the wet season as well, no difference was found with regards to the medians (Table 2).

10   Salinity and N$_2$O concentrations were correlated in the dry season (r = -0.62), but uncorrelated in the wet season (Fig. 2c). By the town of Sebuyau at the Lupar river mouth, where the Sebuyau River flows into the South China Sea, N$_2$O was enhanced with concentrations of up to 116.8 nmol L^{-1} in the wet season (not shown in Fig. 2-4). The data from SO218 revealed enhanced N$_2$O concentrations offshore during November 2011 (see Fig. 2c), with a median of 13.0 ± 7.0 nmol L^{-1} (218 ± 119 % saturation, see Table 2).

15   N$_2$O was correlated with DOC (Fig. 2a); this correlation was strong in the dry season (r=0.87) and weak during the wet season (r=0.38). N$_2$O concentrations were not correlated with DIN (Fig. 2b), NO$_3^-$, NH$_4^+$ (not shown) or DO (Fig. 2d). During the dry season, we found no link between N$_2$O concentrations and tidal variations (Fig. 4a). In the wet season, however, N$_2$O exhibited slightly higher concentrations during low tide and its spatiotemporal variation resembled that of CH$_4$ (Fig. 4b).

20   ### 3.3 CH$_4$

Dissolved CH$_4$ concentrations ranged from 5.2 nmol L^{-1} to 59 nmol L^{-1} during MLD dry in 2013 (228 to 2782 % saturation) and from 3.7 nmol L^{-1} to 135 nmol L^{-1} during MLD wet in 2014 (168 to 6003 % saturation) in the Lupar and Saribas estuaries and were spatially variable. The highest value was measured by the town of Sebuyau during MLD wet, whereas the highest median concentrations were detected in the Saribas estuary during the dry season and in the Saribas tributary during

25   the wet season (Fig. 3c,d; Table 3). In general, no seasonal pattern could be identified. Mean and median CH$_4$ concentrations in the Lupar estuary were comparable in the dry and wet seasons. In the Saribas estuary, CH$_4$ concentrations were higher during the dry season but in the Saribas tributary, they were higher during the wet season (Table 3). However, higher maximum concentrations were observed in the wet season in both estuaries and the tributary (Table 3).

CH$_4$ concentrations were not correlated with salinity (Fig. 5c). A relatively low marine end-member concentration was

30   determined during the SO218 cruise: With a median of 3.6 ± 0.2 nmol L^{-1} (176 ± 9 % saturation), CH$_4$ concentrations in the coastal ocean were only slightly enhanced in comparison to the atmospheric equilibrium concentration (see Table 3).

CH_4 was not correlated with DOC (Fig. 5a), DO (Fig. 5d), DIN or suspended particulate matter (not shown), but increased with increasing pCO_2 (Fig. 5b). This relationship was stronger in the wet season (r=0.55) than in the dry season (r=0.15). One striking feature was that CH_4 showed a strong response to the tides (Fig. 4). This is visible for most of the data, even though we changed location during the measurements. Tidal and spatial variations are overlapping in Fig. 4, but the tidal variation seems to dominate. This is confirmed by one stationary measurement that we conducted over night at one station on the Saribas tributary in 2014 (Fig. 4b): CH_4 peaked 4-fold during low tide when compared to the concentration at high tide.

3.4 N_2O and CH_4 flux densities

Median N_2O and CH_4 flux densities are listed in Table 4. Both the highest N_2O flux density and the highest CH_4 flux density were computed for the Saribas tributary. During both seasons, N_2O flux densities from the Saribas tributary were up to one order of magnitude higher than from the Lupar and the Saribas estuaries. Annual average N_2O flux densities were low for both Lupar and Saribas, amounting to 1.3 ± 0.3 mmol m^{-2} yr^{-1} and 1.9 ± 1.6 mmol m^{-2} yr^{-1}, respectively. The N_2O flux density from the Saribas tributary was one order of magnitude higher (12.0 ± 7.5 mmol m^{-2} yr^{-1}).

The CH_4 flux density observed on the Saribas tributary during the wet season was approximately five times higher than the flux densities from Lupar or Saribas during any season. As a result, the annual average flux from the Saribas tributary (89.2 ± 55.2 mmol m^{-2} yr^{-1}) was approximately four times as high as those computed for the Lupar and Saribas estuaries, which were comparable (22.5 ± 5.4 mmol m^{-2} yr^{-1} and 23.0 ± 19.1 mmol m^{-2} yr^{-1}, respectively).

In total, 4 ± 1 t N_2O-N yr^{-1} and 60 ± 17 t CH_4-C yr^{-1} were emitted from the Lupar estuary and 3 ± 2 t N_2O-N yr^{-1} and 28 ± 25 t CH_4-C yr^{-1} from the Saribas (Table 4). Using the emission factor of Mosier et al., (1998), we obtained emission estimates of 11 t N_2O-N yr^{-1} for the Lupar and 4 t N_2O-N yr^{-1} for the Saribas estuary.

4. Discussion

4.1 Eutrophication in the Lupar and Saribas estuaries

Blackwater rivers and their estuaries usually have very low nutrient concentrations (<1 µmol L^{-1} NO_3^-, Kselik and Liong 2004; <5 µmol L^{-1} NO_3^-, Alkhatib et al., 2007). Although the Lupar and Saribas rivers are not blackwater rivers, they have several blackwater tributaries (Kselik and Liong 2004; Müller et al., 2016), and 30.5 % and 35.5 % of their catchments are covered by peat (Müller et al., 2016). Therefore, rather low nutrient concentrations were expected. However, several villages and smaller towns are found along the shore of both estuaries, and there is cultivation of sago and oil palm in the catchments (Fig. 1b).

Estuarine DIN concentrations were higher than in the unpolluted freshwater end-member of the Lupar River, indicating that the estuary was indeed slightly eutrophic during the time of our measurements. This eutrophication can be attributed both to the release of DIN during respiration of organic matter, which was shown to be pronounced in the Lupar and Saribas

estuaries (Müller et al., 2016), especially in the dry season (see discussion below), and to anthropogenic input. These processes were also identified as important sources of inorganic nutrients in the Siak River, a eutrophic blackwater river in central Sumatra, Indonesia (Baum and Rixen, 2014). The DIN concentrations in the Lupar and Saribas estuaries were similar to those reported by Baum and Rixen (2014) for the Siak River.

5   Eutrophication can lead to enhanced estuarine primary production and consequently to hypoxia. This was not observed. Although organic matter was respired in the estuaries (Müller et al., 2016), oxygen depletion was relatively moderate in the surface water due to a quick replenishment from the overlying air, as suggested by the high gas exchange velocity (Table 4). Since we did not measure oxygen profiles, we can only speculate about the oxygen levels in the bottom water. The high turbulence in the water likely prevented stratification and promoted the ventilation of the water column and, therefore, may

10 have prevented the development of anoxic bottom waters.

4.2 N_2O

Dissolved N_2O concentrations were mostly close to atmospheric equilibrium concentrations (i.e. 100% saturation), which is in line with other comparable studies in the tropics and subtropics (Richey et al., 1988; Zhang et al., 2010; Rao and Sarma 2013; Borges et al., 2015). High N_2O concentrations were reported for eutrophic and hypoxic coastal waters in the western

15 Indian continental shelf (up to 533 nmol L^{-1}, Naqvi et al., 2000) and for the Peruvian upwelling (up to 986 nmol L^{-1}, Arevalo-Martinez et al., 2015). Similarly, N_2O concentrations in the subtropical Brisbane estuary were higher than in the Lupar and Saribas (median concentrations between 7.2 and 12.3 nmol L^{-1}), ranging between 9.1 and 45 nmol L^{-1} (Musenze et al., 2014).

The low N_2O concentrations in the Lupar and Saribas estuaries are not surprising. Even though these estuaries were slightly

20 eutrophic, the DIN concentrations were still below the average for tropical non-blackwater rivers (Baum and Rixen, 2014). For estuaries with low DIN concentrations, low N_2O concentrations are expected (Zhang et al., 2010). Interestingly, enhanced N_2O was measured offshore during cruise SO218. Either a source of N_2O exists on the continental shelf, or the enhanced N_2O concentrations are due to interannual variability: The SO218 cruise took place in 2011, while the measurements in the Lupar and Saribas estuaries were performed in 2013 and 2014. Ultimately, the SO218 measurements

25 were performed at the onset of the monsoon season, so possibly, seasonal variability plays a role. This is considered most likely, as it is in line with the tendency towards higher and more variable N_2O concentrations during MLD wet when compared to MLD dry in the Saribas tributary.

Stronger oxygen depletion and higher DIN concentrations suggest higher respiration rates during the dry season (Müller et al., 2016). In accordance with this, N_2O was well correlated with DOC and salinity during the dry season, suggesting that it

30 originated mainly from respiratory activity in the upper estuary. In this study, samples were not collected for salinities<4, so we cannot make this claim with certainty. However, previous studies suggest that the highest N_2O concentrations are usually encountered at low salinities in the vicinity of the turbidity maximum (Robinson et al., 1998, Barnes and Owens, 1999, Zhang et al., 2010). On the other hand, N_2O maximum concentrations along estuaries may also occur at intermediate

salinities (de Wilde and de Bie, 2000). This seems to have been the case during our wet season campaign, where we observed the highest N_2O concentrations at salinities between 10-20 (Fig. 2c). N_2O concentrations were not correlated with salinity during the wet season and the correlation with DOC was weak, suggesting that additional sources of N_2O existed in the estuary and obscured these relationships. The nature of this additional estuarine source is indicated by the covariation of

5   N_2O and CH_4. The variability of both gases was linked to the tidal cycle, which was not the case for N_2O during MLD dry (see Fig. 4). This implies that N_2O and CH_4 had the same source during the wet season and that this source was located within the estuary at intermediate salinities. In line with the tidal variability, we propose production of both N_2O and CH_4 in estuarine sediments or in tidal creeks as a common source of both gases

The most striking feature of the spatial distribution of N_2O was its strong variability, with enhanced concentrations in the

10   Saribas tributary during both seasons, indicating a local source. The most obvious candidate for a point source is anthropogenic, i.e. sewage. However, NO_3^-, NO_2^-, and NH_4^+ were not enhanced in the same way as N_2O, suggesting that DIN concentrations are a poor predictor for estuarine N_2O concentrations (see discussion below).

4.3 CH_4

Similar to N_2O, dissolved CH_4 concentrations were relatively moderate. For example, while CH_4 concentrations in the

15   partially hypoxic Pearl River estuary ranged between 23 and 2984 nmol L^{-1} (Chen et al., 2008), median CH_4 concentrations in our study area varied between 4-64 nmol L^{-1}. Similarly, the CH_4 concentration range reported by Musenze et al. (2014) for the Brisbane estuary, Australia, was substantially higher (31-578 nmol L^{-1}) than in this study, although both the DOC concentration range and the DO saturation range were similar. This is surprising, as the peat-draining tributaries are extremely oxygen-depleted and contain large amounts of organic matter (Müller et al., 2015). These conditions are usually

20   suitable for CH_4 production. Although we do not have data on the river end-member CH_4 concentration, we can infer from the lack of correlation between CH_4 and salinity that freshwater input was not the main source of CH_4 in the estuaries. Since CH_4 is a poorly soluble gas, a large fraction might be released to the atmosphere before reaching the estuary and the coastal ocean. Another possible explanation is methane oxidation, which was shown to remove large fractions of CH_4 in some estuaries (deAngelis and Scranton 1993, Abril et al. 2007). Although CH_4 concentrations tended to be higher during the wet

25   season, a clear seasonal pattern of CH_4 concentrations was not apparent, which is in line with observations at other tropical (Barnes et al., 2006; Teodoru et al., 2014) and subtropical (Musenze et al., 2014) sites.

The generally positive relationship between CH_4 and pCO_2 has been observed in other tropical aquatic systems (Teodoru et al., 2014, Borges et al., 2015) and is indicative of organic matter decomposition as a source of both gases. The strong response of CH_4 to tidal variations indicates that CH_4 is produced in the sediments and released when the hydrostatic

30   pressure drops during falling tide. The tidal variability of CH_4 (and N_2O in the wet season) can also be interpreted as indication of the contribution of intertidal sediments and tidal creeks to the CH_4 concentrations in these estuaries. The importance of tidal creeks (Middelburg et al., 2002) and tidal pumping (Barnes et al., 2006; Borges and Abril, 2011) for CH_4 concentrations in estuaries is widely recognized.

4.4 N_2O and CH_4 flux densities and emissions

With the exception of the Saribas tributary (F_{annual} = 12.0 ± 7.5 mmol m^{-2} yr^{-1}), N_2O flux densities were quite low (1.3-1.9 mmol m^{-2} yr^{-1}) and at the lower end of the range reported for Indian estuaries (-0.4-5.2 mmol m^{-2} yr^{-1}, Rao and Sarma, 2013). CH_4 flux densities (22.5-89.2 mmol m^{-2} yr^{-1}) were within the ranges reported for other tropical sites: Koné et al. (2010), for
5   example, determined flux densities of 28.5-123.4 mmol m^{-2} yr^{-1} for stratified lagoons of Ivory Coast; Shalini et al. (2006) report flux densities of 19.7-102.2 mmol m^{-2} yr^{-1} for Pulicat lake, India; and Biswas et al. (2007) measured CH_4 flux densities between 0.7 and 49 mmol m^{-2} yr^{-1} in the estuaries of the Sundarban mangrove ecosystem. However, we caution that the comparison suffers from the different approaches to determining the gas exchange velocity k. Koné et al. (2010), Shalini et al. (2006), Biswas et al. (2007) and Rao and Sarma (2013) used empirical equations relating k to wind speed, while we
10   used estimates based on floating chamber measurements. We refer to our discussion in Müller et al. (2016), where we showed that our estimates derived by floating chamber measurements yielded higher values than if we had used empirical relationships with wind speed. We argued that floating chamber measurements offered a better representation of the actual flux than gas exchange models that rely on empirical relationships with wind speed, which were initially derived for the open ocean (Wanninkhof, 1992) and do not consider current-induced turbulence as a driver of gas exchange. Musenze et al.
15   (2014) used empirical models for both the wind-related and the current-related gas exchange velocity and added them up to derive flux estimates for the Brisbane estuary. Not surprisingly, the fluxes they report were much higher than in the aforementioned studies, with 0.8-28.0 mmol N_2O m^{-2} yr^{-1} and 7.5 to 636 mmol CH_4 m^{-2} yr^{-1}. Compared with these estimates, the N_2O and CH_4 fluxes from Lupar and Saribas are quite low, which is consistent with the lower N_2O and CH_4 concentrations as discussed above.

20   On the basis of our floating chamber measurements (see Müller et al, 2016) we computed an overall annual flux of 7 t N_2O-N for the Lupar and Saribas estuaries. This is only half of the estimate (15 t N_2O-N yr^{-1}) computed using the Mosier et al. (1998) emission factor. The reason is obviously the missing relationship between DIN concentrations and N_2O emissions in the studied system. Although across estuaries, increasing DIN is generally associated with increasing N_2O (Murray et al., 2015), the relationship is not linear: Zhang et al. (2010) found a polynomial relationship between DIN and N_2O across
25   estuaries in different geographic locations. The emission factor from Mosier et al. (1998), in contrast, is based on constant N_2O/DIN ratio. Therefore, it is not surprising that for low DIN environments, as our study site, the use of emission factors leads to a considerable bias. In line with the data presented here, Borges et al. (2015) did not find a relationship between N_2O and DIN from measurements in several tropical and sub-tropical African rivers and estuaries. This could indicate that this relationship is not applicable in tropical systems and demonstrates the need of further studies in low latitudes to improve
30   estimates of global N_2O emissions from estuaries.

4.5 Implications for future land use change

Nutrient loads to estuaries are predicted to increase in the future in most of Southeast Asia (Seitzinger and Kroeze, 1998). Our results imply that eutrophication in peat-dominated estuaries does not automatically lead to enhanced N_2O emissions. However, the localized elevation of N_2O concentrations, as observed on the Saribas tributary, suggests that estuarine N_2O concentrations might be impacted by local anthropogenic sources. Indeed, it has been shown that N_2O emissions from peat soils depend on land use and that cultivated sites generally exhibit higher N_2O fluxes to the atmosphere (Hadi et al., 2000). It is likely that this behavior is mirrored in the aquatic systems as well.

As CH_4 emissions from peatlands depend largely on the water table (Couwenberg et al., 2010), CH_4 fluxes from peatlands are enhanced under sago (Melling et al., 2005) and rice (Couwenberg et al., 2010) and reduced under oil palm (Melling et al., 2005). The cultivation of sago in the catchment of the Saribas tributary might therefore partially explain the observed high CH_4 fluxes from the Saribas tributary. The future development of CH_4 dynamics in estuaries in this region in dependence of land use change is hard to predict, as there are potentially counteracting effects of the conversion of peatlands to oil palm and other industrial crops, which require different agricultural practices (flooding versus drainage).

5. Conclusions

Overall, we found that the two tropical estuaries of the rivers Lupar and Saribas in a peat-dominated region in Malaysia were small to moderate sources of N_2O and CH_4 to the atmosphere. DIN concentrations were slightly enhanced compared to the unpolluted riverine end-member. This eutrophication did not lead to hypoxia or to enhanced N_2O concentrations. DIN was generally a poor predictor of N_2O, which provides further evidence that the use of emission factors for the calculation of N_2O fluxes from tropical estuaries is inappropriate. Although predictions about the future development of the Southeast Asian monsoon are highly uncertain and locally variable, it is likely that rainfall will moderately increase in this region (Christensen et al., 2013). Our results suggest that this may increase the N_2O and probably also the CH_4 emissions from estuaries, as the concentrations of both gases were more variable during the wet season, with higher maximum concentrations of both gases and additional sources of N_2O in the estuaries. For our study area, additional sampling at the peak of the monsoon season would be desirable in order to consolidate these statements. Yet, our results provide a first account of the seasonality in these systems and underline the fact that time series measurements (seasonal sampling) are vital for the understanding of N_2O and CH_4 fluxes from aquatic systems in monsoonal regions.

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Tables

		DIN (μmol L^{-1})					N export (t yr^{-1})
		Min	**Max**	**Mean**	**Median**	**SD**	
Lupar	**dry**	20.9	30.8	23.6	22.2	3.6	4532
	wet	11.9	21.7	18.2	19.7	3.2	
Saribas	**dry**	25.5	37.6	31.0	30.0	6.1	1554
	wet	10.0	18.0	14.0	14.0	5.6	
Saribas tributary	**dry**	20.5	30.0	24.3	22.4	5.0	n.d.
	wet	10.9	18.2	13.0	11.4	3.5	

Table 1: Estuarine DIN concentration medians for the spatial extent that was covered in 2013 and the estimated inorganic N export to the South China Sea.

		Concentrations (nmol L^{-1})					Saturations (%)				
		Min	Max	Mean	Median	SD	Min	Max	Mean	Median	SD
Lupar	**dry**	7.2	9.3	7.7	7.6	0.4	106	116	108	108	1
	wet	6.6	13.8	7.7	7.2	1.0	102	208	116	109	15
Saribas	**dry**	7.3	8.4	7.9	7.9	0.2	110	118	114	113	2
	wet	8.2	19.3	9.0	8.7	1.2	118	592	134	126	46
Saribas tributary	**dry**	8.1	13.4	11.8	12.3	1.5	117	184	165	169	19
	wet	9.1	24.4	13.5	11.9	4.3	130	340	189	169	59
Coastal ocean		10.1	27.3	15.8	13.0	7.0	168	462	266	218	119

Table 2: N$_2$O concentrations and saturations in the Lupar, Saribas and the Saribas tributary and in the coastal ocean. Values for the estuaries are given for the spatial extent of the rivers that was covered in 2013.

		Concentrations (nmol L^{-1})					Saturations (%)				
		Min	Max	Mean	Median	SD	Min	Max	Mean	Median	SD
Lupar	**dry**	7.3	42.3	18.7	10.6	12.2	339	1910	837	486	520
	wet	3.7	61.2	24.4	13.5	20.3	168	2799	1104	615	915
Saribas	**dry**	8.3	58.8	28.2	25.6	15.5	397	2782	1331	1188	727
	wet	9.0	68.5	15.1	12.2	9.1	401	3050	671	545	395
Saribas tributary	**dry**	5.2	53.3	20.6	12.4	16.9	228	2458	942	554	784
	wet	23.3	113.9	63.2	64.0	27.4	1040	5058	2773	2786	1198
Coastal ocean		3.3	3.7	3.5	3.6	0.2	166	188	177	176	9

Table 3: CH$_4$ concentrations and saturations in the Lupar, Saribas and the Saribas tributary and in the coastal ocean. Values for the estuaries are given for the spatial extent of the rivers that was covered in 2013.

		k_{600} (cm h^{-1})	Flux density (nmol m^{-2} s^{-1})		Annual average flux density (mmol m^{-2} yr^{-1})		Flux (t N yr^{-1} and t C yr^{-1})	
			N$_2$O	CH$_4$	N$_2$O	CH$_4$	N$_2$O	CH$_4$
Lupar	**dry**	n.d.	0.04 ± 0.01	0.59 ± 0.14	1.3 ± 0.3	22.5 ± 5.4	4 ± 1	60 ± 17
	wet	20.5 ± 4.9	0.04 ± 0.01	0.84 ± 0.20				
Saribas	**dry**	n.d.	0.04 ± 0.03	1.01 ± 0.84	1.9 ± 1.6	23.0 ± 19.1	3 ± 2	28 ± 25
	wet	13.2 ± 11.0	0.08 ± 0.07	0.45 ± 0.37				
Saribas tributary	**dry**	n.d.	0.39 ± 0.24	0.81 ± 0.50	12.0 ± 7.5	89.2 ± 55.2	n.d.	n.d.
	wet	23.9 ± 14.8	0.37 ± 0.23	4.84 ± 3.00				

Table 4: k_{600} values and median N$_2$O and CH$_4$ areal and total fluxes from the Lupar, Saribas and the Saribas tributary. The uncertainties relate to the maximum variability of the k_{600} value, as the k_{600} uncertainty propagation was responsible for approximately 96% of the flux uncertainty. Values are given for the spatial extent of the rivers that was covered in 2013.

Figures
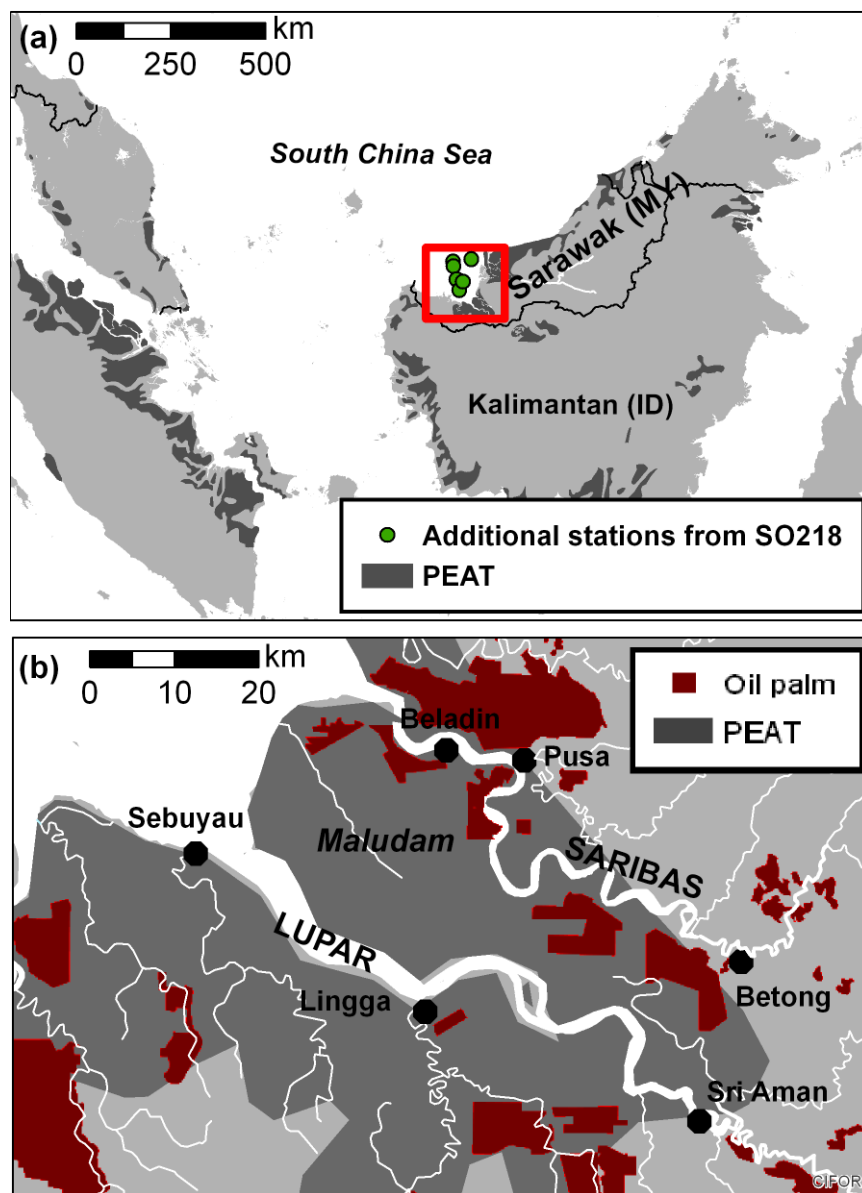
Figure 1: Map of the study area showing (a) the location of Sarawak on the island of Borneo and the cruise track of the R/V *Sonne* in November 2011 (SO218). (b) Close-up map of the Lupar and Saribas estuaries, enclosing the Maludam peninsula, showing the major settlements along the rivers and estuaries. Peat areas are indicated by the dark grey area, oil palm plantations as of CIFOR (2014) are shown in red.
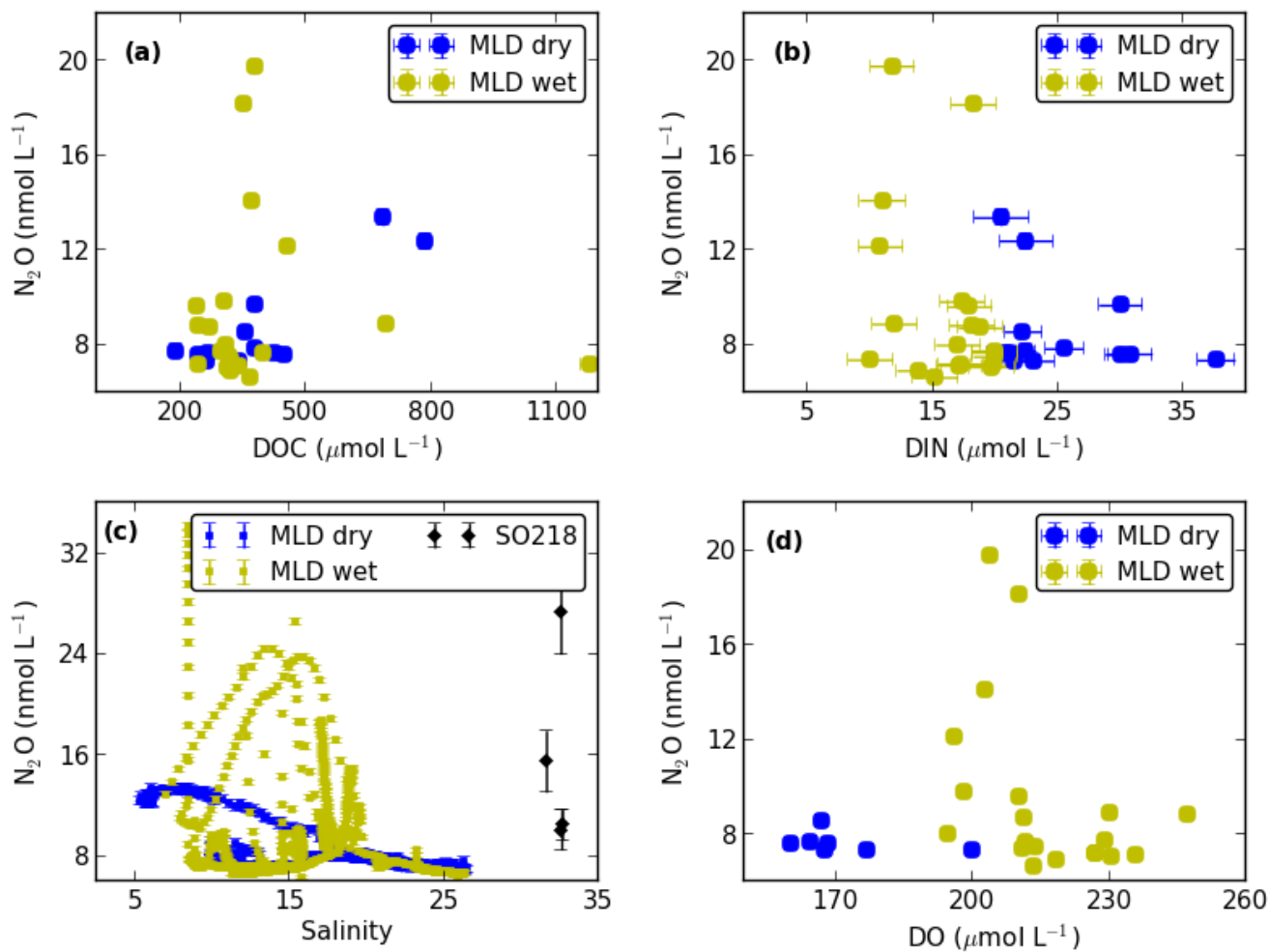
Figure 2: Relationship of nitrous oxide concentrations with (a) dissolved organic carbon (DOC), (b) dissolved inorganic nitrogen (DIN), (c) salinity and (d) dissolved oxygen (DO). MLD refers to the campaigns on the Lupar and Saribas estuaries in the dry and wet season, respectively, SO218 denotes data from the R/V *Sonne* cruise.
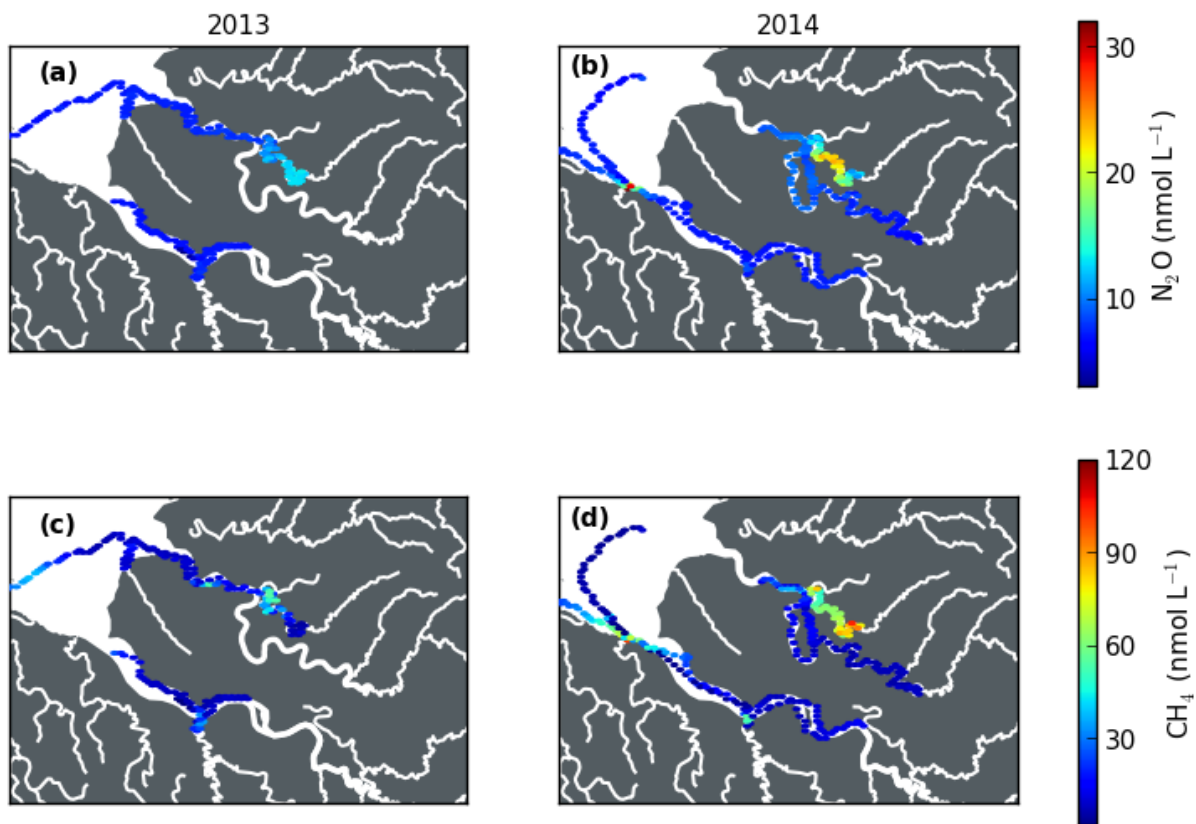
Figure 3: Dissolved N$_2$O (a+b) and CH$_4$ (c+d) concentrations measured during the 2013 (left) and 2014 (right) MLD campaigns.
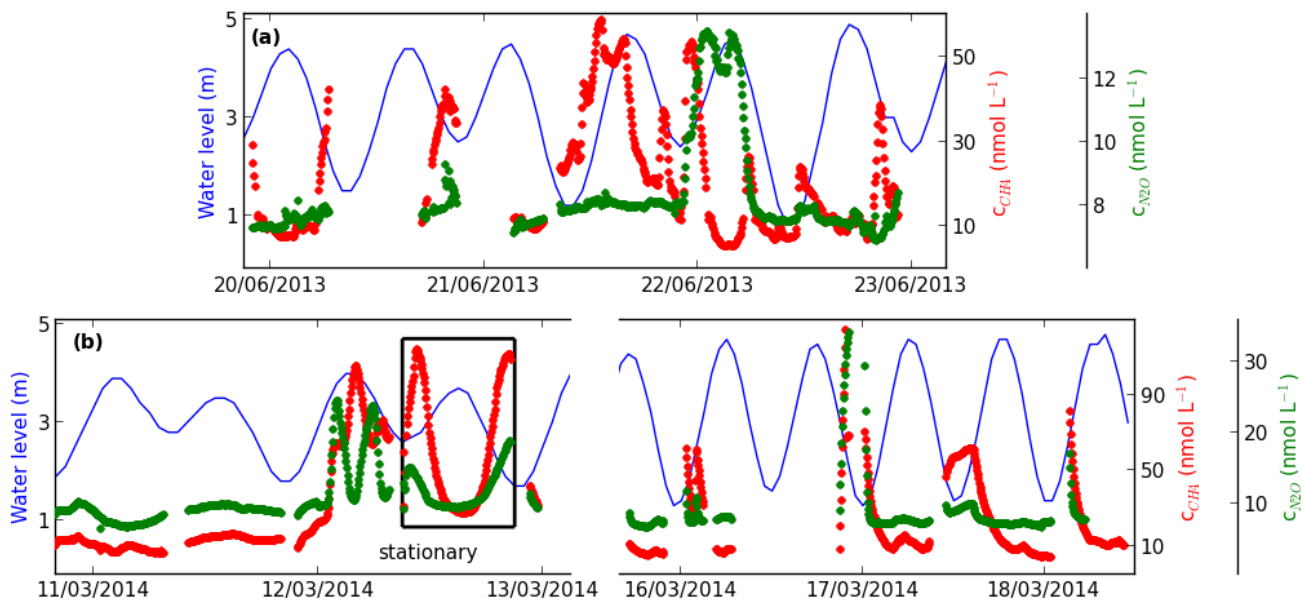
Figure 4: Time series of methane and nitrous oxide concentrations in the Lupar and Saribas estuaries measured during the dry season (2013) campaign (upper panel) and the wet season campaign (lower panel) and the water level as predicted for Pulau Lakei (+1 h for Lupar and Saribas). Spatial, temporal and tidal variations are overlapping in the Figure. One stationary measurement, as recorded on the Saribas River in 2014, is denoted with the black box. Note the discontinuous time axis in the lower panel.
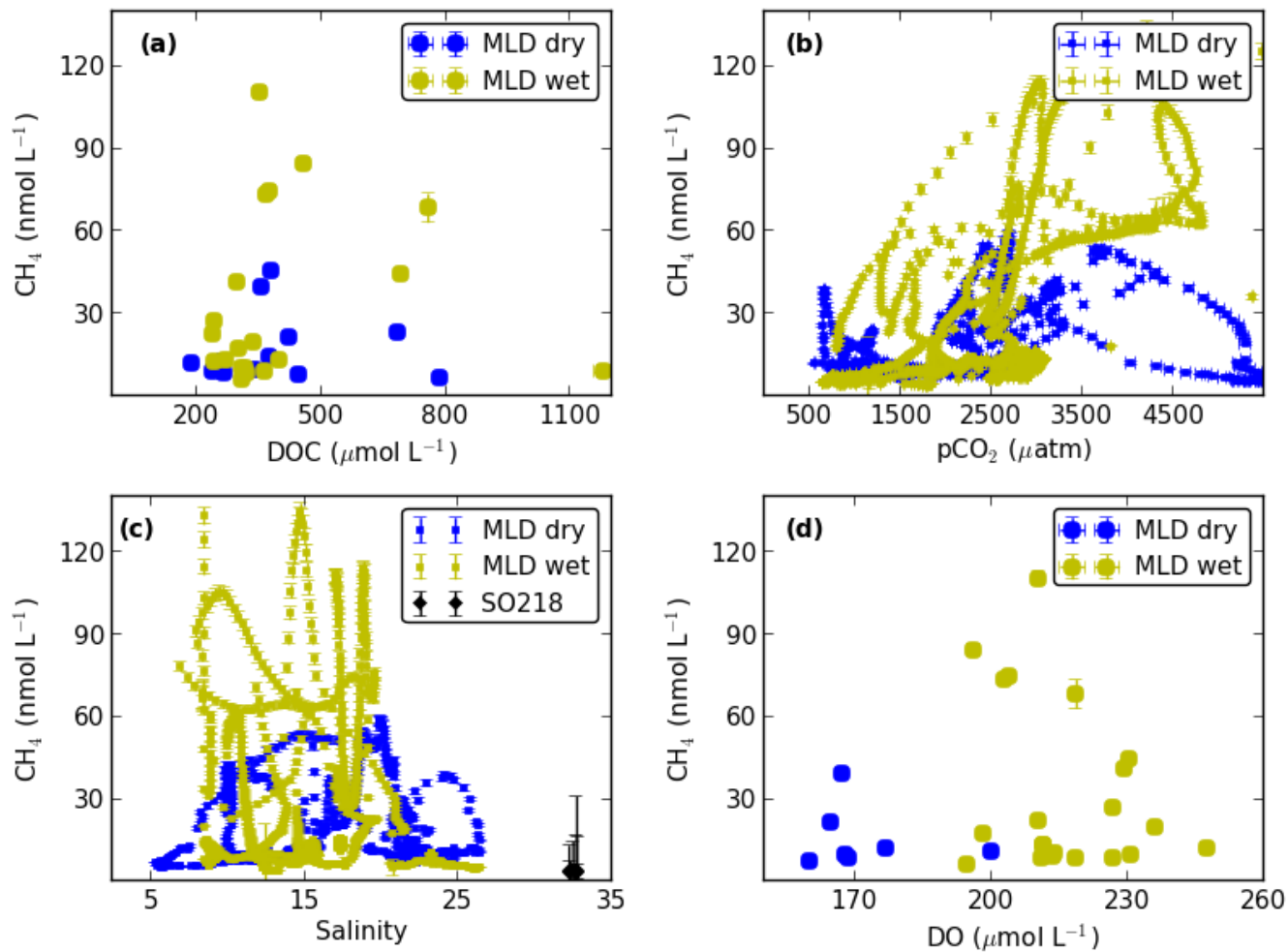
Figure 5: Relationship of methane concentrations with (a) dissolved organic carbon (DOC), (b) pCO$_2$, (c) salinity and (d) dissolved oxygen (DO). MLD refers to the campaigns on the Lupar and Saribas estuaries in the dry and wet season, respectively, SO218 denotes data from the R/V *Sonne* cruise.