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Nitrous oxide (N_2O) and methane (CH_4) in rivers and estuaries of northwestern Borneo

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Abstract

Nitrous oxide (N_2O) and methane (CH_4) are atmospheric trace gases which play important roles of the climate and atmospheric chemistry of the Earth. However, little is known about their emissions from rivers and estuaries which seem to contribute significantly to the atmospheric budget of both gases. To this end concentrations of N_2O and CH_4 were measured in the Rajang, Maludam, Sebuyau and Simunjan Rivers draining peatland in northwestern (NW) Borneo during two campaigns in March and September 2017. The Rajang River was additionally sampled in August 2016 and the Samunsam and Sematan Rivers were additionally sampled in March 2017. The Maludam, Sebuyau, and Simunjan Rivers are typical 'blackwater' rivers with very low pH (3.7 – 7.8), very high dissolved organic carbon (DOC) concentrations (235 – 4387 mmol L^{-1}) and very low O_2 concentrations (31 – 246 µmol L^{-1}; i.e. 13 – 116 % O_2 saturation). The spatial and temporal variability of N_2O and CH_4 concentrations (saturations) in the six rivers/estuaries was large and ranged from 2.0 nmol L^{-1} (28 %) to 41.4 nmol L^{-1} (570 %) and from 2.5 nmol L^{-1} (106 %) to 1372 nmol L^{-1} (57,459 %), respectively. We found no overall trends of N_2O with O_2 or NO_3^-, NO_2^-, NH_4^+ and there were no trends of CH_4 with O_2 or dissolved nutrients or DOC. N_2O concentrations showed a positive linear correlation with rainfall. We conclude, therefore, that rainfall is the main factor determining the riverine N_2O concentrations since N_2O production/consumption in the 'blackwater' rivers themselves seems to be low because of the low pH. CH_4 concentrations were highest at salinity = 0 and most probably result from methanogenesis as part of the decomposition of organic matter under anoxic conditions. CH_4 in the concentrations in the 'blackwater' rivers showed an inverse relationship with rainfall. We suggest that CH_4 oxidation in combination with an enhanced river flow after the rainfall events, might be responsible for the decrease of the CH_4 concentrations. The rivers and estuaries studied here were an overall net source of N_2O and CH_4 to the atmosphere. The total annual N_2O and CH_4 emissions were 1.09 Gg N_2O yr^{-1} (0.7 Gg N yr^{-1}) and 23.8 Gg CH_4 yr^{-1}, respectively. This represents about 0.3 – 0.7 % of the global annual riverine and estuarine N_2O emissions and about 0.1 – 1 % of the global riverine and estuarine CH_4 emissions. Therefore, we conclude that rivers and estuaries in NW Borneo –despite the fact their water area covers only 0.05 % of the global river/estuarine area– contribute significantly to global riverine and estuarine emissions of N_2O and CH_4.

1. Introduction

Nitrous oxide (N_2O) and methane (CH_4) are atmospheric trace gases which influence the climate and atmospheric chemistry of the Earth (IPCC, 2013; WMO, 2014). They act as greenhouse gases in the troposphere and are indirectly involved in stratospheric ozone depletion. Emission estimates indicate that rivers and estuaries contribute significantly to the atmospheric budget of both N_2O and CH_4. N_2O emission estimates for rivers and estuaries range from 0.05 to 3.3 Tg N_2O yr^{-1} and from 0.09 to 5.7 Tg N_2O yr^{-1}, respectively (see overview in (Maavara et al., 2019)). Thus, the combined riverine and estuarine emissions may contribute up to 32 % of the global natural and anthropogenic emissions of N_2O (28.1 Tg N_2O yr^{-1}; IPCC, 2013). CH_4 emission estimates for rivers and estuaries are in the range of 1.5 – 26.8 Tg CH_4 yr^{-1} (Bastviken et al., 2011; Stanley et al., 2016) and 0.8 – 6.6 Tg CH_4 yr^{-1} (see overview in (Borges and Abril, 2011)), respectively. The combined emissions from rivers and estuaries can contribute up to 6% of the global natural and anthropogenic atmospheric emissions of CH_4 (556 Tg CH_4 yr^{-1}; (IPCC, 2013)). As indicated by the wide range of the estimates cited above, the emission estimates of both gases are associated with a high degree of uncertainty, which is mainly caused by an inadequate coverage of the temporal and spatial distributions of N_2O and CH_4 in rivers and estuaries and the inherent errors of the model approaches to estimate their exchange across the water/atmosphere interface (see e.g. (Alin et al., 2011; Borges and Abril, 2011)).

N_2O is produced by microbial processes such as nitrification (i.e. oxidation of ammonia, NH_3, to nitrite, NO_2^-) in estuarine waters (see e.g. (Barnes and Upstill-Goddard, 2011)) and heterotrophic denitrification (i.e. reduction of nitrate, NO_3^-, to dinitrogen, N_2) in river sediments (Beaulieu et al., 2011). The yields of N_2O from these processes are enhanced under low oxygen (i.e. suboxic) conditions (see e.g. (Brase et al., 2017; Zhang et al., 2010)), whereas N_2O can be reduced to N_2 under anoxic conditions via sedimentary denitrification in rivers (see e.g. (Upstill-Goddard et al., 2017)). Apart from ambient oxygen (O_2) concentrations, riverine and estuarine N_2O production is also dependent on the concentrations of dissolved inorganic nitrogen, DIN (= $NH_4^+ + NO_{2-} + NO_3^-$) and organic carbon (Quick et al., 2019). There seems to be a general trend towards high estuarine/riverine N_2O concentrations when DIN concentrations are high as well (Barnes and Upstill-Goddard, 2011; Quick et al., 2019; Zhang et al., 2010). However, this trend masks the fact that in many cases the spatial and temporal variability of riverine and estuarine N_2O is often not related to DIN (see e.g. (Borges et al., 2015; Brase et al., 2017; Müller et al., 2016a; Quick et al., 2019)).

CH_4 is produced during microbial respiration of organic matter by anaerobic methanogenesis in riverine and estuarine sediments (see e.g. (Borges and Abril, 2011; Romeijn et al., 2019; Stanley et al., 2016)). A significant fraction of the CH_4 produced in sediments can be oxidized to carbon dioxide (CO_2) via anaerobic CH_4 oxidation in sulphate-reducing zones of estuarine sediments (see e.g. (Maltby

et al., 2018)) and aerobic CH_4 oxidation in riverine sediments (see e.g. (Shelley et al., 2017)). When released to the overlying riverine/estuarine water CH_4 can be oxidized by aerobic CH_4 oxidation before reaching the atmosphere (see e.g. (Borges and Abril, 2011; Sawakuchi et al., 2016; Steinle et al., 2017)).

In general, the temporal and spatial distributions of N_2O and CH_4 in rivers and estuaries are driven by the complex interplay of microbial production and consumption pathways (see above) as well as physical processes such as input via shallow groundwater, river discharge, tidal pumping, release to the atmosphere and export to coastal waters (Barnes and Upstill-Goddard, 2011; Borges and Abril, 2011; Quick et al., 2019; Stanley et al., 2016).

Peatlands, which are found in the tropics and at high latitudes, constitute one of the largest reservoirs of organic-bound carbon worldwide (Minasny et al., 2019; Page et al., 2011; Treat et al., 2019; Yu et al., 2010). Rivers and streams draining peatlands have exceptionally high concentrations of dissolved organic carbon (DOC) and low pH and, thus, belong to the 'blackwater' river type which is also found in southeast (SE) Asia (see e.g. (Alkhatib et al., 2007; Martin et al., 2018; Moore et al., 2011))..

Despite the fact that a number of studies about N_2O and CH_4 emissions from peatlands in southeast (SE) Asia have been published (see e.g. (Couwenberg et al., 2010; Hatano et al., 2016; Jauhiainen et al., 2012), only a few studies about their emissions from peatland draining rivers in SE Asia have been published so far (Jauhiainen and Silvennoinen, 2012; Müller et al., 2016a). Therefore, our knowledge about the biogeochemistry and emissions of N_2O and CH_4 from peatland draining rivers is still rudimentary at best.

Here we present measurements of dissolved N_2O and CH_4 in six rivers and estuaries in northwestern (NW) Borneo during August 2016, March 2017 and September 2017. The objectives of our study were (i) to measure the distributions of dissolved N_2O and CH_4, (ii) to identify the major factors influencing their distributions and (iii) to estimate the N_2O and CH_4 emissions to the atmosphere.

2. Study site description

Discrete samples of surface water were taken at several stations along the salinity gradients of the Rajang, Maludam, Sebuyau and Simunjan Rivers in NW Borneo during two campaigns in March and September 2017 (Figure 1, Table 1). The Rajang River was additionally sampled in August 2016 and the Samunsam and Sematan Rivers were additionally sampled in March 2017. The environmental settings of the river basins are summarized in Table 2. Based on the areas affected by oil palm plantations and logging in combination with our own observations during several samplings

campaigns, we classified the Rajang and Simunjan river basins as ‘disturbed’, the Maludam, Sebuyau, Sematan and Samunsam river basins as ‘undisturbed’ (Table 2).

3. Methods

3.1 Measurements of N_2O and CH_4

Water was collected from 1 m depth by using a Niskin sampler. Subsamples for N_2O and CH_4 were taken as duplicates or triplicates in 20 or 37 mL glass vials. The vials were first rinsed with sample water, then filled to the maximum (without air bubbles), and finally sealed on the spot using a crimper. The samples were kept on ice for a maximum of 3 hours. When returned to the field station, 50 µL of saturated aqueous mercuric chloride ($HgCl_2$) solution was immediately added to stop any biological activity and samples were stored at 4 °C until shipment. The samples were shipped to GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany, for further analysis within a few weeks after sampling. For the determination of the N_2O and CH_4 concentrations we applied the static-headspace equilibration method followed by gas chromatographic separation and detection with an electron capture detector (ECD, for N_2O) and a flame ionization detector (FID, for CH_4) as described in (Bastian, 2017) and (Kallert, 2017). Calibration of the ECD and FID were performed with standard gas mixtures of 348.4 – 1476.1 ppb N_2O and 1806.10 – 3003.79 ppb CH_4 in synthetic air which have been calibrated against NOAA-certified primary gas standards in the laboratory of the Max Planck Institute for Biogeochemistry in Jena, Germany.

Dissolved N_2O/CH_4 concentrations (C_{obs} in nmol L^{-1}) were calculated with

$$C_{obs} = x'PV_{hs} / (RTV_{wp}) + x'\beta P \qquad (1),$$

where x' is the dry mole fraction of N_2O or CH_4 in the headspace of the sample, P is the ambient pressure (set to 1013.25 hPa), V_{hs} and V_{wp} are the volumes of the headspace and the water phase, respectively. R stands for the gas constant (8.31451 m^3 Pa K^{-1} mol^{-1}), T is the temperature during equilibration and β is the solubility of N_2O or CH_4 (Weiss and Price, 1980; Wiesenburg and Guinasso Jr., 1979). The estimated mean relative errors of the measurements were +/- 9 % and +/- 13 % for N_2O and CH_4, respectively. These comparably high relative errors most probably resulted from the long storage time (six – seven months after sampling) for some of the samples. The higher mean measurement error of the CH_4 samples (compared to the N_2O measurements) was attributed to the fact that CH_4 samples are more sensitive to storage time than N_2O samples (Wilson et al., 2018).

3.2 Ancillary measurements

Water temperature, dissolved oxygen, and salinity were recorded with an Aquaread® 2000. Nutrient measurements are described in detail in (Sia et al., 2019). In short, all samples were collected within the upper 1 m (surface) using pre-washed bottles via a pole-sampler to reduce contamination from the surface of the boat and engine coolant waters (Zhang et al., 2015). Samples were filtered through a 0.4 μm pore-size polycarbonate membrane filters (Whatman) into pre-rinsed bottles, conserved with concentrated $HgCl_2$ solution and kept in a cool, dark room. Nutrients were determined utilizing a Skalar SANplus auto analyser with an analytical precision <5%. pH was measured using a YSI Aquaread® multiple parameters probe (AP-2000). The measurements of dissolved organic carbon (DOC) are described in detail in (Martin et al., 2018). The performance of the DOC measurements was monitored by using deep-sea water samples with certified a DOC concentration of 42 – 45 μmol L^{-1} provided by the Hansell Laboratory, University of Miami. Our analyses consistently yielded slightly higher concentration for the reference water, with a long-term mean (± 1 sd) of 47 ± 2.0 μmol L^{-1} (n = 51). The DOC data are available from the supplementary material in (Martin et al., 2018).

3.3 Computations of saturations and flux densities

The saturations (*Sat*, %) for N_2O, CH_4 and O_2 were calculated as

$$Sat = 100\ C_{obs} / C_{eq} \quad (2)$$

where C_{eq} is the equilibrium concentration of $N_2O/CH_4/O_2$ calculated according to (Weiss and Price, 1980), (Wiesenburg and Guinasso Jr., 1979) or (Weiss, 1970), respectively, with the *in-situ* temperature and salinity as well as the mean dry mole fractions of N_2O/CH_4 at the time of the sampling. Mean monthly N_2O/CH_4 dry mole fractions of 329/1841 10^{-9} (ppb), 331/1880 ppb and 330/1852 ppb for August 2016, March 2017 and September 2017, respectively, were measured at the atmospheric monitoring station Bukit Kototabang, located on the west coast of Sumatra (Indonesia). This station is operated by the NOAA/ESRL Global Monitoring Division program and data are available from http://www.esrl.noaa.gov/gmd. A saturation < 100 % indicates a concentration lower than the theoretical equilibrium concentration (i.e. undersaturation) and a saturation > 100 % indicates supersaturation.

Flux densities (*F*, $nmol \cdot m^{-2} \cdot s^{-1}$) were calculated as

$$F = k_w\ (C_{obs} - C_{eq}) \quad (3)$$

$$k_w = k_{600}\ (Sc/600)^{-0.5} \quad (4)$$

k_w is the gas transfer velocity and *Sc* is the Schmidt number, which was calculated with the equations for the kinematic viscosity of water (Siedler and Peters, 1986) and the diffusion of N_2O or CH_4 in

water (Jähne et al., 1987; Rhee et al., 2009). k_{600} was determined in a study for the Lupar and Saribas Rivers which are located in close vicinity to the Maludam River (Müller et al., 2016a; Müller et al., 2016b). Both rivers have similar environmental and morphological settings in comparison to the rivers studied here. Therefore, we assume that the k_{600} values measured by (Müller et al., 2016a) are representative for the rivers in NW Borneo studied here. Mean k_{600} range from 13.2 +/- 11 cm h^{-1} to 23.9 +/- 14.8 cm h^{-1}. On the basis of the data in (Müller et al., 2016a) we computed a mean k_{600} of 19.2 cm h^{-1} (5.33 10^{-5} m s^{-1}) which we used to estimate the flux densities of N_2O and CH_4. This k_{600} is in good agreement with the mean k_{600} for rivers < 100 m wide (22.4 +/- 14.3 cm h^{-1}) and estuaries/rivers > 100 m wide (10.3 +/- 7.7 cm h^{-1}) listed in (Alin et al., 2011) which range from 6.0 to 35.3 and 4.8 to 30.6 cm h^{-1}, respectively. k_w in rivers depends on the turbulence at the river water/atmosphere interface, which in turn is mainly affected by water current velocity, water depth and river bed roughness and to a lesser extent by the wind speed (Alin et al., 2011; Borges and Abril, 2011). Since the k_{600} reported by (Müller et al., 2016a) were determined only during the wet season (March 2014), our mean k_{600} is biased because it does not account for a lower k_{600} which is to be expected during the dry season (resulting from a lower water current velocity (Alin et al., 2011)). This results in an overestimation of the flux densities.

3.4 Rainfall data

In order to account for the regional variability of the rainfall in NW Borneo, we used rainfall data with a 3 h resolution recorded at the weather stations in Kuching, Bandar Sri Aman and Sibu (all in NW Borneo). The rainfall data were provided by World Weather Online (Dubai, UAE, and Manchester, UK) and are available via https://www.worldweatheronline.com/. Representative weather stations were chosen for each river basin studied here and allocated as follows: The rainfall data for the Simunjan, Sematan and Samunsam River basins are represented by the data from Kuching, the Maludam/Sebuyau, and the Rajang River basins are represented by the data from the Bandar Sri Aman and Sibu weather stations, respectively. We also included the N_2O and CH_4 concentrations data from two measurement campaigns to the Lupar and Saribas Rivers in June 2013 and March 2014 (Müller et al., 2016a). The Lupar and Saribas data were associated with the rainfall data from the weather station in Bandar Sri Aman. Accumulated rainfall amount was computed by summing up the 3 h rainfall data for the periods of one to four weeks prior to the sampling dates.

4 Results and Discussion

All rivers showed low concentrations of DIN in the range from 1.1 to 29 µmol L^{-1} (Table 1). NO_3^- concentrations ranged from below the detection limit of 0.14 µmol L^{-1} up to 19 µmol L^{-1} and NH_4^+ concentrations were in the range of 0.3 to 17 µmol L^{-1}. The Maludam, Sebuyau, and Simunjan Rivers can be classified as ‘blackwater’ rivers with low pH (3.7 – 4.8), high DOC concentrations (1960 –

4387 µmol L^{-1}) and low O_2 concentrations (31 – 95 µmol L^{-1}; 13 – 39 % saturation) at salinity = 0 (Table 1). Comparable settings have been reported from other tropical 'blackwater' rivers in SE Asia as well (Alkhatib et al., 2007; Baum et al., 2007; Moore et al., 2011; Rixen et al., 2008; Wit et al., 2015).

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4.1 Nitrous oxide

The measured ranges of N_2O concentrations and saturations are listed in Table 3 and the distributions of N_2O saturations along the salinity gradients are shown in Figure 2. N_2O concentrations (saturations) were highly variable and ranged from 2.0 nmol L^{-1} (28 %) in the Rajang River (at salinity = 0 in
255 August 2016) to 41.4 nmol L^{-1} (570 %) in the Simunjan River (at salinity = 0 in March 2017). N_2O concentrations in the Rajang, Maludam and Sebuyau Rivers were generally higher in September 2017 compared to March 2017 (Figure 2a-c). A decreasing linear trend of the N_2O saturations with salinity was only observed for the Rajang River in March 2017 (Figure 2a) indicating a conservative mixing and no N_2O sources or sinks along the salinity gradient. Our results are in general agreement with the
260 N_2O measurements in the Lupar and Saribas Rivers (which are located in close vicinityof the Maludam River) in June 2013 and March 2014: (Müller et al., 2016a) measured N_2O concentrations (saturations) from 6.6 to 117 nmol L^{-1} (102 to 1679 %) in the Lupar and Saribas Rivers. Salinity and N_2O concentrations in the Lupar and Saribas Rivers were negatively correlated in June 2013 but were not correlated in March 2014 (Müller et al., 2016a). In contrast to our study, no N_2O undersaturations
265 have been observed by (Müller et al., 2016a). Our results are at the lower end of N_2O concentrations reported from rivers around the globe which can range from extreme undersaturation (down to about 3 %, i.e. almost devoid of N_2O) as measured in a tropical river in Africa (Borges et al., 2015) to extreme supersaturation (of up to 12,500 %) as measured in an agriculture dominated river in Europe (Borges et al., 2018).

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Maximum N_2O saturations measured in March 2017 were in the range from 106 % to 142 % for the rivers classified as undisturbed (Maludam, Sebuyau, Sematan and Samunsam) whereas the maximum saturation for the rivers classified as disturbed (Rajang and Simunjan) were in the range from 329 % to 570 % (Tables 2 and 3) indicating higher emissions from the disturbed rivers. The maximum N_2O
275 saturations in September 2017 ranged from 329 % to 390 % and no differences were observed between undisturbed and disturbed rivers (Table 3).

We found no overall trends of N_2O with O_2 or NO_3^-, NO_2^-, NH_4^+ and DIN. Therefore, it is difficult to decipher the major consumption or production processes of N_2O or to locate the influence of (local)
280 anthropogenic input of nitrogen compounds on riverine N_2O cycling. This is in line with results from studies of other tropical rivers (Borges et al., 2015; Müller et al., 2016a). There are, however, occasional observations of N_2O correlations with O_2/nutrients in tropical rivers which were attributed

to river types such as swamp and savannah rivers (Upstill-Goddard et al., 2017). Figure 3 shows the N_2O concentrations along the pH gradients. Obviously there are no trends except for an enhancement of the N_2O concentrations in September 2017. N_2O production via nitrification depends on the prevailing pH because nitrifiers prefer to take up ammonia (NH_3). The concentration of dissolved NH_3 is dropping significantly at pH < 8 – 9 (Bange, 2008) because of its easy protonation to ammonium (NH_4^+). A low pH of about 5 – 6 can reduce nitrification (NH_4^+ oxidation) significantly as it was recently shown for the Tay Ninh River in Vietnam (Le et al., 2019). Moreover, the optimum for a net N_2O production by nitrification, nitrifier-denitrification and denitrification lies between a pH of 7 – 7.5 (Blum et al., 2018). Therefore, a net N_2O production may be low in the 'blackwater' rivers studied here because of their low pH (see Table 1). The observed N_2O supersaturations, therefore, might have been mainly the result of external inputs of N_2O-enriched waters or groundwater. The observed N_2O undersaturations were most probably resulting from heterotrophic denitrification which could have taken place either in organic matter-enriched anoxic river sediments or in anoxic environments of the surrounding soils. However, the main factor for riverine N_2O under- or supersaturation might be rainfall, because rainfall events determine the height of the water table in the surrounding soils which, in turn, determines the amount of suboxic/anoxic conditions favourable for N_2O production or consumption (Jauhiainen et al., 2016). See also discussion in Section 4.3.

4.2 Methane

The measured ranges of CH_4 concentrations and saturations are listed in Table 3 and the distributions of CH_4 saturations along the salinity gradients are shown in Figure 4. CH_4 concentrations (saturations) were highly variable and ranged from 2.5 nmol L^{-1} (106 %) in the Simunjan River (at salinity = 0 in September 2017) to 1372 nmol L^{-1} (57,459 %) in the Simunjan River (at salinity = 0 in March 2017). (Please note that we also measured a CH_4 concentration of 14,999 nmol L^{-1} (624,070 %) at one station in the Simunjan River at salinity = 0 in March 2017 which, however, was not included in Figure 4 and which was excluded in the emission estimates because of statistical reasons.) CH_4 saturations in the Rajang, Maludam, Sebuyau and Simunjan Rivers were higher in March 2017 compared to September 2017. Maximum CH_4 concentrations were measured at salinity = 0 and there was a general decrease of CH_4 concentrations with increasing salinity. Exceptions from this trend occurred at individual stations in the Maludam, Sebuyau and Samunsam Rivers which point to local sources of CH_4 (Figure 3). The range of CH_4 concentrations (saturations) from our study is larger compared to the concentration range measured in the Lupar and Saribas Rivers (3.7 – 113.9 nmol L^{-1}; 168 – 5058 %) (Müller et al., 2016a). (Borges et al., 2015) reported a maximum CH_4 concentration (saturation) of 62,966 nmol L^{-1} (appr. 954,000 %) in their study of tropical rivers in Africa which is much higher than the maximum concentration measured in our study. We found no differences in the CH_4 saturations between the rivers classified as undisturbed and those classified as disturbed in both March and September 2017.

We found no overall trends of CH_4 with O_2 or dissolved nutrients or DOC along the salinity gradients. There are, however, occasional observations in tropical rivers of CH_4 relationships with O_2 which were attributed to different river types such as swamp and savannah rivers (Upstill-Goddard et al., 2017). High CH_4 concentrations, which were often associated with high DOC and low O_2 concentrations at salinity = 0 and pH < 7 (see Figure 3b), might have been produced by methanogenesis in anoxic riverine sediments rich in organic material or in anoxic parts of the surrounding soils drained by the rivers. The decrease of CH_4 with increasing salinity can be attributed to the gas exchange across the river water/atmosphere interface in combination with CH_4 oxidation (Borges and Abril, 2011; Sawakuchi et al., 2016).

4.3 N_2O/CH_4 concentrations and rainfall

Mean N_2O concentrations showed linear correlations with accumulated rainfall during different periods from one to four weeks before the dates of sampling (Figure 5, Table 6). Enhanced N_2O emissions from (peat) soils are usually associated with rainfall when the water table approaches the soil surface (Couwenberg et al., 2010; Jauhiainen et al., 2016). A high water table, in turn, allows decomposition of previously deposited fresh organic material (Jauhiainen et al., 2016) and, thus, will result in favourable conditions for microbial N_2O production mainly via denitrification in a suboxic/anoxic soil environment (Espenberg et al., 2018; Pihlatie et al., 2004). N_2O production via nitrification may be less important at high water table (Pihlatie et al., 2004; Regina et al., 1996). Therefore, the positive linear relationship of the riverine N_2O concentrations with rainfall might result from enhanced N_2O production in the adjacent soils drained by the rivers. A decreasing trend of N_2O concentrations which would be expected to be caused by enhanced river discharge after the rain events –which in turn can lead to dilution of the concentrations and enhanced fluxes across the river/atmosphere interface (Alin et al., 2011)– is obviously outcompeted by an enhanced input of N_2O.

In contrast to N_2O, the response of riverine/estuarine CH_4 concentrations to increasing rainfall is not resulting in increasing CH_4 concentrations (Figure 5). When considering the periods of 1 or 1.5 weeks of accumulated rainfall there seems to be a pronounced decrease of CH_4 concentrations with increasing rainfall (Figure 5c and Table 6). This trend is no longer significant when considering the periods of 2 - 4 weeks of accumulated rainfall (Table 6). A closer inspection of the data reveals that the response to increasing rainfall seems to be different for individual rivers/estuaries. There is a clear negative relationship with rainfall for the Maludam, Sebuyau and Simunjan Rivers, whereas no obvious trends were observed for the other rivers (Figures 5c and d). Under the assumption that rainfall is a predictor for river discharge/high water we can argue that our results are in agreement with the often observed inverse relationship between CH_4 concentrations and river discharge (Anthony et al., 2012; Bouillon et al., 2014; Dinsmore et al., 2013; Hope et al., 2001). This relationship can be explained by an interplay of various processes such as: (i) decrease of CH_4 concentrations caused by a

higher water flow (i.e. dilution under the assumption that the net CH_4 production does not change significantly), (ii) higher flux across the river/atmosphere interface during periods of higher discharge (caused by an enlarged river surface area and/or a more turbulent water flow) (Alin et al., 2011), and (iii) the enhancement of CH_4 oxidation during high waters: (Sawakuchi et al., 2016) showed that CH_4 oxidation in 'blackwater' rivers of the Amazon basin was maximal during the high water season.

4.4 Emission estimates

The N_2O flux densities from the six rivers studied here are comparable to the N_2O flux densities from other aqueous and soil systems reported from Borneo and other sites in SE Asia, see Table 4. The corresponding CH_4 flux densities are higher than the CH_4 flux densities reported for the Lupar and Saribas Rivers but much lower than the flux densities from drainage canals in Central Kalimantan and Sumatra (Jauhiainen and Silvennoinen, 2012) (Table 4). Our CH_4 flux densities are, however, comparable to recently published CH_4 eddy covariance measurements (Tang et al., 2018) in the Maludam National Park, which is drained by the Maludam River, and measurements of the CH_4 release from peat soils when the water table is high and CH_4 from rice paddies (Couwenberg et al., 2010), see Table 4. The mean annual N_2O and CH_4 emissions for the individual rivers were calculated by multiplying the mean flux density, *F*, for each river (Table 4) with the river surface area given in Table 2. The results are listed in Table 5. The resulting total annual N_2O emissions for the rivers in NW Borneo - including the emissions from the Lupar and Saribas Rivers (Müller et al., 2016a) - are 1.09 Gg N_2O yr^{-1} (0.7 Gg N yr^{-1}). This represents about 0.3 – 0.7 % of the global annual riverine and estuarine N_2O emissions of 166 – 322 Gg N_2O (106 – 205 Gg N yr^{-1}) recently estimated by (Maavara et al., 2019). The total annual CH_4 emissions from rivers in NW Borneo are 23.8 Gg CH_4 yr^{-1}. This represents about 0.1 – 1 % of the global riverine and estuarine CH_4 emissions of 2300 – 33,400 Gg CH_4 yr^{-1} (the emission range is based on the minimum and maximum estimates given in (Bange et al., 1994; Bastviken et al., 2011; Borges and Abril, 2011; Stanley et al., 2016). However, we caution that our estimates are associated with a high degree of uncertainty because (i) our data are biased by the fact that for some rivers it was not possible to cover the entire salinity gradient, (ii) seasonal and interannual variabilities of the N_2O and CH_4 concentrations are not adequately represented in our data set, (iii) the wind speed-driven gas exchange in estuaries is not adequately represented, and (iv) the mean k_{600} used here is most probably too high (see Section 3.3) resulting in an overestimation of the emissions.

5 Summary and Conclusions

N_2O and CH_4 were measured in the Rajang, Maludam, Sebuyau and Simuntan Rivers and Estuaries in NW Borneo during two campaigns in March and September 2017. The Rajang River was additionally sampled in August 2016 and the Samunsam and Sematan Rivers were additionally sampled in March

2017. The spatial and temporal variability of N_2O and CH_4 concentrations was large. N_2O concentrations (saturations) ranged from 2.0 nmol L^{-1} (28 %) in the Rajang River (at salinity = 0 in August 2016) to 41.4 nmol L^{-1} (570 %) in the Simunjan River (at salinity = 0 in March 2017). CH_4 concentrations (saturations) were in the range from 2.5 nmol L^{-1} (106 %) in the Simunjan River (at salinity = 0 in September 2017) to 1372 nmol L^{-1} (57,459 %) in the Simunjan River (at salinity = 0 in March 2017). N_2O concentrations showed a positive linear correlation with rainfall. We conclude, therefore, that rainfall, which determines the N_2O production/consumption in the surrounding soils, is the main factor determining the riverine N_2O concentrations. N_2O production in the 'blackwater' rivers themselves seems to be low because of the low pH. CH_4 concentrations were highest at salinity = 0 and most probably results from methanogenesis as part of the decomposition of organic matter under anoxic conditions. CH_4 concentrations in the 'blackwater' rivers showed an inverse relationship with rainfall. We suggest that enhanced CH_4 oxidation in combination with a higher flux across the river/atmosphere interface during periods of higher river flow (after rainfall events), is responsible for the reduction of the CH_4 concentrations along the salinity gradient. The rivers and estuaries studied here were an overall net source of N_2O and CH_4 to the atmosphere. The total annual N_2O and CH_4 emissions were 1.09 Gg N_2O yr^{-1} (0.7 Gg N yr^{-1}) and 23.8 Gg CH_4 yr^{-1}, respectively. This represents about 0.3 – 0.7 % of the global annual riverine and estuarine N_2O emissions and about 0.1 – 1 % of the global riverine and estuarine CH_4 emissions. Rivers and estuaries in NW Borneo contribute only 0.05 % (= 7.9 10^2 km^2 including the surface areas of the Lupar and Saribas Rivers; (Müller et al., 2016a) to the global water surface area of rivers and estuaries (= 1.7 10^6 km^2; (Maavara et al., 2019)). Therefore we conclude that rivers and estuaries in NW Borneo contribute significantly to the global riverine and estuarine emissions of both N_2O and CH_4.

The environment of Borneo (and SE Asia) is affected by rapid changes due to (i) anthropogenic activities such as conversion of peatland into oil palm plantations etc. (see e.g. (Austin et al., 2018; McAlpine et al., 2018; Schoneveld et al., 2019)) and (ii) climatic changes (see e.g. (Sa'adi et al., 2017a, b; Tang, 2019)) which, in turn, could significantly affect N_2O and CH_4 emissions from soils (see e.g. (Jauhiainen et al., 2016; Oktarita et al., 2017)). But little is known about how these changes will affect N_2O and CH_4 emissions from aqueous systems such as rivers and estuaries in the future. The obvious relationship of N_2O and CH_4 concentrations and rainfall could be used to predict future concentrations and its associated emissions to the atmosphere. However, the trends of rainfall and river discharge in Borneo show a high local variability and no general common trend (Sa'adi et al., 2017a; Tang, 2019). Therefore, predictions of future trends of N_2O and CH_4 emissions will be associated with high degree of uncertainty. In order to improve our knowledge to predicted future changes of N_2O and CH_4 riverine/estuarine emissions we suggest establishing regular measurements in the rivers and along the salinity gradients. This will help deciphering the temporal and spatial variability of N_2O and CH_4 emissions from tropical rivers and estuaries. Moreover, studies of the

relevant production/consumption pathways (and their main driving factors) for both gases are required. A suitable framework for this could be the recently published concept of the global N_2O Ocean Observation Network (N2O-ON) (Bange et al., 2019).

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Author contribution

MM, CHS, AM and HWB designed the study. CHS performed the sample preparation during the campaigns. DB and JK performed the N_2O/CH_4 measurements with support from AK. HWB prepared the ms with contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interests.

Data availability

All N_2O/CH_4 data presented here are archived in and available from the MEMENTO (the MarineE MethanE and NiTrous Oxide) database: https://memento.geomar.de .

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8 Tables

Table 1: Overview of sampling and sampled ranges of salinity, pH as well as O_2 concentration and saturation (in %, given in parenthesis) and concentrations of dissolved inorganic nitrogen (DIN = NO_3^- + NO_2^- + NH_4^+), silicate (SiO_2) and dissolved organic carbon (DOC). All concentrations are given in µmol L^{-1}. na stands for not available and Stat. stands for sampling station. DOC data were taken from (Martin et al., 2018).

River	Date	# of Stat.	Range of					
			Salinity	pH	O_2	DIN	SiO_2	DOC
Rajang	20 – 27 Aug ‘16	30	0 – 32	6.5 – 8.1	85 – 153 (42 – 73)	6.7 – 29	4.0 – 179	na
	4 – 7 Mar ’17	14	0 – 30	6.0 – 8.2	142 – 237 (58- 109)	8.1 – 18	16 – 158	96 – 201
	5 – 14 Sept ‘17	8	0 – 18	6.9 – 8.2	164 – 227 (76 – 90)	6.7 – 14	12 – 98	na
Maludam	9 Mar ‘17	9	0 – 20	3.7 – 7.6	34 – 213 (13 – 100)	3.9 – 10	5.8 – 32	266 – 4387
	14/15 Sept ‘17	9	0 – 15	4.1 – 6.7	43 – 155 (17 – 74)	2.1 – 3.0	0.1 – 8.0	3072 – 3245
Sebuyau	11 Mar ‘17	11	0 – 24	4.3 – 7.8	43 – 246 (18 – 116)	2.9 – 13	33 – 78	206 – 1968
	15 Sept ‘17	5	0 – 10	7.2 – 7.7	65 – 179 (27 – 75)	1.1 – 13	0.9 – 44	235 – 2052
Simunjan	12 Mar ‘17	6	0 – 0.4	4.7 – 6.3	31 – 81 (13 – 34)	2.2 – 16	73 – 114	2016 – 3039
	17 Sept ‘17	6	0 – 4.6	4.7 – 6.7	95 – 131 (39 – 53)	2.0 – 13	1.4 – 2.6	925 – 1960
Sematan	9 Mar ‘17	5	0 – 28	6.8 – 8.3	184 – 208 (81 – 102)	5.9 – 10	6.3 – 141	100 – 240
Samunsam	11 Mar ‘17	5	0 – 27	6.3 – 8.2	174 – 208 (72 – 102)	3.9 – 6.6	9.7 – 98	87 – 1188

Table 2: Summary of the environmental settings of the river basins. Based on the area percentage of oil palm, logging and our own surveys and observations, we classified the river basins into undisturbed (U) and disturbed (D). All areas are given in km^2.

River	Areas					Remarks	Classification
	Total Basin	Peatland[1]	Oil palm plantations[2]	Logging[3]	River water surface[4]		
Rajang	50,000[5]	3844	4514	29,379	455[5]	The longest river in Malaysia. Major town is Sibu (163,000 population). Smaller townships are Kapit, Kanowit and Sarikei. There is a large number of villages and longhouses (traditional buildings inhabited by local communities) located along the river and its tributaries. Two hydroelectric power plants were built at two tributaries in the upper Rajang basin. The river mouth is surrounded by peat lands, and most of these peat lands have been converted to commercial oil palm plantations.	D
Maludam	197	172	16	0	0.36	The upstream of the river is surrounded by the Maludam National Park. The Maludam Peninsula is bordered by the Lupar and Saribas Rivers and is the biggest undisturbed peat forest in Malaysia. The National Park had been subjected to selective logging before it was gazetted as a totally protected area in 2000. Well preserved peat land. There are oil palm cultivations near the few villages.	U
Sebuyau	538	288	24	0	2.11	Major town is Sebuyau (14,000 population), surrounded by a few villages. Other agricultural activities were observed.	U
Simunjan	788	346	240	0	4.73	Major town is Simunjan (22,000 population), a few villages. Two streams combine to form the main Simunjan River. One of the streams passes an oil palm mill which discharges into the river.	D
Sematan	287	0	0	0	1.47	Major town is Sematan (7,600 population), small villages. We observed agricultural activities by the local people.	U
Samunsam	163	0	0	0	0.85	Well preserved tropical forest. Some peat in the upper catchment area.	U

[1] Estimate is based on 'Wetlands International'."Malaysia peat lands". Accessed through Global Forest Watch on 22nd November 2018 (www.globalforestwatch.org).

[2] Estimate is based on 'Oil palm concessions'. Accessed through Global Forest Watch on 22nd November 2018 (www.globalforestwatch.org).

[3] Estimate is based on 'Managed forest concessions'. Accessed through Global Forest Watch on 22nd November 2018 (www.globalforestwatch.org).

[4] Area estimates are based on the length and width of the primary course and main tributaries of the rivers. Length and width of the rivers were estimated using Google Earth (multiple readings).

[5] Estimate from (Staub et al., 2000).

Table 3: Overview of N_2O and CH_4 concentrations, saturations and flux densities in rivers and estuaries of NW Borneo.

River	Date	N_2O			CH_4		
		concentration nmol L^{-1}	saturation %	flux density nmol m^{-2} s^{-1}	concentration nmol L^{-1}	saturation %	flux density nmol m^{-2} s^{-1}
Rajang	Aug '16	2.0 – 14.1	28 – 215	-0.33 – 0.48	13.2 – 233	719 - 9988	0.77 – 15
	Mar '17	5.9 – 24.0	100 – 329	0 – 1.08	11.1 – 1008	455 – 40,598	0.34 – 62
	Sept '17	18.6 – 24.6	277 – 390	0.76 – 1.22	7.4 – 150	350 – 6019	0.35 – 9.05
Maludam	Mar '17	4.5 – 6.7	62 – 106	-0.20 – 0.03	312 – 829	12,603 – 32,988	19 – 50
	Sept '17	10.8 – 20.7	150 – 331	0.23 – 1.00	3.3 – 18	163 – 717	0.09 – 0.93
Sebuyau	Mar '17	3.5 – 7.7	55 – 118	-0.18 – 0.08	8.4 – 1228	396 – 50,774	0.41 – 78
	Sept '17	12.8 – 23.0	176 – 335	0.36 – 1.08	6.4 – 29	299 – 1285	0.28 – 1.79
Simunjan	Mar '17	2.5 – 41.4	35 – 570	-0.31 – 2.20	39 – 1372 (14,999)[1]	1642 – 57,459 (624,070)[1]	2.37 – 88
	Sept '17	5.1 – 26.5	73 – 365	-0.13 – 1.24	2.5 – 21	106 – 878	0.01 – 1.18
Sematan	Mar '17	4.3 – 8.2	71 – 109	-0.11 – 0.04	8.6 – 12	433 – 47,055	0.43 – 72
Samunsam	Mar '17	4.0 – 9.5	67 – 142	-0.13 – 0.19	16.5 – 978	830 – 43,807	0.95 – 63

[1] This extreme value was not included in further computations.

695 Table 4: Overview of N_2O and CH_4 flux densities from aqueous and soils ecosystems in SE Asia. (na stands for not available/not measured.)

Site	Location	N_2O flux density, nmol m^{-2} s^{-1}		CH_4 flux density, nmol m^{-2} s^{-1}		Measurement or sampling dates	Reference
		Range	Mean[1]	Range	Mean[1]		
				Aqueous systems			
Rajang River/Estuary	Sarawak, NW Borneo	-0.33 – 1.22	0.53	0.34 – 62	5.52	Aug. 2016; Mar.; Sept. 2017	This study
Maludam River/Estuary	Sarawak, NW Borneo	-0.20 - 1.00	0.32	0.09 – 50	15.9	March 2017; September 2017	
Sebuyau River/Estuary	Sarawak, NW Borneo	-0.18 – 1.08	0.39	0.28 – 78	15.4	March 2017; September 2017	
Simunjan River/Estuary	Sarawak, NW Borneo	-0.31 – 2.20	0.50	0.01 – 88	18.7	March 2017; September 2017	
Sematan River/Estuary	Sarawak, NW Borneo	-0.11 – 0.04	-0.05	0.43 – 72	21.1	March 2017	
Samunsam River/Estuary	Sarawak, NW Borneo	-0.13 – 0.19	0.05	0.95 – 63	21.7	March 2017	
Lupar River/Estuary	Sarawak, NW Borneo	0.04 – 0.04	*0.04*	0.59 – 0.84	*0.72*	June 2013; March 2014	(Müller et al., 2016a)
Saribas River/Estuary	Sarawak, NW Borneo	0.04 – 0.08	*0.06*	0.45 – 1.01	*0.73*	June 2013; March 2014	
Saribas River tributary	Sarawak, NW Borneo	0.37 – 0.39	*0.38*	0.81 – 4.84	*2.83*	June 2013; March 2014	
Drainage canal, Kalimantan, settled	Central Kalimantan, S Borneo	-0.02 – 0.03	0	0 – 943	119	September 2007; April 2008	(Jauhiainen and Silvennoinen, 2012)
Drainage canal, Kampar, settled	Riau, eastern central Sumatra	0.03 – 5.80	0.73	0 – 3672	776	September 2007; April 2008	
Drainage canal, Kampar, disturbed	Riau, eastern central Sumatra	0.02 – 0.84	0.20	2.17 – 281	64.4	September 2007; April 2008	
				Soil systems			
Forest	Sarawak, NW Borneo	-0.03 – 0.20	*0.08*	-0.10 – 0.19	*0.04*	August 2002 - July 2003	(Melling et al., 2005, 2007)
Sago plantation	Sarawak, NW Borneo	0.01 – 1.75	*0.88*	-0.17 – 2.36	*1.10*	August 2002 - July 2003	
Oil palm plantation	Sarawak, NW Borneo	0.01 – 0.58	*0.29*	-0.76 – 0.11	*-0.33*	August 2002 - July 2003	
Undrained forest	Central Kalimantan, S Borneo	-0.09 – 1.16	0.02	na	na	Dry/wet seasons in 2000/2001	(Jauhiainen et al., 2012)
Drained forest	Central Kalimantan, S Borneo	-0.42 – 22.9	1.11	na	na	Dry/wet seasons in 2001/2002; monitoring 2004 – 2007	
Drained recovering forest	Central Kalimantan, S Borneo	-0.06 – 0.45	0.02	na	na	Dry/wet seasons in 2001/2002	
Drained burned peat	Central Kalimantan, S Borneo	-0.70 – 0.88	0.11	na	na	Dry/wet seasons in 2001/2002; monitoring 2004 – 2007	
Agricultural peat in Kalampagan	Central Kalimantan, S Borneo	-0.95 – 0.89	0.12	na	na	Dry/wet seasons in 2001/2002	
Agricultural peat in Marang	Central Kalimantan, S Borneo	-0.86 – 0.59	0.07	na	na	Dry/wet seasons in 2001/2002	
Canopy soil of oil palm	Jambi, eastern central Sumatra	na	0.001	na	0.0004	February 2013 - May 2014	(Allen et al., 2018)
Drained burned land	Central Kalimantan, S Borneo	na	0.001	na	21.1	July 2011	(Ishikura et al., 2018)
Drained forest	Central Kalimantan; S Borneo	na	0.08	na	0.23	July 2011	
Undrained forest	Central Kalimantan, S Borneo	na	0.15	na	17.6	July 2011	
Drained agricultural land (fertilized)	Various locations in SE Asia	0.81 – 29.3	10.3	0.05 – 6.74	*3.39*	Various dates	(Couwenberg et al., 2010): Review of results from various studies.
Drained, open vegetation (abandoned, not fertilized)	Various locations in SE Asia	-0.12 – 0.45	0.08	na	na	Various dates	
Forested (drained and undrained peat swamp, agro-forestry)	Various locations in SE Asia	-0.06 – 1.51	0.39	-0.73 – 11.6	*5.45*	Various dates	
Rice paddies	Various locations in SE Asia	-0.04 – 0.23	0.07	7.17 – 98.1	*52.7*	Various dates	
Peat soil	Various locations in SE Asia	na	na	0 – 52.1	26.0	Various dates	
Maludam Natl. Park	Sarawak, NW Borneo	na	na	na	23.1	November – December 2013	(Tang et al., 2018)

[1] Values in italics indicate a mean flux density computed from the range given in the table (when no mean flux density was given in the ref.)

Table 5: Mean annual emissions of N_2O and CH_4 from rivers and estuaries in NW Borneo. The estimates for the Lupar and Saribas Rivers are from (Müller et al., 2016a).

River	Emissions	
	Gg N_2O yr^{-1}	Gg CH_4 yr^{-1}
Rajang	0.33	1.27
Maludam	0.20	3.65
Sebuyau	0.24	3.53
Simunjan	0.32	4.30
Sematan	-0.03	5.99
Samunsam	0.03	4.99
Lupar	0.01	0.08
Saribas	0.01	0.04
Sum	1.09	23.8

Table 6: Correlation coefficents (r) of the linear correlations between the accumulated rainfall for different periods before the dates of sampling and the average N_2O/CH_4 concentrations of the various rivers and estuaries. Values in bold are significant at the 99% level and values in italics are significant at the 95% level; n = 17.

Weeks of accumulated rainfall before sampling	N_2O	CH_4
1	**0.7059**	***0.5744***
1.5	**0.8075**	***0.5781***
2	**0.8095**	0.4671
2.5	**0.8220**	0.3746
3	**0.8232**	0.4363
3.5	**0.7203**	0.1871
4	**0.7018**	0.3114

Figure Captions

Figure 1: Map of the study area with locations of the sampling stations. Sampling stations from August 2016 are displayed in red circles, from March 2017 in blue triangles, and from September 2017 in green diamonds. Major cities are highlighted in bold plus symbols. Inset is adapted from (Staub et al., 2000).

Figure 2: N_2O saturations along the salinity gradients of (a) Rajang, (b) Maludam, (c) Sebuyau, (d) Simunjan, (e) Sematan and (f) Samunsam. The dashed lines indicate the equilibrium (100%) saturation. The open circles depict measurements from August 2016, the filled red circles depict measurements from March 2017 and the filled blue circles depict measurements from September 2017.

Figure 3: Concentrations of N_2O (a) and CH_4 (b) from rivers/estuaries along the pH gradients. The open red squares depict data from August 2016, the filled red squares depict data from March 2017 and the filled blue triangles depict data from September 2017. The vertical bars in (a) and (b) roughly indicate salinity = 0. Concentrations to the left of the vertical bar are at salinity = 0 and concentrations to the right of the vertical bars are at salinity >0. The horizontal bar in (a) indicates the equilibrium concentration of N_2O. Please note that in August 2016 only the Rajang River was sampled.

Figure 4: CH_4 saturations along the salinity gradients of (a) Rajang, (b) Maludam, (c) Sebuyau, (d) Simunjan, (e) Sematan and (f) Samunsam. The dashed lines indicate the equilibrium (100%) saturation. The open circles depict measurements from August 2016, the filled red circles depict measurements from March 2017 and the filled blue circles depict measurements from September 2017.

Figure 5: Average N_2O and CH_4 concentrations for the individual rivers and esturaries vs. the accumulated rainfall amount during one (a, c) and three weeks (b, d) before the dates of sampling. We also included the average N_2O and CH_4 concentrations for the Lupar, Saribas Rivers and Saribas tributary from (Müller et al., 2016a).

6 Figures

Figure 1.

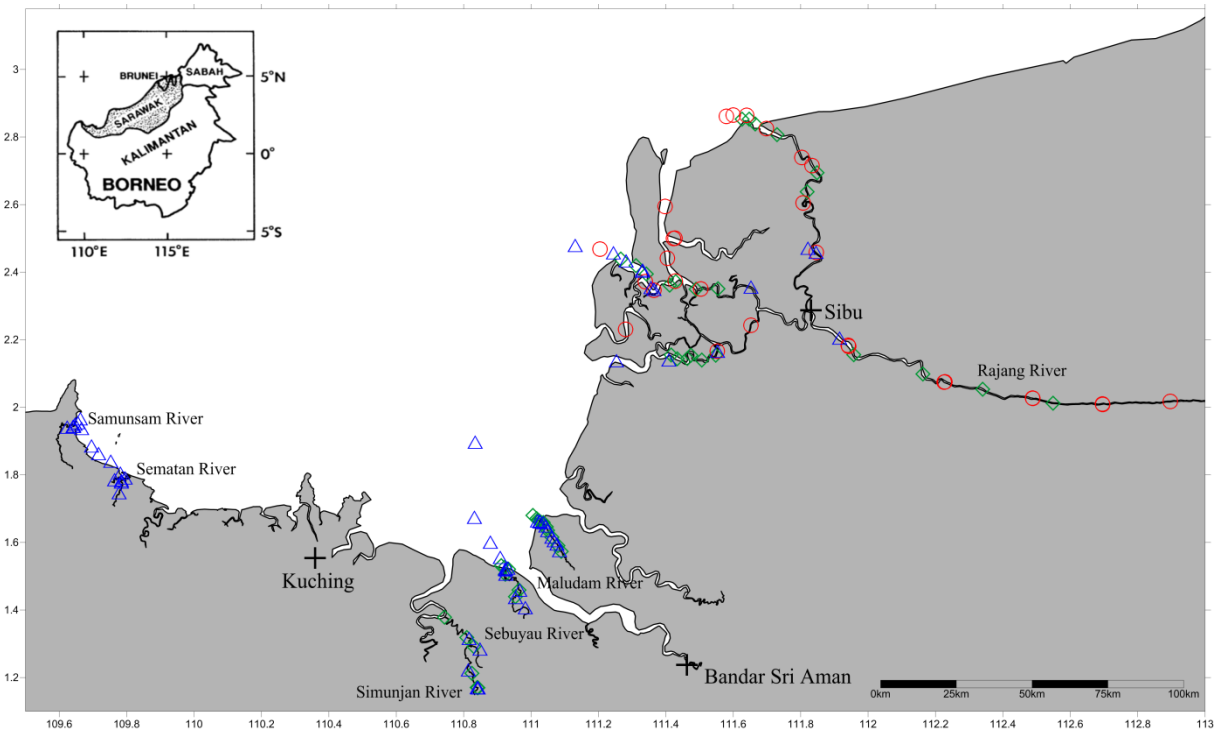
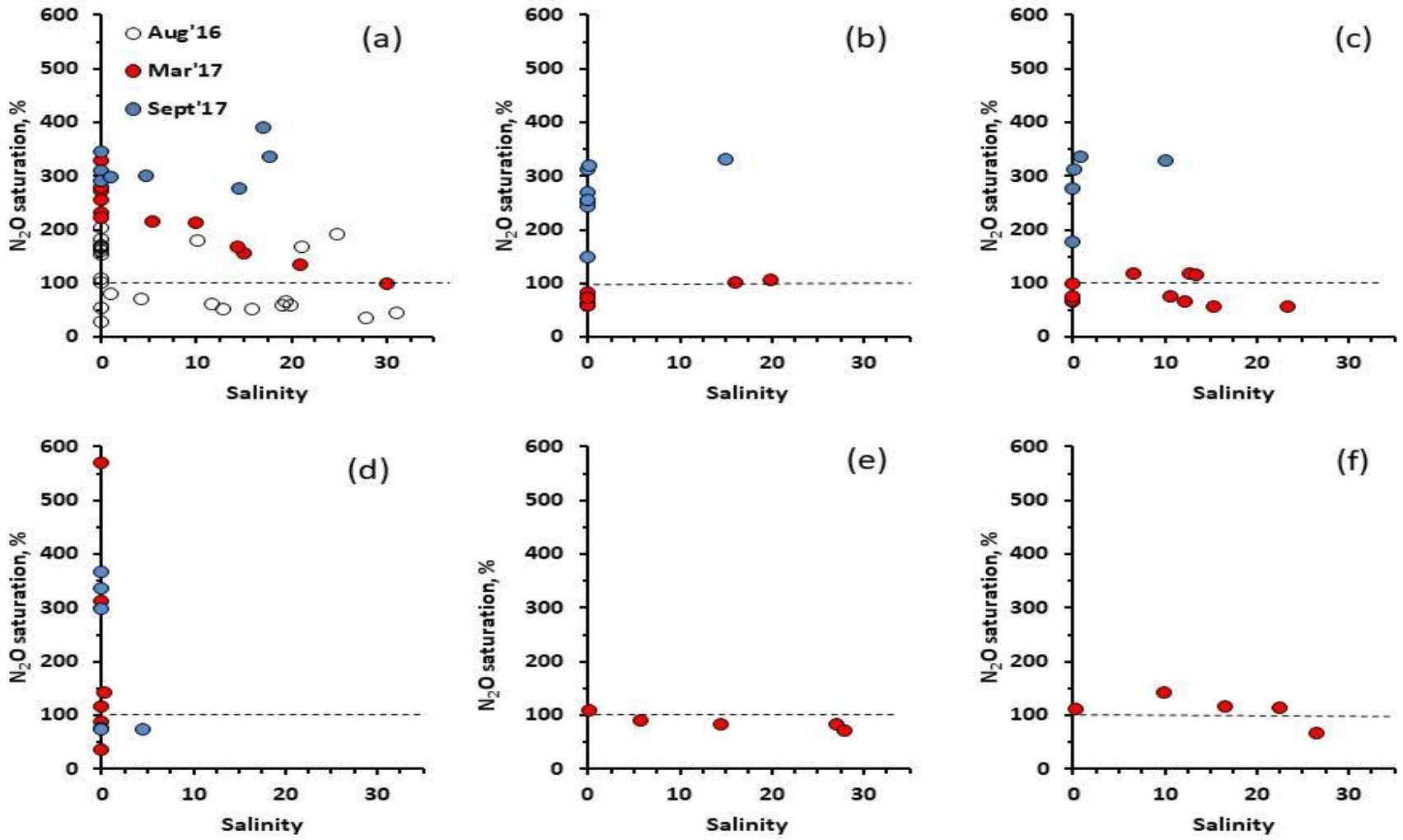


Figure 2.


Aug'16
Mar'17
Sept'17
(a)
(b)
(c)
(d)
(e)
(f)
N2O saturation, %
Salinity
0
100
200
300
400
500
600
0
10
20
30

740

Figure 3.

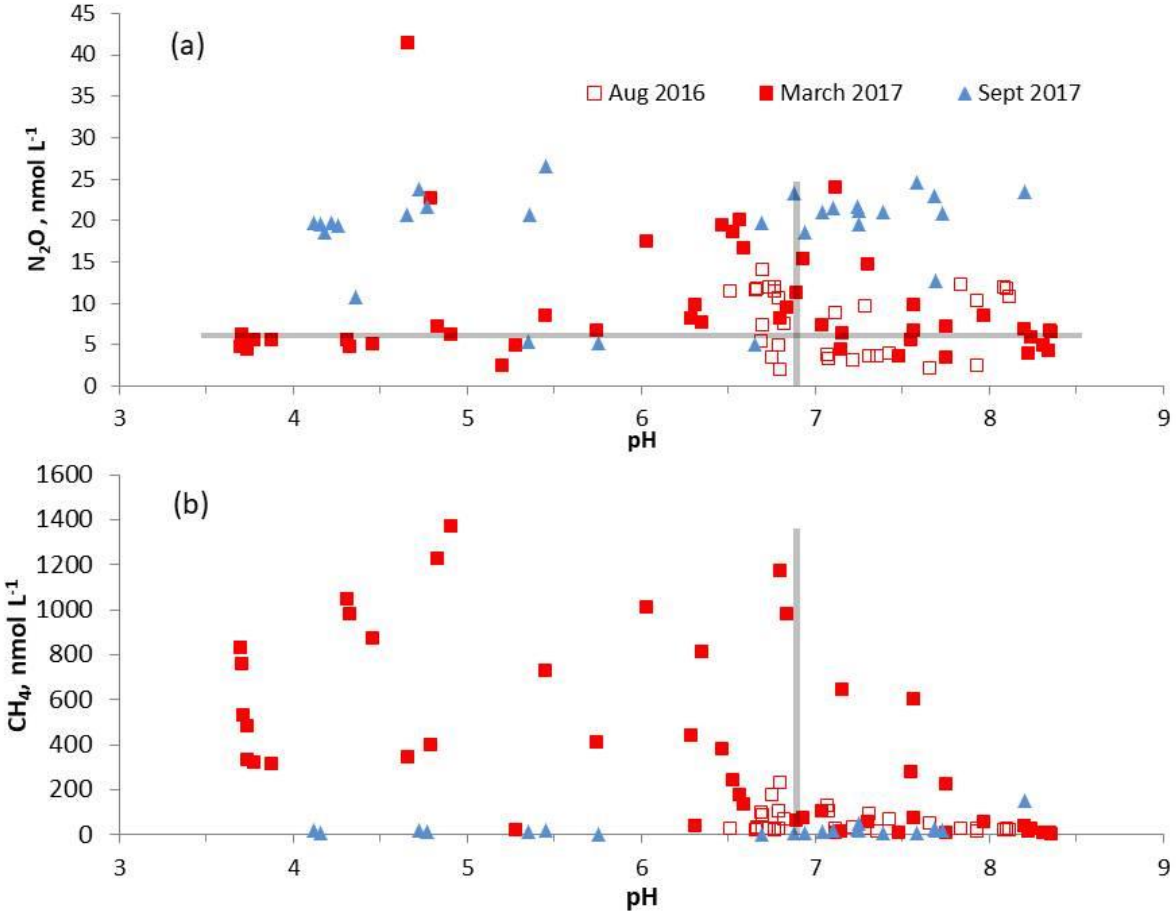
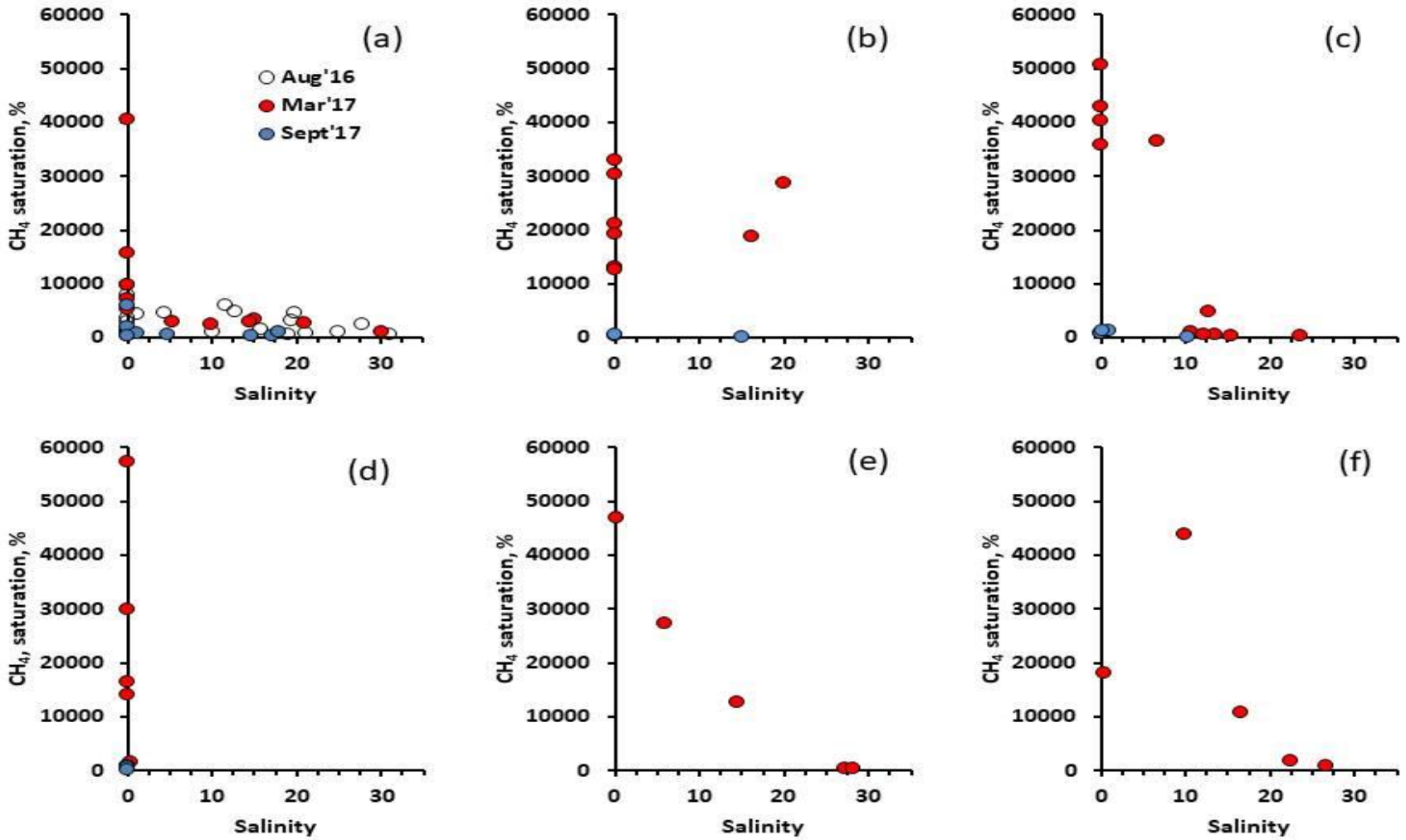
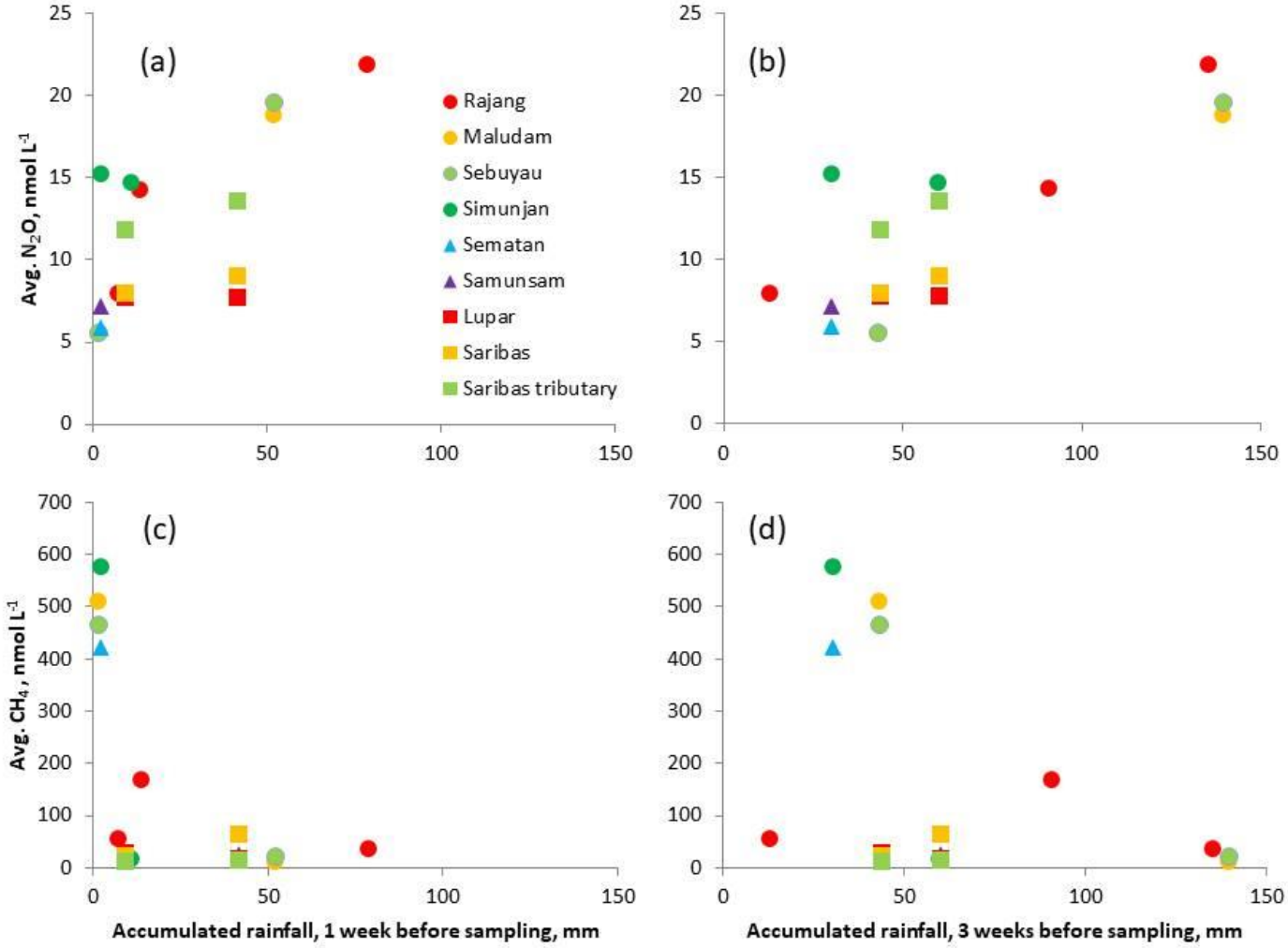


Figure 4.


(a)
Aug'16
Mar'17
Sept'17
(b)
(c)
(d)
(e)
(f)
CH4 saturation, %
CH4, saturation, %
Salinity
0
10000
20000
30000
40000
50000
60000
0
10
20
30

745 Figure 5


(a)
(b)
(c)
(d)
Avg. N_2O, nmol L^{-1}
Avg. CH_4, nmol L^{-1}
Rajang
Maludam
Sebuyau
Simunjan
Sematan
Samunsam
Lupar
Saribas
Saribas tributary
Accumulated rainfall, 1 week before sampling, mm
Accumulated rainfall, 3 weeks before sampling, mm