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Lateral carbon fluxes and CO_2 outgassing from a tropical peat-draining river

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Abstract

Tropical peatlands play an important role in the global carbon cycle due to their immense carbon storage capacity. However, pristine peat swamp forests are vanishing due to deforestation and peatland degradation, especially in Southeast Asia. CO_2 emissions associated with this land use change might not only come from the peat soil directly, but also from peat-draining rivers. So far, though, this has been mere speculation, since there was no data from undisturbed reference sites. We present the first combined assessment of lateral organic carbon fluxes and CO_2 outgassing from an undisturbed tropical peat-draining river. Two sampling campaigns were undertaken on the Maludam river in Sarawak, Malaysia. The river catchment is covered by protected peat swamp forest, offering a unique opportunity to study a peat-draining river in its natural state, without any influence from tributaries with different characteristics. The two campaigns yielded consistent results. Dissolved organic carbon (DOC) concentrations ranged between 3222 and 6218 µmol L^{-1} and accounted for more than 99 % of the total organic carbon (TOC). Radiocarbon dating revealed that the riverine DOC was of recent origin, suggesting that it derives from the top soil layers and surface runoff. We observed strong oxygen depletion, implying high rates of organic matter decomposition and consequently CO_2 production. The measured median pCO_2 was 7795 and 8400 µatm during the two campaigns, respectively. Overall, we found that only 26±15 % of the carbon was exported by CO_2 evasion, while the rest was exported by discharge. CO_2 outgassing seemed to be moderated by the short water residence time. Since most Southeast Asian peatlands are located at the coast, this is probably an important limiting factor for CO_2 outgassing from most of its peat-draining rivers.

1 Introduction

Southeast Asian peat soils are a globally important carbon pool. They store 68.5 Gt carbon, which corresponds to 11–14 % of the global peat carbon (Page et al., 2011).

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Peat consists of layered dead organic material. Decay is inhibited due to permanent waterlogging, low pH and scarcity of oxygen. The main reason for slow decomposition rates in peat is the enzyme phenol oxidase, which is activated by bimolecular oxygen (Freeman et al., 2001): at low oxygen and low pH, phenol oxidase activity is inhibited (Pind et al., 1994). That allows phenolic compounds to accumulate, which, in turn, inhibit those enzymes required for peat decomposition. Under natural conditions, organic matter accumulates faster than it decomposes, and the peatland acts as a net carbon sink. Coastal peatlands in Southeast Asia, in particular, were said to be the most effective terrestrial ecosystems with regards to long-term carbon sequestration (Dommain et al., 2011).

However, most Southeast Asian peatlands are currently undergoing severe disturbance due to anthropogenic activities, such as deforestation, drainage, and conversion of peatlands into plantations. It has been estimated that only 11 % of the peatlands in Sumatra and Kalimantan (Indonesia) remain covered by peat swamp forest (PSF) (Miettienen and Liew, 2010). In Malaysia, 23 % of the peatlands were classified as undisturbed or relatively undisturbed, and 17 % in Sarawak, a Malaysian state in northwestern Borneo, where most of Malaysia's peatlands are located (Wetlands International, 2010). Entirely pristine PSFs in Sarawak make up only 1.5 % (Wetlands International, 2010). In the context of climate change, the vulnerability of the tropical peatland carbon store to human perturbation has been noted with concern. Both (1) vertical carbon fluxes, i.e., carbon dioxide (CO_2) emissions (Hirano et al., 2012), and (2) lateral carbon fluxes (Moore et al., 2013; Evans et al., 2014) indicate its increasing instability.

(1) Many studies suggest that disturbed peat soil turns from a carbon sink into a carbon source to the atmosphere (Hooijer et al., 2010; Hirano et al., 2012). The reason is that drainage lowers the water level in the peat soil, exposing the top layers to aerobic conditions. The activity of phenol oxidase, however, increases dramatically with increasing oxygen availability (Pind et al., 1994). Therefore, peat decomposition in a drained peatland is accelerated, which releases CO_2 to the atmosphere (Couwenberg et al., 2010). Additionally, degraded peat is susceptible to burning, which causes

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large CO_2 emissions as well (Page et al., 2002; van der Werf et al., 2004; Gaveau et al., 2014). The prevalence of fire differs between countries, presumably due to different preventive and suppressive measures: Langner and Siegert (2009) showed that fire affects relatively larger areas in the Indonesian part of Borneo (Kalimantan) than in the Malaysian part and Brunei.

(2) Lateral carbon fluxes primarily concern the dissolved organic carbon (DOC) export from peat-draining rivers. It is well established that peat-draining rivers receive large amounts of DOC from the peat soils (Baum et al., 2007; Alkhatib et al., 2007; Moore et al., 2011). Because of that, they usually exhibit a dark water color (Baum et al., 2007), which is why they are often referred to as "blackwater" rivers. Baum et al. (2007) estimated that Indonesian rivers alone account for 10 % of the global riverine DOC export to the ocean. It was shown that these DOC fluxes, too, respond to anthropogenic change (Evans et al., 2014). Moore et al. (2013) showed that disturbed tropical peatlands released more and older organic carbon to rivers in comparison to an undisturbed site. They also speculated that this might lead to increased CO_2 outgassing from peat-draining rivers in response to anthropogenic change, but they did not assess CO_2 evasion in their study.

Peat-draining rivers are potential sources of CO_2 to the atmosphere: Pind et al. (1994) suggested that the rate of peat degradation might increase in the adjacent aquatic system, where oxygen and pH conditions might be more favorable for phenol oxidase activity than in the peat soil itself. Through the water–air interface, oxygen can diffuse into the river and facilitate in-stream DOC decomposition. This, in turn, consumes the supplied oxygen, potentially leading to hypoxic or anoxic events (Rixen et al., 2008). At the same time, CO_2 is produced, leading to CO_2 supersaturation of the river water with respect to the atmosphere, and consequently to CO_2 evasion. Indeed, high CO_2 fluxes have been reported from temperate peat-draining rivers (Hope et al., 2001; Billett et al., 2007), which is in line with the emerging consensus that streams and rivers generally tend to be sources of CO_2 to the atmosphere (e.g., Richey et al., 2002;

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Cole et al., 2007; Aufdenkampe et al., 2011; Butman and Raymond, 2011; Bouillon et al., 2012; Raymond et al., 2013).

CO_2 emissions from tropical peat-draining rivers have not been quantified so far and their response to anthropogenic change is unclear. Obviously, the quantification of the anthropogenic effect on riverine CO_2 emissions in tropical peatlands requires the comparison between disturbed and undisturbed peat-draining rivers. To the best of our knowledge, an undisturbed system has not been documented in terms of CO_2 outgassing yet. It is very likely that the emerging research on CO_2 dynamics in tropical peat-draining rivers will focus on disturbed systems, simply due to the fact that pristine sites have become extremely rare and are hardly accessible. Nevertheless, baseline data are indispensable for the quantification of the anthropogenic effect on both lateral, riverine organic carbon fluxes and CO_2 emissions from tropical peat-draining rivers.

In this study, we present, for the first time, measurements of both total organic carbon (TOC) and CO_2 fluxes in a tropical blackwater river draining an intact peat dome. We measured surface water pCO_2, dissolved oxygen (DO) and particulate and dissolved organic carbon along with a number of ancillary parameters, as well as CO_2 fluxes to the atmosphere in the Maludam river in Sarawak, Malaysia.

2 Materials and methods

2.1 Study area

Our study area is the Maludam National Park (NP), which is located on the Maludam peninsula (between 1°24′–1°40′ N and 111°0′–111°16′ E) in the Malaysian state of Sarawak. Sarawak comprises the northwestern part of the island of Borneo and is separated from the Malaysian peninsula by the South China Sea. It has a tropical climate and high rainfall throughout the year. Precipitation in Kuching, the capital city of Sarawak, ranges from 196 mm in June to 675 mm in January at the peak of the northwestern monsoon, which occurs between November and February, and

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amounts to 4101 mm yr^{-1} (average for the period between 1961–1990, figures from DWD). Sarawak holds the largest share of Malaysia's peatlands (Joosten, 2012), which cover about 14 659 km^2 or 12 % of the state's area (Chai, 2005). They are mainly found in the coastal region and were initiated during the Middle and Late Holocene between 7000 and 4000 BP (Dommain et al., 2011). Sarawak's peatlands are rainwater-fed and were originally forested (Joosten, 2012). However, in recent years, PSFs in Sarawak have been cleared mostly for commercial crops like oil palm, sago, and rubber (Wetlands International, 2010).

The Maludam peninsula hosts Malaysia's largest peat dome. The Maludam NP encompasses an area of 432 km^2 (Forest Department, 2014). Two adjacent areas with a total of 91.3 km^2 were proposed for extension to protect and preserve the central portion of the peat area (Chai, 2005). Peat thickness reaches up to 10 m (Melling et al., 2007). The forest is characterized as mixed peat swamp forest at the edge of the dome, and Alan bunga forest in the center (Melling et al., 2007), with *Shorea albida* being the dominant species in the upper storey (Anderson, 1963). Kselik and Liong (2004) reviewed precipitation and evaporation data from meteorological stations in the vicinity of the park and concluded that a moisture deficit is not expected, suggesting that the water supply for the peat dome is provided year-round.

Prior to the establishment of the NP, commercial logging threatened parts of the Maludam PSF. Gazetted as NP in 2000, the PSF has to a great extent recovered and has regained a canopy height of 30–35 m (Melling and Tang, 2012). For our study, the most important feature of the Maludam peat dome is the fact that the soil was not drained (Vaessen et al., 2011). Consequently, the peat soil has not been exposed to aerobic conditions and remained intact.

The Maludam river runs through the center of the peat dome and lies, to its largest part, inside the NP (Fig. 1). It is lined by several dominant species that include *Pandanus andersonii*, which is frequently found in Alan bunga forest (Anderson, 1963), several species of *Syzygium* (*Eugenia*), the herb *Hanguana malayana*, and the fan palm *Licuala petiolulata* (Chai, 2005). The only village along the river (ca. 5000 inhab-

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itants) is located downstream of the NP boundary, 1.5 km before the river discharges into the South China Sea. The Maludam river drains a catchment of 91.4 km^2 (Lehner et al., 2006), which is covered by PSF (except for a small coastal strip). The only physico-chemical data reported for the Maludam river that we are aware of is one data point published by Kselik and Liong (2004). These authors report tea-colored, acidic, nutrient-low and oxygen-depleted water, which is typical for peat-draining rivers, as described above. However, the paucity of the data highlights the need for further studies.

We collected samples in March 2014 and March 2015, a few weeks after the monsoon season, so that it can be assumed that samples were taken during decreasing discharge. In 2015, Sarawak had experienced a severe flood during the peak of the monsoon in January. Our campaign during that year took place in the beginning of March, whereas samples were taken during late March in 2014.

11 stations along a 12 km stretch of the Maludam river (total length: ~ 24 km; see Fig. 1) were covered in 2014, and 14 stations along approximately the same stretch in 2015. In 2014, one sample was taken in the village at the beginning of the cruise. Then, we started at the furthest point upstream and collected samples at a spatial frequency of approximately 1 km on our way downstream during one day. In 2015, the first six samples were collected on the way upstream and the remaining eight samples during two subsequent days on the way downstream. No bigger rainfall events occurred during the campaigns.

Our sampling aimed at assessing the carbon budget in the river and quantifying the related CO_2 emissions to the atmosphere. In 2014, we took 9 samples inside and 2 outside the NP; in 2015, 13 out of 14 samples were taken inside the park. In the village, the water level was influenced by tides (yet salinity was zero). Unless stated otherwise, our findings are based on the NP samples.

2.2 Sampling procedure

Water samples were taken from ca. 1 m below the water surface. For dissolved organic carbon (DOC) and total dissolved nitrogen (TDN), samples were filtered through

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0.45 µm syringe filters, acidified with 21 % phosphoric acid to pH < 2 and frozen. Analysis for DOC and TDN was performed by combustion at 720 °C using a Shimadzu TOC-VCSH with TNM-1 analyzer equipped with a non-dispersive infrared sensor and a Shimadzu ASI-V automatic sampler.

Three of the 2014 samples were also analyzed for ^{14}C-DOC at the Leibniz-Laboratory for Radiometric Dating and Isotope Research in Kiel, Germany. One measurement had to be discarded due to analytical reasons. The $^{14}C/^{12}C$ ratio was determined with accelerator mass spectrometry (AMS) and compared to an international standard (NIST Oxalic Acid standard 2 – OxII). The values were normalized to a $\delta^{13}C$ of −25 ‰ according to Stuiver and Polach (1977). Values are reported in percent modern carbon (pMC), whereas 100 pMC refers to the atmospheric radiocarbon concentration in the year 1950 AD (Stuiver and Polach, 1977).

Particulate material was collected on pre-weighed and pre-combusted glass fiber filters (Whatman, 0.7 µm). The net sample weight was determined. For the determination of nitrogen, a definite amount of each sample was filled into tin cups. For organic carbon, silver cups were used, inorganic carbon was removed by addition of 1 N HCl and the samples were dried at 40 °C. The elemental analysis was performed by flash combustion using a Eurovector EA3000. For stable carbon isotope analysis, samples were filled into silver cups as well, inorganic carbon was removed as described above and $\delta^{13}C$ was determined with a Thermo Finnigan DELTAplus mass spectrometer.

Samples for $\delta^{13}C$ in dissolved inorganic carbon (DIC) were taken directly from the sampling bottle, preserved with 100 µL $HgCl_2$ per 24 mL sample and the bottle was sealed with Parafilm. For analysis, ∼ 50 µL of 98 % phosphoric acid were filled into a vial. The vial was closed and the headspace was exchanged with He gas. 4 mL of sample water were then injected through the septum using a syringe. $\delta^{13}C$ was determined in duplicates using a Thermo Scientific MAT 253 mass spectrometer.

CO_2 measurements were performed using two different techniques. In 2014, a headspace method was used with an Li-820 infrared CO_2 analyzer. We sampled 300 mL of water in a 600 mL conical flask and closed the top with a lid. The lid was

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connected to the CO_2 analyzer, whereas the inlet was connected to a tube sampling the headspace air, and the outlet reached down to the bottom of the flask. This forced the sampled air to bubble through the water and enabled a faster equilibrium between water and air. Normally, this is achieved by shaking the sampling bottle (e.g., Cole et al., 1994, Abril et al., 2015). In our case, we were able to observe how the equilibrium was achieved. The water pCO_2 was then calculated according to Dickson et al. (2007), SOP4, using solubility constants for CO_2 from Weiss (1974). In this acidic environment, we were able to simplify the calculations presented by Dickson et al. by assuming that DIC consists essentially of CO_2 and that the fractions of carbonate and bicarbonate are negligible (see Supplement). The reproducibility of this headspace method was tested in the lab with a closed bucket of tap water. pCO_2 in the water from this bucket was measured 10 times and the standard deviation was calculated. This revealed a variability of $< 2.5\,\%$. The Li-820 was calibrated in the lab before and after the sampling with three secondary standards with different CO_2 mixing ratios (380, 1000, 3500 and 5000 ppm).

In 2015, pCO_2 was continuously monitored using a Contros HydroC CO_2 Flow Through Sensor. Note that the Contros sensor was only calibrated up to 1500 µatm CO_2 by the manufacturer and nonlinear at high concentrations. In order to correct for this nonlinearity, we conducted six additional headspace measurements with the Li-820 on the spot and scaled the Contros data accordingly for the measured range. Details are provided in the Supplement.

In order to quantify the CO_2 flux, we conducted floating chamber measurements. The floating chamber used in 2014 had a volume of 8.7 L and enclosed a surface area of $0.05\,m^2$ with the water. The chamber used in 2015 was smaller with a volume of 3 L and a surface area of $0.03\,m^2$. The edges extended approximately 1 cm into the water. In order to maintain ambient pressure in the headspace, the chambers were equipped with a long vent tube. For the duration of one floating chamber measurement (ca. 5 min), the impact of the vent on the headspace concentrations can be considered negligible. Five floating chamber measurements were conducted during each cruise

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and only when the boat was drifting freely. The flux F was calculated from the slope of the concentration vs. time curve, according to

$$F = \frac{\Delta c}{\Delta t}\frac{pV}{RTA},$$

where $\Delta c/\Delta t$ is the fitted slope ($\mu mol\,mol^{-1}\,s^{-1}$), p is the pressure (Pa), V is the volume (m^3), R is the universal gas constant ($8.314\,J\,mol^{-1}\,K^{-1}$), T the temperature (K) and A the surface area (m^2). Fluxes were converted to $g\,C\,m^{-2}\,d^{-1}$ (per water surface unit area). The corresponding exchange velocities were calculated with

$$k = \frac{F}{K_0\left(pCO_2^{water} - pCO_2^{air}\right)}.$$

pCO_2^{water} refers to the water pCO_2 and pCO_2^{air} to the average ambient pCO_2, which was measured with the Li-820 between the stations. For the purpose of comparison, k was normalized to a Schmidt number of 600, corresponding to CO_2 in freshwater at 20 °C. The Schmidt number is the ratio of the kinematic viscosity of the water and the diffusion coefficient of the gas. It was calculated according to Wanninkhof (1992). In order to better constrain our findings, we calculated k_{600} also using the parameterization of Raymond et al. (2012) (see Table S1).

At each station, we measured pH, dissolved oxygen (DO), conductivity and water temperature in the surface water and ambient air temperature. In 2015, we measured pH and DO continuously between the stations. DO and conductivity were measured with a WTWMulti 3420, using an FDO 925 oxygen sensor and a TetraCon 925 conductivity sensor. For pH measurements, we used a HANNA HI 8424 pH meter in 2014, and a Sentix 940 IDS pH sensor in 2015, both of which were calibrated with the same two technical buffers directly before the cruise. Water temperature was measured with the temperature sensors integrated in the oxygen probe. In 2014, we measured additional salinity and temperature profiles with a CastAway CTD.

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As we conducted no in-situ measurement of the flow velocity, we estimated it from the drift during the stations, at which the motor was off and the boat drifted freely. To this end, we used the GPS information of the CTD at the beginning and the end of the cast, and the duration of the cast to calculate the flow velocity. Additional flow velocity estimates were obtained with a separate GPS, which was evaluated before and after the floating chamber measurements, during which the boat floated freely as well.

2.3 Discharge and carbon yield calculation

No gauging data exist for the Maludam river. Therefore, we estimated the discharge Q from the difference between precipitation P (in $\mathrm{mm\,yr^{-1}}$) and evapotranspiration ET (in $\mathrm{mm\,yr^{-1}}$):

$$Q = (P - \mathrm{ET})A,$$

where A is the catchment area ($\mathrm{m^2}$). Although this approach has been said to deviate from the actual runoff in the short-term, it can be a useful approach in a steady state (Dai and Trenberth, 2002), especially if gauging stations are rare or lacking. For P, we used daily rainfall records from Maludam village for the year 2013, which were provided by the Department of Irrigation and Drainage Sarawak (DID). Since our approach of calculating discharge cannot resolve seasonal variations for the reason given above, we used the annual average precipitation for the year 2013. For ET, we drew on three different estimates from the literature: one estimate was for a lowland rainforest in central Sarawak (Kumagai et al., 2005), and two were for an undisturbed PSF in central Borneo (Moore et al., 2013; Hirano et al., 2014).

We multiplied Q with the average total organic carbon (TOC) concentration (C_{TOC}) and divided by the catchment area A in order to determine the average TOC yield exported by discharge (see Table S2). The CO_2 yield was determined from the areal flux and the assumption that streams cover 0.89 % of the catchment area, according to the value used by Raymond et al. (2013) for the COSCAT 1328 (COSCATs: COastal Seg-

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mentation and related CATchments), which contains our study area (Meybeck et al., 2006).

3 Results

3.1 Physico-chemical characteristics

The Maludam river is a typical blackwater river. The water exhibited a brown color and low pH. In the NP, all samples contained freshwater, as indicated by a low conductivity between 72.5 and 100.3 $\mu S\,cm^{-1}$ (2014). In the village, conductivity was as high as 235.0 $\mu S\,cm^{-1}$. Following Moore et al. (2011), we classify this data point as one with seawater influence. pH was consistently low with a median of 3.8 in 2014 and 3.7 in 2015, respectively (Table 1). Note that for the 2014 measurements, we have pH data only for the first five stations because of a failure of the sensor. However, the small standard deviation of 0.2 suggests that the pH does not vary much and that the median value of 3.8 can be considered representative for the river's spatial extent, consistent with the 2015 median and standard deviation. The acidic character of the Maludam river is typical for blackwater rivers and in agreement with the results from previous studies of Malaysian peat-draining rivers (Kselik and Liong, 2004; Gasim et al., 2007; Irvine et al., 2013).

The total dissolved nitrogen (TDN) median was $49 \pm 6\,\mu mol\,L^{-1}$ in 2014 and $57 \pm 3\,\mu mol\,L^{-1}$ in 2015. TDN concentrations increased slightly in flow direction (Fig. 2b). The river was strikingly undersaturated in oxygen, ranging from 29 to 58 $\mu mol\,L^{-1}$ in 2014 and from 26 to 42 $\mu mol\,L^{-1}$ in 2015. Note that in 2014, two data points are missing (kilometers ~ 3 and 7.5, see Fig. 3) due to a failure in data storage. Initially, DO decreased in flow direction (both years) down to a minimum, which was located approximately six kilometers from the river mouth. From there, it increased again up to an oxygen maximum of 201 $\mu mol\,L^{-1}$ in the village (2014 data, Fig. 3).

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3.2 Organic carbon

DOC concentrations varied between 3420 and 6218 µmol L^{-1} in 2014, with a median of 3768 µmol L^{-1}, and between 3222 and 3734 µmol L^{-1} in 2015, with a median of 3612 µmol L^{-1} (Table 1) and increased slightly in flow direction (see Fig. 2a), while DO decreased (see Fig. 3). The age determination of our two samples from 2014 revealed that DOC contained 106.6 ± 0.3 pMC and 106.1 ± 0.4 pMC, indicating a large contribution of modern carbon to the overall sample age. The calibration for post-bomb carbon was achieved with the program CALIBomb (Reimer et al., 2004) and yields a probability distribution for the sample's mean calendar age on both sides of the bomb-peak (see Fig. S3). Since our samples were taken in an undisturbed system, we considered the younger solution to be more likely. Accordingly, the most probable mean sample age is 2005–2007 AD and 2006–2008 AD (one sigma) for the two samples, respectively. That means that the DOC in the Maludam river is derived from carbon that was fixed from the atmosphere during the last decade.

The Maludam river water contained very little particulate material. On average, DOC accounted for 99.5 % (2014) and 99.6 % (2015) of TOC (Table 1), which is consistent with observations in Indonesian peat-draining rivers (Baum et al., 2007; Moore et al., 2013). Median POC concentrations were 21 µmol L^{-1} in 2014 and 16 µmol L^{-1} in 2015 with little variation in the NP (see Fig. 2c). In 2014, elevated POC concentrations were only found between the NP boundary and the village (see Fig. 2c). The atomic carbon-to-nitrogen (C/N) ratio in particulate organic matter ranged between 7.4 and 21.3 in 2014 and 13.7 and 45.5 in 2015, which is consistent with a mixed signal of phytoplankton (6–7) and higher plant terrestrial organic matter (> 20, Hedges et al., 1986a, 1997). $\delta^{13}C$ in POC varied only slightly between the stations and ranged from −29.35 to −28.55 ‰ (average −28.89 ‰, 2014 data only).

Precipitation in Maludam in 2013 ranged from 89 mm in June to 769 mm in December and summed up to 3576 mm yr^{-1}. Discharge was estimated to be 4.8 m^3 s^{-1} with the ET value used by Moore et al. (2013) for an undisturbed PSF (ET = 1903 mm yr^{-1}),

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$5.6\,m^3\,s^{-1}$ with the ET estimate of Hirano et al. (2014) for the same PSF (ET = $1636\,mm\,yr^{-1}$) and $5.9\,m^3\,s^{-1}$ with the ET estimate of Kumagai et al. (2005) for lowland rainforest in central Sarawak (ET = $1545\,mm\,yr^{-1}$). The average discharge thus obtained was $5.5 \pm 0.6\,m^3\,s^{-1}$ (average ± largest deviation). With median TOC concentrations of $3861 \pm 890\,\mu mol\,L^{-1}$ and $3645 \pm 175\,\mu mol\,L^{-1}$ and a catchment size of $91.4\,km^2$, we estimated an average total organic carbon (TOC) yield of $87 \pm 10\,g\,C\,m^{-2}\,yr^{-1}$ for 2014 and $82 \pm 9\,g\,C\,m^{-2}\,yr^{-1}$ for 2015, respectively. The uncertainties were calculated by propagation of uncertainties (Gaussian error propagation), whereas the standard deviation of the TOC concentration, the uncertainty of discharge and the uncertainty of the catchment size were considered (see Table S3). For both years combined, the TOC yield from the Maludam catchment was $85 \pm 9\,g\,C\,m^{-2}\,yr^{-1}$.

3.3 CO_2

pCO_2 ranged between 6130 and 8943 µatm in 2014 and between 8126 and 8694 µatm in 2015 and exhibited some spatial variations. It decreased in flow direction in the uppermost part of the studied river stretch (Fig. 4a, km14–10, 2014 data). Then, pCO_2 increased slightly, and decreased again between the NP boundary and the village. CO_2 concentrations showed a weak negative relationship with DO (Fig. 5b).

Within the observed variability, pCO_2 was similar in 2014 (7795 ± 900 µatm, median ± one standard deviation) and in 2015 (8400 ± 135 µatm). $\delta^{13}C$ in DIC ranged between −28.85 to −28.18 ‰ and averaged −28.55 ‰ (2014 data). Under acidic conditions, the carbonate system is shifted towards more free CO_2. At a pH of 3.7–3.8, CO_2 accounts for > 99 % of DIC. Atmospheric pCO_2 averaged 420 µatm in 2014 and 419 µatm in 2015.

The floating chamber measurements differed markedly among each other and revealed areal fluxes between 5.6 to $28.5\,g\,C\,m^{-2}\,d^{-1}$ in 2014 and 1.8 to $10.0\,g\,C\,m^{-2}\,d^{-1}$ in 2015 (see Fig. 4b). The highest fluxes were observed at the most upstream and most downstream spots in 2014 (see Fig. 4b). The average piston velocity normal-

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ized to a Schmidt number of 600 was $15.6 \pm 9.7\,\mathrm{cm\,h^{-1}}$ (average ± standard deviation; largest deviation of a single measurement from the mean was $15.1\,\mathrm{cm\,h^{-1}}$) in 2014 and $6.3 \pm 3.3\,\mathrm{cm\,h^{-1}}$ (largest deviation: $5.0\,\mathrm{cm\,h^{-1}}$) in 2015. The standard deviation was used for the further calculation of the propagation of uncertainties (see Table S3). For the Raymond et al. (2012) model equations, the stream velocity V, the slope S, mean depth D and discharge Q were required. As velocity, we used the mean of our estimates based on the drift during the stations in 2014 ($V = 0.2\,\mathrm{m\,s^{-1}}$). The slope was calculated after determination of the elevation at the source and at the river mouth using the GTOPO30 digital elevation model for ESRI's ArcGIS (USGS-EROS, 2010, $S = 25\,\mathrm{m}/24\,000\,\mathrm{m}$). We assumed a depth D of ~ 4 m based on measurements during December 2014 (unpublished). The piston velocities k_{600} obtained in this way ranged from 6.8 to $31.8\,\mathrm{cm\,h^{-1}}$ (for details see Tab. S1), which is the same order of magnitude as the estimates based on our floating chamber measurements. We calculated a mean flux for the Maludam river with $k_{600} = 15.6\,\mathrm{cm\,h^{-1}}$ of $12.7 \pm 6.8\,\mathrm{g\,C\,m^{-2}\,d^{-1}}$ for 2014 and with $k_{600} = 6.3\,\mathrm{cm\,h^{-1}}$ of $5.5 \pm 2.6\,\mathrm{g\,C\,m^{-2}\,d^{-1}}$ for 2015. Although these CO_2 fluxes are quite different with regards to the absolute numbers, they exhibit a consistent spatial pattern: from Fig. 4b, it can be seen that the measurements in 2015 were concentrated around the central part of the river stretch, where lower fluxes were observed also in 2014. In contrast, enhanced outgassing was observed in the most upstream and most downstream part of the sampled stretch. Therefore, it can be assumed that the discrepancy between the two estimates actually represents some of the spatial variability along the river stretch.

The areal CO_2 fluxes determined for 2014 and 2015, respectively, translate into CO_2 yields of $41 \pm 23\,\mathrm{g\,C\,m^{-2}\,yr^{-1}}$ and $18 \pm 9\,\mathrm{g\,C\,m^{-2}\,yr^{-1}}$, or an average CO_2 yield of $30 \pm 16\,\mathrm{g\,C\,m^{-2}\,yr^{-1}}$. The uncertainties were calculated from the uncertainty associated with the gas exchange velocity and the Raymond et al. (2013) estimate of a 0.89 % stream coverage was assigned an uncertainty of 18 %, which corresponds to the deviation from the stream coverage for the neighboring COSCAT (see Table S3). In order to partition lateral and vertical flux, we calculated the combined lateral and vertical carbon

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export and estimated the percentage of carbon exported by evasion. Accordingly, CO_2 evasion accounted for 32 % of the carbon export in 2014 and for 18 % of the carbon export in 2015. If both years are taken together, the combined carbon export was $114 \pm 26\,g\,C\,m^{-2}\,yr^{-1}$, 26 ± 15 % of which were evaded to the atmosphere as CO_2.

4 Discussion

4.1 Organic matter decomposition

DOC, oxygen and CO_2 dynamics in freshwaters and peat-draining rivers are closely linked through the process of organic matter decomposition. During the oxidation of organic matter, oxygen is consumed and CO_2 is produced. This view is confirmed for our study site by the $\delta^{13}C$ in DIC (average −28.55 ‰), which, at the pH of 3.7–3.8, consists of > 99 % CO_2. These $\delta^{13}C$ values are similar to those measured in peat and leaves (Baum, 2008). Since the isotopic fractionation during organic matter decomposition is negligible (Rozanski et al., 2001), the $DI^{13}C$ values provide strong evidence that the DIC (CO_2) originates from the decomposition of terrestrial DOM. Enhanced CO_2 is generally associated with oxygen depletion. We observed this link, but it was weak in our study. Probably, both the DO-DOC and the DO-CO_2 relationship are partially obscured by a natural variability, as seen in other studies (e.g., Rixen et al., 2008). For example, although we think that primary productivity is small, the fact that the samples were taken during different times of the day might have an impact. This would cause higher oxygen values during the day than in the early morning. Additionally, we sampled different locations during 2014 and 2015. As a result, spatial variability of, e.g., the exchange velocity might have caused some bias. In that case, the data would be biased towards higher oxygen concentrations, because due to different diffusivities, the consumed oxygen is replaced faster by invasion than the produced CO_2 is emitted. Although it cannot be fully resolved which other processes might play a role, the general

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link between DO, DOC and CO_2 concentrations is observed in the Maludam river as expected.

One important factor that controls DOC decomposition and thereby pCO_2 is the DOC concentration. In the Maludam river, we observed increasing DOC in flow direction, indicating that DOC inputs are larger than DOC decomposition. The $DO^{14}C$ indicates that this organic material is of recent origin, which is consistent with the notion that undisturbed peatlands exhibit modern fluvial $DO^{14}C$ across different climatic regions (Evans et al., 2014) and that rivers generally convey relatively young DOC (Marwick et al., 2015). It does also provide evidence of the stability of the peat column, i.e. DOC inputs are mainly derived from upper soil layers or surface runoff. This is in agreement with the classical view that the hydraulic conductivity, i.e. the movement of water through the soil, is high in the upper peat layer and small in the saturated zone (Rieley and Page, 2008). This means that the water that enters the stream is a mixture of surface runoff and subsurface flow from upper soil layers. Therefore, the DOC is derived from these two sources as well, whereby enhanced surface runoff might lead to a dilution of the DOC concentrations. This is in line with the slightly lower DOC concentrations in 2015: Samples were taken earlier in the month, so that runoff was possibly still higher due to the receding monsoon. The young age of the riverine DOC implies that the CO_2 production is sustained by a relatively young carbon pool, which is in agreement with radiocarbon studies from the Amazon (Hedges et al., 1986b; Mayorga et al., 2005).

4.2 Total organic carbon flux

On a global perspective, the DOC concentrations in the Maludam river range among the highest reported for streams and rivers (Alkhatib et al., 2007; Baum et al., 2007; Moore et al., 2011, 2013). Similarly, the TOC yield of $85 \pm 9\,g\,C\,m^{-2}\,yr^{-1}$ for the Maludam catchment is among the highest reported for tropical peat-draining rivers so far. Baum et al. (2007) suggested that the organic carbon yield mainly depends on the peat coverage in the catchment. In Maludam, the peat coverage is 100 %, and the only other studies that we are aware of that reported data from a tropical catchment

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with 100 % peat are those of Moore et al. (2011), (2013). They determined a TOC yield of 63 g C m^{-2} yr^{-1} for an undisturbed inland Bornean peat swamp forest and 97 g C m^{-2} yr^{-1} for disturbed sites (Moore et al., 2013), all of which were located in the Sebangau catchment in Central Kalimantan, Indonesia. Although these TOC yields are in a similar range as the one we are reporting for Maludam, the riverine DOC concentrations in the Maludam river were lower (3612–3768 µmol L^{-1}) than those at the undisturbed site in the Sebangau catchment (5667 ± 42 µmol L^{-1}, Moore et al., 2013). Possibly, this has to do with the different hydrological conditions: while no moisture deficit is expected for Maludam (Kselik and Liong, 2004), the Sebangau site usually has a three months dry period (Moore et al., 2011), so that the soil is not always fully saturated with water. Therefore, the DOC concentrations in the Sebangau tributaries might actually resemble those in the peat pore waters, while in Maludam, under saturated conditions, fresh rainwater would not fully infiltrate into the soil, but lead to a dilution of the riverine DOC. The fact that both sites end up with a similar TOC yield can be attributed to the higher discharge of the Maludam river if compared to the Sebangau sites, owing to 27 % higher rainfall in Maludam (3576 mm) than in Central Kalimantan (2810 mm, Moore et al., 2013).

4.3 CO_2 flux

The average estimated areal CO_2 fluxes of 5.5 ± 2.6 and 12.7 ± 6.8 g C m^{-2} d^{-1} are not unusually high. Aufdenkampe et al. (2011) report an average areal outgassing for tropical streams of 7.5 g C m^{-2} d^{-1}, which falls within this range. In consideration of the high DOC concentrations and degradation rates in the Maludam river, one could have expected higher pCO_2 and consequently higher areal emissions. The partitioning of lateral and vertical flux revealed that approximately three times as much carbon is transported laterally than evaded to the atmosphere as CO_2. The CO_2 concentration might mainly be moderated by the short residence time of the water in the Maludam river (33 h). This could be true for many peat-draining rivers in Indonesia and Malaysia, since the peat is mostly located in the coastal areas. Using the Harmonized World Soil

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Database (FAO, 2009) and the Analysis tools (Proximity/Buffer) in ArcGIS 10.1 (ESRI, USA), we determined the percentage of peatlands on Sumatra and Borneo that were located within a coastal strip of a defined width (Fig. 6). This revealed that 70 % of the peatlands on the islands of Sumatra and Borneo, which host the majority of all Southeast Asian peatlands, lie within 40 km of the coastline. Even at very low flow velocities, as in the Maludam river, this short distance translates into a time constraint that moderates biological processing. At faster flow velocities, this effect should be even more obvious.

4.4 Uncertainties of the presented estimates

Our findings are subject to some considerable uncertainties. The major conclusions are drawn from the comparison of (1) TOC yield and (2) CO_2 yield. Both yields were calculated based on certain assumptions and are thus subject to different sources of uncertainty.

(1) The TOC yield was calculated from the median TOC concentration, discharge and the catchment size. For a robust estimate, ideally, TOC concentrations and discharge should be measured simultaneously during different seasons. This would ensure that enhanced TOC export during peak discharge and flooding events would be captured. However, at present stage, continuous measurements in this remote area were not possible due to a lack of infrastructure. The results presented here rely on TOC concentrations measured after the monsoon season. Seasonal variability was not assessed in our study and arguably represents its most important limitation. However, the seasonal variability of at least the DOC concentrations is not expected to be large. Firstly, following the discussion of Moore et al. (2011), plant growth is sustained year-round in this monsoonal climate. Secondly, as reasoned above, a moisture deficit in the Maludam PSF is unlikely. Therefore, a "flushing effect", whereby DOC accumulates in peat pores during the dry season and is washed into the river at the onset of the wet season (Moore et al., 2011), is not expected.

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However, the very rough estimate of discharge that we provided is another, and possibly the larger, source of uncertainty. Our calculation of an annual average discharge did naturally not attempt to resolve seasonal variability. The assumption of steady state, which is the basis of this discharge estimate, is not always granted. Moore et al. (2011) showed that discharge in the Sebangau catchment was twice as high during the wet season if compared to the dry season. Baum et al. (2007) even found a six-fold higher discharge during a wet season campaign if compared to their result from a dry season campaign. It is likely that these large fluctuations have an effect on the TOC export, which we did not capture with our approach. Therefore, further simultaneous measurements of discharge and the TOC concentration are definitely desirable to resolve details about the variability of the TOC flux.

(2) The CO_2 yield was calculated from the CO_2 flux and the Raymond et al. (2013) estimate of the stream coverage in this COSCAT. To start with the latter, estimating the stream surface area especially in swamps or flooded areas is very challenging. The estimate of Raymond et al. (2013) seemed to us the most robust estimate available. However, it was derived for the entire COSCAT, so breaking this estimate down to the catchment scale might introduce some bias. We compared the stream coverage to the one reported for the neighboring COSCAT (Indonesia) and used the deviation of the two as an approximate uncertainty estimate. Certainly, a field survey would be the best way to estimate the stream surface area – however, this way, headwater streams and small tributary channels might be overlooked and the surface area thus be underestimated.

The largest uncertainty associated with the calculated CO_2 flux arguably stems from the uncertainty associated with the gas exchange velocity. Here, we used a floating chamber to derive the gas exchange velocity. This method has been subject to quite some debate. One objection is that floating chambers shelter the water surface from wind and thus reduce the gas exchange (Frankignoulle, 1988). However, due to the dense canopy, the Maludam river is not so exposed to wind stress, so that this bias is probably small. Others argue that floating chambers disrupt the water surface and thus

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artificially enhance the gas exchange (Matthews et al., 2003; Vachon et al., 2010). We tried to avoid this by using a relatively light floating chamber with small extensions into the water to make it more stable (Müller et al., 2015), and by employing the floating chamber only when the boat was drifting freely.

5 Conclusion

In summary, our study provided further evidence that tropical peat-draining rivers exhibit the highest riverine DOC concentrations worldwide. We showed that the peat carbon in this undisturbed system is securely stored in the peat column, and suggested that only DOC from the top soil layers is leached into the aquatic system, where it is diluted and partially remineralized. However, measured against the high DOC concentrations, CO_2 emissions from the Maludam river were quite moderate. We attributed this mainly to the short water residence time. Since most Sumatran and Bornean peat-draining rivers are located at the coast, we expect the TOC yield to dominate over the CO_2 yield in most of these systems. To date, it remains unclear how the described carbon dynamics are changing under anthropogenic pressure. Upon anthropogenic disturbance, the DOC export from peat soils tends to change both in quantity and quality: the DOC export increases and the DOC is older, i.e. derived from deeper soil layers (Moore et al., 2013; Evans et al., 2014). In the Sebangau catchment, the increased export of DOC was due to higher discharge, not due to higher DOC concentrations. Under naturally saturated conditions, as in Maludam, drainage would cause the water level to drop below the surface, so that increasing DOC concentrations would have to be expected upon disturbance. Increasing DOC concentrations, in turn, would lead to increasing CO_2 emissions, even if the short water residence time represents a limiting factor.

For future research, our study can serve as a reference, representing the conditions in an undisturbed tropical peat-draining river, and allowing for the quantification of anthropogenic effects on tropical peatland ecosystems in future research.

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Table 1. Median values ± one standard deviation for the main parameters measured in the Maludam river (NP stations only).

Parameter	2014	2015
pH	3.8 ± 0.2	3.7 ± 0.2
Dissolved oxygen (µmol L^{-1})	46 ± 11	31 ± 4
Water temperature (°C)	26.1 ± 0.4	25.4 ± 0.1
DOC (µmol L^{-1})	3768 ± 842	3612 ± 166
POC (µmol L^{-1})	21 ± 3	16 ± 10
% DOC in TOC	99.5 ± 0.1	99.6 ± 0.3
pCO_2 (µatm)	7795 ± 900	8400 ± 135
TDN (µmol L^{-1})	49 ± 6	57 ± 3

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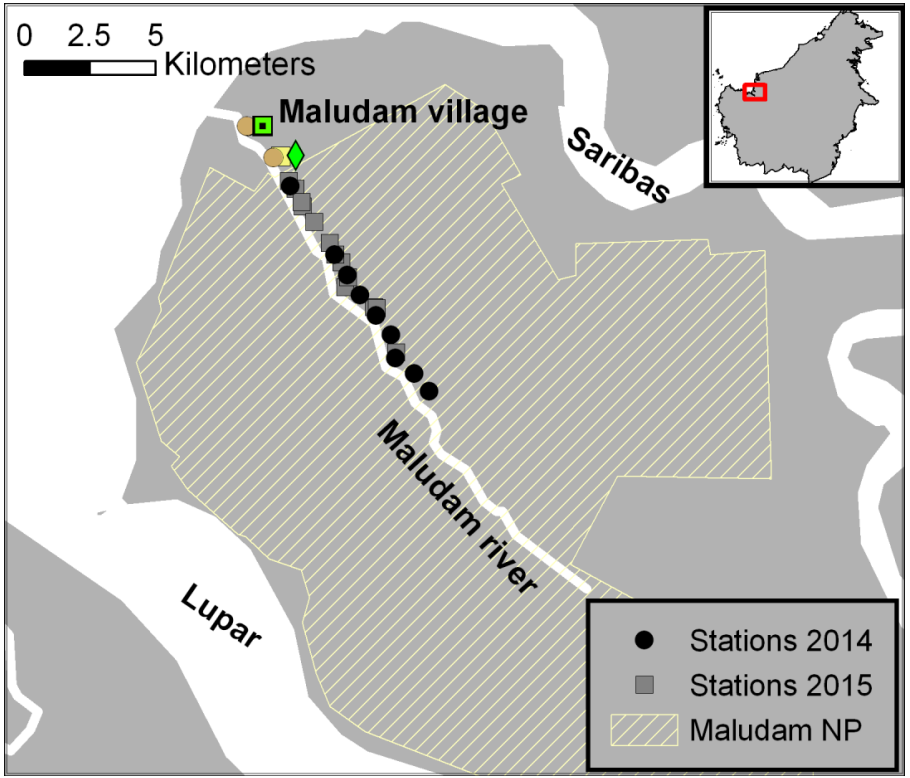

Figure 1. Map showing the location of the Maludam national park (NP) between the rivers Lupar and Saribas. The dots denote sampling locations, the diamond shows the location of a waste water treatment plant, and the green square indicates the location of Maludam village. The yellow markers refer to sampling stations outside the NP.

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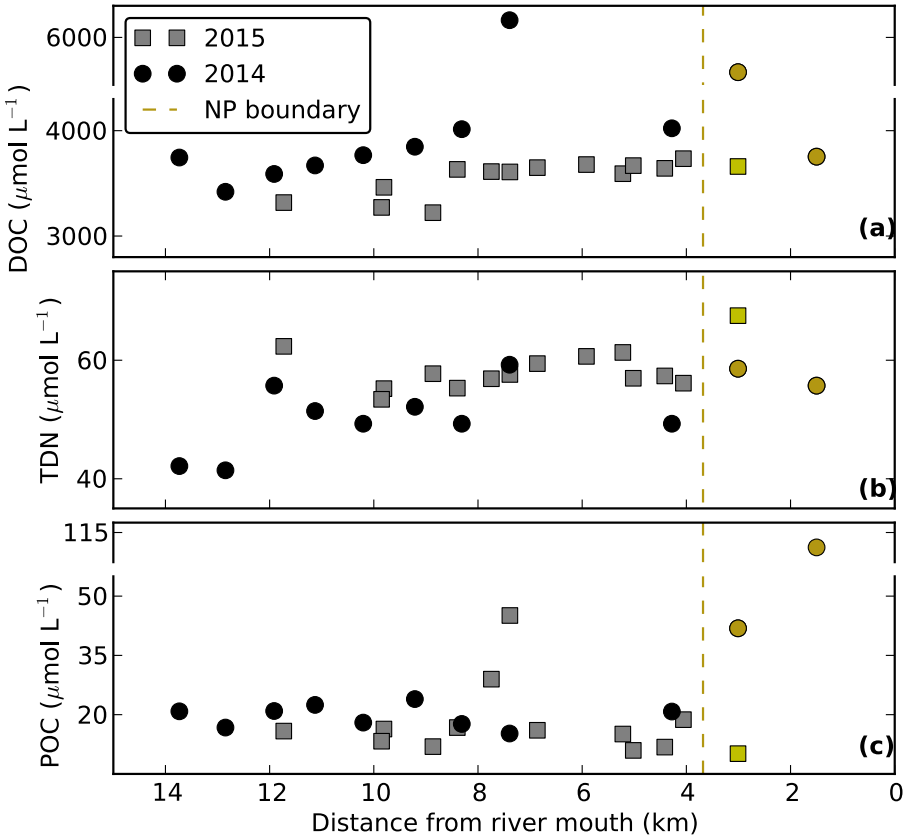

Figure 2. DOC, TDN and POC as measured along the river stretch. Flow direction is from left to right. Note the discontinuous vertical axis in **(a)** and **(c)**. The yellow markers to the right of the dashed line refer to sampling stations outside the NP.

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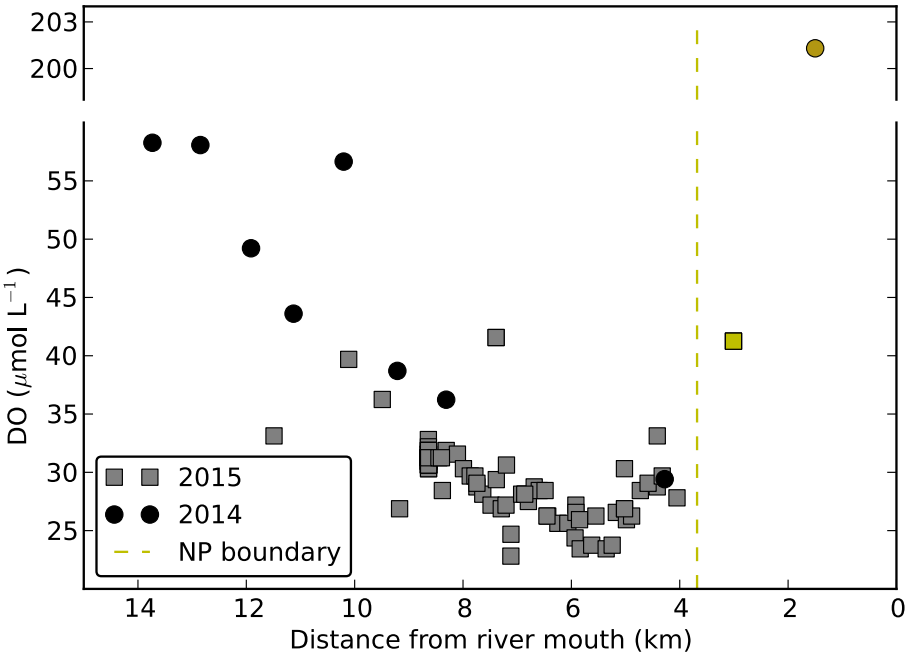

Figure 3. Dissolved oxygen concentrations in the Maludam river. Flow direction is from left to right. Note the discontinuous vertical axis. The yellow markers to the right of the dashed line refer to sampling stations outside the NP.

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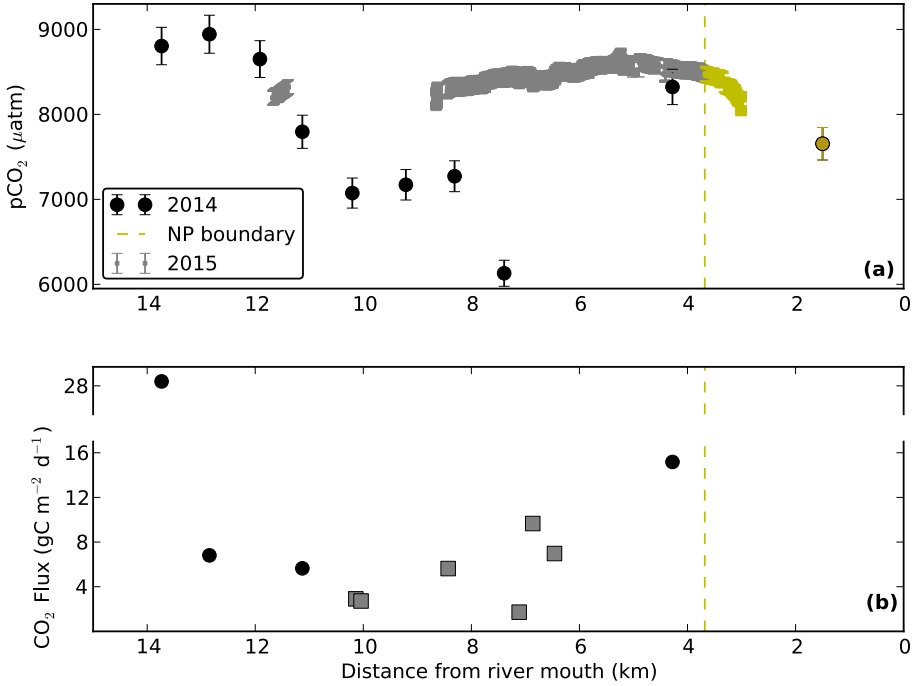

Figure 4. pCO_2 **(a)** and CO_2 fluxes **(b)** as measured along the spatial extent of the Maludam river. Flow direction is from left to right. The yellow markers on **(a)** to the right of the dashed line refer to sampling stations outside the NP. Note the discontinuous vertical axis in **(b)**.

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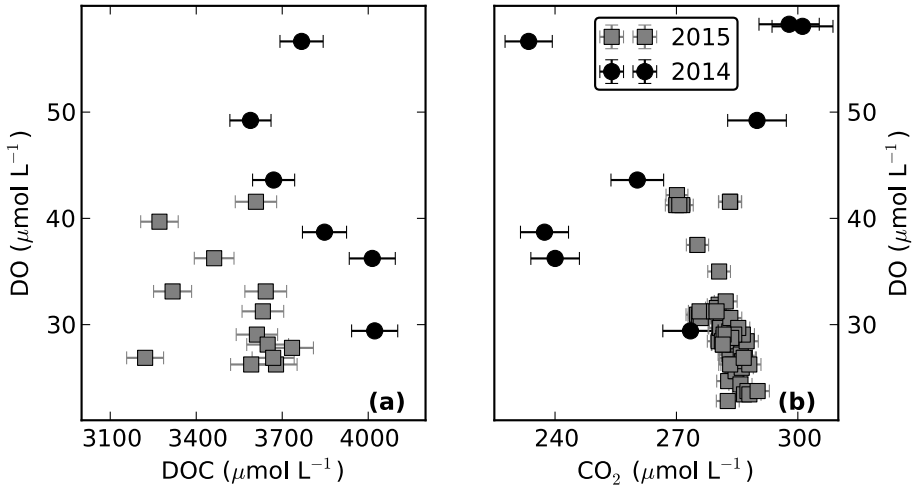

Figure 5. DO vs. DOC **(a)** and DO vs. CO_2 **(b)** reveal a weak linkage between these parameters in the river.

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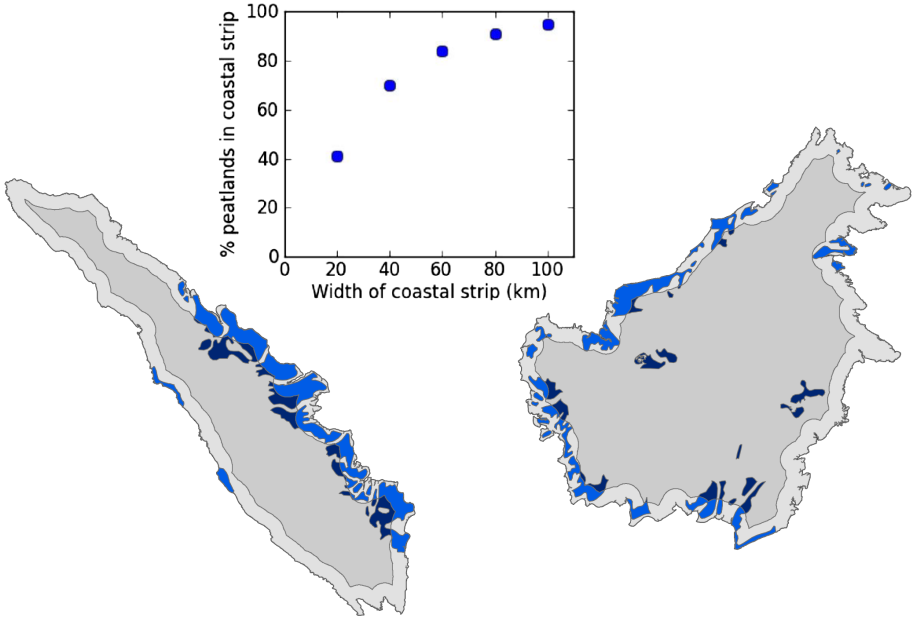

Figure 6. Distribution of peatlands along the coastlines of Sumatra and Borneo as of FAO (2009). The light grey area refers to a 40 km wide coastal strip.

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