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Fate of peat-derived carbon and associated CO$_2$ and CO emissions from two Southeast Asian estuaries

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CO₂ and CO emissions from Southeast Asian estuaries
D. Müller et al.
Abstract

Coastal peatlands in Southeast Asia release large amounts of organic carbon to rivers, which transport it further to the adjacent estuaries. However, little is known about the fate of this terrestrial material in the coastal ocean. Although Southeast Asia is, by area, considered a hotspot of estuarine CO$_2$ emissions, studies in this region are very scarce. We measured dissolved and particulate organic carbon, carbon dioxide (CO$_2$) partial pressure and carbon monoxide (CO) concentrations in two tropical estuaries in Sarawak, Malaysia, whose coastal area is covered by peatlands. We surveyed the estuaries of the rivers Lupar and Saribas during the wet and dry season, respectively. The spatial distribution and the carbon-to-nitrogen ratios of dissolved organic matter (DOM) suggest that peat-draining rivers convey terrestrial organic carbon to the estuaries. We found evidence that a large fraction of this carbon is respired. The median $p$CO$_2$ in the estuaries ranged between 618 and 5064 µatm with little seasonal variation. CO$_2$ fluxes were determined with a floating chamber and estimated to amount to 14–272 mol m$^{-2}$ yr$^{-1}$, which is high compared to other studies from tropical and subtropical sites. In contrast, CO concentrations and fluxes were relatively moderate (0.3–1.4 nmol L$^{-1}$ and 0.8–1.9 mmol m$^{-2}$ yr$^{-1}$) if compared to published data for oceanic or upwelling systems. We attributed this to the large amounts of suspended matter (4–5004 mg L$^{-1}$), limiting the light penetration depth. However, the diurnal variation of CO suggests that it is photochemically produced, implying that photodegradation might play a role for the removal of DOM from the estuary as well. We concluded that unlike smaller peat-draining tributaries, which tend to transport most carbon downstream, estuaries in this region function as an efficient filter for organic carbon and release large amounts of CO$_2$ to the atmosphere. The Lupar and Saribas mid-estuaries release 0.4 ± 0.2 Tg C yr$^{-1}$, which corresponds to approximately 80% of the emissions from the aquatic systems in these two catchments.
1 Introduction

Southeast Asian peatlands store 68.5 Gt carbon (Page et al., 2011) and represent a globally important carbon pool. Parts of this organic carbon are released to the aquatic system and exported to the coastal ocean. It has been estimated that due to the presence of peatlands, Indonesia alone accounts for 10 % of the dissolved organic carbon (DOC) exported to the ocean globally (Baum et al., 2007). Peat-draining rivers usually exhibit extraordinarily high DOC concentrations (Alkhatib et al., 2007; Moore et al., 2011, 2013; Müller et al., 2015). Although a small fraction of this DOC is respired in the river, the larger part is transported downstream (Müller et al., 2015), ultimately reaching the estuary and the coastal ocean. So far, the fate of this carbon fraction remains unclear, and data particularly in this region is scarce.

Globally, the view prevails that terrestrial organic carbon is respired in estuaries. Therefore, they are net heterotrophic (Duarte and Prairie, 2005) and act as a source of carbon dioxide (CO$_2$) to the atmosphere, releasing 150 Tg C annually (Laruelle et al., 2013). On the other hand, Cai (2011) suggested that terrestrial organic carbon might in fact bypass the estuarine zone, and that it is actually organic carbon from intertidal flats that sustains net heterotrophy in estuaries.

The question whether or not the terrestrial organic carbon is retained in estuaries is of particular interest in peat-dominated regions with high riverine carbon loads like Southeast Asia. On the one hand, peat-derived organic matter consists mainly of lignin and its derivates (Andriesse, 1988) and is thus relatively recalcitrant to degradation. In addition, short water residence times might constrain organic matter decomposition (Müller et al., 2015). On the other hand, high organic carbon loads together with high temperatures would suggest high microbial activity both in the water column and in the sediment, leading to high decomposition rates.

Additionally, photodegradation was proposed as an important removal mechanism for terrestrial organic matter in the ocean (Miller and Zepp, 1995). Chromophoric dissolved organic matter (CDOM) absorbs light, mainly in the UV region. The absorbed
photons initiate abiotic photochemical reactions, during which DOC is oxidized to carbon monoxide (CO) and CO₂ (Stubbins, 2001), with the CO₂ production being 14 to 20 times larger than CO production (Vähätalo, 2010). Photochemistry might be of particular importance in estuaries (Ohta et al., 2000), where CDOM concentrations and CO production rates are high, making estuaries a significant source of CO to the atmosphere (Valentine and Zepp, 1993). What adds to it, is that dissolved organic matter (DOM) in estuaries is largely of terrestrial origin, and terrestrial CDOM was found to be more efficient in producing CO than marine CDOM (Zhang et al., 2006). Ultimately, recalcitrant peat-derived organic matter might be subject to photobleaching (Vähätalo, 2010) and would then be more readily available for bacterial respiration, supporting net heterotrophy.

In order to investigate if and how peat-derived organic carbon is processed in tropical estuaries, we studied organic carbon, dissolved CO₂ and CO in two Malaysian estuaries, both of which receive terrestrial carbon from rivers draining a peat-dominated catchment.

2 Materials and methods

2.1 Study area

Sarawak is Malaysia’s largest state and located in the northwest of the island of Borneo, which is divided between Indonesia, Brunei and Malaysia. It is separated from Peninsular Malaysia by the South China Sea. Sarawak has a tropical climate. The mean annual air temperature in Sarawak’s capital Kuching (1.56° N, 110.35° E) is 26.1 °C (average 1961–1990, DWD, 2007). Rainfall is high throughout the year, but pronounced during the northeast monsoon, which occurs between November and February.

Our study focused on two macrotidal estuaries in western Sarawak. The coastal area of western Sarawak is covered by peatlands. The largest peat dome is found on the Maludam peninsula. It is rainwater-fed and covered by dense peat swamp forest,
which has been protected ever since Maludam was gazetted as national park in 2000. The peninsula is enclosed by the rivers Lupar and Saribas (Fig. 1). Six channels from the Maludam peat swamp forest drain into the Lupar river and six into the Saribas, respectively (Kselik and Liong, 2004). With reference to their catchment areas, the peat coverage in the Lupar and Saribas basins is 30.5 and 35.5%, respectively (FAO, 2009). The catchment sizes are 6558 km² (Lupar) and 1943 km² (Saribas) (Lehner et al., 2006).

Sampling was performed during two ship cruises in 2013 and 2014. The 2013 cruise took place in June (18–23 June) during the dry season. The 2014 cruise was performed in March (10–19 March), right after the end of the monsoon season. We sampled 20 stations in 2013 and 26 stations in 2014 (Fig. 1). Here, we report the data separately for the outer (salinity > 25), mid-(salinities 2–25) and upper estuaries (salinity < 2). In 2014, we went further upstream than in 2013. Therefore, when it comes to the mid-estuaries, we report medians for the “2013 spatial extent”, i.e. refer to the spatial coverage of 2013.

2.2 Discharge and flow velocity

We estimated river discharge \((Q)\) from the difference between precipitation \((P)\) and evapotranspiration \((ET)\). Precipitation was taken from NOAA NCEP Reanalysis data set for the nearest upstream grid \((0.95°\ N, \ 110.625°\ E, \ www.esrl.noaa.gov/psd/data/reanalysis/reanalysis.shtml)\). Evapotranspiration was taken from the literature (Kumagai et al., 2005). Ultimately, we derived \(Q = (P - ET) \cdot A\), where \(A\) is the catchment area \((m^2)\). The rivers’ flow velocity was estimated from the drift during the stations, when the boat drifted freely. To this end, we used the GPS information of a CTD at the beginning and the end of the cast, and the duration of the cast to calculate the flow velocity (2014 data only).
2.3 Water chemistry

Salinity and temperature profiles were measured at each station with a CastAway CTD. Additionally, water pH, dissolved oxygen (DO) and conductivity were measured in the surface water with a WTW Multi3420, using an FDO 925 oxygen sensor, a SenTix 940 pH sensor and a TetraCon 925 conductivity sensor. Apparent oxygen utilization (AOU) was calculated as the difference between the saturation oxygen concentration and the measured oxygen concentration.

\[ \text{AOU} = \text{O}_{2}^{\text{sat}} - \text{O}_{2}^{\text{meas}} \]  

(1)

Oxygen solubility for a given temperature and salinity was calculated with constants from Weiss (1970).

Samples for determination of dissolved inorganic nitrogen (DIN) concentrations were taken at every station from approximately 1 m below the water surface. The water was filtered through a Whatman glass microfibre filter (pore size 0.7 µm), preserved with a mercuric chloride (HgCl₂) solution and stored cooled and upright until analysis. Concentrations of nitrate (NO₃⁻), nitrite (NO₂⁻) and ammonia (NH₄⁺) were determined spectrophotometrically (Grasshoff et al., 1999) with an Alliance Continuous Flow Analyzer.

2.4 Organic carbon and carbon isotope analysis

Dissolved organic carbon (DOC) samples were filtered (pore size 0.45 µm) and acidified with 21 % phosphoric acid until the pH had dropped below 2. DOC concentrations were determined through high temperature combustion and subsequent measurement of the evolving CO₂ with a non-dispersive infrared detector. In 2014, those samples were also analyzed for total dissolved nitrogen (TDN) using a Shimadzu TOC-VCSH with TNM-1 analyzer. Dissolved organic nitrogen (DON) was then calculated by subtracting DIN from TDN.

Particulate material was sampled by filtering water through pre-weighed and pre-combusted Whatman glass fiber filters. The net sample weight was determined. 1 N 8305
hydrochloric acid was added in order to remove inorganic carbon and samples were
dried at 40 °C. Organic carbon and nitrogen contents were determined by flash com-
bustion with a Euro EA3000 Elemental Analyzer. The abundance of the stable isotope
$^{13}$C was determined with a Finnigan Delta plus mass spectrometer.

Samples for determination of $\delta^{13}$C in dissolved inorganic carbon (DIC) were pre-
served with HgCl$_2$, sealed against ambient air and stored cool, upright and in the dark
until analysis. Vials were prepared with 50 µL of 98 % H$_3$PO$_4$ and a He headspace.
Depending on the salinity, 1–4 mL sample volume was injected through the septum using
a syringe. The prepared sample was allowed to equilibrate for 18 h and $\delta^{13}$C was
determined with a Thermo Scientific mass spectrometer (MAT 253).

2.5 CO$_2$ and CO measurements

In order to determine partial pressures of dissolved CO$_2$ and CO in the water, we used
a Weiss equilibrator (Johnson, 1999). Water from approximately 1 m below the surface
was pumped through the equilibrator at a rate of approximately 20 L min$^{-1}$. Dry air
mole fractions of CO$_2$ and CO in the equilibrator’s headspace were determined with
an in-situ Fourier Transform InfraRed (FTIR) trace gas analyzer. The instrument was
manufactured at the University of Wollongong, Australia, and is described in detail by
Griffith et al. (2012). FTIR spectra were averaged over five minutes, and dry air mole
fractions were retrieved using the software MALT5 (Griffith, 1996). The gas dry air
mole fractions were corrected for pressure, water and temperature cross-sensitivities
with empirically determined factors (Hammer et al., 2013). Calibration was performed
twice during each ship cruise with a suite of secondary standards ranging from 380
to 10 000 ppm CO$_2$ and 51 to 6948 ppb CO. The relevant concentration range was
re-evaluated after the cruises.

The equilibrator headspace air circulated between the FTIR and the equilibrator at
a rate of 1 L min$^{-1}$ in a closed loop, allowing for continuous monitoring of the CO$_2$
and CO mixing ratios in the headspace. The equilibrator and the sampling lines were
covered with aluminum foil to avoid CO photoproduction in the sampled air. Water
temperature was measured both in the equilibrator and in the water using a Pico PT-104 temperature data recorder. Ambient air temperature and pressure were recorded over the entire cruise with a Vaisala SP-1016 temperature data recorder and a PTB110 barometer, respectively. Gas partial pressures for dry air \( p_{\text{Gas}_{\text{dryair}}} \) were calculated from the FTIR measurements and our records of ambient pressure. We corrected for the removal of water (Dickson et al., 2007) using

\[
p_{\text{Gas}} = p_{\text{Gas}_{\text{dryair}}}(1 - VP(H_2O)),
\]

where \( p_{\text{Gas}} \) is the corrected gas partial pressure and \( VP(H_2O) \) is the water vapor pressure, which was calculated with the equation given in Weiss and Price (1980).

Equilibrator measurements have been widely used for trace gas measurements in estuarine surface water (Chen et al. (2013) and references therein). For \( \text{CO}_2 \), the response time is usually short (< 10 min) and the error associated with a remaining disequilibrium between water and headspace air is 0.2 % for a Weiss equilibrator (Johnson, 1999). \( \text{CO}_2 \), in contrast, takes much longer to reach full equilibrium, and an error of up to 25 % must be taken into account for measurements with a Weiss equilibrator (Johnson, 1999).

In the freshwater region, we were unable to carry out FTIR measurements, because the sampling spots could not be reached by ship. Instead, we performed headspace equilibration measurements of discrete samples with an Li-820 \( \text{CO}_2 \) analyzer, which was calibrated with the same secondary standards as the FTIR. We filled a 10 L canister with 9.5 L of sample water (2014: 0.6 L flask filled with 0.35 L of sample water) and left ambient air in the headspace. We connected the Li-820 analyzer inlet to the headspace and the outlet to the bottom of the canister, so that air could bubble through the sample water, accelerating the equilibration process. The \( p_{\text{CO}_2} \) obtained from headspace equilibration measurements was corrected for water vapor pressure as well.
Following common practice, we will report CO$_2$ levels in terms of CO$_2$ partial pressure ($p$CO$_2$), but convert CO partial pressure to molar concentrations using solubilities according to Wiesenburg and Guinasso (1979).

2.6 Flux estimation

In 2014, we performed direct flux measurements with a floating chamber (FC). The FC was an upside-down flower pot with a volume of 8.7 L and a surface area of 0.05 m$^2$ which it enclosed with the water. Its walls extended 1 cm into the water. The chamber headspace was connected to the Li-820 CO$_2$ analyzer, and CO$_2$ concentrations in the chamber were recorded over time. The concentration change was fitted linearly and the water-to-air CO$_2$ flux $F$ (in µmol m$^{-2}$ s$^{-1}$) was calculated according to

$$F = \frac{dc}{dt} \frac{pV}{RTA},$$

where $\frac{dc}{dt}$ is the slope of the fitted curve (µmol mol$^{-1}$ s$^{-1}$), $p$ is the pressure (Pa), $V$ is the chamber volume (m$^3$), $R$ is the universal gas constant, $T$ the temperature (K) and $A$ the surface area (m$^2$). The gas exchange velocity was calculated with

$$k_{CO_2} = \frac{F}{K_0 \left( pCO_2^\text{water} - pCO_2^\text{air} \right)},$$

where $k_{CO_2}$ is the gas exchange velocity (m s$^{-1}$) of CO$_2$ and $pCO_2^\text{air}$ is the atmospheric CO$_2$ partial pressure, which was measured with the Li-820 CO$_2$ analyzer during the cruises. For comparisons, $k_{CO_2}$ was normalized to a Schmidt number of 600 (Schmidt number Sc relates the diffusivity of the gas to the viscosity of the water):

$$\frac{k_{600}}{k_{CO_2}} = \left( \frac{600}{Sc_{CO_2}} \right)^{-n}$$
with \( n = 0.5 \) for rough surfaces (Jähne et al., 1987). The relationship with the Schmidt number was also exploited for calculating CO fluxes. Schmidt numbers were calculated from water temperature for both saline and freshwater (\( \text{CO}_2 \): Wanninkhof (1992), CO: Raymond et al. (2012) for freshwater, Zafiriou et al. (2008) for saltwater), and evaluated for the in-situ salinity assuming a linear dependency (Borges et al., 2004). Atmospheric CO mole fractions were obtained from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling for the nearest station (Novelli and Masarie, 2014), which was Bukit Kotobatang, Indonesia (0.202° S, 100.3° E).

Since many flux estimates in the literature were obtained using exchange velocities derived from empirical equations, we calculated \( k \) also using the wind speed parameterization from Wanninkhof (1992) for comparison. Wind speed data were taken from the NOAA NCEP Reanalysis data set for the closest coastal grid (2.85° N, 110.625° W). Here, we chose the most downstream grid because the upstream grid, which we picked for precipitation, is over land, where wind speeds might be much lower than in the estuary. We considered daily wind speeds for the time period of both our 2013 and 2014 cruise.

3 Results

3.1 Discharge

Annual average precipitation from 1980–2014 amounted to 3903 mm yr\(^{-1}\) in the chosen grid, corresponding to an average precipitation of 325 mm month\(^{-1}\). The precipitation during June 2013 was below average (246 mm) and above average (364 mm) in March 2014. Both values do not deviate much from the historical averages during 1980–2014 (March: 367 mm, June: 234 mm, see Fig. 2). In the following, we will refer to our measurements in June 2013 as representative of the dry season, and those in March 2014 as representative of the wet season.
With an average evapotranspiration of 4.2 mm d\(^{-1}\) (Kumagai et al., 2005), we estimated the average annual discharge for the Lupar river to be 490 and 160 m\(^{3}\) s\(^{-1}\) for the Saribas river. The flow velocities were estimated to be 2.5 ± 1.4 m s\(^{-1}\) (average ± largest deviation from average) for the Lupar river, 0.7 ± 0.7 m s\(^{-1}\) for the Saribas and 0.8 ± 1.0 m s\(^{-1}\) for the Saribas tributary. Note that the measurements were taken during different stages of the tidal cycle, which explains the large variability.

### 3.2 Water chemistry

Our data covered a salinity range of 0–30.6 in 2013 and 0–31.0 in 2014. pH ranged between 6.7 and 8.0 in the dry season (2013) and between 6.8 and 7.6 in the wet season (2014) and was positively correlated with salinity (\(r = 0.8\), data from both years). Notably, at salinity zero, pH was higher than suggested by this correlation, and ranged between 6.7 to 7.3 (both seasons).

DIN concentrations were generally rather low. During the dry season, DIN ranged between 1.7 and 87.1 µmol L\(^{-1}\), whereas most concentrations were between 15 and 30 µmol L\(^{-1}\). In the wet season, DIN concentrations ranged between 3.4 and 21.7 µmol L\(^{-1}\). The medians for the individual estuaries show that overall, DIN concentrations were slightly higher in the dry season (Table 1).

Dissolved oxygen was mostly slightly undersaturated. Oxygen saturation was lower in the dry season than in the wet season (Table 1), with oxygen saturation ranging between 63.6 to 94.6 % (2013) and 79.0–100.4 % (2014). These values correspond to an AOU between 14 and 93 µmol L\(^{-1}\) (2013) and −1 and 52 µmol L\(^{-1}\) (2014), respectively. Negative AOU suggests net oxygen production and was only observed once in the outer estuary.

### 3.3 Organic carbon

DOC ranged from 80 to 784 µmol L\(^{-1}\) in the dry season and from 172 to 1180 µmol L\(^{-1}\) in the wet season and was negatively correlated with salinity (Fig. 3), indicating that
freshwater supplies DOC to the estuary, while seawater has a dilution effect. However, the end-member determined from the salinity-DOC correlation was not confirmed by the samples taken in the upper estuaries: the calculated end-member for Lupar was \(673 \pm 274 \mu mol L^{-1}\) (intercept of the regression curve ± standard error of the estimate), the measured freshwater DOC median was \(89 \mu mol L^{-1}\) (2013) and \(208 \mu mol L^{-1}\) (2014). For Saribas, the calculated end-member was \(425 \pm 54 \mu mol L^{-1}\), and the measured value was \(312 \mu mol L^{-1}\) (2013, Table 1). This discrepancy is owed to the fact that the peatlands, which are likely the main source of allochthonous organic carbon, are located in the coastal area, downstream of our freshwater stations (Fig. 1).

In a different study, we found DOC concentrations in a peat-draining river on the Maludam peninsula between \(3612\) and \(3768 \mu mol L^{-1}\) (Müller et al., 2015). With the average \(3690 \mu mol L^{-1}\) as a second zero-salinity end-member, we estimated how much carbon derives from peat-draining tributaries from the Maludam peninsula using a simple three-point mixing model (Fig. 3). The Maludam contribution \(f\) (in %) was calculated as

\[
f = \frac{EM_{\text{calc}} - EM_{\text{meas}}}{EM_{\text{Maludam}} - EM_{\text{meas}}} \cdot 100,\]

with \(EM_{\text{calc}}\) the calculated end-member, \(EM_{\text{meas}}\) the measured end-member and \(EM_{\text{Maludam}}\) the peat-draining rivers’ end-member. Accordingly, 15% of the DOC in the Lupar river is derived from peat-draining tributaries, and 3% of DOC in the Saribas river. The total DOC export to the ocean from Lupar and Saribas was estimated from the calculated zero-salinity end-members (673 and 425 \(\mu mol L^{-1}\), respectively), assuming that they provide an average of non-peat and peat freshwater inputs, and annual average discharge. Accordingly, Lupar and Saribas together convey \(0.15 \pm 0.05\) Tgyr\(^{-1}\) DOC to the South China Sea (Table 4).

Both the Lupar and the Saribas estuary were very turbid. Suspended particulate matter (SPM) ranged from 3.7 to 5003.6 mgL\(^{-1}\) in 2013 and from 13.8 to 3566.7 mgL\(^{-1}\) in 2014. SPM was highest at intermediate salinities in the Lupar river, suggesting the existence of an estuarine turbidity maximum (ETM). Particulate organic carbon (POC)
was higher during the dry season (Table 1), ranging from 51 to 4114 µmol L\(^{-1}\) in 2013 and from 17 to 2907 µmol L\(^{-1}\) in 2014. The atomic carbon-to-nitrogen (C/N) ratio of particulate organic matter (POM) ranged between 8.5–14.1 in 2013 and 8.1–13.8 in 2014. \(\delta^{13}C\) values ranged between –28.5 and –25.5 ‰ in 2013 and –27.6 to –24.4 ‰ in 2014. In contrast, the C/N ratio in the dissolved organic matter (DOM) was much higher: it ranged between 10.9 and 81.8 (2014 data), whereas the lowest value was measured on the Lupar river, upstream of the Maludam peninsula, and the highest value was measured on the Lupar river at the mouth of a peat-draining left-bank tributary (see Fig. 1). The average for all samples was 40.6.

Since POC was not conservatively transported through the estuary, the export of POC to the South China Sea was estimated from the median POC concentration and discharge (see Supplement). 0.15 Tg C yr\(^{-1}\) are estimated to be delivered from the Lupar, and another 0.06 Tg C yr\(^{-1}\) from the Saribas (Table 4). Taken together with the DOC export, this implies that Lupar and Saribas deliver approximately 0.36 ± 0.30 Tg organic carbon to the South China Sea every year, more than half of which is bound to particles.

### 3.4 CO\(_2\) and CO

In both years, both CO\(_2\) and CO were found to be above atmospheric equilibrium, indicating that the Lupar and Saribas estuaries were net sources of these gases to the atmosphere.

CO\(_2\) ranged from 297.3 to 5504.0 µatm in 2013 and from 326.5 to 5014.1 µatm in 2014. CO\(_2\) increased with decreasing salinity, indicating that high CO\(_2\) can be attributed to freshwater input (Fig. 5). However, matters were different for the freshwater samples. The measured freshwater end-member CO\(_2\) was relatively moderate (1021–1527 µatm). Table 2 summarizes the median \(p\)CO\(_2\) values in the outer, mid- and upper estuaries. It can be seen that like DOC, CO\(_2\) was highest in the mid-estuaries. The difference between dry and wet season \(p\)CO\(_2\) was marginal (see Fig. 5). Although ex-
cess CO$_2$ (in µmolL$^{-1}$) was weakly correlated with AOU for the individual datasets, higher AOU in the dry season did not concur with higher excess CO$_2$ (Fig. 6) with the exception of the Saribas tributary (see discussion below).

Interestingly, Saribas and its tributary had a higher CO$_2$ level (i.e., higher CO$_2$ at the same salinity) than Lupar, but not higher DOC. $\delta^{13}$C-DIC ranged from $-0.85$‰ in the lower estuary to $-15.70$‰ in the freshwater region and varied approximately linearly with salinity (not shown).

CO ranged from < 0.1 to 6.6 nmolL$^{-1}$ in the dry season (2013) and from 0.2 to 12.4 nmolL$^{-1}$ in the wet season (2014) and was spatially variable (Fig. 5). Median values are summarized in Table 2. CO concentrations were higher during daytime than during the night, independent of the boat’s location (Fig. 7). In both years, maximum CO concentrations were observed around noon and in the early afternoon. CO concentrations were not correlated with salinity, DOC, POC or SPM (not shown).

### 3.5 CO$_2$ and CO fluxes

The CO$_2$ fluxes measured with the floating chamber showed large spatial variations and ranged from 63 to 935 mmol m$^{-2}$ d$^{-1}$. The lowest flux was measured in the Saribas mid-estuary, and the highest flux was measured on the Saribas tributary. $k_{600}$ values were averaged for the individual rivers and are reported with the largest deviation of a single measurement from the mean. The Saribas tributary, which was the smallest of the studied rivers, had the highest $k_{600}$ of $23.9 \pm 14.8$ cm h$^{-1}$. The largest river, Lupar, had a high $k_{600}$ of $20.5 \pm 4.9$ cm h$^{-1}$ as well, which is probably owed to the high flow velocity (2.5 m s$^{-1}$). The Saribas main river had a $k_{600}$ of $13.2 \pm 11.0$ cm h$^{-1}$, with large spatial variability. The wind speed averaged 3.0 m s$^{-1}$ during our 2013 sampling period and 2.3 m s$^{-1}$ during the 2014 sampling period. The average $k_{600}$ calculated with W92 were one order of magnitude lower than the experimentally determined ones, with 3.1 cm h$^{-1}$ during the dry season and 1.9 cm h$^{-1}$ during the wet season.
Atmospheric $pCO_2$ averaged 403.6 µatm in the dry season (2013) and 414.4 µatm in the wet season (2014). CO$_2$ fluxes were calculated for every datapoint using updated solubilities, $pCO_2$ values and exchange velocities and the average atmospheric partial pressure. The two estimates that were obtained for the two different seasons (2013 spatial extent) were averaged and the uncertainty was estimated from the uncertainty associated with the gas exchange velocity, which proved to cause the largest error. CO fluxes were derived in the same way. Atmospheric CO monthly averages from the NOAA ESRL data set were available from 2004 to 2013. For our dry season data, we used the monthly average for June 2013 (77.91 ppb, corresponding to 77.49 natm), and for our wet season data, we calculated the average CO mixing ratio in March for the years that were available (145.93 ppb, corresponding to 145.58 natm).

The calculated CO$_2$ and CO fluxes in the outer, mid- and upper estuaries are summarized in Table 3. CO$_2$ fluxes ranged between 14 and 272 mol m$^{-2}$ yr$^{-1}$ and CO fluxes between 0.8 and 1.9 mmol m$^{-2}$ yr$^{-1}$. Fluxes for the outer estuary were derived for the Lupar river (Fig. 5). Estimates for the upper estuaries were based on our $pCO_2$ measurements in the freshwater region and the average $k_{600}$ of Lupar and Saribas, respectively (Table 3).

Like $pCO_2$, the CO$_2$ fluxes were highest in the mid-estuaries, ranging between 76 and 272 mol m$^{-2}$ yr$^{-1}$. The CO flux from Lupar was twice as high in the mid-estuary than in the outer estuary.

In order to calculate the total flux from these estuaries, we estimated the estuarine surface area of both systems in ArcGIS (for details see Supplement). The Lupar estuary has a surface area of 220 km$^2$, which corresponds to 3% of the catchment area, and the Saribas (excluding the tributary) estuary has a surface area of 102 km$^2$ (5% of the catchment). The total flux for the Lupar is $0.31 \pm 0.09$ and $0.09 \pm 0.08$ Tg C yr$^{-1}$ for the Saribas (see Table 4). The contribution of CO to these terms is negligible. The contribution of the upper estuaries and rivers was calculated by assuming that they cover 0.89% of the catchment area (Raymond et al., 2013). For the percentage of the catchment that is covered by peat, we used a previously published estimate for the areal flux.
from a peat-draining river in this region \( F_{\text{peat, areal}} = 167-386 \text{ mol m}^{-2} \text{yr}^{-1} \), Müller et al. (2015), we used the average of \( 277 \pm 110 \text{ mol m}^{-2} \text{yr}^{-1} \). For the rest, we used the flux that we determined for the upper estuary \( F_{\text{UE, areal}} = 60 \pm 14 \) and \( 33 \pm 28 \text{ mol m}^{-2} \text{d}^{-1} \) for Lupar and Saribas, respectively). The calculations and the error budget are detailed in the Supplement.

Accordingly, the Lupar upper estuary and river network add \( 0.09 \pm 0.03 \text{ Tg C yr}^{-1} \) and the Saribas \( 0.02 \pm 0.01 \text{ Tg C yr}^{-1} \) (Table 4). Taken together, the Lupar and Saribas estuaries and rivers release approximately \( 0.5 \pm 0.2 \text{ Tg CO}_2 \text{ C yr}^{-1} \) to the atmosphere, approximately 80 % of which comes from the mid-estuaries.

4 Discussion

4.1 Sources of carbon in the estuaries

It is striking that both DOC and CO\(_2\) exhibit their maximum concentrations at intermediate salinities, and that the concentration that would be expected for the zero-salinity endmember is overestimated if based on the correlation with salinity. As indicated above, we attribute this to the location of the peatlands. On the northwestern coast of Borneo, tidal intrusion can reach up to 200 km inland (Kselik and Liong, 2004). In the Lupar and Saribas river, saltwater intrusion reaches beyond the extent of the peatlands. Since they likely provide major organic carbon inputs, maximum DOC and CO\(_2\) concentrations are observed at intermediate salinities.

The C/N ratios observed in particulate organic matter (POM) were compared to those reported for peat, leaves (Baum, 2008) and phytoplankton (Fig. 4). Accordingly, the C/N in POM (8.1–14.1) is likely a mixed signal from marine and terrestrial sources (Fig. 4), which is in agreement with the relatively low \( \delta^{13} \text{C} \) values. The C/N ratios in the dissolved organic matter (DOM) clearly suggest a terrestrial origin (average: 40.6) and are consistent with both plant and peat derived organic matter (Fig. 4). Based on the calculated zero-salinity end-members, we estimated that 15 % of the DOC in the Lupar
and 3\% of the DOC in the Saribas estuary were derived from peat-draining tributaries. This is not as much as expected, given that peatlands cover 30.5 and 35.5\% of the catchments. Therefore, there must be retention of DOC in the estuary.

### 4.2 Fate of carbon in the estuaries

Likely, a part of the DOC that reaches the Lupar and Saribas estuaries is retained through adsorption and flocculation, which are promoted by mixing of saltwater and freshwater masses. Ertel et al. (1991) found that 1 to 12\% of DOC was converted to POC during laboratory experiments due to changes in salinity. The transformation of DOC to POC in the presence of saltwater was attributed both to particle precipitation and to adsorption of DOM onto riverine particles. Due to the high SPM concentrations in the Lupar and Saribas estuaries, we think that adsorption could be an important process there as well. A partial conversion of DOC to POC is consistent with the high POC concentrations and with the C/N ratios in POM.

Additionally, we found evidence that DOC is respired in the estuary. To begin with, like DOC, CO$_2$ is highest in the mid-estuary. The correlation of AOU and CO$_2$ and the depletion in $\delta^{13}$C-DIC suggest that this CO$_2$ derives mainly from aerobic respiration of organic matter. This respiration might be promoted by two processes. Firstly, the addition of DOC by peat-draining tributaries contributes substrate for in-situ CO$_2$ production. Secondly, estuarine CO$_2$ levels are usually highest in the ETM (Abril and Borges, 2004), where high turbidity limits the light penetration depth and thereby also photosynthetic CO$_2$ uptake. At the same time, the residence time of organic matter is prolonged (Abril et al., 1999), and particle-attached bacteria get the chance to decompose organic matter (Crump et al., 1998), resulting in pronounced net heterotrophy.

Although $p$CO$_2$ is relatively high, oxygen depletion is quite moderate in comparison. For example, Chen et al. (2008) measured CO$_2$ partial pressures between 690 to 2680 µatm in the eutrophicated Pearl river estuary (see Table 5) along with AOU up to 239 µmolkg$^{-1}$, resulting in hypoxia at the river mouth. Although we found similarly high and even higher $p$CO$_2$, oxygen depletion was much less pronounced. This suggests
that more oxygen is available in the Lupar and Saribas estuaries. Reaeration might be more efficient, i.e. oxygen fluxes across the air–water interface are higher, which could be explained by a high gas exchange velocity, consistent with our measurements, and a shallower water column.

In addition to estuarine respiration, the diurnal CO cycle observed in the Lupar and Saribas estuaries (Fig. 7) suggests that photodegradation is another pathway for DOC removal. This diurnal pattern is well known for ocean surface water and explained by a balance of light-dependent production of CO and microbial consumption (Conrad and Seiler, 1980; Conrad et al., 1982; Ohta, 1997). Average CO concentrations in the Lupar and Saribas estuaries were lower than in the East China Sea and Yellow Sea (average 2.25 nmol L\(^{-1}\), Yang et al. (2011), see Table 5), which can be attributed to the high turbidity. A high concentration of suspended particulates limits the light penetration depth and increases microbial CO consumption (Law et al., 2002). On the other hand, CO can also be produced by particles (Xie and Zafiriou, 2009), which would have the opposite effect. Since we did not observe a correlation of CO and SPM, this relationship seems to be rather complex. Ultimately, another reason for the low CO concentrations could be that the terrestrial DOM in the Lupar and Saribas estuaries is not so susceptible to photodegradation, which would be in contrast to other studies (Valentine and Zepp, 1993; Zhang et al., 2006).

However, it would be too fast to conclude that photochemistry is only of little relevance for the DOM removal in our study area. First of all, most CO is probably produced directly at the water surface and might quickly escape to the atmosphere. We might not have captured this volatile CO fraction with our measurements, since we sampled water from 1 m below the surface. CO concentrations usually decline rapidly with water depth (Ohta et al., 2000), so the numbers presented here can be considered conservative. Secondly, the relevance of photochemistry amounts to more than CO production. Amon and Benner (1996) suggested that photochemical processes play a key role in the breakdown of DOM into compounds that are more readily available for bacterial respiration, such as formaldehyde, acetaldehyde, glyoxylate and pyruvate. However, the
overall relevance of photochemistry for the removal of DOM in our study area remains a bit uncertain and would merit further investigation.

4.3 Comparison dry season vs. wet season

Expectedly, the differences between dry season and wet season DOC were marginal, which is in agreement with other studies in this region. Moore et al. (2011) argued that DOC concentrations vary only little, because DOC is released to rivers throughout the year due to the high precipitation. They found that merely POC concentrations exhibited a clear seasonality, with higher concentrations during the dry season. Consistently, this was also observed in our study. The higher AOU and DIN values in the dry season indicate that respiration was higher then, possibly due to enhanced respiration of POC. The higher availability of POC in the dry season was most obvious in the Saribas and its tributary, whereas in the latter, the hypothesis of POC-enhanced respiration is confirmed by slightly higher $p$CO$_2$. For Lupar and the Saribas main river, though, we did not observe any major differences between wet and dry season $p$CO$_2$ and CO concentrations. The weak seasonal variability has some general implications for the research in our study area, which is mostly based on single campaigns and not on continuous measurements due to poor infrastructure. The little variation that we observe between our wet and dry season measurements could imply that single measurement campaigns in this region provide better insights than previously assumed. However, measurements at the peak of the monsoon season would be desirable to confirm this hypothesis.

4.4 CO$_2$ and CO fluxes

It has been previously suggested that Southeast Asian estuaries are rather moderate sources of CO$_2$ to the atmosphere, because of low wind speeds and consequently low transfer velocities (Chen et al., 2013). We cannot confirm this notion with our measurements. CO$_2$ emissions from both the Lupar mid-estuary ($119 \pm 28 \text{ mol m}^{-2} \text{ yr}^{-1}$)
CO\textsubscript{2} and CO emissions from Southeast Asian estuaries

D. Müller et al.

and the Saribas tributary (272 ± 167 mol m\textsuperscript{-2} yr\textsuperscript{-1}) are higher than the global average of 37.4 mol m\textsuperscript{-2} yr\textsuperscript{-1} for mid-estuaries (Chen et al., 2012). Similarly, the value reported for small deltas in this region is 41.8 mol m\textsuperscript{-2} yr\textsuperscript{-1} (Laruelle et al., 2013), which is also lower than the fluxes from Luper and the Saribas tributary. The fluxes from the Saribas mid-estuary appear to be higher than those values, too (76 ± 64 mol m\textsuperscript{-2} yr\textsuperscript{-1}), but we cannot ascertain this because of the large uncertainty range. Interestingly, the fluxes that we found are also more than one order of magnitude higher than areal fluxes reported for Indian monsoonal estuaries (Sarma et al., 2012) and for other Malaysian rivers (Chen et al., 2013), see Table 5. However, flux estimates depend critically on the gas exchange velocity: both Sarma et al. (2012) and Chen et al. (2013) used the W92 parameterization for calculating the gas exchange velocity. In order to see whether the discrepancy between our results and theirs is a consequence of the different gas exchange velocities used, we recalculated fluxes for our study area using W92 (see Table 5). This way, we obtained fluxes between 2 and 31 mol m\textsuperscript{-2} yr\textsuperscript{-1}. The values for the mid-estuaries (12–31 mol m\textsuperscript{-2} yr\textsuperscript{-1}) are still higher than the values of Chen et al. (2013) and could indicate that the presence of peatlands makes quite a difference for CO\textsubscript{2} emissions from tropical estuaries.

CO flux estimates were in a similar range as those obtained for the Mauritanian upwelling (Kitidis et al., 2011), those reported for the Equatorial Pacific upwelling (Ohta, 1997) and for the East China Sea and Yellow Sea (Yang et al., 2011) (see Table 5). However, if we use our W92 estimates for comparison, it seems that CO fluxes are rather low in our study area, consistent with the observation that CO concentrations appear to be rather low, as discussed above.

Both the CO\textsubscript{2} flux estimates and the CO flux estimates presented in this study and elsewhere depend critically on the gas exchange velocity. The W92 exchange velocities differed considerably from our experimental values, yielding much lower fluxes. We believe that the W92 parameterization, which was derived for the ocean, is not suitable for estuaries, though frequently used. It does not account for the turbulence created by tidal currents and water flow velocity. Borges et al. (2004) showed that the contribution
of the water-current related gas exchange velocity to the total gas exchange velocity was substantial at low wind speeds, which are prevalent in our case, too. Therefore, we think that it is more accurate to use empirically determined exchange velocities over wind speed parameterizations.

The performance of FCs has been a matter of debate. Arguments exist both for FCs leading to over- and underestimation of the flux: because they shield the water surface from wind, they may reduce the gas exchange (Frankignoulle, 1988). However, in our case, the FC-derived exchange velocities were much higher than the W92 ones, so that here, the question is rather whether the FC lead to an overestimation of the flux. This would have been the case if the chamber had created artificial turbulences. Indeed, this has been discussed as one of the major weaknesses of the FC method (Matthews et al., 2003; Vachon et al., 2010), although FCs are more susceptible to disruptions in low-turbulence environments than in high-turbulence environments (Vachon et al., 2010). In contrast, a recent study found a rather good agreement between floating chamber and eddy covariance measurements on a river (Huotari et al., 2013), which suggests that the accuracy of FC measurements is also a matter of design. We intended to avoid creation of artificial turbulence by (1) using short wall extensions of the chamber into the water (ca. 1 cm), which is thought to decrease the artificial turbulence by making the chamber more stable (Matthews et al., 2003), and (2) letting the chamber float freely next to the boat.

Taken together, Lupar and Saribas deliver 0.4 Tg organic carbon to the South China Sea every year and release 0.5 Tg yr\(^{-1}\) to the atmosphere as CO\(_2\). Approximately 80\% of the evasion from aquatic systems in the two catchments came from the mid-estuaries. This is noteworthy, since it was recently shown that CO\(_2\) emissions from a blackwater stream on the Maludam peninsula are actually relatively moderate. Müller et al. (2015) showed that due to the short water residence time, 64–84\% of the carbon that this peat-draining river conveyed was exported laterally. Our results imply that a large fraction of this carbon is respired in the adjacent estuaries and released to the atmosphere.
Within the uncertainties, we can state that the aquatic CO$_2$ emissions appear to be approximately as high or higher than the TOC export (Table 4). Since only 15 and 3% of the DOC in the Lupar and Saribas estuaries were derived from peat-draining tributaries, additional DOC from marine sources or intertidal flats might support net heterotrophy in the estuaries. Another factor adding to the high CO$_2$ fluxes is the large variability of pH. pH varied spatially by 1.3 (2013) and 0.8 (2014). This can partially be attributed to the inputs from peat-draining rivers, which are highly acidic (Kselik and Liong, 2004; Müller et al., 2015). Lower pH shifts the carbonate system towards more free CO$_2$, supporting the release of CO$_2$ to the atmosphere in the mid-estuaries.

Conclusively, while the residence time in the peat-draining tributaries might be insufficient to allow for the transformation of peat-derived organic matter, respiration in the estuary is supported by the prolonged residence time and high oxygen availability. Acidic, high-DOC water from peat-draining tributaries contributes to the emission of large quantities of CO$_2$ to the atmosphere.

5 Conclusions

Overall, we conclude that these estuaries in a peat-dominated region receive substantial amounts of terrestrial organic carbon, parts of which are contributed by peat-draining tributaries. We found evidence that aerobic respiration removes DOC, resulting in net heterotrophy. Possibly, DOC degradation is supported by photochemistry, but to assess the magnitude and importance of this pathway, further investigation is required. Additionally, we hypothesize that a fraction of the DOC is physically removed by adsorption. This highlights how these estuaries function as an efficient filter between land and ocean. Unlike small peat-draining rivers, which tend to export most organic carbon downstream, the adjacent estuaries seem to trap a large fraction of this terrestrial organic carbon. This means that the carbon export to the continental shelf is reduced, at the price of CO$_2$ production and, ultimately, emission from the estuary.
Acknowledgements. We would like to thank the Sarawak Biodiversity Center for permission to conduct research in Sarawak waters (Permit No. SBC-RA-0097-MM and export permit SBC-EP-0040-MM). We thank Hella van Asperen (University of Bremen, Germany), Nastassia Denis, Felicity Kuek, Joanne Yeo, Hong Chang Lim, Edwin Sia (all Swinburne University, Malaysia) and all scientists and students from Swinburne University and the University of Malaysia Sarawak who were involved in the sampling campaigns and the preparation. Lukas Chin and the crew members of the SeaWonder are acknowledged for their extensive support. We would also like to acknowledge Innovasi Samudra Sdn Bhd for the loan of the CTD equipment. The authors thank Matthias Birkicht and Dorothee Dasbach (ZMT Bremen, Germany) for their help in the lab performing the analyses. Ultimately, we acknowledge the University of Bremen for funding this study through the “exploratory project” in the framework of the University’s Institutional Strategy.

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FAO: Harmonized World Soil Database, FAO, Rome, Italy and IIASA, Laxenburg, Austria, 2009. 8304, 8334


8326
Carbon dioxide and CO emissions from Southeast Asian estuaries

D. Müller et al.

Abstract

Introduction

Conclusions

References

Tables

Figures


Table 1. Dissolved organic carbon (DOC), particulate organic carbon (POC) and dissolved inorganic nitrogen (DIN) median concentrations and oxygen saturation in the Lupar and Saribas estuary.

<table>
<thead>
<tr>
<th></th>
<th>DOC (µmol L⁻¹)</th>
<th>POC (µmol L⁻¹)</th>
<th>DIN (µmol L⁻¹)</th>
<th>DO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dry</td>
<td>wet</td>
<td>dry</td>
<td>wet</td>
</tr>
<tr>
<td>Saribas OE</td>
<td>n.d. 244*</td>
<td>n.d. 42*</td>
<td>n.d. 18*</td>
<td>n.d. 100.4*</td>
</tr>
<tr>
<td>Lupar ME</td>
<td>340 338</td>
<td>456 650</td>
<td>22 20</td>
<td>70.8 94.4</td>
</tr>
<tr>
<td>Saribas ME</td>
<td>258 281</td>
<td>766 292</td>
<td>30 14</td>
<td>82.8 85.8</td>
</tr>
<tr>
<td>Saribas tributary</td>
<td>685 374</td>
<td>2040 281</td>
<td>22 11</td>
<td>n.d. 82.8</td>
</tr>
<tr>
<td>Lupar UE</td>
<td>89 208</td>
<td>79 131</td>
<td>5 5</td>
<td>84.4 93.3</td>
</tr>
<tr>
<td>Saribas UE</td>
<td>312* n.d.</td>
<td>4114* n.d.</td>
<td>19* n.d.</td>
<td>63.6* n.d.</td>
</tr>
</tbody>
</table>

OE: Outer estuaries (salinity > 25).
ME: Mid-estuaries (salinity 2–25, for the 2013 spatial extent of the rivers).
UE: upper estuaries.
* denotes that only one data point was available.
Table 2. Median CO₂ partial pressures and CO concentrations, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$p$CO₂ (µatm)</th>
<th>CO (nmol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dry</td>
<td>wet</td>
</tr>
<tr>
<td>Lupar OE</td>
<td>618 ± 44</td>
<td>662 ± 36</td>
</tr>
<tr>
<td>Lupar ME</td>
<td>2461 ± 574</td>
<td>1849 ± 881</td>
</tr>
<tr>
<td>Saribas ME</td>
<td>2240 ± 442</td>
<td>2235 ± 304</td>
</tr>
<tr>
<td>Saribas tributary</td>
<td>5064 ± 840</td>
<td>2925 ± 789</td>
</tr>
<tr>
<td>Lupar UE</td>
<td>1527 ± 38</td>
<td>1021 ± 357</td>
</tr>
<tr>
<td>Saribas UE</td>
<td>1159 ± 29</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

OE: Outer estuaries (salinity > 25).
ME: Mid-estuaries (salinity 2–25, for the 2013 spatial extent of the rivers).
UE: Upper estuaries.
Values are median ± one standard deviation.
Table 3. \( \text{CO}_2 \) and CO fluxes measured in the Lupar and Saribas estuaries.

<table>
<thead>
<tr>
<th></th>
<th>( F\text{CO}_2 ) (mol m(^{-2}) yr(^{-1}))</th>
<th>( F\text{CO} ) (mmol m(^{-1}) yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OE</td>
<td>ME</td>
</tr>
<tr>
<td>Lupar</td>
<td>14 ± 3</td>
<td>119 ± 28</td>
</tr>
<tr>
<td>Saribas</td>
<td>n.d.</td>
<td>76 ± 64</td>
</tr>
<tr>
<td>Saribas tributary</td>
<td>n.d.</td>
<td>272 ± 167</td>
</tr>
</tbody>
</table>

OE: Outer estuaries (salinity > 25).
ME: Mid-estuaries (salinity 2–25, for the 2013 spatial extent of the rivers).
UE: upper estuaries.
Table 4. Total CO$_2$ fluxes estimated for the Lupar and Saribas aquatic systems. All numbers are in Tg C yr$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>Lupar</th>
<th>Saribas</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ emissions from rivers (peat)</td>
<td>0.06 ± 0.02</td>
<td>0.02 ± 0.01</td>
<td>0.08 ± 0.03</td>
</tr>
<tr>
<td>CO$_2$ emissions from UE and rivers (non-peat)</td>
<td>0.03 ± 0.01</td>
<td>&lt; 0.01</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>Total riverine CO$_2$ emissions</td>
<td>0.09 ± 0.03</td>
<td>0.02 ± 0.01</td>
<td>0.11 ± 0.04</td>
</tr>
<tr>
<td>Estuarine CO$_2$ emissions</td>
<td>0.31 ± 0.09</td>
<td>0.09 ± 0.08</td>
<td>0.40 ± 0.17</td>
</tr>
<tr>
<td>Total aquatic emissions</td>
<td>0.40 ± 0.12</td>
<td>0.12 ± 0.10</td>
<td>0.52 ± 0.22</td>
</tr>
<tr>
<td>DOC export</td>
<td>0.12 ± 0.05</td>
<td>0.03 ± 0.01</td>
<td>0.15 ± 0.05</td>
</tr>
<tr>
<td>POC export</td>
<td>0.15 ± 0.18</td>
<td>0.06 ± 0.07</td>
<td>0.21 ± 0.25</td>
</tr>
<tr>
<td>TOC export</td>
<td>0.27 ± 0.23</td>
<td>0.09 ± 0.07</td>
<td>0.36 ± 0.30</td>
</tr>
</tbody>
</table>
Table 5. Comparison of CO\textsubscript{2} and CO values for partial pressure and concentration, respectively, and fluxes for different tropical and subtropical sites.

<table>
<thead>
<tr>
<th>CO\textsubscript{2} Site</th>
<th>$pCO\textsubscript{2}$ (µatm)</th>
<th>$FCO\textsubscript{2}$ (mol m\textsuperscript{-2} yr\textsuperscript{-1})</th>
<th>$k$ model</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>outer estuaries</td>
<td>618–662</td>
<td>14</td>
<td>FC</td>
<td>This study</td>
</tr>
<tr>
<td>in Sarawak, MY</td>
<td>2</td>
<td></td>
<td>W92</td>
<td></td>
</tr>
<tr>
<td>mid-estuaries</td>
<td>1849–5064</td>
<td>76–272</td>
<td>FC</td>
<td>This study</td>
</tr>
<tr>
<td>in Sarawak, MY</td>
<td>12–31</td>
<td></td>
<td>W92</td>
<td></td>
</tr>
<tr>
<td>upper estuaries</td>
<td>1021–1527</td>
<td>33–60</td>
<td>FC</td>
<td>This study</td>
</tr>
<tr>
<td>in Sarawak, MY</td>
<td>6–7</td>
<td></td>
<td>W92</td>
<td></td>
</tr>
<tr>
<td>Malaysian estuaries</td>
<td>n.d.</td>
<td>0.4–6.3</td>
<td>W92</td>
<td>Chen et al. (2013)</td>
</tr>
<tr>
<td>Indonesian estuaries</td>
<td>n.d.</td>
<td>8.5–54.1</td>
<td>W92</td>
<td>Chen et al. (2013)</td>
</tr>
<tr>
<td>Brazilian estuaries</td>
<td>162–8638</td>
<td>0.3–63.9</td>
<td>RC01</td>
<td>Noriega and Araujo (2014)</td>
</tr>
<tr>
<td>Indian estuaries</td>
<td>300–18 492</td>
<td>−0.01–132.1</td>
<td>W92</td>
<td>Sarma et al. (2012)</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>CO Site</th>
<th>CO (nmol L\textsuperscript{-1})</th>
<th>$FCO$ (mmol m\textsuperscript{-2} yr\textsuperscript{-1})</th>
<th>$k$ model</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>outer estuaries</td>
<td>0.3–0.7</td>
<td>0.9</td>
<td>FC</td>
<td>This study</td>
</tr>
<tr>
<td>in Sarawak, MY</td>
<td>&lt; 0.1</td>
<td></td>
<td>W92</td>
<td></td>
</tr>
<tr>
<td>mid-estuaries</td>
<td>0.4–1.4</td>
<td>0.8–1.9</td>
<td>FC</td>
<td>This study</td>
</tr>
<tr>
<td>in Sarawak, MY</td>
<td>0.1–0.3</td>
<td></td>
<td>W92</td>
<td></td>
</tr>
<tr>
<td>Seto Inland Sea and Ise Bay, JP</td>
<td>n.d.</td>
<td>0.7–4.0</td>
<td>LM86</td>
<td>Ohta et al. (2000)</td>
</tr>
<tr>
<td>Equatorial Pacific</td>
<td>1.9–7.7</td>
<td>1.4–1.6</td>
<td>LM86</td>
<td>Ohta (1997)</td>
</tr>
<tr>
<td>Mauritanian upwelling</td>
<td>0.1–6.2</td>
<td>1.7–3.5</td>
<td>N00</td>
<td>Kitidis et al. (2011)</td>
</tr>
<tr>
<td>East China and Yellow Sea</td>
<td>0.1–7.0</td>
<td>0.4–6.8</td>
<td>W92</td>
<td>Yang et al. (2011)</td>
</tr>
</tbody>
</table>

The gas exchange velocity $k$ used to calculate the flux was determined using different approaches:

FC = floating chamber measurements.
N00 = Nightingale et al. (2000).
LM86 = Liss and Merlivat (1986).
Figure 1. Map of the study area. The stations are indicated by the grey and black dots, peat soils (histosols) are indicated in green (as of FAO, 2009).
Figure 2. Average monthly precipitation during 1980–2014 (black), monthly precipitation in 2013 (green) and 2014 (red). The bars indicate the rainfall during our sampling months. It can be seen that the rainfall pattern was not much different from the historical average during these periods.
Figure 3. Dissolved organic carbon (DOC) concentrations vs. salinity in the Lupar (a) and Saribas (b) estuaries. The red marker refers to the zero salinity end-member in the peat-draining tributaries. The lines indicate mixing of the different water masses.
Figure 4. Carbon-to-nitrogen (C/N) ratios in dissolved organic matter (a) and in particulate organic matter (b). Blue markers refer to samples from 2013, yellow markers refer to samples from 2014. The individual rivers are denoted by different symbols. Lines refer to the C/N ratios that would be expected for tropical peat and leaves (Baum, 2008) and for phytoplankton.
Figure 5. Salinity (a and b), CO$_2$ partial pressures (c and d) and CO concentrations (e and f) measured during the two cruises in 2013 (left column) and 2014 (right column).
Figure 6. Apparent oxygen utilization (AOU) vs. excess CO$_2$. Blue markers refer to samples from 2013, yellow markers refer to samples from 2014. The individual rivers are denoted by different symbols.
Figure 7. CO concentrations depending on the hour of the day local time. The black areas refer to night-time hours, while the light area denotes the daylight hours. All data are gathered in this figure, 2013 and 2014 data are distinguished with different colors and symbols.