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## ***Interactive comment on “Fate of peat-derived carbon and associated CO<sub>2</sub> and CO emissions from two Southeast Asian estuaries” by D. Müller et al.***

**D. Müller et al.**

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We thank Anonymous Referee 1 for the positive evaluation of our manuscript and the constructive feedback. Please find detailed answers to all general and specific comments below.

*General Comments: The authors describe a series of observations along two Tropical estuaries in Malaysia. Specifically, the authors present measurements of POC, DOC, CO<sub>2</sub>, CO concentrations and their respective isotopic signatures. In addition air-sea exchange measurements using a floating chamber are presented. These observations are discussed in the context of C-export from land to sea, C-transformations along*

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*this route and emissions of CO<sub>2</sub> and CO to the atmosphere. The authors found that substantial transformations of terrestrial C occur in the estuary, related primarily to biological (respiration) and photochemical processes. These processes moderate the export of organic C to the adjacent shelf and result in substantial efflux of CO<sub>2</sub>/CO from the estuary to the atmosphere. This is a very well written paper which provides rare data in an environment which is not well understood in the context of C-cycling and emission of greenhouse gases. I am sure that this work involved considerable logistical difficulties, but I really enjoyed the ingenuity shown by the authors in overcoming these. I have a number of comments which the authors should address, but have no hesitation in recommending this paper for publication in BG.*

*Specific Comments:*

*1) Abstract: The authors state that ‘suspended matter. . . limiting the light penetration depth’ was responsible for lower CO fluxes compared to other regions. I agree with this statement, but not everyone is a photochemist, so the authors should clearly state that suspended matter would be expected to suppress CO photoproduction.*

This will be pointed out in the Abstract of the revised manuscript as suggested.

*2) p.8303, line 24: What is the tidal range for the two “macrotidal” estuaries?*

The reported tidal range at the reference port for these two rivers, Pulau Lakei, is 3.1 m (Mean higher high water – mean lower low water). In the rivers themselves, tidal ranges of 3.5 m (Lupar) and 4 m (Saribas) are reported with reference to this port. In the publication, we will add this information.

*3) p.8302, line 7: The authors state the “peat draining rivers exhibit extraordinarily high DOC. . .”. Please give some representative values and references for the non-expert reader.*

We will add three references (Müller et al., 2015, Moore et al., 2011, 2013) and state that DOC concentrations of up to 5667  $\mu\text{mol/L}$  have been measured in tropical peat-draining rivers (Moore et al., 2013).

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4) p. 8304, lines 10-15: *Data are grouped by salinity for the two campaigns, but was there a geographic overlap as well? e.g. Did the “mid-estuary” regions overlap at all or were they in different places because of differences in river discharge?*

There was a geographic overlap. Although this is not explicitly indicated, it can be seen in Figure 5. Note that the salinity distribution of the Lupar river is not displayed in this Figure, this was a technical issue. We will submit the revised Figure with the revised manuscript (see attachment). Additionally, we will indicate in the Results section that although water with higher salinities progressed slightly upstream during the dry season, the wet and dry mid-estuary location overlapped. We will also change the terminology to lower, middle and upper estuary, as mid-estuary salinities were also observed in the (geographically) outer estuary.

5) *Section 2.2: In the absence of measurements, the calculation of river discharge probably contains substantial uncertainty, but I find the authors’ approach very clever. The same applies to section 2.6, where a “flower pot” was modified to serve as a gas exchange chamber. It is nice to see that ingenuity and that the authors are honest about the materials they used in the field.*

Discharge measurements would have certainly reduced the uncertainty of our estimates, but unfortunately, they were not available. We thank the referee for his sympathy with logistical constraints.

6) p. 8305, line 5: *How was the pH calibrated? With NBS/NIST buffers or borate buffers? What activity scale is pH reported on? Total-scale? NBS-scale? Please clarify this as the scale can make a difference of 0.2 units in seawater.*

We used NIST buffers and report pH values on NBS scale. We will add this information in the revised text.

7) p.8305, line 18: *How long were nutrient/DOC samples stored for?*

Both DOC and nutrient samples were stored up to two months until analysis. They were preserved as indicated in the text and kept frozen until analysis. We will indicate the duration of storage in the revised text.

8) p.8306, line 7: *What was the volume of the vials used for delta-13-C-DIC? What reference are the results reported against? PDB?*

We used 10 ml vials for the determination of d13C-DIC. The results are reported against PDB. We will add this information in the revised text.

9) p. 8306. line 14: *How was the equilibrated air “dried” before FTIR?*

We used a Nafion<sup>®</sup> drier and a magnesium perchlorate moisture trap, as described in Griffith et al. 2012. We will point this out with reference to Griffith et al. in the revised text.

10) p.8306, lines 23: *Where did the gas standards come from? What were they reevaluated against after the cruises? Please give suppliers of secondary and primary standards.*

The reference gases are gravimetrically prepared gas mixtures (Deuste Steininger). They were re-calibrated against WMO reference scale (for the available range of concentrations) at the Max-Planck-Institute for Biogeochemistry in Jena, Germany. This information will be added in the revised manuscript. The “re-evaluation” seems to be misleading. We referred to the fact that we did measure all reference gases up to 10000 ppm CO<sub>2</sub>, but then we saw that maximum CO<sub>2</sub> mixing ratios were only up to 5000 ppm. Therefore, we used only those data points for calibration that covered the range of measured values. We will rephrase this in the revised manuscript.

11) p.8314, lines 12-14: *The authors should clarify that these flux rates for CO/CO<sub>2</sub> refer to their flux-chamber data, not the calculated flux from Wanninkhof, 1992 (W92). Perhaps the use of a subscript throughout the manuscript would help differentiate these, e.g. FFC from FW92*

This seems to be a good way to clarify which flux we refer to. This will be done in the revised manuscript.

12) p. 8316, lines 2-3: *The authors state that they did not “expect” the low DOC contribution from peatlands, given that these occupy such a large fraction of the catchments.*

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*The authors should elaborate on this point. I am less “surprised”. My understanding from temperate peatlands is that runoff in these is limited to the uppermost layer of peat and only occasionally (if not rarely) flushes the deeper layers, so their DOC contribution/age/composition does not reflect the amount of C stored in peat. Perhaps the authors could explain why they “expected” a higher contribution.*

Tropical peat swamp forests have a dense vegetation. As we suggested in another publication (Müller et al. 2015), most DOC is actually derived from the upper peat layers or surface runoff. Although the DOC concentrations do indeed not reflect the peat pore water concentrations, they are still quite high. We determined an average DOC concentration of 3690  $\mu\text{mol/L}$  in a peat-draining river on the Maludam peninsula, between the Lupar and Saribas rivers. This is more than ten times higher than the DOC concentrations in the Lupar and Saribas rivers (upland region). Although this particular river flows directly into the South China Sea, many other peat-draining rivers from the Maludam peninsula and from other peatlands in the Lupar and Saribas catchments flow into the Lupar and Saribas estuaries. Therefore, we expected to see a signal of elevated DOC in these estuaries. We will make this clearer in the revised manuscript and extend the discussion at this point.

*13) Section 4.2: The discussion of DOM photochemistry seems thorough, even though the conclusion is that the results are “inconclusive”. Undoubtedly, diurnal CO variability points to a photochemical source, but the authors are correct to point out that this is probably limited by high light attenuation over the whole water column.*

We agree that the diurnal variability of CO clearly indicates a photochemical source. We were unable to quantify in how far the bioavailability of DOC was influenced by photochemistry though, which is why we think this question would merit further investigation.

*14) p. 8320, lines 1-4: The conclusion that W92 is not appropriate for calculating gas exchange in estuaries is not new, but this is frequently neglected elsewhere. In fact this applies to all wind-driven turbulent diffusivity models and the authors are correct to*

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*point this out, but this conclusion should feature more prominently in the abstract. e.g. Wind-driven turbulent diffusivity models (such as W92) are inappropriate in estuaries where turbulence is mainly induced by tidal-flows and river discharge as well as their interactions with channel-morphology rather than wind-shear.*

We will mention this finding in the abstract and the conclusions of the revised manuscript, as suggested.

*15) p. 8321, lines 5-9: The authors state that pH in the estuary may drive the carbonate system to high CO<sub>2</sub>, as observed. Though this is true, one could also argue the opposite, i.e. that high CO<sub>2</sub> reduces pH. I'm not sure that "causality" can be established here. On the one hand, most estuaries are heterotrophic environments where respiration produces CO<sub>2</sub> which would be expected to decrease pH. Nevertheless, the change in ionic strength at the freshwater-seawater interface may also cause a respiration-independent decrease in pH which could increase CO<sub>2</sub>.*

Our thought was that the input of acidic waters from peat-draining rivers might decrease pH. On the other hand, certainly, respiratory CO<sub>2</sub> might have an effect on pH as well. We agree that it is difficult to determine the direction of the causality with the available data, but we will try to provide a more balanced and extended discussion at this point.

*16) Conclusions: This section is good, but the authors should highlight the inadequacy of wind-driven turbulent diffusivity models for calculating fluxes in estuaries.*

This will be done as mentioned in our reply to comment 14.

## References

Griffith et al. 2012: A Fourier transform infrared trace gas and isotope analyser for atmospheric applications. *Atmospheric Measurement Techniques* 5, 2481–2498. doi:10.5194/amt-5-2481-2012

Moore et al. (2011): Fluvial organic carbon losses from a Bornean blackwater river. *Biogeosciences*, 8, 901–909. doi:10.5194/bg-8-901-2011

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Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/12/C5220/2015/bgd-12-C5220-2015-supplement.pdf>

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Interactive comment on Biogeosciences Discuss., 12, 8299, 2015.

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# ***Interactive comment on “Fate of peat-derived carbon and associated CO<sub>2</sub> and CO emissions from two Southeast Asian estuaries” by D. Müller et al.***

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We thank Anonymous Referee 2 for the constructive feedback and useful comments on our manuscript. We replied in detail to all general and specific comments below.

## *General remarks*

*The paper presents a high quality dataset from a not well studied region. The topic of carbon cycling in coupled systems, in this case peatlands, streams, and estuaries is highly interesting and fits to the focus of the journal. The data are new and strongly deserve publication. To accept this manuscript, however, a number of critical points have to be addressed: The main problem with the manuscript is that the data do not*

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*really fit to the story. The rivers are dominated by upland areas, just passing the peat area on their way to the ocean. The authors state that only 3 and 15% of the DOC in the rivers stems from the peat area. Thus, the link between the peatlands and the stream biogeochemistry is not really convincing. I recommend to re-write the story with a focus on the turnover of land derived organic carbon in the estuaries.*

We did detect much lower DOC concentrations than expected, but we think that this in itself is a quite interesting finding. DOC concentrations in a peat-draining river on the Maludam peninsula were more than ten times higher than the freshwater end-member in the Lupar and Saribas rivers (Müller et al., 2015). Although this particular river discharges directly into the South China Sea, other rivers flow from Maludam directly into the Lupar and Saribas estuaries. Similarly, there are several other tributaries to the Lupar and Saribas estuaries that flow through peat. We were wondering where all this peat-derived carbon ends up. Our results do show elevated DOC in the mid-estuaries, but it is not as high as expected. We agree that the rivers carry a mixed signal. Therefore, we agree that the title of the manuscript could be changed to “Fate of terrestrial organic carbon and associated CO<sub>2</sub> and CO emissions from two Southeast Asian estuaries”. Under this title, we will discuss the different sources of terrestrial carbon (peat/ non-peat) in a more balanced way.

*A second shortcoming of the paper is the absence of data on methane emissions. Since the authors used a FTIR, I am pretty sure that they have also data on methane. Probably, they saved those data for another paper. However, for the actual manuscript I consider data on methane production and emission indispensable.*

It is correct that we conducted simultaneous measurements of CO<sub>2</sub>, CO, CH<sub>4</sub> and N<sub>2</sub>O. A first draft of the manuscript included all four gases, making it very complex and unfocused. Therefore, we decided to present only CO<sub>2</sub> and CO, because we found that those two gases tell us something about the fate of terrestrial organic carbon in these estuaries. CH<sub>4</sub>, surprisingly, did not. The factors influencing CH<sub>4</sub> production and emission seem to lie outside the focus of this study, which is the terrestrial organic carbon that rivers convey to the estuary. Therefore, we think by adding the CH<sub>4</sub> data,

the manuscript would become more complex, longer, less concise, while the added information would not help us resolve the fate of terrestrial organic carbon in these estuaries. We thus prefer not to add this data.

*My third point is that the fate of organic carbon in aquatic systems cannot be understood without the inclusion of the sediments. This is especially relevant in such large scale studies, where spatial patterns of carbon cycling are usually heavily influenced by sedimentation and benthic metabolism. The authors probably do not have data on sediment quality or carbon turnover. However, it should be possible to discuss the possible role of sediments using relevant literature.*

Unfortunately, we have no data on sedimentation or benthic metabolism. We will restructure our discussion and include the role of sediments in the revised manuscript with reference to the literature as suggested.

#### *Detailed remarks*

*8301, I.8: It is not clear to me why different units were used for CO<sub>2</sub> and CO. I suggest to use either partial pressure or concentration.*

This arose from the fact that most papers report either CO<sub>2</sub> data or CO data, but not both. CO<sub>2</sub> is almost always reported as CO<sub>2</sub> partial pressure. CO is almost exclusively reported as concentration. In the attempt to stick to both conventions, we chose different units for CO<sub>2</sub> and CO. Actually, those authors who do report several gases simultaneously choose partial pressure or mole fraction for CO<sub>2</sub> and molar concentrations for other trace gases for the convenience of the readership, e.g., Borges et al., 2015; Bouillon et al., 2012; Teodoru et al., 2015.

*8303, I.2: DOC is probably not completely oxidized to CO and CO<sub>2</sub>, but a major reaction-product is (modified) DOC.*

This is a valid point, we will rephrase that CO and CO<sub>2</sub> are photochemically produced from DOC.

*8303, I.24: Not being an expert in marine science I do not know the meaning of the*

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word “macrotidal”.

In the revised manuscript, we will indicate the meaning of this word by giving the tidal range (3-4 m) for these estuaries.

*8304, I23: Explain all abbreviations (in this case CTD).*

This will be done in the revised manuscript.

*8304, I.24: Wasn't the boat drift affected by wind?*

This is a good point, although this effect was probably minor compared to the water flow velocity. Since we do not use velocity data for any further calculations, this bias has no further effect, but we agree that this must be mentioned, which we will do in the revised manuscript. The only time we actually refer to the flow velocity data is when we try to identify the reason for the high gas exchange velocity in the Lupar river. We think that this interpretation remains valid despite the uncertainty associated with our flow velocity estimate.

*8305, section 2.3: give companies and country for instruments*

This information will be added.

*8305, I.13: Do these filters really have a defined pore-size of 0.7  $\mu\text{m}$ ?*

Yes, the specification of these filters indicates that they have a particle retention of 0.6-0.8  $\mu\text{m}$ , meeting the requirements of EPA method TCLP (Toxicity Characteristic Leaching Procedure).

*8308, I.1-3: Better use same unit for both gases.*

As stated above, we prefer using partial pressure for CO<sub>2</sub> and concentrations for CO in order to make it more convenient for readers from the CO<sub>2</sub> community and CO community to use our data without converting it to different units.

*8308, I.14: How long were the chamber measurements? A few minutes per measurement? Did you check the temperature in the chamber. There might be substantial warming under the tropical sun.*

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The chamber measurements usually lasted between 5 and 10 minutes. The small size of the chamber allowed for these relatively short deployment periods. Unfortunately, we did not monitor the temperature in the chamber, but we assumed that heating of the (white) chamber is limited during this short time period. We will add two sentences about this in the discussion of floating chamber performance.

*8309, I.1: Was the surface rough?*

Yes, the surface was rough due to the high flow velocity of the rivers and tidal currents. Especially the Lupar river exhibited substantial turbulence.

*8301, section 3.2: I wonder whether the estuary was fully mixed all the time. This is important if the samples are considered to be representative for the whole water column.*

We agree that full mixing is a strong assumption. Actually, vertical salinity profiles measured with the CTD indicate that the Saribas estuary was well-mixed, but occasionally slight stratification occurred in the Lupar estuary. We did not measure vertical profiles of any of the water chemistry parameters, like oxygen, DIN, DOC or pH. In the Methods section, we stated that our samples were taken from ca. 1 m below the surface, but in the revised manuscript, we will clarify in this section that we are talking about surface salinity, surface concentrations etc.

*83011, I.27 How deep were the estuaries? I wonder whether a large part of the turbidity originates from re-suspended sediment rather than river discharge.*

The estuaries were on average between 6 and 9 m deep. Locally, the estuaries were as shallow as 2 m, so that resuspension of sediments is likely a source of the turbidity. This is why we speculated that we hit the estuarine turbidity maximum during our cruise. For the purpose of this manuscript, it is probably less relevant to postulate the existence of a turbidity maximum and more relevant to make it clear to the reader that we assume that sediment resuspension was a significant source of turbidity in the estuary. We will rephrase and try to make it clearer in the revised manuscript.

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*8313, I.1: The weak correlation between O<sub>2</sub> and CO<sub>2</sub> is a hint that CO<sub>2</sub> was not regulated by metabolic processes but by chemical reactions and transport processes. We will be more precise about the correlation between AOU and CO<sub>2</sub> in the revised manuscript. In the dry season, it was strong for the Lupar estuary, but weak for the Saribas (Lupar:  $r = 0.71$ ,  $p = 0.01$ , Saribas:  $r = 0.52$ ,  $p = 0.18$ ). During the wet season, a correlation could be established for the Lupar estuary ( wet season:  $r = 0.62$ ,  $p = 0.14$ ) but not for the Saribas due to the limited number of data points. We will give the correlation coefficients in the revised manuscript. In general, it seems like oxygen depletion concurs with an elevation of excess CO<sub>2</sub>; however, this signal is not unambiguous. Overall, CO<sub>2</sub> is probably driven by a combination of metabolism, chemical reactions and transport.*

*8313, I.12: Wasn t there a diurnal cycle of CO<sub>2</sub>? If not, that is another hint that CO<sub>2</sub> was not controlled by metabolism.*

A diurnal cycle of CO<sub>2</sub> was not observed. A diurnal cycle of CO<sub>2</sub> would be expected if autotrophy was important. However, we think that CO<sub>2</sub> is mainly heterotrophic, because we consider photosynthesis limited due to the high turbidity. Heterotrophic respiration does not necessarily exhibit a diurnal cycle, unless driven by temperature variations. That means that if we do not observe a diurnal CO<sub>2</sub> cycle, this does not necessarily mean that there is no metabolism.

*8314, I.3: I do not completely understand, which k values were used in this calculations. In the revised manuscript, we are going to use subscripts  $k_{600_{FC}}$  and  $k_{600_{W92}}$ , as well as  $F_{FC}$  and  $F_{W92}$ , so that it is clear which k values were used.*

*8314: The whole section contains a lot of method descriptions. I wonder whether some text can be moved to the method section.*

We will move some of the descriptions to section 2.6.

*8314, I.25: I guess you mean the “total flux between water and atmosphere for the Lupar was . . .”*

Yes, we will specify this in the revised manuscript as suggested.

*8314, I.28: Is this the best way to estimate river surface area? Maybe you should try to multiply river length with an estimated mean width.*

As detailed below, we decided to follow your suggestion and remove rivers from the GHG budget. Therefore, the riverine surface area is no longer required.

*8314, I.26: What about CH<sub>4</sub>?*

Its contribution to the total C emissions from these estuaries is less than 1% in terms of CO<sub>2</sub>-equivalents (assuming a global warming potential of methane of 28 times that of carbon dioxide on a 100 year time horizon), but as discussed above, we would rather leave the CH<sub>4</sub> data out.

*8315, I.1: I do not understand why a mean river flux was used to determine the flux from the peatland.*

For rivers flowing through peat, we used an areal flux estimate (flux between water surface and air) for a peat-draining river. For rivers flowing through other areas, we used an areal flux estimate from the upper estuary. Since we will remove rivers from the budget, this description will not be found in the revised manuscript any more.

*8315, I.2: What is the “rest”?*

The “rest” refers to rivers that are not flowing through peatland. As stated above, this part will no longer be found in the text.

*8315, last section: I wonder whether the GHG fluxes from the river network should be included in the budget or if it is probably better to concentrate on the estuary. The database for the streams is suboptimal, because, e.g. small tributaries are neglected.*

With our estimates of riverine CO<sub>2</sub> emissions, we wanted to show the importance of the estuary for CO<sub>2</sub> outgassing. However, we acknowledge that our estimate of the riverine surface area and the negligence of headwater streams causes a very high uncertainty. Therefore, we will follow your suggestion and remove the rivers from the budget.

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*8315, I.13: It looks a bit like the classical zonation of processes in a reservoir as nicely explained in the book of Thornton (Reservoir Limnology, 1990). Metabolic processes are often highest in the intermediate section of reservoirs, because when the stream is entering the lentic waterbody, that is the site of sedimentation and also plankton development. It would be extremely interesting to have some information about the sediments along the stream-estuary transition.*

We will include benthic metabolism as a potential source of carbon dioxide and sedimentation as a potential sink in the discussion.

*8316, I.15: Above you say that the correlation between AOU and CO<sub>2</sub> was bad. What is true? Maybe show data.*

The data is shown in Figure 6, but we will add correlation coefficients in the Results section to make it clearer.

*8316, I.28: pH has a strong influence on the CO<sub>2</sub> concentration. Do you know the pH of the streams draining the peatlands and is it possible that the CO<sub>2</sub> concentration is mostly regulated by pH changes and geochemical reactions?*

Yes, we measured a pH of 3.8 in a peat-draining river on the Maludam peninsula. We refer to the publication in our text, but we will add the value in the revised manuscript. We will also extend the discussion of the pH-CO<sub>2</sub> relationship. In the discussion paper, this discussion is found on p. 8321, I. 5-9. We agree that this might be a bit late and a bit short and therefore, we will shift (and extend) this discussion to section 4.2.

*8317, I.2: Since you know k<sub>600</sub>, you can easily calculate reaeration from the measured oxygen concentrations in the water.*

That is correct, but since we cannot do the same thing for the Chen et al. 2008 data, the value wouldn't compare to anything.

*8317, I.14: What is the mechanism of CO production from particles?*

Irradiation of POM can produce CO, CO<sub>2</sub> and DOC. Xie et al. 2009 found that in coastal waters, CO photoproduction from particulates was 10-35% that of CDOM. We

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will add some additional explanation in the revised manuscript.

*8317, I.29: There is much more literature about the effect of UV on the degradability of DOM. Please improve the discussion at this point.*

We will include additional references while keeping the discussion brief and concise and without too much speculation.

*8319, section 4.4: I suggest to discuss also the role of temperature as a regulator of the fluxes.*

Generally, increasing temperature would lead to an increasing gas exchange velocity and decreased solubility of CO<sub>2</sub> and CO, so it would be expected that fluxes increase with increasing temperature. Our data doesn't show this very clearly though, probably because the spatial heterogeneity obscured the temperature effect, as shown in the Supplement. We will add a sentence about this in the revised manuscript, but we would prefer not to add an additional Figure.

*8320, I.5: Better "floating chambers" instead of "Fcs".*

This will be changed, except in the subscripts and Tables.

*8321, I.6: Yes – the pH is important. That discussion has to be extended and placed earlier in the paper.*

This will be done as indicated above.

*8336, Figure 3: I do not fully understand the lines.*

The lines indicate mixing of the two different freshwater end-members: The freshwater DOC concentration measured upstream in the Lupar and Saribas rivers and the peat-freshwater DOC concentration. The point where the regression line hits the vertical axis is the calculated freshwater end-member, as indicated in Section 3.3. In order to make this clearer, we will add labels ( $EM_{meas}$ ,  $EM_{Maludam}$ ,  $EM_{cal}$  as in Eq. 6) in the revised Figure and remove the "mixing" lines while keeping the regression lines.

*8339, Figure 6: I suggest to include a 1:1 line*

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We will include a 1:1 line in the revised Figure.

*8340, Figure 7: I guess the location of the measurements was variable during the diurnal cycles. Was the boat also moving in the darkness or is there a possible bias towards non-moving measurements during the night?*

Yes, the location was variable, which we indicated in the text (“CO concentrations were higher during daytime than during the night, independent of the boat’s location (Fig. 7).”, p. 8313, l.9-11). We will add a similar sentence in the Figure caption. Although we frequently moved until the late evening and sometimes started moving before sunrise, there is a potential bias towards non-moving measurements during the night. However, many of the “dark” data points that were recorded while the boat was moving (e.g., between 6.30 pm and 10 pm) show the indicated pattern with highest CO concentrations during daytime, so we think that our conclusion, that CO is photochemically produced, remains valid.

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Zambezi River and major tributaries, and their importance in the riverine carbon budget. *Biogeosciences* 12, 2431–2453. doi:10.5194/bg-12-2431-2015

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# Fate of terrestrial organic carbon and associated CO<sub>2</sub> and CO emissions from two Southeast Asian estuaries

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## Abstract



Southeast Asian rivers convey large amounts of organic carbon, but little is known about the fate of this terrestrial material in estuaries. Although Southeast Asia is, by area, considered a hotspot of estuarine CO<sub>2</sub> emissions, studies in this region are very scarce. We measured dissolved and particulate organic carbon, as well as carbon dioxide (CO<sub>2</sub>) partial pressures and carbon monoxide (CO) concentrations in two tropical estuaries in Sarawak, Malaysia, whose coastal area is covered by carbon-rich peatlands. We surveyed the estuaries of the rivers Lupar and Saribas during the wet and dry season, respectively. Carbon-to-nitrogen ratios suggest that dissolved organic matter (DOM) is largely of terrestrial origin. We found evidence that a large fraction of this carbon is respired. The median *p*CO<sub>2</sub> in the estuaries ranged between 640 and 5064 μatm with little seasonal variation. CO<sub>2</sub> fluxes were determined with a floating chamber and estimated to amount to 14–272 mol m<sup>-2</sup> yr<sup>-1</sup>, which is high compared to other studies from tropical and subtropical sites. Estimates derived from a merely wind-driven turbulent diffusivity model were considerably lower, indicating that these models might be inappropriate in estuaries, where tidal currents and river discharge make an important contribution to the turbulence driving water-air gas exchange. Although an observed diurnal variability of CO concentrations suggested that CO was photochemically produced, the overall concentrations and fluxes were relatively moderate (0.4–1.4 nmol L<sup>-1</sup> and 0.8–1.9 mmol m<sup>-2</sup> yr<sup>-1</sup>) if compared to published data for oceanic or upwelling systems. We attributed this to the large amounts of suspended matter (4–5004 mg L<sup>-1</sup>), limiting the light penetration depth and thereby inhibiting CO photoproduction. We concluded that estuaries in this region function as an efficient filter for terrestrial organic carbon and release large amounts of CO<sub>2</sub> to the atmosphere. The Lupar and Saribas mid-estuaries deliver 0.4 ± 0.2 Tg C yr<sup>-1</sup> to the South China Sea as organic carbon and release approximately the same amount to the atmosphere as CO<sub>2</sub>.

# 1 Introduction



Estuaries are net heterotrophic systems (Duarte and Prairie, 2005; Cole et al. , 2007) and act as a source of carbon dioxide (CO<sub>2</sub>) to the atmosphere, releasing 150 TgC annually (Laruelle et al., 2013). Southeast Asia is considered one of the hotspot regions of aquatic CO<sub>2</sub> emissions to the atmosphere (Regnier et al., 2013), because many Southeast Asian rivers exhibit high organic carbon concentrations (Alkhatib et al., 2007; Moore et al., 2011, 2013; Müller et al., 2015). It has been estimated that Indonesian rivers alone account for 10% of the dissolved organic carbon (DOC) exported to the ocean globally (Baum et al., 2007), which was attributed to the presence of tropical peatlands. Southeast Asian peatlands store 68.5 Gt carbon (Page et al., 2011) and represent a globally important carbon pool. DOC concentrations in Southeast Asian peat-draining rivers range up to 5 μmol L<sup>-1</sup> (Moore et al., 2013). Although a small fraction of this DOC is respired in the river and released to the atmosphere as CO<sub>2</sub>, 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.

Peat-derived organic matter consists mainly of lignin and its derivatives (Andriessse, 1988) and is thus relatively recalcitrant to degradation. In addition, short water residence times constrain organic matter decomposition (Müller et al., 2015). However, high organic carbon loads and high temperatures suggest high microbial activity both in the water column and in the sediments, 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 carbon monoxide (CO) and CO<sub>2</sub> are produced (Stubbins, 2001), with the CO<sub>2</sub> 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 dissolved organic matter (DOM) is largely of terrestrial origin. Terrestrial CDOM was found to be more efficient in producing CO than marine CDOM (Zhang

et al., 2006), making estuaries a significant source of CO to the atmosphere (Valentine and Zepp, 1993). Ultimately, recalcitrant terrestrial organic matter might be subject to photo-bleaching (Vähätalo, 2010), increasing its bioavailability to the heterotrophic community.

In order to investigate if and how terrestrial organic carbon is processed in tropical estuaries, we studied organic carbon, dissolved CO<sub>2</sub> and CO in two Malaysian estuaries, both of which receive terrestrial carbon from rivers draining a catchment that is partially covered by peat.

## 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 (tidal range 3-4 m). 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), which originate in upland areas. Six channels from the Maludam peat swamp forest drain into the Lupar estuary 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), whereas the peat is located very close to the coast (Fig. 1). The catchment sizes are 6558 km<sup>2</sup> (Lupar) and 1943 km<sup>2</sup> (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 lower (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](http://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<sup>2</sup>). 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). Note that as boat drift might have been affected by wind, these flow velocity estimates have limited accuracy. However, a very rough estimate of flow velocity is sufficient for our purposes.

## 2.3 Water chemistry

Salinity and temperature profiles were measured at each station with a CastAway CTD (conductivity, temperature, depth; Sontek, USA). Additionally, water pH, dissolved oxygen (DO) and conductivity were measured in the surface water with a Multi3420, using an FDO 925 oxygen sensor, a SenTix 940 pH sensor and a TetraCon 925 conductivity sensor (WTW, Germany). The pH sensor was calibrated with NIST (National Institute of Standards and Technology, formerly National Bureau of Standards, NBS) buffers and is reported on NBS scale. Apparent oxygen utilization (AOU) was calculated as the difference between the

saturation oxygen concentration and the measured oxygen concentration.

$$\text{AOU} = \text{O}_2^{\text{sat}} - \text{O}_2^{\text{meas}} \quad (1)$$

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

5 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  $\mu\text{m}$ ), preserved with a mercuric chloride ( $\text{HgCl}_2$ ) solution and stored cooled and upright until analysis (approx. two months after sampling). Concentrations of nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ) and ammonia ( $\text{NH}_4^+$ ) were determined spectrophotometrically (Grasshoff et al., 1999) with a Continuous Flow Analyzer (Alliance, Austria).

## 2.4 Organic carbon and carbon isotope analysis

15 Dissolved organic carbon (DOC) samples were filtered (pore size 0.45  $\mu\text{m}$ ) and acidified with 21 % phosphoric acid ( $\text{H}_3\text{PO}_4$ ) until the pH had dropped below 2. Samples were stored frozen until analysis (approx. two months after sampling). DOC concentrations were determined through high temperature combustion and subsequent measurement of the evolving  $\text{CO}_2$  with a non-dispersive infrared detector. In 2014, those samples were also analyzed for total dissolved nitrogen (TDN) using a TOC-VCSH with TNM-1 analyzer (Shimadzu, Japan). Dissolved organic nitrogen (DON) was then calculated by subtracting DIN from TDN.

20 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 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 combustion with a Euro EA3000 Elemental Analyzer (Eurovector, Italy). The abundance of the stable isotope  $^{13}\text{C}$  was determined with a Finnigan Delta plus mass spectrometer (Thermo Fisher Scientific, USA).



Samples for determination of  $\delta^{13}\text{C}$  in dissolved inorganic carbon (DIC) were preserved with  $\text{HgCl}_2$ , sealed against ambient air and stored cool, upright and in the dark until analysis (3 – 4 months after sampling). 1 mL vials were prepared with 50  $\mu\text{L}$  of 98 %  $\text{H}_3\text{PO}_4$  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 the  $^{13}\text{C}/^{12}\text{C}$  ratio was determined with mass spectrometry (MAT 253, Thermo Scientific, USA).  $\delta^{13}\text{C}$  values are reported against Pee Dee Belemnite (PDB).

## 2.5 $\text{CO}_2$ and CO measurements

In order to determine partial pressures of dissolved  $\text{CO}_2$  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  $20 \text{ L min}^{-1}$ . Dry air mole fractions of  $\text{CO}_2$  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).

The equilibrator headspace air circulated between the FTIR and the equilibrator at a rate of  $1 \text{ L min}^{-1}$  in a closed loop, whereas the air was dried before entering the analyzer using a Nafion<sup>®</sup> drier and a magnesium perchlorate moisture trap (Griffith et al., 2012). The equilibrator and the sampling lines were covered with aluminum foil to avoid CO photoproduction in the sampled air. 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 gravimetrically prepared gas mixtures (Deuste Steininger) ranging from 380 to 10 000 ppm  $\text{CO}_2$  and 51 to 6948 ppb CO. Those gas mixtures were calibrated against the World Meteorological Organization (WMO) reference scale at the Max-Planck-Institute for Biogeochemistry in Jena, Germany.

Water temperature was measured both in the equilibrator and in the water using a Pico PT-104 temperature data recorder (Pico Technology, UK). Ambient air temperature and

pressure were recorded over the entire cruise with an SP-1016 temperature data recorder and a PTB110 barometer (Vaisala, Finland), 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

$$p_{\text{Gas}} = p_{\text{Gas}_{\text{dryair}}}(1 - \text{VP}(\text{H}_2\text{O})), \quad (2)$$

where  $p_{\text{Gas}}$  is the corrected gas partial pressure and  $\text{VP}(\text{H}_2\text{O})$  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).  $\text{CO}$ , 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 (LICOR, USA), 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  $\text{CO}_2$  levels in terms of  $\text{CO}_2$  partial pressure ( $p_{\text{CO}_2}$ ), but convert  $\text{CO}$  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. The floating chamber was an upside-down flower pot with a volume of 8.7 L and a surface area of 0.05 m<sup>2</sup> which it enclosed with the water. Its walls extended 1 cm into the water. The chamber headspace was connected to the Li-820 CO<sub>2</sub> analyzer, and CO<sub>2</sub> concentrations in the chamber were recorded over time. The concentration change was fitted linearly and the water-to-air CO<sub>2</sub> flux  $F$  (in  $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) was calculated according to

$$F = \frac{dc}{dt} \frac{pV}{RTA}, \quad (3)$$

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

$$k_{\text{CO}_2} = \frac{F}{K_0 (p\text{CO}_2^{\text{water}} - p\text{CO}_2^{\text{air}})}, \quad (4)$$

where  $k_{\text{CO}_2}$  is the gas exchange velocity ( $\text{m s}^{-1}$ ) of CO<sub>2</sub> and  $p\text{CO}_2^{\text{air}}$  is the atmospheric CO<sub>2</sub> partial pressure, which was measured with the Li-820 CO<sub>2</sub> analyzer during the cruises. For comparisons,  $k_{\text{CO}_2}$  was normalized to a Schmidt number of 600 (Schmidt number  $Sc$  relates the diffusivity of the gas to the viscosity of the water):

$$\frac{k_{600}}{k_{\text{CO}_2}} = \left( \frac{600}{Sc_{\text{CO}_2}} \right)^{-n} \quad (5)$$

with  $n = 0.5$  for rough surfaces (Jähne et al., 1987). Schmidt numbers were calculated from water temperature for both saline and freshwater (Wanninkhof, 1992), and evaluated for the in-situ salinity assuming a linear dependency (Borges et al., 2004). CO<sub>2</sub> fluxes were calculated for every datapoint using updated solubilities,  $p\text{CO}_2$  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.

The relationship with the Schmidt number was also exploited for calculating CO fluxes. Schmidt numbers for CO were calculated using the coefficients given in Raymond et al. (2012) for freshwater, and the formula given in Zafiriou et al. (2008) for saltwater. 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 Kototakeng, Indonesia (0.202° S, 100.3° E). 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, and for our wet season data, we calculated the average CO mixing ratio in March for the years that were available. CO fluxes were then calculated in the same way as CO<sub>2</sub> fluxes.

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<sup>-1</sup> in the chosen grid, corresponding to an average precipitation of 325 mm month<sup>-1</sup>. 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  $4.2 \text{ mm d}^{-1}$  (Kumagai et al., 2005), we estimated the average annual discharge for the Lupar river to be 490 and  $160 \text{ m}^3 \text{ s}^{-1}$  for the Saribas river. The flow velocities were estimated to be  $2.5 \pm 1.4 \text{ m s}^{-1}$  (average  $\pm$  largest deviation from average) for the Lupar river,  $0.7 \pm 0.7 \text{ m s}^{-1}$  for the Saribas and  $0.8 \pm 1.0 \text{ m s}^{-1}$  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 the dry season and 0–31.0 in the wet season. Although relatively higher surface salinities were observed further upstream during the dry season if compared to the wet season, the geographical location of the mid-estuaries largely overlapped (Fig. 5a,b). 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 surface 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 in the surface water were generally rather low. During the dry season, DIN ranged between  $1.7$  and  $87.1 \mu\text{mol L}^{-1}$ , whereas most concentrations were between  $15$  and  $30 \mu\text{mol L}^{-1}$ . In the wet season, DIN concentrations ranged between  $3.4$  and  $21.7 \mu\text{mol L}^{-1}$ . 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 of the surface water 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  $93 \mu\text{mol L}^{-1}$  (2013) and  $-1$  and  $52 \mu\text{mol L}^{-1}$  (2014), respectively. Negative AOU suggests net oxygen production and was only observed once in the lower estuary.

### 3.3 Organic carbon

DOC ranged from 80 to 784  $\mu\text{mol L}^{-1}$  in the dry season and from 172 to 1180  $\mu\text{mol L}^{-1}$  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  $673 \pm 274 \mu\text{mol L}^{-1}$  (intercept of the regression curve  $\pm$  standard error of the estimate), the measured freshwater DOC median was 89  $\mu\text{mol L}^{-1}$  (2013) and 208  $\mu\text{mol L}^{-1}$  (2014). For Saribas, the calculated end-member was  $425 \pm 54 \mu\text{mol L}^{-1}$ , and the measured value was 312  $\mu\text{mol L}^{-1}$  (2013, Table 1). This discrepancy indicates that there is a source of DOC in the estuaries. With regards to their location, peatlands seemed a likely source of carbon to the estuaries. In a different study, we found DOC concentrations in a peat-draining river on the Maludam peninsula between 3612 and 3768  $\mu\text{mol L}^{-1}$  (Müller et al., 2015). With the average (3690  $\mu\text{mol L}^{-1}$ ) 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

$$f = \frac{EM_{\text{calc}} - EM_{\text{meas}}}{EM_{\text{Maludam}} - EM_{\text{meas}}} \cdot 100, \quad (6)$$

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 these peat-draining tributaries, and 3% of DOC in the Saribas river. Following Baum et al. (2007), the total DOC export to the ocean from Lupar and Saribas was estimated from the calculated zero-salinity end-members (673 and 425  $\mu\text{mol L}^{-1}$ , respectively), assuming that they provide an average of non-peat and peat freshwater inputs, and annual average discharge. Accordingly, Lupar and Saribas together convey  $0.15 \pm 0.05 \text{ Tg yr}^{-1}$  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  $\text{mg L}^{-1}$  in 2013 and from 13.8 to 3566.7  $\text{mg L}^{-1}$  in 2014.

Particulate organic carbon (POC) was higher during the dry season (Table 1), ranging from 51 to 4114  $\mu\text{mol L}^{-1}$  in 2013 and from 17 to 2907  $\mu\text{mol L}^{-1}$  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 (see Fig. 4b).  $\delta^{13}\text{C}$  values ranged between  $-28.5$  and  $-25.5\text{‰}$  in 2013 and  $-27.6$  to  $-24.4\text{‰}$  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, see Fig. 4a), 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  $\text{C yr}^{-1}$  are estimated to be delivered from the Lupar, and another 0.06 Tg  $\text{C yr}^{-1}$  from the Saribas (Table 4). Taken together with the DOC export, this implies that Lupar and Saribas deliver approximately  $0.36 \pm 0.30$  Tg organic carbon to the South China Sea every year, more than half of which is bound to particles.

### 3.4 $\text{CO}_2$ and CO

In both years, both  $\text{CO}_2$  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.  $p\text{CO}_2$  ranged from 297.3 to 5504.0  $\mu\text{atm}$  in 2013 and from 326.5 to 5014.1  $\mu\text{atm}$  in 2014.  $p\text{CO}_2$  increased with decreasing salinity, indicating that high  $p\text{CO}_2$  can be attributed to freshwater input (Fig. 5). However, matters were different for the freshwater samples. The measured freshwater end-member  $p\text{CO}_2$  was relatively moderate (1021–1527  $\mu\text{atm}$ ). Table 2 summarizes the median  $p\text{CO}_2$  values in the lower, mid- and upper estuaries. It can be seen that like DOC,  $p\text{CO}_2$  was highest in the mid-estuaries. The difference between dry and wet season  $p\text{CO}_2$  was marginal (see Fig. 5). Excess  $\text{CO}_2$  (in  $\mu\text{mol L}^{-1}$ ) was uncorrelated with AOU for the Lupar river (dry season:  $r = 0.71$ ,  $p = 0.01$ , wet season:  $r = 0.62$ ,  $p = 0.14$ ). For the Saribas, the correlation was weak in the dry season ( $r = 0.52$ ,  $p = 0.18$ ). Due to the limited number of data points, no correlation could be established for the Saribas during the

wet season (see Fig. 6). Higher AOU in the dry season did not concur with higher excess  $\text{CO}_2$  (Fig. 6) with the exception of the Saribas tributary.

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

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

### 3.5 $\text{CO}_2$ and $\text{CO}$ fluxes

The  $\text{CO}_2$  fluxes measured with the floating chamber showed large spatial variations and ranged from  $63$  to  $935 \text{ mmol m}^{-2} \text{ d}^{-1}$ . The lowest flux was measured in the Saribas mid-estuary, and the highest flux was measured on the Saribas tributary.  $k_{600,FC}$  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  $k_{600,FC}$  of  $23.9 \pm 14.8 \text{ cm h}^{-1}$ . The largest river, Lupar, had a high  $k_{600,FC}$  of  $20.5 \pm 4.9 \text{ cm h}^{-1}$  as well, which is probably owed to the high flow velocity ( $2.5 \text{ m s}^{-1}$ ). The Saribas main river had a  $k_{600,FC}$  of  $13.2 \pm 11.0 \text{ cm h}^{-1}$ , with large spatial variability. The wind speed averaged  $3.0 \text{ m s}^{-1}$  during our 2013 sampling period and  $2.3 \text{ m s}^{-1}$  during the 2014 sampling period. The average  $k_{600,W92}$  calculated with W92 were one order of magnitude lower than the experimentally determined ones, with  $3.1 \text{ cm h}^{-1}$  during the dry season and  $1.9 \text{ cm h}^{-1}$  during the wet season.

Atmospheric  $p\text{CO}_2$  averaged  $403.6 \mu\text{atm}$  in the dry season (2013) and  $414.4 \mu\text{atm}$  in the wet season (2014). Atmospheric  $\text{CO}$  was  $77.91 \text{ ppb}$  in June 2013, corresponding to  $77.49 \text{ natm}$ . The average monthly mean for March was  $145.93 \text{ ppb}$ , corresponding to  $145.58 \text{ natm}$ . The calculated  $\text{CO}_2$  and  $\text{CO}$  fluxes in the lower, mid- and upper estuar-



ies are summarized in Table 3. Fluxes for the lower estuary were derived for the Lupar river (Fig. 5). Estimates for the upper estuaries were based on our  $p\text{CO}_2$  measurements in the freshwater region and the average  $k_{600,FC}$  of Lupar and Saribas, respectively (Table 3).  $\text{CO}_2$  fluxes determined with the floating chamber ( $F_{\text{CO}_2,FC}$ ) ranged between 14 and 272  $\text{mol m}^{-2} \text{yr}^{-1}$  and CO fluxes ( $F_{\text{CO},FC}$ ) between 0.8 and 1.9  $\text{mmol m}^{-2} \text{yr}^{-1}$ . In comparison, using  $k_{600,W92}$ , we obtained  $\text{CO}_2$  fluxes between 2 and 31  $\text{mol m}^{-2} \text{yr}^{-1}$ .

Like  $p\text{CO}_2$ , the  $\text{CO}_2$  fluxes were highest in the mid-estuaries, with  $F_{\text{CO}_2,FC}$  ranging between 76 and 272  $\text{mol m}^{-2} \text{yr}^{-1}$ . The CO flux from Lupar was twice as high in the mid-estuary than in the lower 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  $\text{km}^2$ , which corresponds to 3 % of the catchment area, and the Saribas (excluding the tributary) estuary has a surface area of 102  $\text{km}^2$  (5 % of the catchment). The total water-atmosphere flux for the Lupar was  $0.31 \pm 0.09$  and  $0.09 \pm 0.08 \text{ Tg C yr}^{-1}$  for the Saribas (see Table 4). The contribution of CO to these terms is negligible.


## 4 Discussion


### 4.1 Sources and fate of carbon in the estuaries

#### 4.1.1 Dissolved and particulate organic matter

It is striking that both DOC and  $\text{CO}_2$  are higher in the estuaries than in the freshwater region. This means that carbon is not conservatively transported to the ocean and that a source of both DOC and  $\text{CO}_2$  exists in the estuaries. C/N ratios in DOM (average: 40.6) clearly suggest a terrestrial origin (Fig. 4a). 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. Given that peatlands cover 30.5 and 35.5 % of the catchments, we had expected a larger contribution. DOC concentrations in the Maludam

river, the main river draining the Maludam peninsula, were more than ten times higher ( $3690 \mu\text{mol L}^{-1}$ , Müller et al. (2015)) than the measured freshwater end-member of both Lupar and Saribas. If we assume that all peat-draining tributaries exhibit these high DOC concentrations, elevated DOC concentrations would have been expected in the estuaries as well. Even though the estuarine DOC maximum indicates that peat-draining tributaries are indeed relevant sources of DOC to the estuaries, their contribution is small measured against the extent of peatlands in the catchment. Thus, the simple assumption that high-DOC inputs are proportional to the peatland coverage is not valid in this case, probably because the peatlands are located very close to the coast (Müller et al., 2015).

Likely, a part of the DOC that reaches the Lupar and Saribas estuaries is also 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 these processes could be important as well. A partial conversion of DOC to POC is consistent with the high POC concentrations and with the C/N ratios in particulate organic matter (POM) (8.1–14.1).  is likely a mixed signal from marine and terrestrial sources (Fig. 4b), in agreement with the relatively low  $\delta^{13}\text{C}$  values, which are indicative of both terrestrial soil and vascular plant material and phytoplankton (Bianchi and Bauer, 2011). We thus attribute those high POM concentrations to both river discharge and sediment resuspension due to the tidal currents.

 estuaries, POM may be degraded, deposited or exported to the continental shelf. It was shown that carbon burial in low-energy environments was a relevant sink of carbon in the Yangtze and Hudson estuaries (Zhu and Olsen, 2014). For example, 42 % of the carbon deposited on intertidal sediments of the Scheldt estuary was buried (Middelburg et al., 1995), suggesting that sediments can make a significant contribution to the retention of carbon in estuaries.

## 4.1.2 Controls on CO<sub>2</sub>



The elevated  $p\text{CO}_2$  in the Lupar and Saribas estuaries and the depletion of  $\delta^{13}\text{C}\text{-DIC}$  suggest that respiration plays an important role for the removal of organic matter (OM) in the estuaries as well. Respiration could take place in the water column (pelagic respiration) or in the sediments (benthic respiration).

Generally, pelagic respiration rates are largely controlled by temperature and the availability of organic substrates (Hopkinson and Smith, 2005). The relatively high concentrations of terrestrial organic matter (DOM + POM) and the high temperatures in the Lupar and Saribas estuaries suggest considerable rates of pelagic respiration, which would explain the relatively high  $p\text{CO}_2$  and the correlation of  $\text{CO}_2$  and AOU. Additionally, estuarine  $p\text{CO}_2$  is usually highest in high-turbidity zones (Abril and Borges, 2004), where the light penetration depth and thereby photosynthetic  $\text{CO}_2$  uptake are limited. 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 OM (Crump et al., 1998), resulting in pronounced net heterotrophy. Due to the strong tidal currents in the Lupar and Saribas estuaries, particle sedimentation is probably delayed by turbulence, leaving more time for the pelagic community to respire OM (Hopkinson and Smith, 2005).


Benthic respiration accounts on average for 24 % of the total system production in estuaries (Hopkinson and Smith, 2005). Although this respiration is largely aerobic, OM decomposition can also occur through denitrification, manganese, iron or sulfate reduction and methanogenesis. Middelburg et al. (1995) showed that 58 % of the carbon delivered to intertidal sediments in the Scheldt estuary was remineralized. The produced  $\text{CO}_2$  may be detected in estuarine waters (Cai et al., 1999) or escape to the atmosphere from the exposed sediment surface. This represents an additional  $\text{CO}_2$  flux that we did not account for in our study. Therefore, future work should include the carbon supply to and remineralization rates in intertidal sediments.

Although  $p\text{CO}_2$  is relatively high, oxygen depletion is quite moderate in comparison. For example, Chen et al. (2008) measured  $\text{CO}_2$  partial pressures between 690 to 2680  $\mu\text{atm}$

in the eutrophicated Pearl river estuary (see Table 5) along with AOU up to  $239 \mu\text{mol kg}^{-1}$ , resulting in hypoxia at the river mouth. Although we found similarly high and even higher  $p\text{CO}_2$ , 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.

Another important control on  $p\text{CO}_2$  is pH, which varied spatially by 1.3 (2013) and 0.8 (2014) in the Lupar and Saribas estuaries. This can largely be attributed to the mixing of seawater and freshwater along the estuary, as indicated by the correlation of pH with salinity. Additionally, inputs from peat-draining rivers, which are highly acidic ( $\text{pH} < 4$ , Kselik and Liong (2004); Müller et al. (2015)), might decrease pH. Lower pH shifts the carbonate system towards more free  $\text{CO}_2$ , consistent with the elevated  $p\text{CO}_2$  observed in the Lupar and Saribas estuaries. On the other hand, respiratory  $\text{CO}_2$  might decrease pH. It cannot be ultimately resolved whether the pH drives  $p\text{CO}_2$  or whether respiration drives the pH. In-situ measurements of pelagic and benthic respiration rates could help resolve details about these mechanisms.

#### 4.1.3 Photochemical degradation of organic matter

In addition to respiration, the diurnal CO cycle observed in the Lupar and Saribas estuaries (Fig. 7) suggests that photodegradation is another pathway for the removal of DOC. 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  $2.25 \text{ nmol L}^{-1}$ , 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 photochemically produced from particles (Xie and Zafiriou, 2009).  These authors found that in coastal waters, CO photoproduction from particulates was 10-35 % that of CDOM. We could not establish a clear

relationship between SPM and CO for the Lupar and Saribas estuaries. However, the low CO concentrations suggest that particulates limited CO photoproduction rather than supporting it. 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. UV radiation changes the composition of CDOM (Zhang et al., 2009), which increases its bioavailability (Amon and Benner, 1996; Moran et al., 2000). Tranvik et al. (2000) showed that in nutrient-poor (oligotrophic) systems, the net effect of radiation is an enhancement of bacterial growth, as photochemical reactions increase not only the bioavailability of organic carbon compounds, but also that of nitrogen and phosphorous. It is thus to be assumed that photochemistry plays an important role in our study area, which would merit further investigation.

## 4.2 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 DOC 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  $p\text{CO}_2$ .

For Lupar and the Saribas main river, though, we did not observe any major differences between wet and dry season  $p\text{CO}_2$  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.

### 4.3 CO<sub>2</sub> and CO fluxes



It has been previously suggested that Southeast Asian estuaries are rather moderate sources of CO<sub>2</sub> 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<sub>2</sub> emissions from both the Lupar mid-estuary ( $F_{\text{CO}_2,FC} = 119 \pm 28 \text{ mol m}^{-2} \text{ yr}^{-1}$ ) and the Saribas tributary ( $F_{\text{CO}_2,FC} = 272 \pm 167 \text{ mol m}^{-2} \text{ yr}^{-1}$ ) are higher than the global average of  $37.4 \text{ mol m}^{-2} \text{ yr}^{-1}$  for mid-estuaries (Chen et al., 2012). Certainly, elevated CO<sub>2</sub> fluxes can be partially attributed to high temperatures, which decrease the solubility of CO<sub>2</sub> in water and increase the gas exchange velocity. However, the average value reported for small deltas in this region is  $41.8 \text{ mol m}^{-2} \text{ yr}^{-1}$  (Laruelle et al., 2013), which is also lower than the fluxes from Lupar and the Saribas tributary. The fluxes from the Saribas mid-estuary appear to be higher than those values, too ( $F_{\text{CO}_2,FC} = 76 \pm 64 \text{ mol m}^{-2} \text{ yr}^{-1}$ ), 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. The comparison between  $F_{\text{CO}_2,FC}$  and  $F_{\text{CO}_2,W92}$  revealed a considerable difference (see Table 5). However,  $F_{\text{CO}_2,W92}$  in the mid-estuaries was still higher ( $12\text{--}31 \text{ mol m}^{-2} \text{ yr}^{-1}$ ) than the values of Chen et al. (2013) and could in-

dicate that the presence of peatlands makes a notable difference for CO<sub>2</sub> emissions from tropical estuaries.



CO flux estimates ( $F_{CO,FC}$ ) 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  $F_{CO,W92}$  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<sub>2</sub> 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 floating chambers has been a matter of debate. Arguments exist both for floating chambers 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,  $k_{600,FC}$  were much higher than  $k_{600,W92}$ , so that here, the question is rather whether the floating chamber method 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 floating chamber method (Matthews et al., 2003; Vachon et al., 2010), although chambers 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 floating chamber 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. Our setup could be improved by monitoring the temperature in the chamber headspace, which was not done during this study. We assumed that the temperature increase was limited because of the short time of deployment (5-10 minutes).

Taken together, Lupar and Saribas deliver 0.4 Tg organic carbon to the South China Sea every year and release approximately the same amount of carbon to the atmosphere as CO<sub>2</sub>.

## 5 Conclusions

Overall, we conclude that these estuaries in a peat-dominated region receive considerable amounts of terrestrial organic carbon, only a minor part of which was contributed by peat-draining tributaries, however. Estuarine  $p\text{CO}_2$  was largely driven by aerobic respiration of OM and pH variability. OM degradation was likely supported by photochemistry, as indicated by a diurnal variability of CO concentrations in the surface water. Overall, CO<sub>2</sub> emissions to the atmosphere were substantial if compared to other tropical and subtropical sites, while CO emissions were moderate, because photoproduction was limited by a high turbidity. We suggested that the use of a wind-driven turbulent diffusivity model (W92) leads to a gross underestimation of the fluxes, because it neglects turbulence caused by tidal currents and river discharge. Aside from net heterotrophy, we hypothesized that a fraction of the DOC was removed by adsorption onto estuarine particles. 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<sub>2</sub> production and, ultimately, emission from the estuary.



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**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.

	DOC ( $\mu\text{mol L}^{-1}$ )		POC ( $\mu\text{mol L}^{-1}$ )		DIN ( $\mu\text{mol L}^{-1}$ )		DO (%)	
	dry	wet	dry	wet	dry	wet	dry	wet
Lupar LE	142*	n.d.	62*	n.d.	7*	n.d.	n.d.	n.d.
Saribas LE	n.d.	244*	n.d.	42*	n.d.	18*	n.d.	100.4*
Lupar ME	340	338	456	650	22	20	70.8	94.4
Saribas ME	258	281	766	292	30	14	82.8	85.8
Saribas tributary	685	374	2040	281	22	11	n.d.	82.8
Lupar UE	89	208	79	131	5	5	84.4	93.3
Saribas UE	312*	n.d.	4114*	n.d.	19*	n.d.	63.6*	n.d.

LE: Lower estuary (salinity > 25).

ME: Mid-estuary (salinity 2–25, for the 2013 spatial extent of the rivers).

UE: upper estuary.

\* denotes that only one data point was available.

**Table 2.** Median CO<sub>2</sub> partial pressures and CO concentrations, respectively.

	<i>p</i> CO <sub>2</sub> (µatm)		CO (nmol L <sup>-1</sup> )	
	dry	wet	dry	wet
Lupar LE	640 ± 105	662 ± 36	1.4 ± 2.5	0.7 ± 0.1
Saribas LE	n.d.	n.d.	n.d.	n.d.
Lupar ME	2461 ± 574	1849 ± 881	1.4 ± 1.1	0.5 ± 2.7
Saribas ME	2240 ± 442	2235 ± 304	0.5 ± 0.9	0.7 ± 0.7
Saribas tributary	5064 ± 840	2925 ± 789	0.5 ± 0.7	0.4 ± 0.5
Lupar UE	1527 ± 38	1021 ± 357	n.d.	n.d.
Saribas UE	1159 ± 29	n.d.	n.d.	n.d.

LE: Lower estuary (salinity > 25).

ME: Mid-estuary (salinity 2–25, for the 2013 spatial extent of the rivers).

UE: upper estuary.

Values are median ± one standard deviation.

**Table 3.** CO<sub>2</sub> and CO fluxes in the Lupar and Saribas estuaries determined with a floating chamber.

	<i>F</i> CO <sub>2</sub> (mol m <sup>-2</sup> yr <sup>-1</sup> )			<i>F</i> CO (mmol m <sup>-1</sup> yr <sup>-1</sup> )	
	LE	ME	UE	LE	ME
Lupar	14 ± 3	119 ± 28	60 ± 14	0.9 ± 0.2	1.9 ± 0.5
Saribas	n.d.	76 ± 64	33 ± 28	n.d.	0.8 ± 0.6
Saribas tributary	n.d.	272 ± 167	n.d.	n.d.	0.9 ± 0.6

LE: Lower estuary (salinity > 25).

ME: Mid-estuary (salinity 2–25, for the 2013 spatial extent of the rivers).

UE: upper estuary.

**Table 4.** Total CO<sub>2</sub> fluxes estimated for the Lupar and Saribas aquatic systems. All numbers are in Tg C yr<sup>-1</sup>.



	Lupar	Saribas	Total
Estuarine CO <sub>2</sub> emissions	0.31 ± 0.09	0.09 ± 0.08	0.40 ± 0.17
DOC export	0.12 ± 0.05	0.03 ± 0.01	0.15 ± 0.05
POC export	0.15 ± 0.18	0.06 ± 0.07	0.21 ± 0.25
TOC export	0.27 ± 0.23	0.09 ± 0.07	0.36 ± 0.30

**Table 5.** Comparison of CO<sub>2</sub> and CO values for partial pressure and concentration, respectively, and fluxes for different tropical and subtropical sites.

CO <sub>2</sub>				
Site	$p\text{CO}_2$ ( $\mu\text{atm}$ )	$F\text{CO}_2$ ( $\text{mol m}^{-2} \text{yr}^{-1}$ )	$k$ model	Reference
lower estuaries in Sarawak, MY	662	14	FC	This study
mid-estuaries in Sarawak, MY	1849–5064	76–272	W92	This study
upper estuaries in Sarawak, MY	1021–1527	12–31	W92	
Malaysian estuaries	n.d.	33–60	FC	This study
Indonesian estuaries	n.d.	6–7	W92	
Pearl river estuary, CN	690–2680	0.4–6.3	W92	Chen et al. (2013)
Brazilian estuaries	162–8638	8.5–54.1	W92	Chen et al. (2013)
Indian estuaries	300–18492	n.d.	n.d.	Chen et al. (2008)
		0.3–63.9	RC01	Noriega and Araujo (2014)
		–0.01–132.1	W92	Sarma et al. (2012)
CO				
Site	CO ( $\text{nmol L}^{-1}$ )	$F\text{CO}$ ( $\text{mmol m}^{-2} \text{yr}^{-1}$ )	$k$ model	Reference
lower estuaries in Sarawak, MY	0.7	0.9	FC	This study
mid-estuaries in Sarawak, MY	0.4–1.4	< 0.1	W92	
Seto Inland Sea and Ise Bay, JP	n.d.	0.8–1.9	FC	This study
Equatorial Pacific	1.9–7.7	0.1–0.3	W92	
Mauritanian upwelling	0.1–6.2	0.7–4.0	LM86	Ohta et al. (2000)
East China and Yellow Sea	0.1–7.0	1.4–1.6	LM86	Ohta (1997)
		1.7–3.5	N00	Kitidis et al. (2011)
		0.4–6.8	W92	Yang et al. (2011)

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

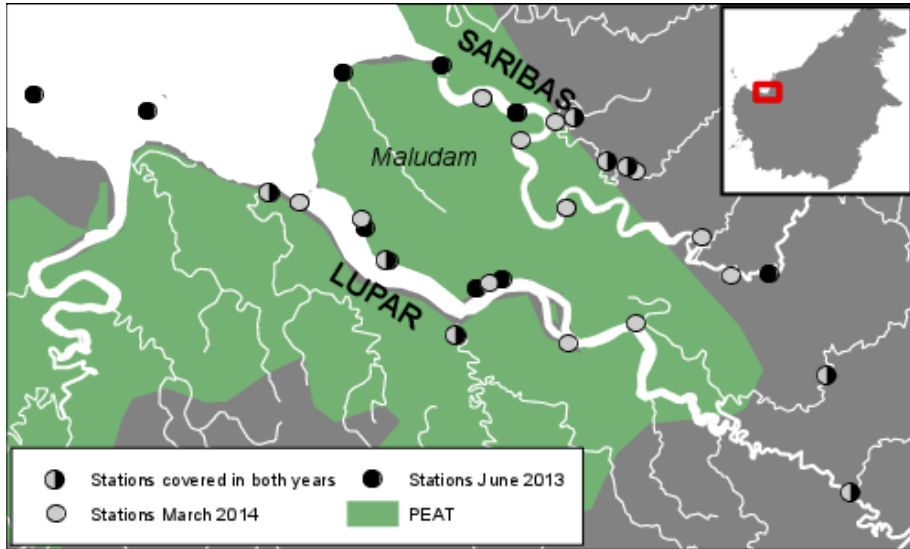
FC = floating chamber measurements.

W92 = Wanninkhof (1992).

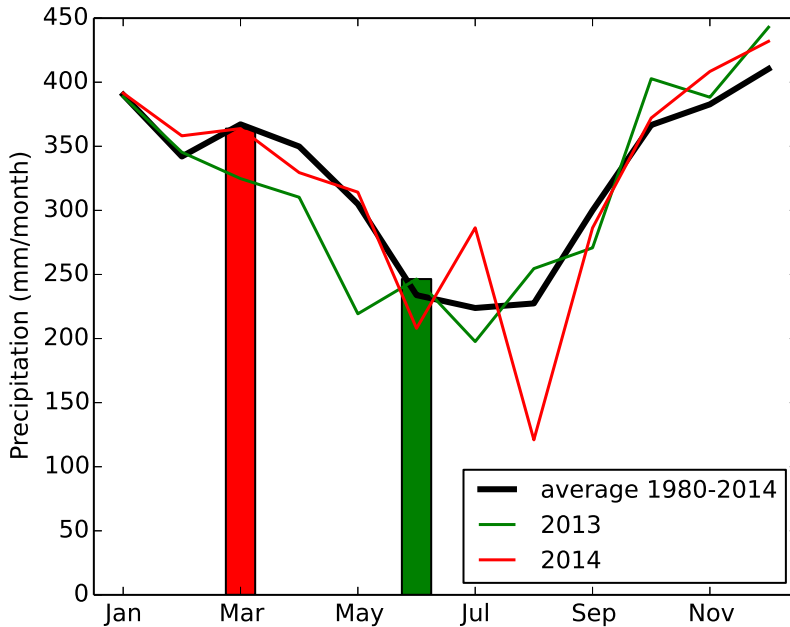
N00 = Nightingale et al. (2000).

LM86 = Liss and Merlivat (1986).

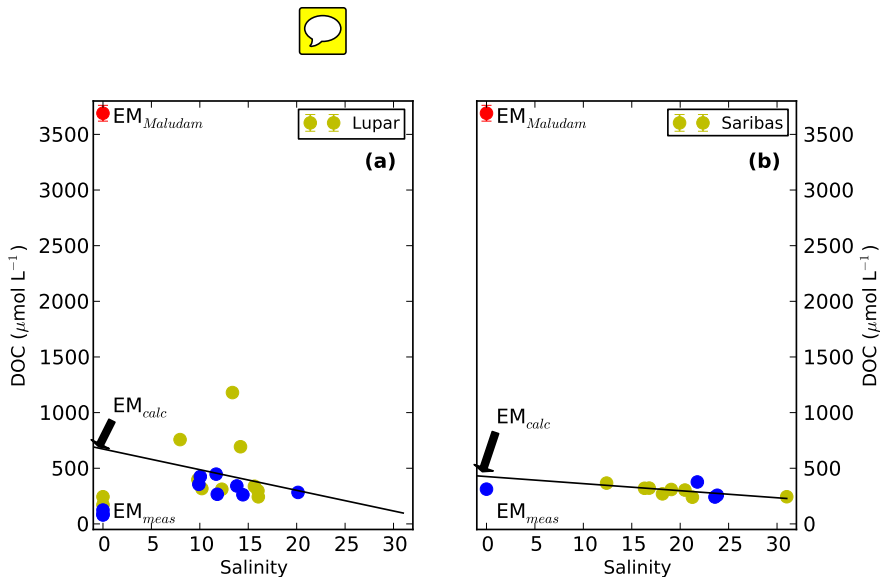
RC01 = Raymond and Cole (2001).



**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).

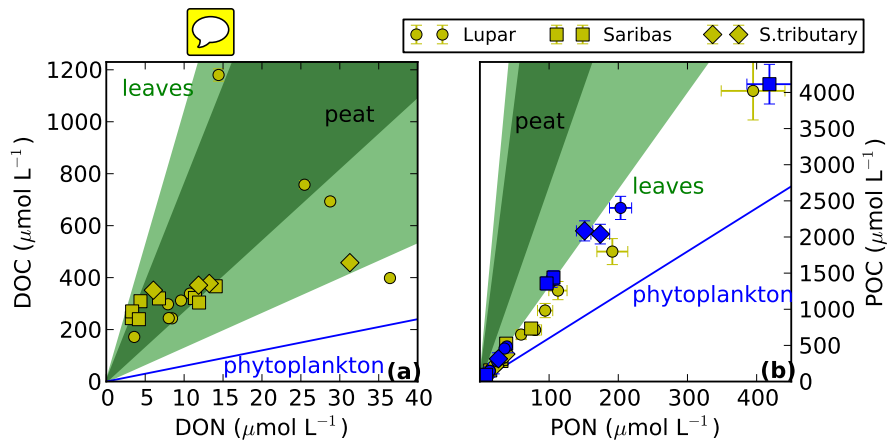


**Figure 2.** Average monthly precipitation during 1980–2014 (black), monthly precipitation in 2013 (green) and 2014 (red). The bars indicate the rainfall during our sampling months. It can be seen that the rainfall pattern was not much different from the historical average during these periods.

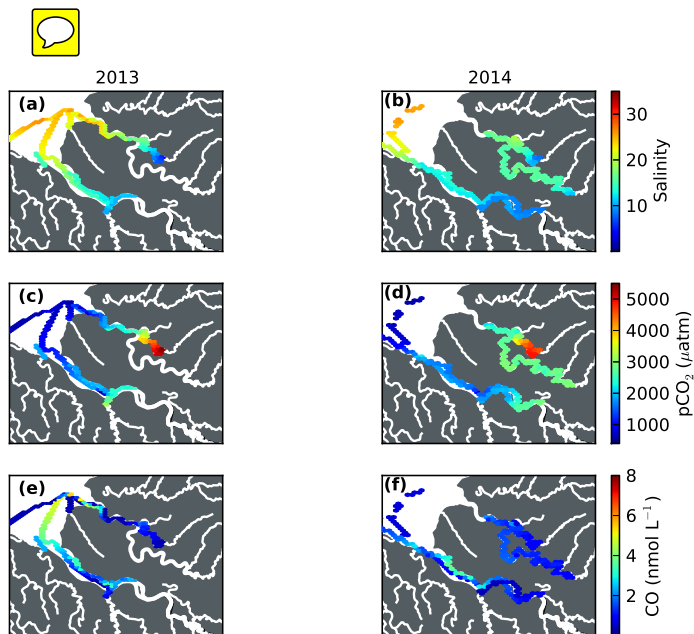


**Figure 3.** Dissolved organic carbon (DOC) concentrations vs. salinity in the Lupar (a) and Saribas (b) estuaries. The red marker refers to the zero salinity end-member in the peat-draining tributaries. The line indicates the DOC-salinity regression line, labels refer to theoretical and measured end-member values as described in the text.

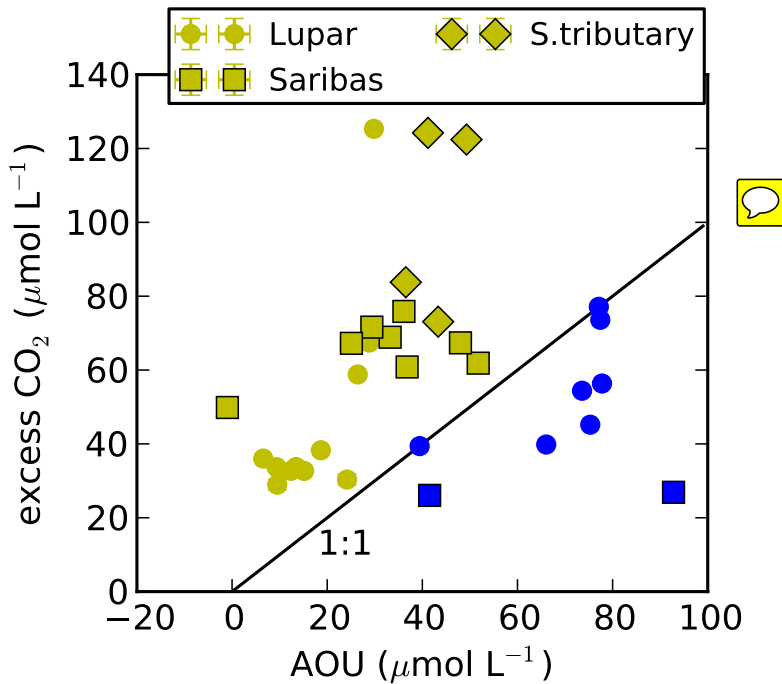




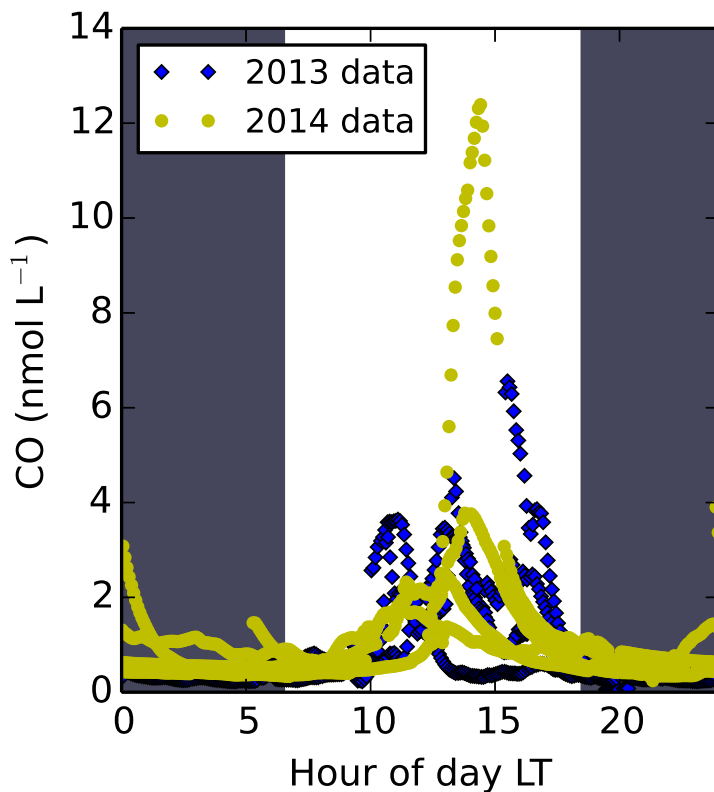
**Figure 4.** Carbon-to-nitrogen (C/N) ratios in dissolved organic matter **(a)** and in particulate organic matter **(b)**. Blue markers refer to samples from 2013, yellow markers refer to samples from 2014. The individual rivers are denoted by different symbols. Lines refer to the C/N ratios that would be expected for tropical peat and leaves (Baum, 2008) and for phytoplankton.



**Figure 5.** Salinity (a and b), CO<sub>2</sub> 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<sub>2</sub>. 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 gathered in this figure, 2013 and 2014 data are distinguished with different colors and symbols. Note that the boat was usually moving during daytime and more often not moving during nighttime.