

## ***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,

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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, I.23: 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 μm?*

Yes, the specification of these filters indicates that they have a particle retention of 0.6-0.8 μm, 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, l.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, l.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, l.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, l.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, l.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, l.25: I guess you mean the "total flux between water and atmosphere for the Lupar was . . ."*

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

*8314, l.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, l.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, l.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, l.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, l.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, l.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, l.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, l. 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, l.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, l.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, l.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, l.5: Better "floating chambers" instead of "Fcs".*

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

*8321, l.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.

#### References

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Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/12/C5227/2015/bgd-12-C5227-2015-supplement.pdf>

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