

Interactive comment on “Nitrous oxide and methane in two tropical estuaries in a peat-dominated region of North-western Borneo” by D. Müller et al.

D. Müller et al.

dmueller@iup.physik.uni-bremen.de

Received and published: 23 March 2016

We thank Anonymous Referee 1 for his helpful comments and suggestions. Our detailed answers can be found below.

This paper describes CH₄ and N₂O distributions in two tropical estuaries. Current literature for estuarine CH₄ and N₂O concentrations is still limited, and this type of study is significant for our scientific understanding and relevant to BG. The paper is well written and reads easily. However, there are several issues that need to be addressed prior to publication.

1) The dataset of CH₄ and N₂O concentrations does not cover the region of low

C1

salinity (0-5), where high CH₄ and N₂O might be expected. Furthermore, no sample was taken at the river-end member. Hence it is hard to take a full picture of trace gas variation in the whole estuary system.

The correlation of N₂O with salinity during the dry season indicates that the freshwater end-member might indeed exhibit the highest N₂O during the dry season. We calculated the expected river end-member using the correlation of N₂O with salinity during the dry season and found concentrations of 9.1 nM, (Lupar, $r = 0.5$), 9.3 nM (Saribas, $r=0.8$) and 15 nM (Saribas tributary, $r=0.9$). For CH₄, this is a bit harder to do, as we did not observe a correlation between methane and salinity. While we agree that the lack of data in the low salinity region deserves a more thorough discussion, which we will include in the revised manuscript in sections 4.2 and 4.3, our main conclusions can be maintained despite the lack of data for the upper estuaries:

- 1) Eutrophication did not lead to enhanced N₂O. - Data from the river end-member would not provide additional information, as eutrophication was not observed in the river end-member.
- 2) DIN was a poor predictor of N₂O. - This was mainly inferred from Figure 2b), a river end-member data point is not likely to change this overall observation.
- 3) Postulation of additional N₂O and CH₄ sources during the wet season. - This conclusion is based mainly on the observation of high N₂O and CH₄ values at salinities 10-20. Of course, it would be extremely interesting to see if a similar observation could be made in the freshwater region.

2) Page 5, line 13: Does the DO sensor calibrated with Winkler titration method?

The FDO 925 sensor was calibrated by the manufacturer (WTW, Germany). According to the manufacturer, user calibration is not required for the specified lifetime of the sensor. Nevertheless, a routine function check was performed in water vapor saturated air, using the check and calibration vessel (FDO (R) check) that was provided with the sensor. This information will be added in the revised manuscript.

C2

3) Page 6, line 25: I think the authors should give a little more detail about the k600 they used. For example, were they measured in situ or calculated by widely used wind-speed related relationships in the literature?

The k600 that we used were derived from CO₂ fluxes measured with a floating chamber in 2014. The measurements are described in detail in Müller et al., 2015a. From simultaneous measurements of the CO₂ flux and the water and air pCO₂, we derived kCO₂ and, ultimately, k600 for these estuaries. In the revised manuscript, we will change the following sentence:

For k, we used k600 values that were reported for the Lupar and Saribas estuaries in Müller et al. (2015a).

to

For k, we used k600 values that were derived for the Lupar and Saribas estuaries using the floating chamber method (Müller et al., 2015a). Floating chamber measurements were conducted at several locations along the estuaries during the wet season campaign and averaged over the spatial extent of the individual estuaries. We argued in Müller et al. (2015a) that the k600 values determined in this way are more appropriate than commonly used wind speed parameterizations, which neglect the influence of tidal currents and the water flow velocity.

4) Table 3 showed that dissolved CH₄ in the Lupar estuary was low and undersaturated (2nM and 88%). What's possible reasons for this?

This seems to be an artifact. The reasons why we think so are the following: 1.) There are only two datapoints directly following each other which indicate undersaturation. 2.) With the exception of CO, all gas concentrations that we could retrieve from the respective spectra indicate undersaturation or atmospheric equilibrium values (N₂O, CH₄ and CO₂). This indicates that atmospheric air was in the measurement cell. 3.) No measurements were taken during the 20 minutes preceding the undersaturation values. A background measurement (empty cell) had been performed before that, and

C3

the cell was filled with atmospheric air afterwards before the measurements of equilibrator air continued. If we reconsider these facts, it seems likely that atmospheric air was still in the cell. We would therefore exclude the two data points from the analysis. The numbers will be corrected in the revised manuscript.

5) Table 4 didn't show k600 for dry season, and the authors should explain what k600 was used for the calculation for dry season. k600 for Saribas tributary and Lupar estuary are almost twice of that for Saribas. Do the authors have any idea of the reason?

We used the same k600 for the dry and wet season. In the revised manuscript, we will add a more detailed description of the k600 values used in the methods section (see comment 3).

We discussed the variability of the k600 values in Müller et al., 2015a and after adding more detailed information in the methods section, the reader will be referred to that publication. There, we reasoned that the strong currents in the Lupar estuary are responsible for the relatively higher k600. The higher gas exchange velocity in the Saribas tributary if compared to the Saribas is consistent with the notion that the gas exchange velocity decreases with increasing stream order (Raymond et al., 2012).

6) Figure 1: Scales should be added and the South China Sea should be located on the map.

The Figure will be revised accordingly.

7) Figure 2: N₂O vs salinity, it was shown that there are great N₂O peaks during wet seasons between the areas with salinity of 12-15, suggesting a significant N₂O source. The authors should discuss this in the text.

On page 10, lines 23-27 of the discussion paper, we tried to combine several lines of evidence as to where this N₂O comes from. Our argument is as follows. 1) There are sources in the estuary (i.e., salinities 10-20) in the wet season which we did not observe in the dry season. 2) Another feature of N₂O that we observed in the wet but not in the dry season was the co-variation of N₂O with CH₄. 3) In the wet season,

C4

both N₂O and CH₄ varied with the tides, with higher concentrations during low tide. We inferred from 1) that there are additional sources of N₂O in the wet season, from 2) that they are sources of both N₂O and CH₄ and from 3) that either tidal creeks or the estuarine sediments constitute this additional source. We will modify the sections 4.2 and 4.3 in the revised manuscript in order to provide a more specific and detailed discussion.

References

Müller et al. (2015a): Fate of peat-derived carbon and associated CO₂ and CO emissions from two Southeast Asian estuaries. *Biogeosciences Discussions* 12:8299-8340, doi: 10.5194/bgd-12-8299-2015

Raymond et al. (2012): Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. *Limnology and Oceanography: Fluids and Environments* 2:41-53. doi: 10.1215/21573689-1597669

Interactive comment on *Biogeosciences Discuss.*, doi:10.5194/bg-2016-4, 2016.