

We thank Ref#2 for the comments which helped to improve the manuscript significantly.

Anonymous Referee #2

The available data set for greenhouse gas concentrations in tropical rivers/estuaries and the resulting emissions to air is small, so this paper makes a potentially valuable contribution in this area. The dataset was interesting and while some trends in the data were reflected in other studies cited, yet other studies found contrasting results that I felt were not duly considered or were ignored. I was therefore looking for some further discussion and my overall impression was that the treatment was a little simplistic in several areas. I therefore consider that some significant modifications to the text are required. These, and some additional minor comments, are listed below.

L150: What certified gas standard values were used?

Reply (R): The standard gas mixtures have been calibrated against certified NOAA gas standards in the laboratory of the MPI for Biogeochemistry in Jena, Germany. Unfortunately, the values of the primary gas standards are not known to us.

L160-164: the mean relative errors of the gas analyses were acknowledged as being rather high and this was ascribed to long storage times. What were the storage times and were these the same for all samples? If not, is there any statistically significant difference between the errors for samples stored for “long” vs “short” times”? Also, was the greater sensitivity of CH₄ to storage shown by Wilson et al (2018) also the case here? This was not clear.

R: We added the mean storage time. Measurements of the Aug'16 samples were finished in Feb'17; measurements of the samples from the Mar'17 campaign were finished in Sept'17, and measurements of the samples from the Sept'17 campaign were finished in Feb'18. We did not see a trend of the mean relative error with storage time or a significant difference between the sampling campaigns.

We think that the greater sensitivity of CH₄ samples is the reason for the higher mean relative error as described in Wilson et al. (2018). We modified the sentence which reads now 'The higher mean measurement error of the CH₄ samples (compared to the N₂O measurements) was attributed to the fact it was shown that CH₄ samples are more sensitive to storage time than N₂O samples (Wilson et al., 2018).'

L168-169: Was the pre-washing protocol described here and the method for collecting ancillary samples also used for gases? The description of dissolved gas sample collection was lacking in detail.

R: Water was collected at 1m depth using a Niskin sampler. Sample vials for N₂O/CH₄ were rinsed with sample water, filled to the maximum (without air bubbles), sealed on the spot using a crimper, and kept on ice for a maximum of 3 hours. When returned to the field station, HgCl₂ was immediately added to stop any biological activity and samples were stored at 4 degree until shipment. We added the missing information to the text.

L173: What was the precision of the DOC analyses? Supplementary data from another paper are cited but the precision should be stated here. Also, there does not seem to be any description of the method used for pH.

R: We added the requested information on the precision of the DOC analyses and the method used for pH. DOC measurement performance was monitored using certified deep-sea water from the Hansell Laboratory, University of Miami (42–45 $\mu\text{mol L}^{-1}$). Our analyses consistently yielded slightly higher values for the reference water, with a long-term mean (± 1 SD) of $47 \pm 2.0 \mu\text{mol L}^{-1}$ ($n = 51$).

L200: It would be useful to briefly consider the scale of the potential errors in the values of k_{600} applied. It was stated that mean values from another (seasonal) study were used but what was the range of values estimated in that study? These values were derived using rivers other than those studied here but are they morphologically similar? As gas exchange in rivers is determined by river flow rates, depth, gradient and bedform, it would be worth commenting on whether these variables are similar for the study rivers and for those from which k_{600} was derived.

R: We modified the text as requested:

1) The standard deviations of the k_{600} data given in Müller et al. (2016) were added.

2) We added ‘Both rivers have very similar environmental and morphological settings in comparison to the rivers studied here.’

3) At the end of the section we added: ‘ k_w in rivers depends on the turbulence at the river water/atmosphere interface, which in turn is mainly affected by water current velocity, water depth and river bed roughness and to a lesser extent by the wind speed (Alin et al., 2011; Borges and Abril, 2011). Since the k_{600} reported by (Müller et al., 2016a) were determined only during the wet season (March 2014), our mean k_{600} is biased because it does not account for a lower k_{600} which is to be expected during the dry season (resulting from a lower water current velocity (Alin et al., 2011)). This results in an overestimation of the flux densities.’

L205: It was stated that the value of k_{600} used here was close to the mean value used in Alin et al (2011) but only their range, which is quite wide, was given.

R: We added the requested information.

L210: Was monthly rainfall data the best resolution available and if not, why was it chosen? The rainfall data on the cited website seem to be available for hourly intervals so it would at least be useful to briefly consider the overall ranges for the months in question based on these higher resolution data.

R: The monthly rainfall data had been chosen because we think it is representative of the typical rainfall patterns. Indeed we refined our analysis by considering now the accumulated rainfall during up to four weeks prior to the date of sampling. For this we used rainfall data with a 3h resolution (available from the same website). We modified the text of Section 3.4 to account for this.

L236, Reference to Figure 2a. There is a spread of N_2O (also CH_4) for some rivers at zero salinity, but given the resolution of these plots are these values all truly riverine or does the plot mask large changes taking place at very low salinities? It is important to unequivocally make this point. To show this more clearly it might be worth considering using composite plots in which the x-axis left of zero salinity is plotted as “distance upstream”. That would clearly show the variability along the length of

the catchment sampled and may help reveal any tributaries with different CH₄/N₂O signatures from the main river in each case. It was also stated that the decreasing trend of N₂O with salinity was only linear in the Rajang in March, but given the errors inherent in the analyses couldn't the Simutan and Sematan (incidentally, these are both labelled "(d)" in the figure caption) also be linear?

R: In order to address the reviewers request we added a new Figure 3 which shows the N₂O and CH₄ concentrations along the pH gradients.

We do not think that the relationships for the Simunjan and Sematan Rivers are linear: Even when taking into account the associated measurement errors the data from the Simunjan River are well below a linear mixing line from endmembers at sal = 0 and sal = 30. There might be linear relationship for the Sematan River, but only when ignoring the data point at sal = 10.

We corrected the typos in the Figures captions.

L256: The lack of overall trends for N₂O (also CH₄) with oxygen and nutrients are stated to be in-line with the results of Borges et al (2015) and Müller et al (2016a) but this is perhaps a bit dismissive of contrasting observations made in other studies. Richey et al (1998), Bouillon et al (2009), Borges et al (2015), Teodoru et al (2015) and Upstill-Goddard et al (2017), among others, did find clear correlations of N₂O with oxygen and nutrients, and Upstill-Goddard et al (2017) noted that N₂O vs oxygen could be positive or negative depending on river "type". Consequently, some wider discussion of the current findings within this context seems warranted.

R: We added a sentence: 'There are, however, occasional observations in tropical rivers of N₂O relationships with O₂ and nutrients which were attributed to different river types such as swamp and savannah rivers (Upstill-Goddard et al., 2017).'

However, there does not seem to be a general (spatial or temporal) trend (we mentioned this in the introduction, see also Stanley et al., 2016). We think, therefore, that a more detailed discussion of results from other rivers (draining other ecosystems) does not improve our understanding of the results from peatland draining rivers presented here.

A some remarks about the references cited by the reviewer:

Bouillon et al. (2009) is missing in the reference list given by the reviewer. In the listed article (Bouillon et al., 2012) we could not find any N₂O/O₂ and N₂O/nutrients correlations. There are no N₂O data in Borges et al. (Sci Rep, 2015). The relationship of N₂O with O₂ mentioned in Richey et al., 1988, is far from being 'clear': 1) there are no statistics given and 2) the trend is only visible indirectly via plots of N₂O/CO₂ and AOU/CO₂. The relationships of N₂O with O₂ or nutrients mentioned in Teodoru et al. (2015) are far from being 'clear': The authors state: 'There was no correlation between N₂O and NH₄⁺ or NO₃⁻, while a positive relation with %DO was only found during wet seasons (data not shown).'

Line 280: Presumably the very high CH₄ sample that was excluded from the discussion was real, and not an artefact. It would be worth stating this, unless there is some reason to suspect otherwise.

R: In fact we considered the very high CH₄ concentration from the Simunjan River as real. In order to clarify this point we replaced 'further computations' with 'emission estimates'.

Line 296-299: Could the explanation of decreasing CH₄ with salinity be a little simplistic? At least one plot (figure 3f) would look almost conservative if the high value at around salinity 10 was excluded. Is the plot therefore indicating “removal” of CH₄ between an intermediate estuarine “endmember” at salinity 10 and the seawater endmember? If so it would be instructive to estimate the degree of removal of the CH₄ signal (by extrapolating the linear portion of the plot at high salinity back to zero and taking the ratio of that number to the salinity 10 value) that could then be ascribed to oxidation and/or gas exchange (notwithstanding that there are a very small number of data points in the plot).

R: A decrease of CH₄ concentration with increasing salinity was observed in the majority of the measurements, see Fig 3 a,c,e and f. No trend was only observed for the data in Fig 3b. (in Fig 3d no measurements were available at salinities >0). Occasionally occurring higher CH₄ concentrations were attributed to local point sources of CH₄. So, we think that it is justified to state that there was a ‘general decrease of CH₄ with increasing salinity’.

We agree that the suggested idea is useful for estimating the riverine CH₄ loss from the data presented in Fig 3f. However, we think that a (too) detailed interpretation of the data (based on only one river out of the six rivers measured) won't help to improve our general understanding of the CH₄ trends in the rivers/estuaries of NW Borneo.

L304 (Section 3.4): I wonder how meaningful it is to plot mean N₂O vs mean monthly rainfall. At the very least, some discussion of the likely errors in this approach might be necessary to establish its validity. Some questions are: is the relationship between rainfall and N₂O constant over different timescales? is it always linear? Could there be a variable lag time following initial rainfall (the length of which might relate to rain intensity and duration and the duration of any dry periods between successive rain events) before the N₂O signal appears in the rivers? What is the likely effect of rainfall on gas exchange (could suppress or enhance it) and simple dilution (which relates to rainfall intensity). The relationship between rainfall, local hydrogeology and river flow may be complex and affect N₂O processing in groundwater flow etc., so some more detailed discussion of the relationships between N₂O and rainfall seems warranted.

R: We refined our analysis by considering the relationship of the average N₂O/CH₄ concentrations with the accumulated rainfall from periods of up to four weeks prior to the date of sampling (= pre-sampling periods). (To this end, we now use rainfall data with a 3h resolution.) The linear N₂O/rainfall relationship is quite robust and does not change when considering varying pre-sampling periods of accumulated rainfall prior to the dates of sampling. To address the question of a variable lag time we now consider periods of 1-4 weeks of accumulated rainfall prior to the dates of sampling. The resulting correlation coefficients are given in the new Table 6. Since the relationship of N₂O and rainfall is robust over the given pre-sampling periods (1-4 weeks) we can conclude that the variability of time lag is negligible. (it would be great to have data on river discharge to answer this question, but these data were not available.) We modified this section.

The (revised) results for CH₄ are more complex: Statistical significant linear relationships occur only when considering periods of 1 or 1.5 weeks before the dates of sampling. We modified this section as well.

To our knowledge the effect of rainfall on the trace gas exchange in rivers has not been investigated so far. We think, therefore, that a discussion about potential effects of rainfall (which is also highly variable in time and space) on riverine gas exchange is too speculative.

L315 onward: Upstill-Goddard et al (2017) found both positive and negative relationships between CH₄ and oxygen in tropical rivers (Congo Basin) dependent upon river “type” (as for N₂O), which was ascribed to the possible presence or absence of macrophytes (as also discussed earlier by Borges et al). The current results should be contrasted with these and other earlier findings.

R: We added a sentence: ‘There are, however, occasional observations in tropical rivers of CH₄ relationships with O₂ which were attributed to different river types such as swamp and savannah rivers (Upstill-Goddard et al., 2017).’

However, there does not seem to be a general (spatial or temporal) trend (we mentioned this in the introduction). We think, therefore, that a more detailed discussion of results from other rivers (draining other ecosystems) does not improve our understanding of the results of peatland draining rivers presented here.

L345: It would be instructive to acknowledge the high degree of uncertainty in the flux estimates and to have some brief discussion of the likely major sources of these.

R: We added ‘[...] (iii) the wind speed-driven gas exchange in estuaries is not adequately represented, and (iv) the mean k₆₀₀ used here is most probably too high (see Section 3.3) resulting in an overestimation of the emissions.’ However, we think that a detailed discussion about the inherent uncertainties of air/river exchange flux densities and emissions is beyond the scope of this article.

Figure 2 and 3 captions. “cycles” should perhaps be “circles”

R: We replaced ‘cycles’ with ‘circles’.