

Interactive comment on “Nitrous oxide (N₂O) and methane (CH₄) in rivers and estuaries of northwestern Borneo” by Hermann W. Bange et al.

Anonymous Referee #1

Received and published: 26 June 2019

The authors report a very valuable data-set of dissolved CH₄ and N₂O concentrations obtained in several estuaries in Borneo. I have a few minor suggestions for improvement/clarification listed below.

L 39 : Please provide ranges of pH, O₂ and DOC. “very high/low” is vague.

L 77 : I suggest replacing “release” by “exchange”, since the direction of the flux is not necessarily always to the atmosphere, as shown here by frequent N₂O depletion in some rivers.

L 96 : CH₄ is also oxidized aerobically in freshwater sediments, in rivers (Kelley et al. 1995) and lakes (Frenzel et al. 1990).

L 111: The number of references seems excessive to back a simple statement on the

C1

occurrence of black water rivers in SE Asia.

L 142: Please specify how was the water collected for the CH₄/N₂O samples? Niskin bottle?

L152: Please provide the values of standards for N₂O/CH₄. Authors state that their standards were calibrated against NOAA standards, but NOAA standards have usually very low CH₄/N₂O values (close to atmospheric equilibrium), but given the reported concentrations, the measured pCH₄ and pN₂O should have strongly deviated from atmospheric equilibrium, unless the gas samples were diluted (in which case this needs to be specified).

L 166: Please specify how was pH measured.

L 171: Did you check if there was an interference of HgCl₂ on NH₄⁺ samples ? Based on personal experience HgCl₂ strongly modifies NH₄⁺ samples for colorimetric measurements.

L 247: Over-saturation of N₂O of 12,480% was reported in an agriculture impacted small stream of the Meuse Basin (Borges et al. 2018).

L 256-273: The authors develop the idea that N₂O production did not occur in black water rivers due to low pH values because of the protonation of NH₃ and the pH-dependent reduction of nitrification and denitrification. Consequently, the authors conclude N₂O production occurred in soils, and that N₂O was subsequently transferred to the river. However, peat soils themselves are also very acid, so the same reasoning of inhibition of N₂O production should also apply to soils. So, why should low pH inhibit N₂O production in river water but not in soils?

L 256-273: The experiments of Le et al. (2019) showed that nitrification was strongly inhibited but still occurred until pH 5.3, and was totally inhibited at pH 5.0. Since N₂O is produced as a by-product of nitrification, it is possible that the N₂O yield increases with decreasing pH (the same way that N₂O yield from nitrification increases with de-

C2

creasing O₂)? Even if this is not the case, the fact that nitrification is inhibited by pH but still occurs down to pH 5.3 still allows the possibility of N₂O production occurring in river water in the sampled sites. So there could still be a case for N₂O being produced in black-water rivers.

L 256-273: While the lowest values of pH in the ranges reported in Table 1 are clearly lower than 5.0 (the value at which nitrification was undetectable in the experiments of Le et al. (2019)), I cannot figure out how many observations of high N₂O coincided with pH < 5.0. It might be useful for the discussion to plot N₂O versus pH to show the reader how many data point of high N₂O occur at pH > and < 5.0.

L 315: Higher discharge/rain also leads to enhanced gas transfer velocities and loss of CH₄ to the atmosphere. Higher discharge/rain also leads to decreased residence time of water (flushing of water), which will decrease the accumulation of CH₄ in the water (even if sources such as sediment flux remain the same). Higher rain (surface runoff) also leads to simple dilution of all solutes (including CH₄).

L 316: A negative relation between CH₄ and discharge is not necessarily a general rule. Teodoru et al. (2015) reported higher CH₄ in the Zambezi River during high-waters and lower CH₄ during low-waters due to variable connectivity with floodplains. At a fixed station in the upper Congo, Borges et al. (2019) showed that the CH₄ seasonal evolution roughly follows the one of discharge. So in both studies a positive relation between CH₄ and discharge was reported.

L 318: Most of the low- vs high-water comparisons of MOX and CH₄ given by Sawakuchi et al. are for white water and clear water rivers, and only for one black river at a single station (Negro). I'm not sure this is sufficient to derive a general rule on methane oxidation in black water rivers.

Further, methane oxidation is a first order process, so should be lower when CH₄ concentrations are lower, so, it's unlikely that CH₄ oxidation is higher when CH₄ concentrations are lower, as stated by the authors.

C3

L 363: I suggest replacing "results" by resulted

Please explain how were the "average" flux calculated. It's unclear how the "average" flux intensities and integrated fluxes were derived to take into account the estuarine geometry. Estuaries are generally wider at the mouth than upstream ("funnel shaped"). So even if high salinity regions show lower flux intensities, their relative contribution to total flux will have more weight (relative larger surface area). To put it in other words a simple average of all of the data points will lead to an over-estimation of the flux intensities because the average will be biased towards low salinity values that in reality correspond to a lower surface of estuary. So, each data point needs to be weighted by a corresponding surface area (section of the estuary), and the average should be surface weighted. This requires a little bit of GIS but is feasible (even with Google Earth).

Figures 2 & 3: it could be useful to add in plots a legend of the symbols.

References

Borges, A., Darchambeau, F., Lambert, T., Bouillon, S., Morana, C., Brouyère, S., Hakoun, V., Jurado Elices, A., Tseng, H.-C., Descy, J.-P., & Roland, F. (2018). Effects of agricultural land use on fluvial carbon dioxide, methane and nitrous oxide concentrations in a large European river, the Meuse (Belgium). *Science of the Total Environment*, 610–611, 342 - 355

Borges AV, F Darchambeau, T Lambert, C Morana, G Allen, E Tambwe, A Toengaho Sembaito, T Mambo, J Nlandu Wabakhangazi, J-P Descy, CR Teodoru, S Bouillon (2019) Variations of dissolved greenhouse gases (CO₂, CH₄, N₂O) in the Congo River network overwhelmingly driven by fluvial-wetland connectivity, *Biogeosciences Discussions*, doi: 10.5194/bg-2019-68

Frenzel P, Thebrath B, Conrad R (1990) Oxidation of methane in the oxic surface layer of a deep lake sediment (Lake Constance). *FEMS Microbiol Ecol* 73:149–158

C4

Kelley CA, Martens CS, Ussler W III (1995) Methane dynamics across a tidally flooded riverbank margin. *Limnol Oceanogr* 40:1112–1129

Teodoru, C. R., Nyoni, F. C., Borges, A.V., Darchambeau, F., Nyambe, I., & Bouillon, S. (2015). Dynamics of greenhouse gases (CO₂, CH₄, N₂O) along the Zambezi River and major tributaries, and their importance in the riverine carbon budget. *Biogeosciences*, 12(8), 2431-2453.

Interactive comment on *Biogeosciences Discuss.*, <https://doi.org/10.5194/bg-2019-222>, 2019.