

# ***Interactive comment on* “Reliable reference for the methane concentrations in Lake Kivu at the beginning of industrial exploitation” by Bertram Boehrer et al.**

**Bertram Boehrer et al.**

bertram.boehrer@ufz.de

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Reply to anonymous Referee #2 Received and published: 9 August 2019

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The authors interested in the measurements of gases concentrations in very deep waters of Lake Kivu. This work is very interesting, since the latest studies were alarming and suggested that methane concentrations in Lake Kivu were increasing, and that a limnic eruption was possible in a near future. This study shows that gases concentrations, and especially methane concentrations, did not increase since the first measure-

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ments made by Schmitz and Tietze, and thus that methane production is not higher than methane oxidation+methane fluxes to the atmosphere. I think that this study is important and overall reliable, with good measurements methods. »»»»» We appreciate the kind words: We also appreciate that the important consequences for political decisions have been recognized by the reviewer.

Actually, I decided to put this manuscript in "major revisions" mainly for grammatical and language reasons, and also because numerous specifications and details must be added.

» We definitely appreciate any comment that is suited to improve the quality and legibility of our paper. Below, we indicate briefly, how we intend to include all comments by anonymous referee #2 in a new final version.

» Only two of his/her points refer to the contents of the paper:

» (1) supposed methane production in a sampling bag over night: The methane production is not relevant. Estimates show that methane production over night may be in the range of  $10E-7$  of the amount of methane recovered from the bags.

» (2) inclusion of chemical data: The chemical data are part of of the documentation of the current status. The most recent publication on chemical composition (Tasssi et al) shows problems and must urgently be replaced. The chemical data should be included in the proper publication in HESS.

Details:

In particular, I have some questions on M&M (please see below). - P2 L3: "large amounts of dissolved methane" => please specify how much, the readers who do not work on Lake Kivu won't know »»»»» we will add the number of  $40 \text{ km}^3$  below 260 m

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- P2 L8-9: "The survey of the management prescription" => What does that mean ?  
»»»»» there have been management prescriptions issued, which the gas companies have to follow. They are subject to survey from time to time.
- P2 L16: "an increasing risk of limninc eruption" »»»»»» Something went wrong in this citation. No such expression in the manuscript
- P2 L17-19: Sentence not clear, please reformulate »»»»»» Not clear which sentence
- P2 L24: "All of them, even the more recent measurements trials, had to struggle with the loss of gas and water while recovering samples to the surface". »»»»»» O.K. the reviewer has proposed to change the sentence into the version that he lists above: it will be accepted.
- P2-3 L29-2: Sentence not clear, please reformulate. »»»»»» We will reformulate this sentence
- P3 L14: separate what ? »»»»»» "in separate" means "separately"
- P3 L23: dissolved solids => which ones? »»»»»» This is the introduction. This is not the place to include a list of measured dissolved solids.
- P4 L5: "Map of Lake Kivu, showing the sampling sites (GIS and DEEP) and the area of the resource zone (below 260m). »»»»»» Proposed change of figure caption will be accepted and implemented.
- P4 L10: "at a maximum depth of 410 m": not clear. Did you make only one depth (410 m) or the depth 410 m was the maximum one, and you also sampled other depths. Please be clearer about the depths sampled. You also sampled the deepest location DEEP, but there is not precision on the depth sampled at this location. So, which depths did you sample at the platform GIS and which depths did you sample at the location DEEP? »»»»»» No this is only the description of the sampling site (5km from Gisenyi at maximum depth 410m); no sampling depths are listed here.

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- P5 L1: Also see the study of Borges et al (2011) for the horizontal variability/homogeneity »»»»» Listing Borges et al here would be misleading, as they have done measurements in the surface layer only, and we refer to horizontal variability below 150m, but Borges et al is already in the references.

- P6 L3: "Gas sampling device, with pump controller...." »»»»» o.k. change will be accepted and implemented in new version

- P7 L8: "over night" => samples were not preserved with anything. »»»»» Right: no conservation as there is no contact with any new substance

(1) Do you consider that any biological activity can occur over night in the water (methane production for example), and thus that the gas composition cannot change during the night? How can you stipulate this? Were the bags well kept in dark? Please give more details and specify.

» It is dark inside the bags, as they have an aluminium layer coated with plastic. In addition, there was no light in the laboratory during the night. While sampling, the bags were kept out of direct sun light. In previous experiments, we had tested the behaviour of samples similar to Kivu over one fortnight and we did not see any changes, neither by production nor by diffusive losses out of the bags (see Horn et al. 2016).

» Of course methane production and methane removal also happens in pelagic waters, although most of the chemical transformation happens at sediment surfaces. We used new bags, hence there was no a-priori infection with methane producing bacteria; in conclusion we expect small rates.

» In Lake Kivu deep water, methane production and removal (oxidation) together with diffusive processes nearly balance each other. Time scales of change are at least 100 to 1000 years. Cutting the diffusive connection (by sampling), would make us expect a relative change in a similar order of magnitude, i.e.  $1/(2 \cdot 365 \cdot 300) \sim 5 \cdot 10^{-6}$  over night in a first order approach estimate.

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» In addition we offer a brief calculation: 1 Liter of Kivu water produces 1 Liter of gas, i.e. roughly 250 ml  $\sim$  0.01 mol of CH<sub>4</sub>; Rates of methane production from pelagic waters were measured by Iversen et al. (1987; Limnol Oceanogr. 32(4), 804-814 in Big Soda Lake). Rates lie in the range of few nmol/(l\*day) and can produce a portion of 10E-7 of the amount of CH<sub>4</sub> already in the bag over night.. Of course, conditions in Lake Kivu can be remarkably different to Great Soda Lake but very unprobably this much. The reviewer should have listed where he took the huge numbers for his assumptions from.

» Using these estimates and the test of methane samples in the sampling bags indicate that there are no noticeable effects from storing samples over night.

- P7 L9: What is the gas in the headspace? »»»»» We are not using the word "headspace" here. The "headspace" results from degassing. No additional gases have been added to the sampling bags. An addition of headspace is only required, if the sample does not produce enough gas to warrant a reliable measurement; this is not needed (and would not be helpful) in Lake Kivu deep water.

- P8 L8-11: Sentence not clear, please reformulate and clarify »»»»» We will edit this sentence, as requested by the reviewer

- P8 L20-24: This conclusion must not be in the M&M. Please move it in the discussion or conclusion sections. »»»»» The wording "in conclusion" does not indicate that we have a major conclusion of the manuscript placed in the wrong section, but we will check this paragraph and modify it accordingly.

- P9 L4-6 : Sentence not clear, please reformulate »»»»» The sentence reads: "If the total gas pressure inside the gas space equals the outside pressure (hydrostatic plus atmospheric pressure), a virtual gas bubble withstands the pressure at depth and persists long enough to start moving upwards through the water column through its own buoyancy." – It is not clear, what the difficulty is for the reviewer.

- P9 L29-31: grammatically not correct, please reformulate. Also, what is a "compen-

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sation reservoir" ? »»»»» o.k. we will deal with this sentence again.

- P10: The norm ISO is not a protocol. The reader needs more details of the analytical methods. Please well describe the steps of the analyses. »»»»» The word protocol is not used on page 10. On purpose, our description of analytical methods is very brief, because they do not form the core of this paper. However the included material must be sufficient to explain procedures and methods. DIN and ISO are clearly referred to: also the reviewer does not explicitly mention a missing detail. Hence we will check the section for completeness carefully again.

- P10 L16: according to Koroleff ??? Reference? »»»»» We will complement this reference in the final version of the paper

- P11 L4: According to DO vertical profiles, 2 field campaigns were conducted during the dry season (27/5/17 and 2/6/17) and 2 field campaigns during the rainy season (9/3/18 and 13/3/18). Why did you choose to make measurements during both seasons? Indeed, this study focuses on very deep waters, where there is no influence of seasonality. Please clarify »»»»» The reviewer is entirely right! There is no seasonality in the deep waters. Other constraints were more important for the choice of sampling dates.

- P11 L7-10 : In the results section, you must not reference other studies. Referencing the literature is a discussion, not results »»»»» o.k if this is bothering the reviewer, we will find another place to list references on meromixis.

- P11 L13: The resolution of the figure 3 is not good, especially the writing. Please improve. Also, please remove the minus in front of the depths - P11 L14: "against depth" => according to depth »»»»» Right! there will be a better resolution figure for the final version

- P12 L1-2: Please add this limit on the graph »»»»» We will find a place to display "ressource zone" and "potential ressource zone" in a display.

- P12 L8: "Successfully" => What does that mean? »»»»» We agree that this is an unfortunate expression. We will remove the word "successfully", as samples from unsuccessful sampling do not exist.
- P 12 L9: The previous results used in this study should be specified above (in the section 2.1). At this stage, it was not clear that the authors did not sample in 27/5 and 2/6 for this study. »»»»» We cannot really follow where the reviewer has difficulties. We clearly list the sampling dates here. The reference to section 2.1 Lake Kivu map / location does not make sense.
- P12 L10-11: Please better describe your results. Example: "CH4 concentrations reached 18 mmol/l at 450m", etc. »»»»» If the reviewer wishes a few descriptive sentences about the findings here, we can add them easily ( we leave this to the editor)
- P13 L1: Please put letters for identify panels, it is easier for the reader (upper panel = A; middle panel = B, etc) »»»»» In more complex depictions, we label the panels, but here, it is easier to refer to upper , middle and lower panel. We believe readers can easily distinguish (editor's choice).
- P13 L2: "from the platform GIS" - P13 L4: Until now, the authors did not use the terms "site 2" and "site 1", but "GIS" and "DEEP". Please stay constant »»»»» We will correct this to remain consistent.
- P14 L2: "greater" => "deeper" »»»»» Writing "at depth deeper than .." is colloquial English. It raises the question whether depth itself can be deep. We propose to change the sentence to "at depths below 400m."
- P14 L5: What is the potential resource zone? Please well define the different zones of the lake, and overall showing them on vertical profiles graphs »»»»» As mentioned above we will include the depth of resource zone and potential resource zone in a display.
- P14 L6-7: It is not a result, it is a discussion »»»»» We will change the sentence

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- P14 L8-9: It is not a result, it is a discussion »»»»» We will change the sentence
- P15 L6: I don't understand "some variability of temperatures"; please clarify »»»»» We will change the sentence
- P15 L8-9: I don't see how you can conclude this, only on the base on the "look" of the vertical profiles. Please detail »»»»» We do not write "look" and we do not conclude anything in these two lines.
- P15 L10-16: Nothing new, already well developed in all the papers on Lake Kivu. Please summarize »»»»» Correct we agree fully! We confirmed these facts for the years 2017 and 2018, as we wrote.
- P15 L20-23: The studies are not properly referenced. Please reformulate; example: "... with previous observations (Schmitz and Kufferath 1952, Tietze 1974, Schmid et al 2005)" »»»»» These are not citations, these are listings of investigators and years of sample collection.
- P16 L5: Methane concentrations (mmol/l) »»»»» we will replace symbols at figure axes by words where advisable.
- P17 L10: Carbon dioxide concentrations (mmol/l) »»»»» Right! we will replace the label at the x-axis.
- P18 L4: The study of Roland et al 2018 is the only study that quantified in situ methane oxidation in Lake Kivu. As the authors talk about methane oxidation, it would be correct to also reference this study »»»»» We were not aware of the Roland paper; we will cite it.
- P18 L16-19: Already said above »»»»» We are not repeating the statement, but refer to the response time to discuss the possibilities that derive from this faster instrument. We think about what needs to be changed here.
- (2) - P19 L15-26: I don't see what these data bring to the manuscript. They are un-

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useful for the purpose of the present study, and they are not well developed »»»»» We clearly oppose the reviewer's statement. He may say that the data do not fit into the focus of the manuscript, but calling them "unuseful" is not correct. These data are very useful for anybody who needs reliable chemical data from Lake Kivu. These data show clear deviations from Tassi et al. and hence form a very important reference. We do not see any other chemical analysis of Kivu pelagic water of a similar quality. The chemical data also form part of the definition of the situation in the lake at the beginning of the industrial exploitation. We expect that in a few years time documented values of chemical composition in the literature will be highly valued. The chemical values are part of the reference and it is correct to list them together with the gas measurements. We do not see why this publication should exclude any important results, and why HESS should not receive the citations.

- P19 L16: "previous ones" »»»»» We will add "previous publications" in stead of "previous ones"

- P19 L20: You did not study Kabuno Bay in the present study »»»»» Right. We will remove the citation of Kabuno Bay

- P19 L21-22: I agree with you, numerous errors are published in the study of Tassi et al 2009 »»»»» (see also above) If the reviewer sees numerous errors in Tassi et al., he / she should encourage and support a new publication of chemical data in a respected journal like HESS to offer a better reference to the science community but also to the local decision takers.

- P19 L22-23: I don't understand why the authors talk about the limit for drinking water in Germany. It does not make sense in this study! »»»»» We are not talking about the limit for drinking water in Germany! We are talking about concentration of chromium in Lake Kivu, and compare this to an internationally respected reference for drinking water. The German limits are familiar to us. We would not know of another reference that would be suited noticeable better.

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- P20 L16 and L19: "on the base on" »»»»» No! Proposed expression "on the base on" is wrong. we retain the correct expression "on the base of"

- P24: The design of the table is not clear and not beautiful. Please improve »»»»» We will make the table "more beautiful"!

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