

Response letter to anonymous referee #1 (C7749–C7751, received and published: 9 January 2014) on Biogeosciences Discuss., 10, 19485-19508, 2013

Referee's Comments:

The presented manuscript describes measurements of CH₄ and N₂O surface emissions, water column concentrations and sediment-water-fluxes of a sub-tropical reservoir. The measurements were made at two sites during one sampling campaign (March 2012). The authors show that there was CH₄ and N₂O evasion from the reservoir to the atmosphere. I agree to this statement, but I have concern regarding the representativeness of the measured values and hence, the quality of the results.

The following points lead to this concern:

- The spatial variability was not resolved adequately, since only 2 sampling sites were used, one for the deeper and one for the shallow water zone. Therefore spatial replication is missing. This point is extremely important since a co-author of this paper showed in another publication that large errors can arise if the variability is not taken into account (Grinham et al., "Quantification of ebullitive and diffusive methane release to atmosphere from a water storage", Atmospheric Environment 2011).

Response: The aim of the presented manuscript was to better understand CH₄ and N₂O production and consumption (in sediments and water column) and emission rates at two sites (one deep and one shallow). We therefore conducted a comprehensive study where we measured total water-air and sediment-water fluxes, as well as CH₄ and N₂O concentrations in water column and pore water. To gain further insights into CH₄ and N₂O production or consumption processes, sediment-water flux incubations were also conducted. The focus of this study was not on spatial variability in emissions as we acknowledge estimating whole storage fluxes is heavily reliant on adequately understanding the ebullition area and rate. However, we are thankful that both referees expressed their concern in regard to the representativeness of the data set in terms of spatial and temporal variability. To address the referee's concerns over spatial variability across the whole storage we conducted an additional study in February 2014. The new study examined the spatial variability of total and diffusive water-air fluxes and gives therefore insights into the representativeness of the comprehensive study results. In particular the new study shows if the CH₄ and N₂O emission data from the comprehensive study agree or differ from other deep and shallow sampling

sites of the dam. Surface floating chambers were deployed in this spatial emission study at four deep and four shallow sites distributed over the whole reservoir (Section 2.2.1 and Fig. 1). The results are presented and discussed in the updated manuscript (Section 3.2, Section 4.2 and Fig. 6).

- Since measurements were made during one campaign, they represent only point measurements. In reservoirs, it was shown that several environmental factors can affect flux rates significantly, e.g. temperature or water level changes. And since the water level in this reservoirs changes, e.g. due to strong precipitation events as indicated in the Methods section (p. 19789, line 2), it can be expected that the flux rates also show strong temporal variations.

Response: This study aimed to understand drivers behind water-air fluxes and we are aware that the five day period of flux measurement cannot be used to quantify natural variability in flux rates across long term temporal scales. Whilst the environmental factors will significantly change flux rates over both short term and long term temporal scales we believe the findings of this study will still be useful in guiding future field and modelling studies. Changes in water level will impact whole storage diffusive fluxes as the surface area will change as well. These changes primarily affect both the rate and area of methane ebullition as changes to sediment bed pressure greatly impact the rate of ebullition.

The methods used to measure the fluxes and concentrations are well established techniques, except of the porewater GHG measurements. The use of Falcon tubes in combination with centrifugation needs to be better described and it is necessary to show, that there was no leakage of gases, since Falcon tubes are not designed to be gastight.

Response: The method used for pore water extraction by centrifugation is now better described in the updated manuscript (Section 2.2.3). Whilst we acknowledge the limitations of this technique to estimate pore water GHG concentrations, care was taken to ensure no headspace was formed during sampling, limiting the loss of dissolved GHG to the gas phase. Method drawbacks related to possible leakages of gases would lead to the underestimation of concentrations. We therefore use this method as a conservative estimate of the greenhouse gas concentrations in pore waters; the high CH₄ concentrations in the pore water clearly showed that sediments are producing CH₄.

The text of the manuscript is well written, but the following points need to be described:

- P. 1949, l. 13-24: How many measurements were made when and where? A table could help to illustrate this to the reader.

Response: The referee comment is assumed to be on page 19489. A table to achieve a better understanding to the reader with all measurement types and a description of the measurement location and time when the studies were conducted is added to the updated manuscript (now Table 1).

- P. 19490, l. 15: Which piston velocity was used? A reference should be added.

Response: The piston velocity k was estimated using the model of Wanninkhof (1992). Detailed information and references are now added to the updated manuscript (Section 2.2.1).

- P. 19491, l. 1-9: How was the equilibration made? This should be described in more detail or a reference should be added. This should be also made for the porewater concentration measurements.

Response: The equilibration to atmospheric pressure was made with ultra-high pure nitrogen gas (BOC gases, Brisbane, Australia) in an inflatable glove bag. Additional information with respect to the equilibration is now added to the manuscript (Section 2.2.2). The equilibration of water column and pore water samples followed the same procedure. This is now addressed in the updated manuscript (Section 2.2.3).

- P. 19493, l. 6-8: How was ebullition considered? Also in incubated sediment cores, gas bubbles can be released and affect the flux rates.

Response: Cores were regularly inspected for signs of ebullition (bubble formation under cap) throughout the incubation times. This information is added to the updated manuscript (Section 2.3). The release of gas bubbles were not detected during our experimental time.

- P. 19495, l. 1-11: The hypolimnion CH_4 concentrations are higher at the deep site than the porewater concentration at the lower site. Does this indicate that there must be higher porewater concentration at the deep site? (Otherwise there would be a flux from the hypolimnion to the sediment.) This should be discussed.

Response: The relative low dissolved methane concentration found at the shallow site sediment pore waters may be due to strong methane consumption in the surface sediment pore waters due to the overlying oxygenated water column. Strong methane consumption in the surface sediment pore waters at the deep site would be unlikely as the overlying water column was continually anoxic. Whilst this was not measured directly partial evidence for this can be inferred from the sediment incubations as rate of methane efflux greatly increased after overlying water become anoxic. This is now included in the discussion (Section 4.1.3).

The figures of the manuscript show the values, but since a logarithmic y-axis was chosen, e.g. for 2, the large differences between days cannot be inferred good enough. The use of a linear scale could help to illustrate the differences better. In the discussion, it would help also to discuss these differences with respect to the precision of the measurements indicated by the error bars.

Response: Linear scales were used for Fig. 2 to illustrate better the differences of flux rates between days as suggested by the referee. The variability in daily emissions is now included in the discussion (Section 4.2).