

## Author's response to reviewer's comments

Interactive comment on “Mineralization of organic matter in boreal lake sediments: Rates, pathways and nature of the fermenting substrates” by François Clayer et al.

### Reviewer 2:

Anonymous Referee #2 Received and published: 15 April 2020

The paper addresses an interesting and fundamentally important question: which fraction of sedimentary organic matter is mineralized through methanogenesis. Based on modeling and analyses of data from two lakes, it argues that organic carbon in negative oxidation states is used preferentially and the hydrogenotrophic pathway of methanogenesis dominates. If true, this may have profound implications for modeling the carbon cycle and interpretations of sedimentary signatures of carbon isotopes. Both the dataset and the model go well beyond the level of detail of typical diagenetic studies, which is indeed a requirement for figuring out the important fine details of organic matter mineralization.

**This important work, however, could be improved in several key areas.**

We are thankful to the reviewer for constructive and rigorous comments. We believe that it helped improve the manuscript.

***Style and clarity:*** The clarity of the narrative deteriorates towards the end of the manuscript. In particular, stating clearly and emphasizing throughout the text the main finding of the work would greatly improve readability. Inferences from modeling of the isotopic profiles could also benefit from a clearer presentation. Key statement such as (Line 265) “practically all CH<sub>4</sub> is produced through hydrogenotrophy” are inferred from modeling  $\delta^{13}\text{C}$  profiles, but I admit I was rather lost following the description, particularly trying to separate the relative contributions of hydrogenotrophic vs acetoclastic methanogenesis.

Thank you for a constructive comment. In consequence, we have (i) clarified the novel aspects (see response to next comment), (ii) better described the modelling and COS estimation approaches, (iii) moved and focused L. 305-317 to section 3.4, (iv) streamlined section 4.3 (L. 406-442) and (v) edited the conclusions (see comments below).

The description of the approach now reads:

“Considering the net reaction rates obtained by inverse modelling, a realistic range of values can be given for each of the effective reaction rates  $R_i$  in each depth interval, as determined by PROFILE, using the general equations described below (Eqs. 3, 4 and 5). The detailed calculations for each  $R_i$  at both study sites are described in section S2.

(...)

Once the range of values have been determined for each of the effective rates  $R_i$  (see Table S2), they can be used in another reaction-transport equation to model the  $\delta^{13}\text{C}$  profiles of CH<sub>4</sub> and DIC. Only sets of  $R_i$  values that yield acceptable modeled  $\delta^{13}\text{C}$  profiles, i.e., which fall within one standard deviation of the measured  $\delta^{13}\text{C}$  profiles (grey area fills in Fig. 4), were kept for COS calculation below (section 2.8). The  $\delta^{13}\text{C}$  modeling procedure is summarized below and described in detail in Section S.2. This procedure takes into account the effect of diffusion, bioirrigation (in Lake Tantaré Basin A) and the isotopic fractionation effect of each reaction  $r_i$ .

(...)

## 2.8 COS calculation

Considering the complete fermentation of metabolizable OM of general formula  $C_xH_yO_z$ , and making two assumptions, described below for clarity, the COS of the fermenting molecule is given by (combining Eq. S8 and S15; see Section S2 for details):

$$\text{COS} = -4 \left( \frac{R_{\text{net}}^{\text{CH}_4} - R_{\text{net}}^{\text{DIC}} - R_{\text{net}}^{\text{Ox}} + R_2}{R_{\text{net}}^{\text{CH}_4} + R_{\text{net}}^{\text{DIC}} + (1 - \chi_M)R_{\text{net}}^{\text{Ox}} - R_2} \right) \quad (9)$$

where  $\chi_M$  is the fraction of oxidants consumed by methanotrophy. Equation (9) is only valid if i) r1 is the only source of substrates for hydrogenotrophy and acetoclasty (this assumption is discussed in Section 4.2 below); and that ii) siderite precipitation (r7) is negligible (Saturation Index for siderite are negative except below 10 cm depth in the sediment of Lake Bédard, this case is considered in Section S2.1.2.2). With values of  $R_{\text{net}}^{\text{CH}_4}$  and  $R_{\text{net}}^{\text{Ox}}$  obtained from PROFILE (section 2.4), values of  $R_1$ ,  $\chi_H$  and  $\chi_M$  constrained by  $\delta^{13}\text{C}$  modeling (section 2.7), Eq. (9) can be used to calculate the COS of the fermenting molecule.”

Statement at L. 265 has been clarified:

“Modeled  $\delta^{13}\text{C}$  profiles were considered acceptable only when they fell within one standard deviation of the measured  $\delta^{13}\text{C}$  profiles (grey area fills in Fig. 4). Acceptable modeled  $\delta^{13}\text{C}$  profiles were obtained only when methanogenesis was 100% hydrogenotrophic, i.e., when  $R_3 = 0$  (see section S2.2.2.1).”

Former L. 305-317 now in section 3.4 read:

“The sharp upward depletion in  $^{13}\text{C}\text{-CH}_4$  leading to a minimum  $\delta^{13}\text{C}\text{-CH}_4$  value at 2.5 cm depth in Lake Tantaré Basin A sediments (Fig. 3a) was unanticipated since it occurs in the methanotrophic zone, i.e., where the remaining  $\text{CH}_4$  is expected to be  $^{13}\text{C}$ -enriched as a result of  $\text{CH}_4$  oxidation. Marked  $^{13}\text{C}\text{-CH}_4$  depletions at the base of the sulfate-methane transition zone, where  $\text{CH}_4$  is consumed via  $\text{SO}_4^{2-}$  reduction, have often been observed in marine sediments (Burdige et al., 2017 and references therein). Such features are generally attributed to the production of  $\text{CH}_4$  by hydrogenotrophy from the  $^{13}\text{C}$ -depleted DIC resulting from the anaerobic  $\text{CH}_4$  oxidation, a process referred to as intertwined methanotrophy and hydrogenotrophy (e.g., Borowski et al., 1997; Burdige et al., 2017; Pohlman et al., 2008). Here the modelled  $\delta^{13}\text{C}\text{-CH}_4$  profile captured the minimum in  $\delta^{13}\text{C}\text{-CH}_4$  in the  $Z_1$  by simply assuming concomitant hydrogenotrophy and methanotrophy in this zone and an upward-increasing  $\alpha_4$  value from 1.085 in the  $Z_3$  to 1.094 in the  $Z_1$  (section S2.2.1 of the SI). A small variation with sediment depth in the fractionation factor  $\alpha_4$  is arguably possible since its value depends on the types of microorganisms producing  $\text{CH}_4$  (Conrad, 2005).”

L. 406-442 now read:

“The COS values determined for the perennially oxygenated Basin A of Lake Tantaré (mean of  $-0.6 \pm 1.1$ ; range of  $-3.2$  to  $2.1$ ; Table 4) are much more variable than for the five other seasonally anoxic lake basins including unrealistic values for October 2015 in the  $Z_1$  ( $-3.2$ ), September 2016 ( $0.4\text{--}0.6$ ) and October 2005 ( $1.8\text{--}2.1$ ). Indeed, the very negative value of  $-3.2$  does not correspond to any degradable compound under anoxic conditions, whereas the positive values of  $0.4\text{--}0.6$  and  $1.8\text{--}2.1$  would involve either amino acids and nucleotides which are very labile (Larowe and Van Cappellen 2011) and tend to be degraded in the water column (Burdige 2007), or oxidized compounds, such as ketones, aldehydes and esters, known to be quickly reduced to alcohols. Possible sources of uncertainty in the COS estimation include mis-quantification of bioirrigation and DIC production through HMW OM fermentation (reaction r2; Corbett et al. 2013). Clayer et al. (2016) provided evidences that sediment irrigation by benthic animals is effective in Lake Tantaré Basin A and that reaction rates are sensitive to the bioirrigation coefficient. Nevertheless, additional simulations show that changing the bioirrigation coefficient by a factor of 2 (increased and decreased) did not result in significant changes in COS values ( $<0.2$ ). Bioirrigation might also be mis-represented. Indeed, the term used in Eq. 2 to calculate this

contribution, i.e.,  $\phi\alpha_{\text{irrigation}}([\text{solute}]_{\text{tube}} - [\text{solute}])$ , is indeed an approximation of intricate 3-D processes variable in space and time (Meile et al., 2005; Boudreau and Marinelli, 1994; Forster and Graf, 1995; Gallon et al., 2008; Riisgård and Larsen, 2005). On the other hand, DIC production through HMW OM fermentation (reaction r2; Corbett et al. 2013) was constrained by default in Lake Tantaré Basin A (Table 4). Indeed, fitting with Eq. 7 the experimental  $\delta^{13}\text{C}$  data does not allow partitioning the production of DIC between r1 and r2 given that both processes share the same fractionation factor ( $\alpha_1 = \alpha_2 = 1.000$ ). Equation 9 indicates that to obtain negative COS values for Lake Tantaré Basin A in September 2006 and October 2005,  $R_2$  should be  $>11 \text{ fmol cm}^{-2} \text{ s}^{-1}$  and  $>110 \text{ fmol cm}^{-2} \text{ s}^{-1}$ , respectively. These  $R_2$  values correspond to transferring  $>9\%$  and  $>44\%$  of the rate of DIC production from  $R_1$  to  $R_2$  for September 2006 and October 2005, respectively. Hence, owing to the imperfection in the COS estimations for Lake Tantaré Basin A, COS values estimated for this site should be treated with caution. Note that the sediment surface was also oxic at the sites Melide and Figino of Lake Lugano in March 1989 (Table 4) as revealed by detectable bottom water  $[\text{O}_2]$  (Table 4), and by low  $[\text{Fe}]$ , undetectable  $\Sigma\text{S}(-\text{II})$  and  $[\text{CH}_4]$  and relatively high  $[\text{SO}_4^{2-}]$  in overlying water (Lazzaretti et al., 1992; Lazzaretti-Ulmer and Hanselmann, 1999). Despite this, the COS values determined for the two sites of Lake Lugano appear realistic and consistent with those calculated for Lakes Tantaré Basin B, Bédard and Jacks. This disparity between Lake Tantaré Basin A and Lake Lugano could be explained by the presence of benthic organisms in the former (Hare et al., 1994) but their absence in the latter, as shown by the presence of varves (Lazzaretti et al., 1992) and the absence of benthos remains in the recent sediments of Lake Lugano (Niessen et al., 1992)."

***Originality:*** Much of the work is an update on the results of Clayer et al. 2018. The text should clearly distinguish the novel aspects, especially how (or if) the difference in conclusions is more than just refinement of the numbers from that previous work. For example, a statement on lines 58-60 reads: "Based on the observation that methanogenesis produced  $\text{CH}_4$  three times faster than  $\text{CO}_2$  . . . Clayer et al. (2018) concluded that the fermenting OM had a markedly negative COS value of -1.9". This parallels the statement in the Abstract, which presumably should highlight the results from this work: "we calculate, from  $\text{CH}_4$  and DIC production rates. . .COS below -0.9". This seems to convey the same information.

We agree. There is some overlap with the results of Clayer et al., 2018, although new datasets are presented and additional data from published work is re interpreted.

We have modified the abstract, introduction and conclusions (see our response to comments "Conclusions" and "Line 454" for changes in the conclusion) to better highlight the novel aspect of the present study.

L. 13-24 now read:

"To test the validity of this assumption, we modeled using reaction-transport equations vertical profiles of the concentration and isotopic composition ( $\delta^{13}\text{C}$ ) of  $\text{CH}_4$  and DIC in the top 25 cm of the sediment column from two lake basins, one whose hypolimnion is perennially oxygenated and one with seasonal anoxia. Furthermore, we modeled solute porewater profiles reported in the literature for four other seasonally anoxic lake basins. A total of seventeen independent porewater datasets are analysed.  $\text{CH}_4$  and DIC production rates associated with methanogenesis at the five seasonally anoxic sites collectively show that the fermenting OM has a mean ( $\pm\text{SD}$ ) carbon oxidation state (COS) value of  $-1.4 \pm 0.3$ . This value is much lower than the value of zero expected from carbohydrates fermentation. We conclude that carbohydrates do not adequately represent the fermenting OM in hypolimnetic sediments and propose to include the COS in the formulation of OM fermentation in models applied to lake sediments to better quantify sediment  $\text{CH}_4$  outflux. This study highlights the potential of mass balancing the products of OM mineralization to characterize labile substrates undergoing fermentation in sediments."

And L. 68-74:

“In this study, the approach described in Clayer et al. (2018), combining concentration and  $\delta^{13}\text{C}$  inverse modeling, is applied to the two newly acquired datasets. These datasets include centimeter-scale vertical porewater profiles of the concentrations and of the stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of  $\text{CH}_4$  and dissolved inorganic carbon (DIC), as well as those of the concentrations of EAs from hypolimnetic sediments of two boreal lake basins showing contrasted  $\text{O}_2$  dynamics: one whose hypolimnion remains perennially oxygenated and the other whose hypolimnion becomes anoxic for several months annually. This procedure enables us to constrain the effective rates of OM mineralization reactions and calculate, using a mass balance equation, the COS of the substrates fermenting in the sediments in these two lake basins. In addition, we modelled solute porewater profiles gathered from the scientific literature or from our data repository for four other seasonally anoxic lake basins to estimate, using the mass balance equation, the COS of the substrates fermenting in these sediments. A total of seventeen independent datasets are analysed to provide additional insight into the COS of the fermenting OM in boreal lakes and the associated mineralization pathways.”

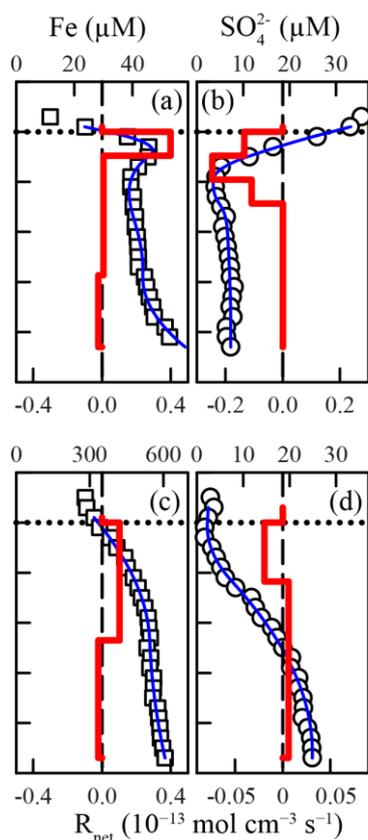
**Justifying the inclusion or omission of processes: The coupling with the sulfur cycle seems particularly suspect. The cryptic oxidation of sulfide coupled to iron oxides is used as an important pathway for  $\text{H}_2$  production. While this reaction is commonly considered (but can be written in various stoichiometries), it is rarely the only reaction that is considered from the complicated network of reactions that comprise the sedimentary Fe and S cycling. Puzzlingly, the modeled  $\text{SO}_4$  and Fe profiles are not shown (line 235). These absolutely need to be shown. The sulfur cycle in this system seems highly unusual. For example (Line 201 and Fig. 2), “ $\text{SO}_4^{2-}$  concentrations reach a minimum between SWI and 5 cm depth, and increase below”. These highly unusual features need to be discussed. How can  $\text{SO}_4$  be produced in anoxic sediment? Does oxidation of  $\text{H}_2\text{S}$  by Fe(III) somehow proceed faster than sulfate reduction? What about precipitation of iron sulfides? Similarly, precipitation of  $\text{CaCO}_3$  does not seem to be considered as a  $\text{CO}_2$  sink, while Line 380 mentions that it had to be considered by the used datasets. Were the saturation indexes negative for the study sites?**

We agree that the description of the reactions was lacking some rigor in section 2.3.

Unraveling the complex Fe and S cycling is, however, out of the scope of this study, we now refer to Couture et al. (2016). Nonetheless, note that these features described at L. 201 are discussed at L. 353-360 which have been modified following the comment of another reviewer as described below. Regarding the precipitation of iron sulfides we now clarify that iron sulfide are currently experiencing dissolution, hence precipitation could be neglected (see below).

As stated L. 144, “the precipitation of carbonates (*can be neglected*) whose saturation index values are negative ( $\text{SI} \leq -1.5$ ) except for siderite (r7) in Lake Bédard ( $\text{SI} = 0.0$  to  $0.7$  below 10 cm depth)”

Finally, we added the modelled Fe and  $\text{SO}_4$  profiles into an additional figure in the supplementary information Fig. S3. and refer to it in the text:



“

**Figure S3: Comparison of the modeled (blue lines) and average (n = 3) measured (symbols) concentration profiles of SO<sub>4</sub> (a and c) and Fe (b and d) in Lakes Tantaré Basin A (a–b) and Bédard (c–d). The horizontal dotted line indicates the sediment-water interface. The thick red lines represent the net solute reaction rate ( $R_{\text{net}}^{\text{solute}}$ ).”**

Regarding reducing Fe and S cycling, it now reads:

“Lastly, sulfide oxidation by iron oxides (r8), which can be a source of SO<sub>4</sub><sup>2-</sup> and H<sub>2</sub> (Clayer et al., 2018; Holmkvist et al., 2011), is also considered. Note that iron sulfide enrichments formed during past decades of elevated atmospheric SO<sub>4</sub> deposition are presently dissolving in Lake Tantaré Basin A (Couture et al., 2016). This process also occurs in the seasonally anoxic Basin B of Lake Tantaré (Couture et al., 2016) and is likely to also occur in Lake Bédard. Hence, other reactions involving reduced S and Fe species, such as pyrite precipitation, are believed to be insignificant for C cycling in the present study and are thus ignored.”

L. 353-360 now read:

“The progressive downward increases in dissolved Fe and SO<sub>4</sub><sup>2-</sup> (Fig. 2e, f, m and n) below ~5 cm depth and decrease in ΣS(-II) (Fig. 2n) observed in the porewaters suggest a net production of H<sub>2</sub> from r8 in both lakes. However, in the Z<sub>1</sub> and Z<sub>2</sub> of Lake Tantaré Basin A, the rate of solid Fe(III) reduction (<3 fmol cm<sup>-3</sup> s<sup>-1</sup>; calculated from Liu et al. 2015) is much lower than that required from r8 (i.e., 1 to 2 times the additional H<sub>2</sub> production of 4R<sub>4</sub> – 2R<sub>1</sub>; 70–424 fmol cm<sup>-3</sup> s<sup>-1</sup>) to produce sufficient amounts of H<sub>2</sub> to sustain the additional hydrogenotrophy. The net production rates of dissolved Fe (<10 fmol cm<sup>-3</sup> s<sup>-1</sup>) and SO<sub>4</sub><sup>2-</sup> (<1 fmol cm<sup>-3</sup> s<sup>-1</sup>) and the net consumption rate of ΣS(-II) (<1 fmol cm<sup>-3</sup> s<sup>-1</sup>) are also consistent with this assertion (Fig. 2).”

***Discussing implications:* If the organic matter used in methanogenesis had negative COS, what happened to the rest of the C pool? Is oxidized OM not mineralized? Or is it mineralized preferentially earlier, in the water column? What are the implications, e.g. for burial, signature of OM in rock record, etc.? The statement on line 450 seems to address it somewhat, but the statement is not clear.**

The implications of our study are now better described although we believe it does not influence burial or the signature of OM in rock record since only a very small fraction of the C pool is mineralized (see below).

Statement on line 450 has been clarified as follows:

“We propose that the most labile compounds are mineralized during OM downward migration in the water column and in the uppermost sediment layers leaving mainly reduced organic compounds to fuel methanogenesis in these sediments.”

L. 334 the following sentences were added regarding the rest of the C pool:

“Considering the sediment accumulation rate and sediment  $C_{org}$  content given in section 2.1, we calculate an average accumulation rate of  $C_{org}$  of  $4.7 \times 10^{-11}$  to  $1.0 \times 10^{-10}$  and  $2.9 \times 10^{-11}$  to  $7.6 \times 10^{-10}$  mol C cm<sup>-2</sup> s<sup>-1</sup> for lakes Tantaré Basin A and Bédard, respectively. Hence, the total sediment OM degradation rate ( $\Sigma R_1 + \Sigma R_2 + \Sigma R_6$ ) of  $1.3 \times 10^{-12}$  and  $1.4 \times 10^{-12}$  reported in this study for lakes Tantaré Basin A and Bédard, respectively, would involve only 1.2–2.8% and 0.2–4.8% of the total  $C_{org}$  deposited. Given that the remaining 95.2–99.8% of the deposited  $C_{org}$  is preserved in the sediment, it is not surprising that the sediment  $C_{org}$  concentration is constant with depth (Fig. 2).”

**It would also help to discuss how special or typical these lakes are, given that the implications seem to include global extrapolations. For example, diagenesis in Lake Tantaré (or is it Lake Bédard? – see below) seems to lack contributions from terminal electron acceptors. How different would this be from a “typical” boreal forest lake?**

To be able to better assess how “typical” our case study lakes are, we added some background information on the sediment OM in Section 2.1. In addition, we included a brief discussion to which degree they are representative of boreal forest lakes.

We added a figure and some information on the sediment OM in section 2.1 as follows:

“The sediment accumulation rates are 4.0–7.3 and 2.4–46.8 mg cm<sup>-2</sup> yr<sup>-1</sup> at the deepest sites of Lake Tantaré Basin A and Lake Bédard, respectively (Couture et al., 2010). The relatively constant organic C ( $C_{org}$ ) content ( $20 \pm 2\%$ ; Fig. 2b), the elevated  $\{C_{org}\}:\{N\}$  molar ratio ( $17 \pm 2$ ; Fig. 2b), the  $\delta^{13}C$  ( $-29\%$ ; Joshani, 2015) and  $\delta^{15}N$  ( $+0.5\%$  to  $-2.5\%$ ; Joshani, 2015) values reported for the sediment OM over the top 30 cm in Lake Tantaré Basin A are typical of terrestrial humic substances (Botrel et al., 2014; Francioso et al., 2005). The  $C_{org}$  content ( $21 \pm 2.7\%$ ; Fig. 2a) and  $\{C_{org}\}:\{N\}$  molar ratio ( $14 \pm 1.9$ ; Fig. 2a) reported over the top 30 cm of Lake Bédard sediments show slightly more variation with depth, but are also typical of terrestrial OM. In addition, the  $\{C_{org}\}:\{S\}$  ratios of both lake basin sediments (50–200) are typical of those reported for soil OM ( $\sim 125$ ; Buffle, 1988).

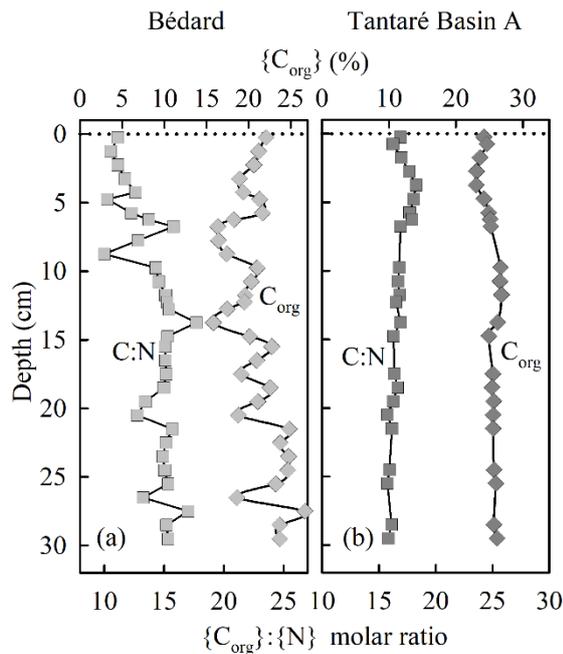


Figure 2: Depth profiles of the organic C concentrations and of the C : N molar ratio in sediment cores collected at the deepest sites of Lake Bédard (a) and Lake Tantaré Basin A (b).”

L. 450 – 453 now read:

“The OM in the sediment of the three boreal lakes, as well as their  $O_2$  seasonal dynamics, are typical of boreal forest lakes. While Lake Bédard experiences prolonged episodes of extended hypolimnetic anoxia, Lake Tantaré Basin B and Jacks Lake show more moderate seasonal anoxia, where some years the hypolimnion of Lake Tantaré Basin B is only hypoxic (Clayer et al., 2016; Carignan et al., 1991). Hence, the selective mineralization of OM described by Clayer et al. (2018), involving that the most labile compounds are mineralized during OM downward migration in the water column and at the sediment surface leaving mainly reduced organic compounds to fuel methanogenesis in the sediments, likely applies to a large portion of boreal lakes.”

**Other criticisms and suggestions:**

**Conclusions:** “fermentation and methanogenesis represent. . .100% of OM mineralization . . . in Lake Tantaré” – Methanogenesis can be fermentation. More importantly, why are there no contributions from terminal electron acceptors? Is it really 100%? Confusingly, Fig. 2 shows that sulfate reduction is clearly active in Lake Tantaré, whereas contributions of terminal electron acceptors are likely smaller in Lake Bédard.

We apologize, this is a mistake, it should be the other way around. The correct sentence now reads:

“Our results show that fermentation and methanogenesis represent about 50% and 100% of OM mineralization in the top 25 cm of the sediments at the hypolimnetic sites in Lake Tantaré Basin A and Bédard, respectively”

**One of the main results seems to be expressed by Eq. 15. Given the range of COS values (-1.4+-0.3), it might be helpful to state the range in the stoichiometric coefficients explicitly.**

Agreed, we have added a sentence L. 460

“Introducing the average COS values reported in this study ( $-1.4 \pm 0.3$ ) into Eq. 15, the coefficients  $a$  and  $b$  would take values of  $2.7 \pm 0.15$  and  $0.65 \pm 0.125$ , respectively, and the  $\text{CH}_4$  and  $\text{CO}_2$  stoichiometric coefficients would be  $0.68 \pm 0.04$  and  $0.32 \pm 0.04$ , respectively.”

**Line 284: “i) when labile OM is depleted, ii) with increasing sediment depth” – aren’t these two statements in practice the same?**

The first statement refers to OM depletion across time, while the other is across space.

**Line 454: “misestimating  $\text{CH}_4$  and  $\text{CO}_4$  production” – not sure what this means. Underestimating the amounts? But early diagenetic models generally work okay and can reproduce measured profiles. Are the differences small enough that they are within uncertainties?**

Early diagenetic models are rarely validated against both  $\text{CH}_4$  and DIC profiles at the same time. Below we also better describe how significant our findings could be for  $\text{CH}_4$  sediment fluxes and oxidant consumption rates.

To better clarify, we modified L. 454 as follows:

“Hence, the current representation of the fermenting OM, i.e.,  $\text{CH}_2\text{O}$ , in process-based biogeochemical models entails a significant risk of underestimating sedimentary  $\text{CH}_4$  production and release to the bottom water and, to a certain extent, of its evasion to the atmosphere under transient environmental scenarios.”

Added the following text L. 460:

“Introducing the average COS values reported in this study ( $-1.4 \pm 0.3$ ) into Eq. 15, the coefficients  $a$  and  $b$  would take values of  $2.7 \pm 0.15$  and  $0.65 \pm 0.125$ , respectively, and the  $\text{CH}_4$  and  $\text{CO}_2$  stoichiometric coefficients would be  $0.68 \pm 0.04$  and  $0.32 \pm 0.04$ , respectively. Note that the same stoichiometric formulation would be obtained for acetoclastic methanogenesis. Under these conditions, fermentation ( $r_1$ ) coupled to methanogenesis ( $r_4$ ) yields  $2.2 \pm 0.4$  times more  $\text{CH}_4$  than DIC for the studied lake sediments. Ignoring the implications of the present study regarding the COS of the fermenting OM could lead to the underestimation of  $\text{CH}_4$  sediment outflux or of the rate of oxidant consumption required to mitigate this efflux by a factor of up to 2.6.”

### **REFs:**

Botrel, M., Gregory-Eaves, I. & Maranger, R. Defining drivers of nitrogen stable isotopes ( $\delta^{15}\text{N}$ ) of surface sediments in temperate lakes. *Journal of Paleolimnology* 52, 419-433 (2014).

Clayer, F., Gobeil, C. and Tessier, A.: Rates and pathways of sedimentary organic matter mineralization in two basins of a boreal lake: Emphasis on methanogenesis and methanotrophy: Methane cycling in boreal lake sediments, *Limnology and Oceanography*, 61(S1), S131–S149, doi:10.1002/lno.10323, 2016.

Conrad, R. (1999). Contribution of hydrogen to methane production and control of hydrogen concentrations in methanogenic soils and sediments. *FEMS Microbiology Ecology*, 28(3), 193–202. <https://doi.org/10.1111/j.1574-6941.1999.tb00575.x>

Couture, R.-M., Gobeil, C. and Tessier, A.: Chronology of Atmospheric Deposition of Arsenic Inferred from Reconstructed Sedimentary Records, *Environ. Sci. Technol.*, 42(17), 6508–6513, doi:10.1021/es800818j, 2008.

Francioso, O., Montecchio, D., Gioacchini, P., and Ciavatta, C. Thermal analysis (TG–DTA) and isotopic characterization ( $^{13}\text{C}$ – $^{15}\text{N}$ ) of humic acids from different origins (2005) *Applied Geochemistry* 20(3), 537-544