

1 **Point-by-point response to the issues raised by referee#1 (Mary Scranton)**

2

3 We thank the referee for the constructive comments and suggestions which have helped to improve the  
4 manuscript.

5 **Referee #1** (*referee's comments are in italics*)

6 *This paper presents an interesting discussion about the importance of methane production by several*  
7 *species of algae under aerobic conditions in the ocean. The authors' experiments are original and*  
8 *convincing but I think they overstate (or ignore) the extent to which this process can result in methane*  
9 *excess concentrations in open ocean surface water. In turn the minor role of that excess production to*  
10 *the atmospheric methane budget is not clearly explained. Below are some substantive criticisms and*  
11 *some minor corrections.*

12 Authors: We appreciate the positive evaluation of our manuscript. The criticisms are addressed and  
13 corrections are made below.

14

15 **Referee #1 Line 17:** *The abstract indicates that the importance of oceanic methane production to the*  
16 *global methane budget is unknown but this is not discussed further in article and is misleading in any*  
17 *case since the ocean is known to be a very small contributor to the atmosphere. I am tired of proposals*  
18 *and papers that use the atmospheric methane budget to justify all studies of basic methane geochemistry.*  
19 *Surely it is enough to note a widespread and unexplained phenomenon which one is trying to explain*  
20 *mechanistically. I suggest adding a sentence or two to the introduction indicating why you are bothering*  
21 *to do this study and de-emphasizing how it might affect global methane budget. You are better off being*  
22 *straightforward and admitting that the real question is that methane is known to be produced in the oxic*  
23 *oceanic mixed layer and after more than 40 years no one really understands why. Give some idea of*  
24 *what actual flux of methane to atmosphere from ocean is thought to be. This HAS been calculated a*  
25 *number of times.*

26 Authors: We agree with the referee and thus have modified the Abstract and Introduction. The first  
27 sentence of the abstract now reads:

28 “Methane (CH<sub>4</sub>) production within the oceanic mixed layer is a widespread phenomenon, while the  
29 underlying CH<sub>4</sub> producing mechanism is still topic of scientific debate”

30 We further added two sentences to the introduction:

31 “The world’s oceans are considered to be a minor source of methane (CH<sub>4</sub>) to the atmosphere (1-3 %,  
32 Saunio et al., 2016). However, in recent years the widespread occurrence of in situ CH<sub>4</sub> production in  
33 the ocean mixed layer has received much attention, since CH<sub>4</sub> formation in the oxygenated ocean mixed  
34 layer challenge the paradigm that biological methanogenesis is a strictly anaerobic process.”

35 We further deleted the sentence “However, partitioning source categories to reduce uncertainties in the  
36 global CH<sub>4</sub> budget is a major challenge (Saunio et al., 2016).”

37 **Referee #1 Line 98:** *(Were cultures axenic? How was this determined? Sterile technique is not enough*  
38 *if bacteria are intrinsic to algal cultures. Bob Guillard told me this when I was using his culture*  
39 *collection. I personally don't think that there are anaerobic bacteria producing methane in rapidly*  
40 *photosynthesizing cultures, but one should be accurate.*

41 Authors: We can't consider our approach as fully axenic and the reviewer is right that it is extremely  
42 difficult to grow algal cultures without bacteria. However, the algal cultures were diluted many times,  
43 resulting in exponential algal growth while minimizing bacterial cell density. This is a common practice  
44 to keep non-axenic algae cultures largely free of bacteria and it was applied in many other physiological  
45 algal studies before, which used non-axenic cultures. Please see also answers regarding comments by  
46 reviewer 2 (manuscript line 98ff and line 381), where we discuss a potential contribution of heterotrophs  
47 and/or methanogenic archaea. Briefly, the correlations we describe clearly show that CH<sub>4</sub> production  
48 depends on algal growth. It is therefore highly unlikely that bacteria are solely responsible for CH<sub>4</sub>  
49 production in our cultures. However, bacteria might be involved in the CH<sub>4</sub> production process. One  
50 scenario which we cannot rule out would be a production of CH<sub>4</sub> precursors by algae and a usage of  
51 these precursors by bacteria to produce CH<sub>4</sub>. While we think that this is less likely than CH<sub>4</sub> production  
52 by algae alone, it would, if true, show that bacteria need algae-produced precursors to produce CH<sub>4</sub>. The  
53 latter scenario would be relevant in the field because algae co-exist with bacteria in the oceans. We have  
54 modified the Discussion and Abstract to make this clear. For more details see reply to reviewer #2  
55 (manuscript line 98ff and line 381).

56

57 **Referee #1 Line 115:** *When calculating the amount of methane produced, was fraction dissolved*  
58 *included? With a large headspace, this may be small but should be mentioned. Were samples*  
59 *equilibrated with headspace before methane measured? The authors mention that oxygen was*  
60 *sometimes supersaturated, but was this relative to headspace or equilibration with ambient air?*

61

62 Authors: The amount of dissolved CH<sub>4</sub> was not included. As requested we have calculated the dissolved  
63 CH<sub>4</sub> concentration by using the equation of Wiesenburg and Guinasso (1979). The dissolved fraction of  
64 CH<sub>4</sub> has now been included in our calculations and added to the total amount of CH<sub>4</sub> produced. As  
65 correctly stated by the referee the addition of the dissolved CH<sub>4</sub> fraction has only a marginal effect on  
66 the overall CH<sub>4</sub> production. Calculation of dissolved CH<sub>4</sub> is mentioned in the method section (2.6) and  
67 a new reference for calculating dissolved CH<sub>4</sub> was added (Wiesenburg and Guinasso, 1979) to the  
68 revised manuscript.

69 Cultures were turned 30 seconds overhead prior to analysis to ensure equilibration between dissolved  
70 and headspace CH<sub>4</sub>. In the preliminary equilibration experiments, we found that further shaking does  
71 not affect the CH<sub>4</sub> measurement and therefore all samples can be considered as equilibrated.

72 We modified the sentence line 260: "The measured oxygen concentrations were always saturated or  
73 supersaturated relative to equilibration with ambient air (S.2)."

74 **Referee #1 Line 133:** Concentrations (final) of added substrates should be given for comparison with  
75 natural concentrations. If possible give concentrations of these substrates in medium at start of  
76 incubation with and without addition of substrate.

77

78 Authors: The final concentration of  $^{13}\text{C}$ -hydrogen carbonate ( $\text{NaH}^{13}\text{CO}_3$ ) was  $48.7 \mu\text{mol L}^{-1}$  and  $10 \mu\text{M}$   
79 for  $^{13}\text{C}_2$ -DMS,  $^{13}\text{C}_2$ -DMSO and  $^{13}\text{C}$ -MSO. Concentrations (final) of added substrates are given in the  
80 manuscript in line 133 for  $\text{NaH}^{13}\text{CO}_3$  and at line 173 for  $^{13}\text{C}_2$ -DMS,  $^{13}\text{C}_2$ -DMSO and  $^{13}\text{C}$ -MSO.

81 Cultures were grown in sterile filtered ( $0.2 \mu\text{m}$   $\emptyset$  pore size) natural North Sea seawater (sampled off  
82 Helgoland, Germany) enriched in nutrients according to F/2 medium. The dissolved inorganic carbon  
83 (DIC) was  $2152 \pm 6 \mu\text{mol L}^{-1}$  (line 104). This value falls within the range of typical DIC concentrations  
84 of North Sea seawater. The added amount of  $\text{NaH}^{13}\text{CO}_3$  corresponds to 2% of the DIC of the North Sea  
85 seawater. This information was added to the revised manuscript: "The DIC value falls within the range  
86 of typical DIC concentrations of North Sea seawater." We added two sentence to the section were we  
87 explain labeling experiments: "For stable carbon isotope experiments  $48,7 \mu\text{mol L}^{-1}$   $^{13}\text{C}$ -hydrogen  
88 carbonate ( $\text{NaH}^{13}\text{CO}_3$ ) in final concentration was added to the F/2 medium. The added amount of  
89  $\text{NaH}^{13}\text{CO}_3$  corresponds to 2% of the DIC of the North Sea seawater ( $2152 \pm 6 \mu\text{mol L}^{-1}$ ), resulting in a  
90 theoretical calculated  $^{13}\text{C}$  value of DIC of  $+2014 \pm 331\%$ ."

91

92 Unfortunately the natural DMS, DMSO and MSO concentrations in our seawater were not determined.  
93 However, the global DMS mean concentration has been reported to be ca. 2 nM (Galí et al., 2018). A  
94 rough estimation can also be made for DMSO concentrations in the ocean as DMSO is generally present  
95 in concentrations 1–2 orders of magnitude greater than DMS (Lee et al., 1999). These estimates are also  
96 in line with data reported from a cruise of the western Pacific Ocean that were reported by Zindler et al.  
97 (2013). The average (total) DMS ,DMSP and DMSO concentrations were ca. 1 nM, 4 nM, and 16 nM  
98 for DMS, DMSP and DMSO respectively. Thus we conclude that the initial substrate concentration in  
99 the seawater is insignificant in comparison to the added amount ( $10\mu\text{M}$ ), the latter being roughly two  
100 orders of magnitude higher than typically reported for oceanic concentrations (please see also reply to  
101 referee#2: line 172). Moreover, intracellular concentrations of methyl-sulfur compounds also play a  
102 significant role. We will discuss this issue below (see answer to next comment).

103

104 **Referee #1 Line 327:** If the labelled methyl groups yield only a small percentage (less than 1%) of total  
105 methane produced where is the other methane coming from? Is this result consistent with field  
106 observations that show only a weak link if any between DMS or DMSO and excess methane in surface  
107 water? This point needs more elaboration since the question of the source of excess methane in seawater  
108 has been plagued by studies that show methane can be produced by a process but that rates are far  
109 lower than are needed to explain natural surface water values. Here is where a link to ambient DMS,  
110 DMSO or MSO concentrations should be made. I think this point is a key issue.

111 Authors: Please note that the main reason for the isotope experiments was to unambiguously show that  
112 the tested compounds might be able to form CH<sub>4</sub> under oxic conditions. The <sup>13</sup>C-labeling experiment  
113 showed that DMS, DMSO, and MSO are potentially important methyl-precursors for CH<sub>4</sub> but the  
114 contribution of these compounds to the overall CH<sub>4</sub> production in cultures of *E. huxleyi* could not be  
115 determined in our experiments due to the complexity of the formation of these compounds in the algal  
116 cells. Hence, the stable isotope labeling approach should be considered as a proof of concept, showing  
117 that methyl groups of all tested substance serve as precursor compounds of CH<sub>4</sub>. Althoff et al. (2014)  
118 and Benzing et al. (2017) suggested a chemical reaction of DMSO, DMS and MSO that leads to CH<sub>4</sub>  
119 formation in eukaryotes, especially, in marine algae containing elevated concentration of these  
120 compounds. We have therefore tested whether the methyl groups of these substances can actually be  
121 converted to CH<sub>4</sub> in marine algae cultures. We made this point clearer in the discussion of the revised  
122 manuscript.

123 The paragraph reads now:

124 “The <sup>13</sup>C-labeling experiment showed that DMS, DMSO, and MSO are potentially important methyl-  
125 precursors for CH<sub>4</sub> but the contribution of these compounds to the overall CH<sub>4</sub> production in cultures of  
126 *E. huxleyi* could not be determined in our experiments due to the complexity of the formation of these  
127 compounds in the algal cells. This can be illustrated by the following. The contribution of a substance  
128 to the total CH<sub>4</sub> released is the product of both the added <sup>13</sup>C-labeled fraction (added to the waters sample  
129 and uptake by the cells) and the internally formed fraction of these compounds (DMS, DMSO, and  
130 MSO) which will roughly show natural <sup>13</sup>C abundance. Therefore the stable isotope value of CH<sub>4</sub> will  
131 be diluted by the fraction of naturally formed methyl sulfur compounds in the algal cells and thus the  
132 contribution of DMS, DMSO, and MSO to CH<sub>4</sub> formation can therefore not be estimated on the basis  
133 of their added amount alone. The <sup>13</sup>CH<sub>4</sub> quantity from conversion of added <sup>13</sup>C labelled substance  
134 contributed 0.03% (<sup>13</sup>C<sub>2</sub>-DMSO) up to 0.84% (<sup>13</sup>C-MSO) to overall released CH<sub>4</sub>. However, even if the  
135 added <sup>13</sup>C labelled compounds might only explain ≤ 1% of CH<sub>4</sub> formed by the algae their overall  
136 contribution (including non-labelled sulfur compounds which we are not able to measure) might provide  
137 a much larger fraction of the released CH<sub>4</sub>. The intracellular DMS concentration can reach 1 mM (Sunda  
138 et al., 2002) in cells of *E. huxleyi*, while the concentration of added <sup>13</sup>C<sub>2</sub>-DMS was 0.01 mM in medium  
139 (final concentration). If intracellular <sup>13</sup>C<sub>2</sub>-DMS was in equilibrium with bulk seawater <sup>13</sup>C<sub>2</sub>-DMS and  
140 all CH<sub>4</sub> would be produced from intracellular DMS, then the contribution of the <sup>13</sup>C labeled compound  
141 would be about 1%. However, even if the biggest fraction of CH<sub>4</sub> in algae cultures was not released by  
142 the <sup>13</sup>C labelled substances, the significant increase in delta notation in <sup>13</sup>C<sub>2</sub>-DMS, <sup>13</sup>C<sub>2</sub>-DMSO and <sup>13</sup>C-  
143 MSO treated cultures above the δ<sup>13</sup>CH<sub>4</sub> values of the control groups demonstrate that <sup>13</sup>C labelled  
144 precursor substances were converted to CH<sub>4</sub> by algal cultures (Fig.4 a-c).

145 This is also indicated, when the absolute conversion quantities of <sup>13</sup>C-labelled substance in algal cultures  
146 are considered: these were ca. nine (<sup>13</sup>C<sub>2</sub>-DMS), three (<sup>13</sup>C<sub>2</sub>-DMSO) and thirty (<sup>13</sup>C-MSO) times higher

147 than in seawater control groups. Hence, the stable isotope labeling approach should be considered as a  
148 proof of concept, that methyl groups of all tested substance serve as precursor compounds of CH<sub>4</sub>.”

149

150 We furthermore deleted the paragraph (line 341-354), since the main points regarding the CH<sub>4</sub>  
151 conversion rates of <sup>13</sup>C labeled compounds were discussed in the section above.

152

153 **Referee #1 Line 400:** *Weller et al may have found a correlation between chlorophyll a and methane*  
154 *concentrations but there were many studies in the older literature (1970s and 80s) where no such*  
155 *correlation was observed. I recommend authors go back and read over some of these earlier papers and*  
156 *confirm that measured production rates from this study can support other previously observed methane*  
157 *fluxes. Also see thesis by Scranton (1977) where methane production was examined in cultures by*  
158 *several species including Emiliani huxleyi (called Coccolithus huxleyi in my thesis) and T. pseudonana.*  
159 *I observed methane production in a much less sophisticated experimental setup and concluded that*  
160 *natural populations of the algae I studied might be adequate to support the widespread supersaturations*  
161 *of methane seen in the open ocean (including in places where no dense algal blooms were observed).*  
162 *Perhaps your results can be compared to mine or to other studies that report cell abundances and air-*  
163 *sea fluxes. A citation to a downloadable copy of my thesis is below. Scranton MI (1977) The marine*  
164 *geochemistry of methane. Citable URI <https://hdl.handle.net/1912/1616>. DOI10.1575/1912/1616.*

165

166 Authors: We followed the recommendation of the reviewer (Mary Scranton) and compared the CH<sub>4</sub>  
167 production rates of *E. huxleyi* reported by Scranton (1977) with those of our study.

168 In line 392 we added: ”We also compared the cellular CH<sub>4</sub> production rates of *E. huxleyi* reported by  
169 Scranton (1977) with those of our study. Scranton (1977) reported a production rate of  $2 \times 10^{-10}$  nmol  
170 CH<sub>4</sub> cell<sup>-1</sup> hr<sup>-1</sup>. This value is close to the production rate of  $1.4 \times 10^{-10}$  nmol CH<sub>4</sub> cell<sup>-1</sup> hr<sup>-1</sup> in our study.  
171 Scranton (1977) concluded from observed CH<sub>4</sub> production rates in laboratory experiments that natural  
172 populations might be adequate to support the widespread supersaturations of CH<sub>4</sub> seen in the open  
173 ocean.”

174 As the referee stated correctly the distribution of chlorophyll has not shown a consistent correlation with  
175 CH<sub>4</sub> distributions in field studies.

176 The following section was added in Chapter 4.3: “In general, the distribution of chlorophyll has not  
177 shown a consistent correlation with CH<sub>4</sub> distributions in field studies. There are studies where no  
178 correlation was observed (e.g. Lamontagne et al., 1975; Foster et al., 2006; Watanabe et al., 1995) or at  
179 least a correlation was found within a few depth profiles (Burke et al., 1983; Brooks et al., 1981). Many  
180 field measurements in oxygenated surface waters in marine and limnic environments have shown  
181 examples where elevated CH<sub>4</sub> concentrations were spatially related to phytoplankton occurrence (e.g.  
182 Conrad and Seifer, 1988; Owens et al., 1991; Oudot et al., 2002; Damm et al., 2008; Grossart, et al.,  
183 2011; Weller et al., 2013; Zindler et al., 2013; Tang et al., 2014; Bogard et al., 2014; Rakowski et al.,

184 2015). Taken together these studies suggest that phytoplankton is not the sole source of CH<sub>4</sub> in  
185 oxygenated surface waters, but importantly they also suggest that phytoplankton is one of the sources  
186 of CH<sub>4</sub>. We therefore compared the CH<sub>4</sub> production rates of our cultures with two field studies for the  
187 Pacific Ocean (Weller et al., 2013) and the Baltic Sea (Schmale et al., 2018) to evaluate the potential  
188 relevance of algal CH<sub>4</sub> production.”

189

190 We followed the reviewer suggestion and added an additional comparison of our CH<sub>4</sub> production rates  
191 by using field study data of Schmale et al., (2018).

192 The respective section reads: “Schmale et al., (2018) reported CH<sub>4</sub> enrichments that were observed  
193 during summer in the upper water column of the Gotland Basin, central Baltic Sea. They furthermore  
194 found that zooplankton is one but not the only CH<sub>4</sub> source in the oxygenated upper waters. While the  
195 authors ruled out a major contribution of algae to the observed sub-thermocline CH<sub>4</sub> enrichment because  
196 of the low sub-thermocline phytoplankton biomass, they considered a primary production associated  
197 CH<sub>4</sub> formation as one likely source in the phytoplankton-rich mixed layer. The average phytoplankton  
198 carbon biomass of the mixed layer was approximately 600 µg L<sup>-1</sup> (averaged from Fig. 9 in Schmale et  
199 al., 2018). For the reported average net CH<sub>4</sub> production rate in the mixed layer (95 pmol CH<sub>4</sub> L<sup>-1</sup> d<sup>-1</sup>),  
200 we calculated that a production rate of 2.5 µg g<sup>-1</sup> POC d<sup>-1</sup> is required if the CH<sub>4</sub> is produced by the algal  
201 biomass. This rate would be within the range of CH<sub>4</sub> production rates observed in our study. These  
202 calculations should be considered as a first rough estimate to assess whether CH<sub>4</sub> production rates of  
203 laboratory grown cultures can significantly contribute to CH<sub>4</sub> supersaturation associated with  
204 phytoplankton. We did not distinguish between species and did not take into account environmental  
205 factors or the complexity of microbiological communities.”

206

207 ***Minor issues***

208 ***Referee #1: Equation 7: There should be a factor of 1000 to convert ratios to per mille values***

209 Authors: We would like to keep equation 7 as is as it follows the recommendations by Coplen (2011)  
210 (“Guidelines and recommended terms for expression of stable isotope-ratio and gas-ratio  
211 measurement”).

212 ***Referee #1 Figure 1: Plot control values here too.***

213 Authors: Control groups in Figure 1 were plotted in the revised manuscript. In order to add control  
214 groups the unit was changed in concentration (ng CH<sub>4</sub> L<sup>-1</sup>).

215

216 ***Referee #1 Line 268: Should it be “were applied” not “where applied”?***

217 Authors: Yes. Corrected.

218

219 ***Referee #1 Line 308: Inoculation OF cells?***

220 Authors: Yes. “of” was added.

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