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Methane Production in Oxic Lake Waters Potentially Increases Aquatic Methane Flux to Air

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ABSTRACT

Active methane production in oxygenated lake waters challenges the long-standing paradigm that microbial methane production occurs only in anoxic conditions, and forces us to rethink the ecology and environmental dynamics of this powerful greenhouse gas. Methane production in the upper oxic water layers places the methane source closer to the air-water interface, where convective mixing and microbubble detrainment can lead to a higher methane efflux than previously assumed.

Microorganisms may produce methane in oxic environments by being equipped with enzymes to counteract the effects of molecular oxygen during methanogenesis, or using alternative pathways that do not involve oxygen-sensitive enzymes. As this process appears to be influenced by thermal stratification, water transparency and primary production, changes in lake ecology due to climate change will alter methane formation in oxic water layers, with far-reaching consequences for methane flux and climate feedback.

34 Introduction

35

36 As a powerful greenhouse gas, methane is projected to have 28 times the warming
37 potential of CO₂ in the coming century.¹ Constraining the global methane budget,
38 however, has been difficult due to uncertainties in its sources and sinks.^{2,3} Methane
39 sources can be broadly classified as biogenic, thermogenic and pyrogenic.⁴ Among the
40 biogenic sources, the prevailing paradigm is that microbial methanogenesis occurs
41 strictly under anaerobic conditions.^{5,6} Consequently, studies of methane dynamics often
42 focus on anoxic and hypoxic habitats. This paradigm has recently been questioned due
43 to the findings that terrestrial fungi,⁷ plants^{8,9} and other eukaryotes¹⁰ can produce
44 significant amounts of methane under oxic conditions. This novel production may
45 substantially contribute to the total atmospheric methane and may even further increase
46 with global warming.¹¹

47

48 Bound by the prevailing paradigm, research on aquatic methane production has
49 often ignored the upper oxic layers. For example, methane sampling in Lake Hallwil,
50 Switzerland over the past decades had been limited to the hypolimnion, but recent
51 measurements revealed a distinct methane peak in the oxic 7-9 m layer (McGinnis,
52 unpublished data). A methane peak has also been recently observed in the surface
53 waters of Lake Geneva (McGinnis, unpublished data). Likewise, decades of methane
54 sampling in Lake Stechlin, Germany had been restricted to the sediment and bottom
55 water, and the methane peak in the oxic metalimnion was not discovered until 2010.¹²
56 Nevertheless, many researchers have reported inexplicable oversaturation of dissolved
57 methane in the upper oxic waters, a phenomenon known as the “methane paradox”
58 because methane production and accumulation are not supposed to occur in well-
59 oxygenated waters.² Conventional explanations for this paradox include input from
60 nearby anoxic sediments and shorelines,^{13,14} and production within micro-anoxic zones
61 such as detritus and animals’ gut.^{15,16,17} Considering the new findings of methane
62 formation in oxic environments on land, a revision to our fundamental understanding of
63 the aquatic methane dynamics is needed.

64

65 **Discovery of ‘oxic methane production’**

66
67 Keppler et al.⁸ first reported that terrestrial vegetation actively releases methane under
68 oxic conditions, and the findings were intensely debated.^{18,19} Additional research further
69 reported methane formation in oxic environments independent of methanogenic
70 microbes.^{20,21} Those studies suggest that eukaryotic methane production involves
71 methionine⁹ and other methylated precursors, and is related to environmental stressors
72 such as reactive oxygen species.^{20,21} Additionally, Angel et al.²² showed that desert soil
73 methanogens actively produced methane under oxic condition by overexpressing
74 oxygen detoxifying genes. Others reported that microbes use methylated metabolites
75 from phytoplankton to produce methane within oxic seawaters.²³⁻²⁷ Collectively these
76 findings show that methanogenesis extends beyond the traditionally perceived anoxic
77 boundaries.

78
79 While the biochemical mechanisms behind this novel methane production remain
80 largely unclear, the mere ability of organisms to do so forces us to re-examine the
81 environmental dynamics of methane in aquatic ecosystems. For the purpose of this
82 paper, we describe this as ‘oxic’ methane production without inferring whether or not the
83 biochemical pathway itself requires oxygen. We review the evidence, its importance for
84 methane flux, and the implications for microbial ecology.

85 86 **Observations in aquatic systems**

87
88 Tables 1 and 2 list reports of over-saturated methane concentrations in oxic sea and
89 lake waters. While not exhaustive, the lists clearly show that the methane paradox is
90 widespread. The reported maximum concentrations are usually much higher in
91 freshwater (high nanomolar to micromolar levels) than in seawater (low nanomolar
92 levels), which is consistent with the fresh-marine “dilution curve” for dissolved
93 methane.⁴⁹ Globally, lakes cover ca. 3.7% of land⁵⁰ or 0.9% of Earth, whereas oceans
94 cover ca. 70% of Earth. Freshwater oxic methane peaks tend to be nearly 1000-fold
95 higher than marine oxic methane peaks, whereas the average oxic methane layer

96 thickness in lakes vs. oceans is ca. 1:10. Simple extrapolation suggests that the total
97 amount of oxic freshwater methane is roughly equal to that of oxic marine methane.

98
99 One challenge in studying oxic methane production is potential interference from
100 nearby anoxic sources. Mesocosms allow the study of the wax and wane of oxic
101 methane production in a more controlled manner and, depending on the mesocosm
102 design, potentially free of influences from the littoral zone and sediment. The IGB
103 LakeLab facility in Lake Stechlin consists of 24 mesocosms (each 9 m diameter x ca. 20
104 m deep). Observed methane oversaturation within the oxygen-rich mesocosm water
105 indicated that oxic methane production was independent of input from the littoral zone
106 (Table 3), consistent with an earlier report.⁴⁷ The mesocosm bottom did not become
107 anoxic; hence, one can rule out methane seepage from anoxic bottom as an
108 explanation for the observations. Similar oxic methane production was observed in
109 smaller mesocosms installed in Lac Cromwell, Canada.⁴⁶ Furthermore, all four of the
110 monitored mesocosms developed oxic-water methane oversaturation despite their
111 different phytoplankton compositions (based on pigments; Table 3), suggesting that oxic
112 methane production was not dependent on a specific phytoplankton taxon.

113
114 Lake Stechlin (max. 70 m) is home to one of the longest-running limnological
115 monitoring programs (>65 years) in north-eastern Germany. Methane production in the
116 upper oxic layer has been repeatedly observed since 2010,^{12,47} coinciding with the
117 phytoplankton growth season, and methane concentration within the upper 25 m was
118 linearly correlated with primary production.⁴⁷ Positive correlations between oxic-water
119 methane and chlorophyll concentrations in several seas and lakes have also been
120 reported.^{46,51} Together, these observations suggest that the oxic methane production is
121 associated with primary production.

122
123 Methane can be rapidly oxidized by methanotrophs to CO₂ in the presence of
124 oxygen, as often seen in the water layer overlying anoxic sediment. Using molecular
125 markers, Grossart et al.¹² detected the presence of methane oxidizers only below the
126 thermocline but not within the oxic methane peak in Lake Stechlin. Murase and

127 Sugimoto⁵² incubated Lake Biwa waters under different light intensities and reported
128 lower oxidation rates in the light. Similar photoinhibition effects were also found in Lake
129 Stechlin⁴⁷ (Table 4). The absence or photoinhibition of methane oxidizers thereby allows
130 for the accumulation of methane in the upper oxic water column.

131

132 **Implications for lake-to-air methane flux**

133

134 Diffusive methane flux F_i from water to the atmosphere is determined by the methane
135 concentration at the surface water C_w , the atmospheric saturation concentration C_{sat} (~3
136 nM) and the physical processes driving the water-air exchange coefficient k (m d^{-1}):⁵³

137

$$138 \quad F_i = k (C_w - C_{sat})$$

139

140 In the case of anoxic bottom methane production in deep stratified lakes, the
141 thermocline acts as a barrier that 1) physically limits the upward flux from bottom water,
142 and 2) allows methanotrophs to oxidize methane within the oxic zone subsequently
143 fortifying that barrier. Hence, significant exposure of dissolved methane to the
144 atmosphere is limited to periods of deep convective mixing or complete lake turnover.
145 However, even in the latter case there is still uncertainty as to how much methane will
146 reach the atmosphere and how much is oxidized.^{54,55}

147

148 With the methane source located in the upper oxic layer instead of the bottom
149 (Fig. 1), methane only needs to be transported over a much shorter distance to reach
150 the water-air interface. Additionally, shallow water mixing (convection), which often
151 occurs diurnally, both exposes higher methane concentrations to the air-water interface
152 and enhances k .⁵³ These fluxes would be particularly important during periods of colder
153 weather and higher winds during the stratified season, and would be further elevated by
154 microbubbles.⁵⁴ These additional mechanisms for releasing methane from the surface
155 are not considered in conventional Fickian diffusion (k) calculations.^{54,56}

156

157 Bastviken et al.⁵⁷ estimates that freshwaters contribute 103.3 Tg CH₄ yr⁻¹ to the
158 atmosphere. Of this, they attribute 9.5% to diffusive fluxes with an average of 0.51 mmol
159 m⁻² d⁻¹ covering arctic to tropical lakes (n = 397). The data, however, rarely included
160 night-time measurements when convection was strongest, and had very limited
161 seasonal studies. Most diffusive fluxes for their budget estimate relied on
162 parameterizations for *k* based on wind speed,^{58,59} which tend to underestimate surface
163 diffusive fluxes, particularly during convective mixing due to surface cooling that strongly
164 drives *k* values⁵³ or microbubble flux enhancement.⁵⁴ Convection-driven *k* can increase
165 the flux as much as five times over the wind parameterization.⁶⁰

166
167 The near-surface oxic methane sources combined with more realistic estimates
168 for transport will increase the estimated contribution to the global budget. As an
169 illustrative example, fluxes from Lake Stechlin ranged from 0.95 mmol m⁻² d⁻¹ in July
170 2014 (avg. surface CH₄ 0.28 μmol L⁻¹, wind speed 1.9 m s⁻¹, our unpublished data) to
171 2.7 mmol m⁻² d⁻¹ in August 2013 (avg. surface CH₄ 0.37 μmol L⁻¹, wind speed 4.2 m s⁻¹).⁵⁴ These values are 1.9-5.3 times higher than Bastviken et al.'s estimates, suggesting
172 that diffusive emissions from lakes, particularly due to the oxic methane peak, could be
173 doubled (~18.5 Tg yr⁻¹) or even higher.

174

175 **Implications for aquatic microbial ecology**

176

177
178 How microbes produce methane under oxic condition is unclear. We consider two
179 possibilities: 1) They use conventional biochemical pathways but are also equipped with
180 ways to counteract the effects of oxygen; 2) They use biochemical pathways that do not
181 involve oxygen-sensitive enzymes as described for the conventional pathways.

182

183 In the conventional pathways, the carbon-borne precursor molecules act as
184 electron acceptors in a series of redox reactions releasing methane as the end product.
185 Although this process is supposedly wide-spread in the oxygen-free ancient ocean, it is
186 wasteful because the energy-rich methane is lost. With the advent of oxygenic
187 photosynthesis, oxygen becomes the preferred electron acceptor as more energy can

188 be generated. This 'switch' from a fully anaerobic metabolism to an exclusively aerobic
189 metabolism requires major changes in the cell's genetic blueprint and biochemical
190 machinery, and leads to an evolutionary divergence of aerobes from their anaerobic
191 ancestors.⁶ Anaerobic organisms became marginalized over time to the remaining
192 anoxic fringe habitats in lakes and oceans. However, some ancestral anaerobes,
193 without committing themselves to whole-sale changes, may have developed ways to
194 neutralize the negative effects of oxygen and continue to occupy the vast but
195 increasingly oxygenated environment. Many oxygen-tolerant microorganisms have the
196 antioxidant enzyme catalase, which can be coded for by a single gene.^{61,62} This strategy
197 appears to be employed by desert soil methanogens.²²

198
199 Alternatively, microbes may use pathways not affected by oxygen (Fig. 2). Karl et
200 al.²³ suggest that microbes in the equatorial Pacific break down methylphosphonate
201 (MPn) and release methane as a by-product. The process requires enzymatic cleavage
202 of the C-P bond and is not oxygen sensitive. The operon for the C-P lyase enzyme
203 PhnJ responsible for breaking the C-P bond⁶³ is widespread across the bacterial
204 domain.⁶⁴ Accordingly, this reaction can be catalysed by numerous phosphorus
205 scavenging microorganisms, and supports the notion that MPn is a main phosphorus
206 source for microbes in oligotrophic waters.^{65,66} While biological phosphonate production
207 is common within the bacterial domain,⁶⁷ currently only one methylphosphonate
208 synthase (mpnS) has been identified originating from the marine *Thaumarchaeota*.⁶⁸
209 These organisms are abundant in the ocean, although they have been reported in some
210 freshwater lakes as well.⁶⁹ Another probable source in freshwater are the
211 *Actinobacteria*, which produce a large diversity of phosphonate compounds.^{70,71} The
212 high abundance of freshwater *Actinobacteria* coupled with known C-P lyase activity of
213 cyanobacteria⁷² may explain the correlation between oxic methane formation and
214 cyanobacteria bloom in Lake Stechlin.¹² Damm et al.²⁵ suggest that arctic microbes
215 metabolize dimethylsulfoniopropionate (DMSP) (requiring enzymatic cleavage of the C-
216 S bond) for energy production and release methane as a by-product, which would
217 require a final step of methyl reduction. However, the methyl reductase Mcr gene
218 complex has not been found in any non-methanogenic genome and has no known

219 structural homolog in *Bacteria*. To allow the process to occur in oxic water, Damm et
220 al.⁷³ theorize that DMSP-utilizing bacteria maintain an anoxic cytoplasm through
221 respiration, although empirical evidence is still missing.

222
223 From an energetic standpoint it is hardly favourable to discard methane as a by-
224 product; nevertheless, the implication of the earlier work is that oxic methane production
225 could be driven by microbes equipped with C-P lyase or C-S lyase,^{23,25} which are
226 common among heterotrophic microbes capable of metabolizing C-1 compounds.⁷⁴ A
227 comparative genomics analysis shows that the majority of enzymes in the various
228 methanogenic pathways are present in non-methanogenic organisms including *Bacteria*
229 (Fig. 2). This along with the presence of several C1 carriers (tetrahydrofolate and
230 tetrahydromethanoptin)⁷⁵ among *Bacteria* allows us to speculate that upon
231 demethylation of C-1 compounds, the methyl group bound to a C1-carrier or an
232 unknown Coenzyme-M homolog is reduced to methane by cellular reductases, for
233 which the methyl-reductase function has not been identified (Fig. 2). Alternative sources
234 of reducing power potentially include: 1) Electron bifurcation that has been described for
235 anaerobic methanogenesis⁷⁶ but not yet for oxic methane production; 2) reducing power
236 dumping by photosystems (in cyanobacteria) or proteorhodopsin (in *Bacteria*),
237 especially under nutrient limitation.

238
239 There is emerging evidence that some microalgal species may directly produce
240 methane by demethylation, completely by-passing the involvement of heterotrophic
241 microbes.⁷⁷ Organosulfur compounds such as methionine, dimethyl sulfoxide and
242 DMSP are commonly produced by algae. It has been reported that, under ambient
243 atmospheric condition, several organosulfur compounds can be chemically converted to
244 methane.⁹ If similar processes are confirmed in algae, methane production in oxic
245 waters would be much more pervasive than previously imagined.

246

247 **Implications for climate and future research directions**

248

249 Cyanobacteria blooms are on the rise due to eutrophication and climate change.⁷⁸
250 Given that strong oxic methane production has been associated with cyanobacteria
251 blooms,¹² this could result in a positive greenhouse feedback. Meanwhile, the fate of the
252 oxic methane source is influenced by stratification pattern and surface mixing events,
253 but these processes may not be fully captured by climate models, especially for small
254 lakes.⁷⁹

255
256 Methane has long been the focus in ecological and climate research, but the
257 current view of its global dynamics is biased by the conventional exclusion of oxic
258 habitats and processes.^{3,4} In light of the new findings discussed here, it is necessary to
259 revisit the century-old understanding of aquatic microbial methane production and
260 address several urgent research areas: 1) More research is needed on the precise
261 biochemical pathway(s) behind oxic methane production, and the use of stable isotopes
262 and tracers can shed light into the different precursor compounds and pathways; 2)
263 Further investigation is warranted on the fate of this novel methane source, including
264 water-to-air exchange and internal consumption via methanotrophy; 3) Isolation and
265 cultivation of the responsible organisms will be needed for detailed physiological
266 studies; 4) It is necessary to revisit the global methane budget by including oxic
267 methane sources, and the role they may play in future climate.

268

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276

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498 Reservoirs in the Climate System. *Limnol. Oceanogr.* **2009**, *54*, 2315-2329.
- 499

500 Table 1. Some examples of studies reporting over-saturated methane concentrations in oxic seawaters.

| Location | Observations | Reference |
|---|---|--|
| Western subtropical N. Atlantic | <ul style="list-style-type: none"> • CH₄ oversaturation in the upper 300 m • Max. 3.5 nM CH₄ overlapping thermocline • Physical transport could not explain observed CH₄ peak | Scranton and Brewer ²⁸ |
| North Atlantic 35°S to 50°N | <ul style="list-style-type: none"> • CH₄ oversaturation in the upper 1000 m; max. ~4 nM CH₄ • CH₄ conc. not correlated with chlorophyll or hydrogen | Conrad and Seiler ²⁹ |
| Southern California Bight, U.S. | <ul style="list-style-type: none"> • CH₄ peak (ca. 8 nM) overlapping thermocline and oxycline • Almost no CH₄ oxidation in the upper 100 m | Ward and Kilpatrick ³⁰ |
| Western North Pacific | <ul style="list-style-type: none"> • High CH₄ (2.2-3.4 nM) within 0-200 m • CH₄ poorly correlated with chlorophyll in upper 100 m | Watanabe et al. ³¹ |
| California coast, U.S.; VERTEX stations | <ul style="list-style-type: none"> • Max. 5.42 nM CH₄ in upper 200 m • Zooplankton guts and sinking particles were suggested as the source | Tilbrook and Karl ³² |
| Arabian Sea | <ul style="list-style-type: none"> • Weakly developed CH₄ max. in the upper 50 m • More pronounced CH₄ max. (up to 8.5 nM) at 150-200 m coinciding max. NO₂ and beam attenuation | Jayakumar et al. ³³ |
| Monterey Bay, U.S. | <ul style="list-style-type: none"> • CH₄ accumulated at thermocline (100-200 m) • CH₄ bubbles from deep water were unlikely the source | Rehder et al. ³⁴ McGinnis et al. ³⁵ |
| Western subarctic gyre of N. Pacific | <ul style="list-style-type: none"> • Up to 12% CH₄ oversaturation in the upper 100 m • Sinking particles were suggested as the source | Sasakawa et al. ³⁶ |
| Fram Strait | <ul style="list-style-type: none"> • High CH₄ (7-9 nM) overlapping high O₂ (380-390 μmol l⁻¹) in upper 20 m | Damm et al. ³⁷ |
| Japan Sea | <ul style="list-style-type: none"> • Average 2.6 nM CH₄ at surface; max. 14 nM at ~50 m • Sediment CH₄ was unlikely the source | Vereshchagina et al. ³⁸ |
| Central Chile upwelling system | <ul style="list-style-type: none"> • 125-550% CH₄ saturation at 0-30 m with >100% O₂ • CH₄ oversaturation coincided with seasonal upwelling, high chlorophyll and high DMSP levels. | Florez-Leiva et al. ³⁹ |
| ALOHA station | <ul style="list-style-type: none"> • CH₄ oversaturation down to 175 m • Max. ~3.6 nM CH₄ coincided with max. 226 μM O₂ | Del Valle and Karl ²⁴ |

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503

504 Table 2. Some examples of studies reporting over-saturated methane concentrations in oxic lake waters.

| Location | Observations | Reference |
|----------------------------------|--|----------------------------------|
| Lake 227, Canada | <ul style="list-style-type: none"> • CH₄ decreased from 282.5 µM at 9 m to ~0.5 µM at 7.5 m • Both CH₄ and oxidation remained low in surface layer | Rudd et al. ⁴⁰ |
| Lake St. George, Canada | <ul style="list-style-type: none"> • CH₄ peak (~5 µM) at 6 m overlapping thermocline, NH₄ and NO₃ peaks; oxidation activity not detectable | Bedard and Knowles ⁴¹ |
| Lake Biwa, Japan | <ul style="list-style-type: none"> • Station A: max. ~175 nM CH₄ coinciding with thermocline and ~250 µmol O₂ l⁻¹ • Station B: max. 205 nM CH₄ coinciding with thermocline and ~188 µmol O₂ l⁻¹ • River runoff, littoral and sublittoral sediments were suggested as the source | Murase et al. ¹³ |
| Lakes in south central Sweden | <ul style="list-style-type: none"> • High CH₄ (~140 µM) near sediment (11 m) • No upper CH₄ peak was observed • High CH₄ oxidation activity below 5 m. | Sundh et al. ⁴² |
| Lake Paul and Lake Peter, USA | <ul style="list-style-type: none"> • CH₄ was nearly zero at thermocline and oxygen peak at 5 m, then increased to 4 µM in the surface layer | Bastviken et al. ⁴³ |
| 10 boreal lakes in Finland | <ul style="list-style-type: none"> • High CH₄ (> 1 µM) in surface layer with 60 to >100% O₂ saturation in some of the lakes | Juutinen et al. ⁴⁴ |
| Sakinow Lake, Canada | <ul style="list-style-type: none"> • CH₄ was low (0.02-0.1 µM) at thermocline depth (~20 m), then increased to ~0.35 µM at the surface • CH₄ bubbles from sediment could not explain high CH₄ in surface water | Vagle et al. ⁴⁵ |
| Lake Constance, Germany | <ul style="list-style-type: none"> • High CH₄ (1.5 µM) above thermocline • Lateral transport from littoral zone was suggested as the source | Hofmann et al. ¹⁴ |
| Lake Stechlin, Germany | <ul style="list-style-type: none"> • Low CH₄ (<0.2 µM) in hypolimnion • Max. ~1.4 µM CH₄ in metalimnion overlapping oxygen peak • Methanotrophs absent in metalimnion • Experiments confirmed active CH₄ production in oxic water | Grossart et al. ¹² |
| Lac Cromwell, Canada | <ul style="list-style-type: none"> • High CH₄ (0.10-0.53 µM) in mesocosms under oxic condition (45.6-128.6% O₂ saturation) | Bogard et al. ⁴⁶ |
| Nine lakes in NE Germany | <ul style="list-style-type: none"> • CH₄ positively correlated with O₂ in surface waters • Euphotic zone CH₄ positively correlated with primary production • Ebullition from sediment was unlikely the source | Tang et al. ⁴⁷ |
| Lake Lugano, Switzerland | <ul style="list-style-type: none"> • High CH₄ (up to 180 nM) in the upper oxic layer in stratification season • Vertical profiles suggest excess CH₄ from a near-surface source | Blees et al. ⁴⁸ |

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Table 3. Methane measurements in four mesocosms within the LakeLab in September, 2012. The mesocosms were 20 m deep with a thermocline at ca. 8 m, and were dominated by different phytoplankton based on pigment composition. The table shows methane concentration, maximum and minimum methane concentrations and the corresponding dissolved oxygen (D.O.) depths are shown. Pigments were measured by BBE (Kiel) probe; temperature and oxygen were measured by (Weilheim) submersible probe; CH₄ of discrete depth water samples was measured by standard headspace method.^{12,47}

| Dominant phytoplankton | Surface CH ₄ (μM) | Max. CH ₄ (μM) | D.O. (mg l ⁻¹) | Depth (m) | Min. CH ₄ (μM) | D.O. (mg l ⁻¹) |
|--------------------------------|------------------------------|---------------------------|----------------------------|-----------|---------------------------|----------------------------|
| Green algae | 0.11 | 0.11 | 11.6 | 3 | 0.05 | 8.7 |
| Chryptophyte and cyanobacteria | 0.11 | 0.12 | 11.6 | 3 | 0.03 | 8.7 |
| Green algae and diatoms | 0.10 | 0.12 | 6.9 | 15 | 0.06 | 8.0 |
| Green algae | 0.23 | 0.23 | 9.13 | 0 | 0.13 | 8.3 |

Table 4. Methane oxidation rates under light and dark conditions. Values for Lake Biwa are calculated for the first 3 days from Fig. 2B and 2C of Murase and Sugimoto.⁵²

| Location | Methane oxidation rate (nmol L ⁻¹ d ⁻¹) | | Reference |
|-------------------------|---|------|-----------------------------------|
| | Light | Dark | |
| Lake Biwa (thermocline) | 0.33 | 2.67 | Murase and Sugimoto ⁵² |
| Lake Biwa (hypolimnion) | 26 | 55 | |
| Lake Stechlin | 89 | 103 | Tang et al. ⁴⁷ |

Figure Legend

Fig. 1. Comparison of two scenarios of methane dynamics in a stratified water column; a: The traditional scenario where methane is produced in the anoxic sediments, transported upward by diffusion and ebullition, and is rapidly consumed by methane oxidation in the hypolimnion, resulting in no or little methane outflux from the system; b: The alternative scenario where oxic methane production occurs in the surface layer. Convective mixing, microbubble detrainment and diffusion in the epilimnion result in higher methane outflux from the system. Downward diffusion also fuels methane oxidation in the hypolimnion. Thermocline is indicated by the dashed line.

Fig. 2. Known and hypothetical methanogenesis pathways. EC numbers for catalysing enzymes marked in green are found in genome annotation of non-methanogenic organisms including *Bacteria* (i.e. non Archaea; based on KEGG taxonomy and PATRIC). Precursor compounds reported for oxic methane production are marked in blue (authors' unpubl. data marked by *). Pathways known to require anoxic environments are grouped in black frames. Known and hypothesized pathways that occur in oxic conditions are grouped within solid or dashed red frames, respectively. See text for details.

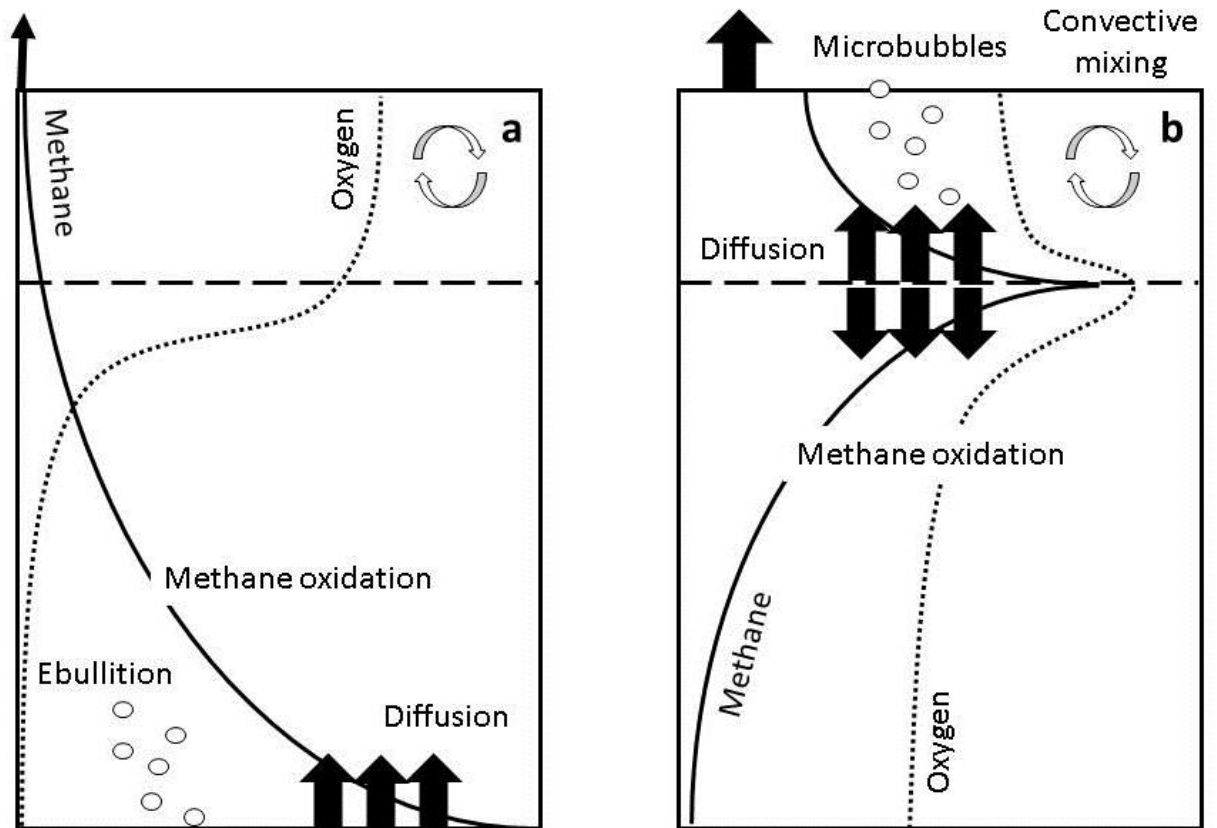


Figure 1. Comparison of two scenarios of methane dynamics in a stratified water column; a: The traditional scenario where methane is produced in the anoxic sediments, transported upward by diffusion and ebullition, and consumed by methane oxidation in the hypolimnion, resulting in no or little methane outflux from the system; b: An alternative scenario where oxic methane production occurs in the surface layer. Convective mixing, microbubble detrainment and diffusion in the epilimnion result in higher methane outflux from the system. Downward mixing fuels methane oxidation in the hypolimnion. Thermocline is indicated by the dashed line.

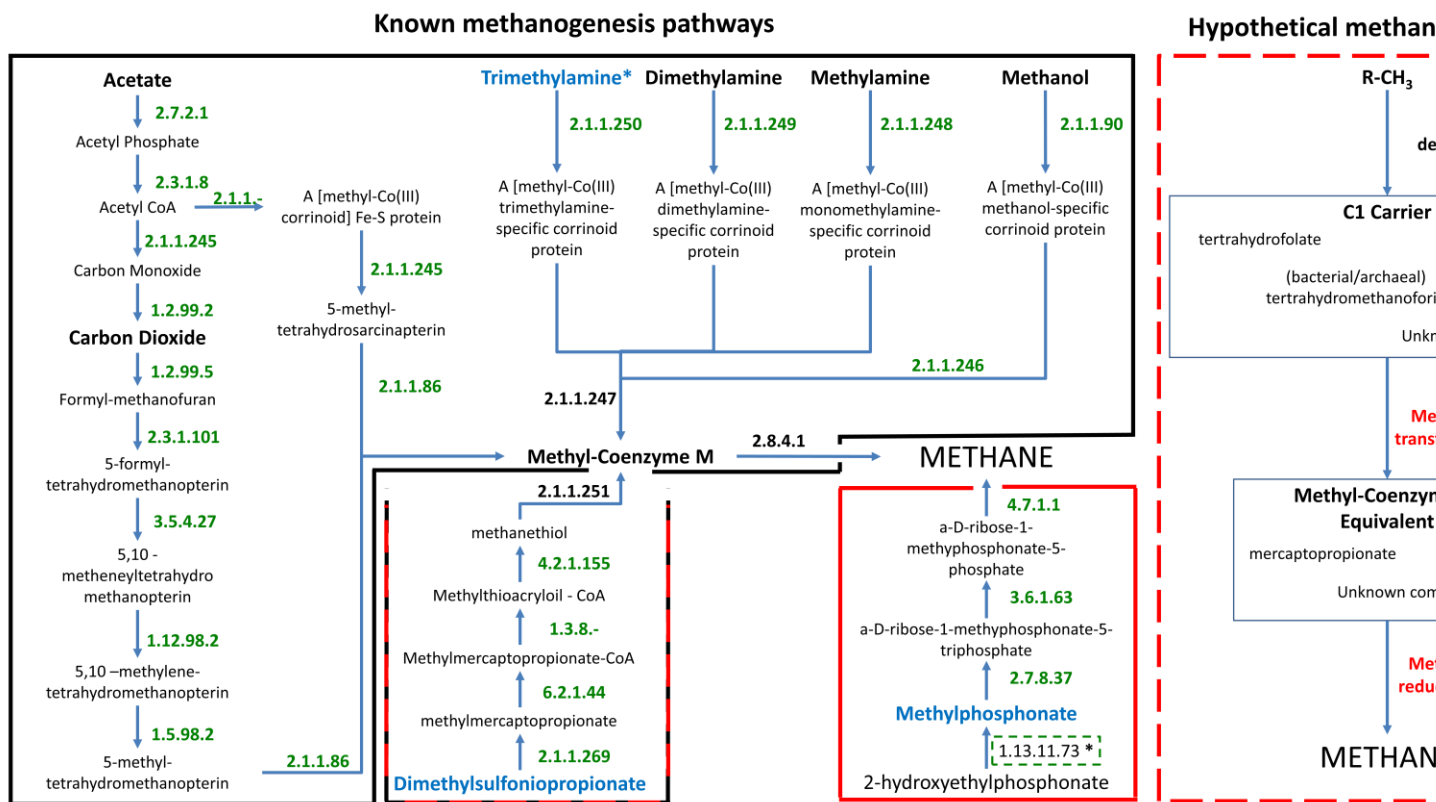


Figure 2. Known and hypothetical methanogenesis pathways. EC numbers for catalysing enzymes may be found in genome annotation of non-methanogenic organisms including Bacteria (i.e. non Archaea; based on taxonomy and PATRIC). Precursor compounds reported for oxic methane production are marked in blue. Data marked by *). Pathways known to require anoxic environments are grouped in black frames. Known and hypothesized pathways that occur in oxic conditions are grouped within solid or dashed red frames, respectively, for details.

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Methane Production in Oxic Lake Waters Potentially Increases Aquatic Methane Flux to Air

Kam W. Tang, Daniel F. McGinnis, Danny Ionescu, Hans-Peter Grossart

