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1 Incubation Experiments, Observations and Modeling Highlight the Key
2 Role of Dimethylmercury on Seawater Methylmercury Distributions

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18 Key words:

19 Methylated Mercury, Enriched Stable Isotopic Tracer Experiments, Atlantic Ocean, Mediterranean
20 Sea, 1D Water Column Model, Marine Hg Cycle

21
22 Short Synopsis Statement:

23 Explaining ambient methylated mercury concentrations in seawater requires considering both
24 dimethylmercury and monomethylmercury, along with their formation rates and stability.

25 Abstract

26 The origin of the bioaccumulative neurotoxin methylmercury (MeHg) in the ocean remains elusive. The
27 current paradigm suggests that microbial methylation of inorganic Hg within the oceanic water column
28 produces monomethylmercury (MMHg) and potentially dimethylmercury (DMHg). Reaction rates and
29 main drivers governing MeHg levels (sum of MMHg and DMHg) are poorly constrained. We conducted
30 ambient Hg species measurements and enriched isotopic tracer experiments in waters of two
31 contrasting marine environments, the oligotrophic Mediterranean Sea (MED) and the mesotrophic
32 Atlantic Ocean (ATL). Maximum subsurface MeHg levels were ~2 times higher in the MED compared
33 to the ATL, essentially driven by higher DMHg concentrations (0.45 ± 0.06 vs 0.16 ± 0.02 pM).

34 Methylation was only detectable in unfiltered subsurface waters and presumably biotically driven. The
35 highest methylation rate (MMHg to DMHg) was observed in subsurface MED waters while reduction
36 and demethylation rates were highest in surface waters of both environments. Experimental reaction
37 rates and the potential microbial activity (based on 16S rDNA) aligned with ambient Hg species
38 distributions.

39 Assuming high DMHg stability and applying our fast experimental DMHg formation rates, a newly
40 developed 1D water column model (MED) successfully reproduced MeHg species distribution,
41 suggesting DMHg plays a key role in the global marine Hg cycle.

42 1. Introduction

43 Monomethylmercury (MMHg) is of global concern due to the capacity of this neurotoxin to biomagnify
44 across trophic levels [1]. The primary exposure pathway to MMHg for humans is the consumption of
45 marine fish [2]. The Minamata Convention aims to reduce human exposure to Hg, by reducing
46 anthropogenic Hg emissions, with substantial progress made since its ratification [3]. Mercury remains
47 of concern since anthropogenic activities have led to an approximately threefold increase of oceanic
48 surface Hg concentrations compared to pre-anthropogenic levels [4].

49 Once Hg has entered the ocean it can undergo a series of abiotic and biotic transformations (e.g.
50 methylation, demethylation, reduction, oxidation) [5]. The main Hg species found in the ocean are
51 monomethylmercury (MMHg), dimethyl Hg (DMHg), elemental Hg (Hg(0)), and inorganic mercuric Hg
52 (Hg(II))[6]. Due to analytical constraints operationally defined Hg species such as methylated mercury
53 (MeHg) as the sum of MMHg and DMHg and dissolved gaseous Hg (DGM) the sum of Hg(0) and DMHg
54 are commonly reported [7].

55 Despite considerable efforts, a lack of understanding persists on Hg transformation pathways likely
56 governing ambient Hg species concentrations. The limitations of our current understanding of MeHg
57 cycling in the ocean is exemplified by the limited reproducibility of MeHg observations in oceanic
58 waters by coupled biogeochemical models [8,9]. The prevailing scientific consensus agrees on biotic *in*
59 *situ* Hg methylation [10,11] as the major source of MeHg in oceanic waters, with its distribution often
60 closely linked to microbial organic matter degradation [12–14].

61 The importance of anaerobic microorganisms (e.g. sulfate-reducing bacteria, iron-reducing bacteria,
62 methanogenic archaea) in mediating methylation is well known in anoxic environments, with the
63 *hgcAB* genes encoding for Hg methylation [15]. Microbes thriving in oxic marine waters bear similar
64 Hg transformation genes but their importance in Hg methylation is still debated [16–18]. Incubation
65 experiments evidence the methylation of Hg(II) in oxic marine waters [10,11]. The cycling of DMHg in
66 seawater is less understood, but it appears to be connected to the formation and decomposition of
67 MMHg [10,19–22].

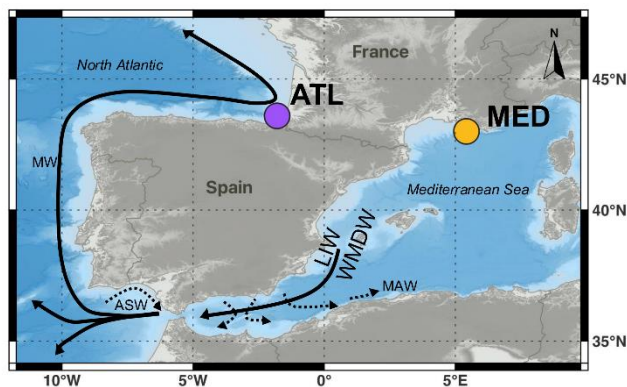
68 The *mer operon*, broadly distributed among prokaryotes [23–25], encodes for enzymes mediating
69 reduction (MerA) and demethylation (MerB). The presence and activity of the *mer operon* in the global
70 ocean, even under low ambient oceanic Hg(II) and MeHg concentrations, has been demonstrated for
71 *Alteromonadales* (*merA*, *merB*), *Rhodobacterales* (*merA*), *Flavobacteriales* (*merA*, *merB*), and
72 *Sphingobacteriales* (*merB*) among others [26,27].

73 The main objective of this study was to investigate potential Hg species reaction rates and drivers. We
74 selected two contrasted marine environments with different productivity and Hg species distribution,
75 I) offshore, oligotrophic waters of the northwestern Mediterranean Sea (MED) and II) coastal,
76 mesotrophic waters of the Bay of Biscay, northeastern Atlantic Ocean (ATL). We conducted sampling
77 campaigns during spring bloom in the MED in May 2021 and in the ATL in May 2022. We measured
78 ambient Hg species concentrations (THg, MMHg, DMHg, DGM) along vertical profiles, conducted
79 enriched isotope tracer incubation experiments and microbial diversity analysis (16S rDNA sequencing)
80 at biogeochemically relevant depths. We use the determined rate constants and reaction pathways in
81 a 1D water column model set-up to test the plausibility of our rates.

82 2. Material & Methods

83 2.1. Study Sites

84 Sampling was conducted on the 4th of May 2021 (MED station; 43° 0' 16.128" N, 5° 25' 21.792" E, 1500
85 m), northwestern Mediterranean Sea onboard the research vessel Antédon II, shortly after a wind
86 driven upwelling event (1st to 3rd May) [28]. For the North Atlantic (ATL) station sampling was
87 conducted on the 10th of May 2022 in the southeastern Bay of Biscay (ATL station; 43° 35' 43.8" N, 1°
88 47' 42.6012" W, 760 m) in onboard the research vessel Côte de la Manche. The MED station is an
89 oligotrophic off-shore station , with no major riverine influence nearby [29], while the ATL station is a
90 mesotrophic station under the influence of the Adour River [30]. A description of the two study areas
91 is given in the SI.



100

101 Figure 1. Illustrates the two sampling points in the two studied environments in the Mediterranean
102 Sea and the North Atlantic. Arrows indicate main patterns of oceanic currents [31], dashed lines
103 indicate surface currents and solid lines subsurface currents. LIW = Levantine Intermediate Waters,
104 WMDW = Western Mediterranean Deep Waters, MW = Mediterranean Waters, MAW = Modified
105 Atlantic Waters, ASW = Atlantic Surface Water. Map created with Qgis. Underlying bathymetry from
106 GEBCO.

107 2.2. Water Sampling and Sample Handling

108 Samples were obtained from acid cleaned (1 % HCl) 10 L GOFLO (General Oceanics) bottles mounted
109 to an epoxy-painted trace metal clean carousel, following ultra-trace metal clean protocols [32].
110 Sampling bottles were thoroughly rinsed with the corresponding water without filtration and filled
111 without head-space. Samples for total Hg (THg) (MED, ATL) were sampled into 60 mL FEP bottles
112 (Nalgene) and kept at +4°C until analysis. For the ATL, DGM was sampled into 500 mL FEP/PFA bottles
113 (Nalgene), purged onto gold coated sand traps (Au-traps) and stored at -20°C until analysis. For the
114 MED, DGM was sampled into 125 mL PET bottles (VWR) and kept at +4°C until analysis. DMHg (MED,
115 ATL) was sampled into 500 mL FEP/PFA bottles (Nalgene), directly purged onto graphitized carbon
116 (Carbotraps) and kept at -20°C until analysis. The DMHg-purged sample was acidified to 0.5% (v/v) with
117 HCl (Optima™) for MMHg analysis and an unpurged sample was acidified in the same way for MeHg
118 analysis [33] and stored dark in double zip closed bags at +4°C until analysis.

119 For the ATL, seawater for incubation experiments was sampled at the surface (SML), Chlorophyll
120 maximum (DCM), Oxygen minimum (min O₂), deep water (DW) (Figure 2) and filled into 1 L FEP/PFA
121 bottles (Nalgene), or 5 L PE containers. Dedicated samples were filtered using an acid cleaned filtration
122 tower (Nalgene) with acid cleaned 0.2 µm PP (Pall) or 0.22 µm PVDF membranes (Merck Millipore).
123 The respective sampling bottles containing seawater for incubations were then stored in double zip
124 closed bags, dark at +4°C until the start of the experiments the following day.

125 Filters to investigate the bacterial community composition (16S rDNA) were sampled in replicates by
126 the filtration of 1 L of seawater onto a PP 0.2 µm membrane (MED; Pall) or sterile 0.2 µm cellulose
127 acetate filter (ATL; Sartorius, Thermo Fisher Scientific) and stored in sterile cryotubes at -80°C until
128 extraction.

129 2.1. Determination of Ambient Hg Species

130 Measurements were conducted following established protocols, all reagents were prepared with
131 ultrapure water obtained from a Milli-Q system (Millipore, 18.2 MΩ cm) using analytical grade
132 reagents. THg was analyzed following a modified USEPA method 1631 by Bromine monochloride (BrCl)

133 oxidation, stannous chloride (SnCl_2) reduction purge and trap followed by cold vapor atomic
134 fluorescence spectrometry (CV-AFS, Brooks Rand, Model 3) the day after sampling [34]. For the MED,
135 DGM samples were analyzed the day after sampling on the same instrument without oxidation and
136 reduction and a higher sample volume (~ 125 mL), as previously described elsewhere [35]. For the ATL,
137 DGM samples were analyzed by double amalgamation on gold-CV-AFS [36,37] within 10 days of
138 sampling, DMHg was analyzed by cryogenic trapping GC-ICPMS [33,38] within 30 days of sampling.
139 MeHg and MMHg were analyzed by species-specific isotope dilution analysis followed by GC-ICPMS
140 [33,39] within 30 days of sampling.

141 2.2. Incubation Experiments

142 All incubations were conducted in triplicates, following an established protocol [40]. Briefly, samples
143 were amended to ~ 10 pM of $^{199}\text{Hg}(\text{II})$ and ~ 1 pM of MM^{201}Hg and incubated the day after sampling
144 under natural light or dark conditions in water baths on the rooftop of MIO (MED; Mediterranean
145 Institute of Oceanography, Marseille) or on the lower deck on board the research vessel (ATL).
146 Additional experiments to follow the formation of DMHg were conducted for the MED under dark
147 conditions for DCM, min O_2 and DW. For the ATL, the applied protocol allows to differentiate between
148 the formation of Me^{199}Hg or MM^{199}Hg from added $^{199}\text{Hg}(\text{II})$ [40]. All experiments were conducted on
149 unfiltered and filtered waters ($0.2 \mu\text{m}$), the latter considered as abiotic control, removing the majority
150 of particles and living cells [41–43]. Incubation samples (aqueous) were analyzed by GC-ICPMS applying
151 quadruple species-specific isotope dilution [20,21], and traps (Au-, carbo-) were analyzed by cryogenic
152 trapping GC-ICPMS [22].

153 Reaction rates were calculated assuming pseudo-first order reaction kinetics from a two-point
154 (demethylation, methylation of $\text{Hg}(\text{II})$) or a one point incubations (reduction, reductive demethylation,
155 methylation of MMHg to DMHg). Demethylation was calculated as the slope of
156 $\ln(\text{MM}^{201}\text{Hg}/\text{MM}^{201}\text{Hg}_{t_0})$, all other rates constants were calculated assuming a linear increase of the
157 reaction product (reduction, reductive demethylation, methylation of $\text{Hg}(\text{II})$ and MMHg). Additional
158 information on incubations can be found in the SI.

159 2.3. Ancillary Parameters

160 Temperature, Salinity, Oxygen and Fluorescence were measured *in situ* with a conductivity
161 temperature density (CTD) probe (Seabird SBE 911plus), equipped with an Oxygen Sensor (Seabird SBE
162 43), beam transmissometer (SeaBird Scientific C-Star) and fluorometer (Chelsea Aquatracka III). DNA
163 from *in situ* samples was extracted using the DNeasy PowerSoil Pro Kit (QIAGEN, Germany) according
164 to the manufacturer's instructions and stored at -20°C. The 16S rDNA sequencing analysis through
165 MiSEQ was performed following established methods and details can be found in the SI.

166 2.4. Quality assessment and Quality control

167 Method detection limit for ambient THg was 30 fM based on 3 x SD of the blank signal, for DGM 5.5 fM
168 based on 3 x SD of purge blank measurements, for DMHg 0.38 fM based on the background equivalent
169 concentration (BEC), and for MeHg and MMHg 15 and 12 fM based on the BEC. Relative standard
170 deviation (RSD) for replicate samples for THg was usually better than 6 % at ~1 pM, and was
171 determined for DGM with 9.6 % at 0.09 pM (n = 3), for DMHg with 7 % at 0.11 pM (n = 3), for MeHg
172 with 4.7 % at 0.07 pM, and for MMHg with 7.9 % at 0.05 pM (n = 3). The RSD for each species was
173 similar or better than the established measurements uncertainty for THg [44], DGM [45], MMHg and
174 DMHg [33].

175 2.5. 1D Water column Model

176 We conducted a modeling exercise in order to test the feasibility of newly determined DMHg formation
177 rates (~6 times faster than in current models) in this study and their impact on ambient Hg species
178 distribution. To model the Hg speciation at the MED station, we use the GOTM-ECOSMO-MERCY
179 modeling system. We chose to model only the MED station, as lateral and bottom influences can be
180 considered to be of minor importance in contrast to the ATL station. GOTM is a hydrodynamic 1D
181 model that calculates the turbulence of a vertical water-column by solving the 1D transport equation
182 of momentum, salinity, and temperature. Thus, the model only has a vertical and no horizontal
183 resolution [46,47].

184 ECOSMO is an end to end ecosystem model including the 7 biological functional groups for
185 phytoplankton, zooplankton, macrobenthos, and fish [48]. MERCY is a Hg cycling model including
186 speciation of Hg(0), Hg(II) HgS, MMHg(I), and DMHg in water, sediment, and biota, the partitioning of
187 Hg(II) and MMHg(I) between the dissolved, particulate, and colloidal phases, and the air-sea exchange
188 of Hg(0) and DMHg [49]. Based on our hypothesis that DMHg formation is biotically mediated, we scale
189 our maximum DMHg formation rate determined to remineralization.

190 The coupled GOTM-ECOSMO-MERCY model was run for 20 years whereof the first 19 years were
191 discarded as spin-up period. For a detailed description of the GOTM model, the modeled Hg species,
192 and the reaction rates, please refer to the SI.

193 3. Results & Discussion

194 3.1. Biogeochemical Characteristics of the Two Study Sites

195 The MED station is representative for warm, oligotrophic waters, while the ATL station is
196 representative for mesotrophic waters. We observed higher salinity (S) and temperatures (T) in the
197 deepest sampled waters of the MED (800 m depth, S: 38.6, T: 13.4°C) compared to the ATL (750 m
198 depth, S: 35.7, T: 10.3°C). The ATL station also showed a moderate freshwater influence (S: 34.7) from
199 the Adour river extending down to ~79 m until reaching typical Atlantic salinity values (35.4). A relative
200 fluorescence maximum, indicating the DCM depth was observed with typical $\delta^{13}\text{C}$ signatures of
201 phytoplankton for the respective environment [50] at both stations, at ~53 m for the MED ($\delta^{13}\text{C}$: 23.44
202 to 24.7 ‰) and ~43 m for the ATL ($\delta^{13}\text{C}$: 24.65 ‰).

203 At the MED station, oxygen decreased ($\sim 149 \mu\text{mol kg}^{-1}$) accompanied by a slight salinity increase to up
204 to 38.7 down to ~475 m indicative of Eastern Levantine Intermediate Waters forming a relative min O_2
205 zone [51]. Below ~500 m oxygen concentrations increased until the deepest point of sampling (~800
206 m), representative of Western Mediterranean Deep Waters (Figure SI 2).

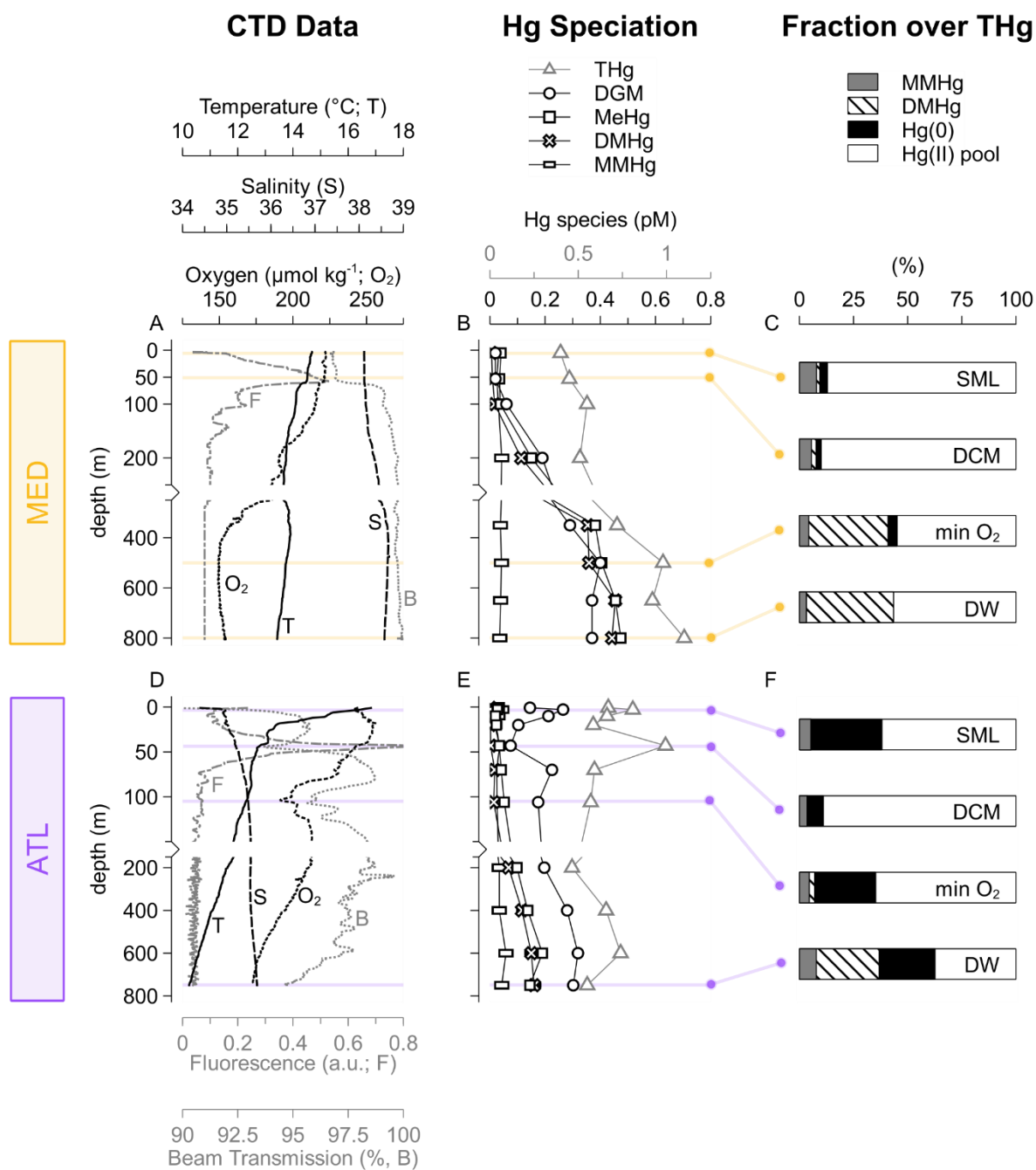
207 For the ATL, we observed a relative subsurface min O_2 at ~104 m ($\sim 191 \mu\text{mol kg}^{-1}$) which coincided with
208 a decrease in beam transmission. Below this relative min O_2 , oxygen increased within the Eastern North
209 Atlantic Central Water, followed by a decrease in oxygen and beam transmission down to the bottom.
210 This decrease in oxygen could be due to the mixing with Mediterranean overflow waters below ~500 m
211 (Figure SI 2), or the influence of remineralization of remobilized particles, described for the Capbreton
212 Canyon [52,53].

213 3.2. Ambient Hg Species

214 Median THg concentrations were comparable between the two study stations, although more variable
215 at the MED with 0.64 pM (interquartile range (IQR) = 0.50 - 0.94 pM) than at the ATL with 0.66 pM (IQR
216 = 0.58 – 0.71 pM). The vertical profiles of THg differed between both stations (Figure 2). For the MED,
217 THg was depleted at the surface, potentially due intense atmospheric exchange, and continuously
218 increased with depth. At the ATL, THg peaked at the DCM depth (~1 pM) without showing a depletion
219 at the surface due to the input of Hg from the Adour River plume [30]. Despite that a decrease in beam
220 transmission below ~600 m possibly suggests a sediment influence, no clear impact on THg
221 concentrations was observed at the deepest sampling point for the ATL station (Figure 2D). Our
222 observations for the MED for THg are in the range of previous observations for the MED [12,29,51,54].
223 In contrast, our observations for the ATL for THg are lower than earlier observations reported at the
224 same station during a higher discharge event of the Adour river [30] but align with previous
225 observations for the North Atlantic, and the Iberian Abyssal Plain [29,55,56].

226 We observed an increase of MeHg with depth at both stations, while MMHg was uniformly distributed
227 along the profiles and remained low (<0.06 pM), at the MED (median = 0.037 pM, IQR = 0.031 – 0.040
228 pM) and ATL station (median = 0.034 pM, IQR = 0.026 – 0.039 pM). In contrast, DMHg increased with
229 depth, reaching concentrations at the MED roughly two times higher (0.45 ± 0.06 pM; maximum \pm
230 measurement uncertainty ($k = 2$)) than at the ATL station (0.16 ± 0.02 pM; maximum \pm measurement
231 uncertainty ($k = 2$)). DMHg always dominated the MeHg pool below ~200 m (Figure 2B, D; Figure SI 3),
232 thus MeHg variations were primarily driven by DMHg levels. Our observations for MMHg
233 concentration levels align with previous studies for the MED [29] and the eastern North Atlantic, which
234 reported similarly low MMHg concentrations (generally below 0.1 pM) [29,55]. DMHg concentrations
235 for both stations were higher [55,57] or within the range of literature values for the respective oceanic
236 basin [29]. The importance of DMHg within the MeHg pool has previously been suggested for the MED
237 [12,29,54,58], ATL [20,29] and other oceanic basins [20,59,60] although contrasting observations have
238 also been reported [55,57,61].

239 Similarly, the importance of DMHg within the DGM pool has been debated, in particular for the MED
240 [51]. Our observations were in the range of literature values [29,30,57,62]. DGM concentrations were
241 comparable between the MED (median = 0.27 pM; 0.05 – 0.37 pM) and the ATL station (median = 0.21
242 pM; IQR = 0.16 – 0.27 pM), although DMHg was more prominent within the DGM pool for the MED
243 (median = 75 %, IQR = 43 – 120 %) than the ATL station (median = 8 %, IQR = 2 – 38 %), overall indicating
244 that Hg(0) was of higher importance in ATL mesotrophic waters than in MED oligotrophic waters.
245 Based on our results, we suggest that DMHg is an important Hg species in particular within the MeHg
246 pool and is key for explaining the differences in observed ambient MeHg maxima and its proportion of
247 THg. This is supported by the consistently low MMHg concentrations in both environments, in contrast
248 to the higher and more variable DMHg levels that dominated the MeHg pool at depth.



249
 250 Figure 2. Illustrates CTD Data, Hg speciation and the relative fraction for each Hg species over the THg
 251 pool for the depths chosen for incubation experiments. The upper row corresponds to the MED and
 252 the lower row to the ATL study site. B, E) Primary x-axes (0 – 1.25) correspond to THg and secondary
 253 x-axes corresponds to DGM, MeHg, DMHg, and MMHg. Please note that the y-axes are broken at 250
 254 m (MED) and 150 m (ATL) to emphasize surface variability. For Hg speciation profiles and relative
 255 fractions, including measurement uncertainties at $k = 2$, refer to Figure SI 3.

256 3.3. Hg Species Transformations

257 We detected methylation of Hg(II) to MeHg and DMHg, as well as the conversion of MMHg to DMHg,
258 exclusively for unfiltered subsurface waters. We consider unfiltered water to be representative of *in*
259 *situ* conditions, including the presence of particles and living cells. These findings, combined with the
260 significance of bacterial activity in marine subsurface waters [63] suggest a particle-dependent, likely
261 biotically driven *in situ* methylation pathway. This aligns with the prevailing scientific consensus that
262 biotic *in situ* methylation predominantly governs MeHg in seawater [6,64].

263 We observed the highest potential methylation for the formation of DMHg from MMHg, at the MED
264 station within min O₂ waters and DW (Figure 3A), followed by the formation of MeHg from Hg(II) in
265 DW at the ATL station (Figure 3D). Highest potential methylation coincided with the highest relative
266 abundance (>8 %) of potential *hgcAB* bearing phyla according to microbial community analysis (16S
267 rDNA) at both stations (Figure 3A, D). Dedicated experiments to investigate the formation of DMHg
268 from MMHg were conducted under dark conditions at the MED station (for DCM, min O₂ and DW). For
269 experiments conducted at the ATL station we examined our purged incubation samples (MM¹⁹⁹Hg, n
270 = 3) and compared them to unpurged samples (Me¹⁹⁹Hg, n = 3), used to calculate methylation rates
271 from Hg(II) to MeHg. We found a significant difference (one tailed t-test, p <0.05) between Me¹⁹⁹Hg
272 and MM¹⁹⁹Hg in DW. In DW, MM¹⁹⁹Hg accounted with ~10 % for the minor fraction of Me¹⁹⁹Hg
273 suggesting the dominant formation of DMHg from Hg(II). In contrast to the methylation observed for
274 min O₂ waters at the ATL station, where the absence of a significant difference suggests that
275 methylation to MM¹⁹⁹Hg was predominant, although the importance of this pathway remains
276 uncertain since methylation levels were close to the detection limit.

277 The potential *in situ* formation of DMHg (min O₂: MED; DW: MED, ATL) observed in incubation
278 experiments aligns with the depths where DMHg dominated the ambient MeHg pool (Figure 2C, F).

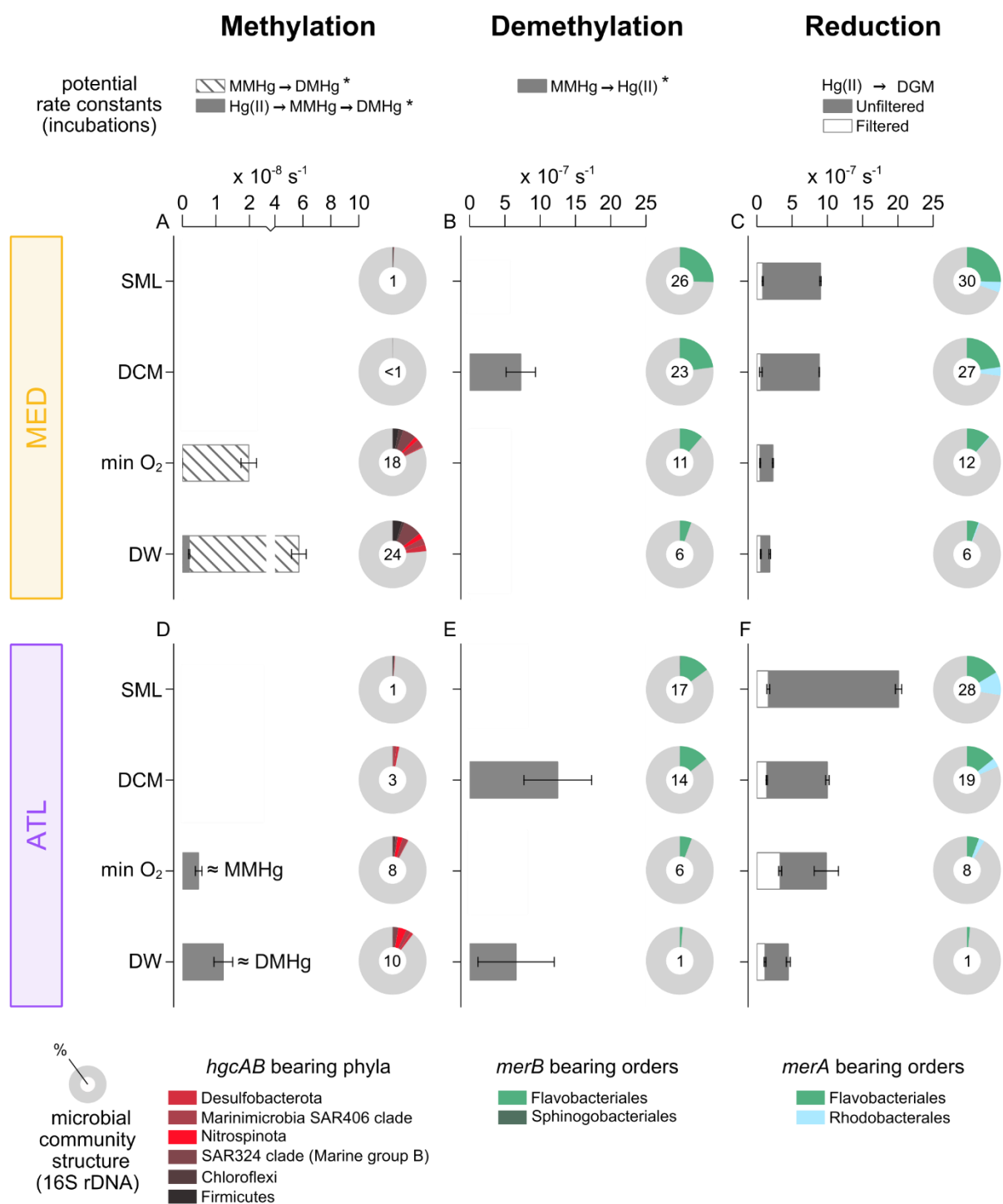
279 Our observed rate constants for the formation of MeHg (from Hg(II) and MMHg) are in agreement with
280 literature data for MeHg formation from Hg(II) (see Table SI 6). In contrast, our highest observed rate

281 constants of DMHg formation from MMHg, were ~3 times higher (see Table SI 8), than highest, species-
282 specific rate constants reported for polar marine waters [10].

283 Light-induced rates for Hg(II) reduction and MMHg demethylation were approximately one order of
284 magnitude faster than dark rates, consistent with previous observations [10,11,30,65,66]. The
285 reduction of Hg(II) was ubiquitous under natural light (Figure SI 5) and dark conditions (Figure 3C, F),
286 with consistently higher rates in the unfiltered samples. Lower rates in filtered samples (0.2 μ m) thus
287 suggest a biotic contribution [67–71] whereas it remains unclear whether reduction was directly
288 mediated by microbial pathways or indirectly induced by biotic activities, e.g. through biogenic organic
289 compounds released by cells. In contrast, the light-dependent demethylation rates of MMHg were
290 relatively similar for unfiltered and filtered incubations (Figure SI 5). Dark demethylation of MMHg was
291 exclusively observed for unfiltered incubations, at similar rates at the DCM at both stations (Figure 3B,
292 E) and in DW only at the ATL station (Figure 3E).

293 Microbial community analysis, conducted on incubated water samples confirmed the presence
294 (>0.1 %, Figure 3) of *Rhodobacterales* (*merA*), *Flavobacteriales* (*merA*, *merB*) in all samples and
295 *Sphingobacteriales* (*merB*) only in surface waters (0.3 ± 0.05 %, $n = 3$) at both stations. In agreement
296 with the highest potential rate observed in incubation experiments for reduction and demethylation
297 in surface waters (SML, DCM), and lowest potential rate in deepest samples (DW). The highest relative
298 abundance of *Rhodobacterales* (*merA*) in the SML at ATL station (11.2 ± 0.2 %, $n = 3$) coincided with
299 the highest dark reduction rate observed in this study. *Mer*-independent reduction pathways, such as
300 the production of reactive oxygen species by heterotrophic bacteria [72,73], extracellular reduction
301 through superoxide formation [74], the use of Hg(II) as an electron acceptor by phototrophs [75,76],
302 and light-dependent processes previously linked to primary productivity [67,71,77], may also be of
303 relevance under our experimental conditions. Similarly, *mer*-independent demethylation pathways
304 may include intracellular *mer*- (see SI 6) and light-independent demethylation mediated by
305 phytoplankton, as demonstrated in laboratory experiments [78], and demethylation by sulfate

306 reducing organisms [79], particularly in DW at the ATL station where we observed dark biotic
307 demethylation.



308

309 Figure 3. Illustrates potential transformation rates as determined in incubation experiments and the
 310 potential to mediate Hg species transformations within the microbial community based on 16S rDNA
 311 analysis. Upper row corresponds to the studied site in the Mediterranean (MED) and lower row to the
 312 Atlantic (ATL). Please note the different x-axes and broken x-axes for A and D. The potential for
 313 methylation within the microbial community is presented at phyla level for known *hgcAB* bearing
 314 microorganisms [15–17,80,81], and for reduction and demethylation was based on orders previously
 315 shown to be actively expressing the *mer-* operon under environmentally relevant conditions [27].
 316 *Potential transformation as evidenced by incubation experiments only observed in the presence of
 317 particles. If no symbol is shown for a certain depth, it indicates that the reaction was not detected at
 318 that specific depth.

319 3.4. The Need to Separate MMHg and DMHg Dynamics

320 The origin of marine MeHg is still debated [82] and the underlying mechanisms governing ambient
321 MMHg and DMHg levels in marine oxygenated waters are not well understood. Methylation of Hg(II)
322 to MMHg, mediated by *hgcAB* bearing microorganisms, is known to occur under anaerobic conditions
323 [15,79,83]. Anoxic micro-niches within sinking particles, have been proposed as potential sites for Hg
324 (II) methylation [14,17] in marine oxygenated waters [84].

325 At the MED site, we observed the formation of DMHg from MMHg in both the min O₂ and DW waters.
326 However, simultaneous methylation of Hg(II) to DMHg was only detected in DW, and was the slowest
327 methylation rate observed and below the DL for MeHg formed in aqueous samples (DL lower by
328 approximately one order of magnitude). Our observations at the MED site and the limited available
329 literature suggest a two-step mechanisms (Hg(II) → MMHg → DMHg) for the formation [10,19] as well
330 as the degradation of DMHg [21,22,60,85,86]. While our results indicate the crucial role of particles for
331 both methylation steps, different biotic or abiotic drivers (e.g. particle size distribution, organic
332 substrate, bacterial diversity and heterotrophic activity) may influence each individual step. It is also
333 possible that the two methylation steps may occur spatially or temporally independent of each other
334 or display distinct sensitivity/reactivity to/with oxygen [10,11,19]. In addition, methylation of Hg(II)
335 may also have occurred in deeper waters but at rates below our DL. We find that studying the dynamics
336 of MMHg and DMHg separately is essential for explaining MeHg maxima in marine oxygenated waters.
337 The importance of distinguishing MMHg and DMHg dynamics, is furthermore exemplified by the
338 discrepancy between MMHg demethylation and MeHg formation rates observed for DW at the ATL
339 station. In our experiments, MMHg demethylation rates were ~2 times higher than the formation of
340 MeHg from Hg(II), suggesting a net demethylation of MeHg. However, MeHg mainly present as DMHg
341 comprised ~26 % of ambient THg in DW, together with the preferential formation of DMHg from Hg(II)
342 in our experiments, point towards the crucial role of DMHg in the system. Published dark
343 demethylation rates (MMHg → Hg(II)) are ~23 times higher (median values, log-transformed) than
344 dark methylation rates (Hg(II) → MeHg) (Table SI 6 and SI 7). Literature data thus indicate a net

345 demethylation globally, which contrasts with the widespread presence of MeHg in the ocean [7].
346 Overall our observations and literature data suggest that a net methylation rate, based solely on the
347 MeHg formation ($\text{Hg(II)} \rightarrow \text{MeHg}$ (MMHg + DMHg)) and demethylation of MMHg ($\text{MMHg} \rightarrow \text{Hg(II)}$),
348 does not fully resolve the biogeochemical MeHg cycle [20,21,59,87,88].

349

350 3.5. Water Column Model

351 Observations of *in situ* DMHg formation rates in oxygenated marine waters are scarce (Table SI 8), with
352 our observed maximum rates ($\text{MMHg} \rightarrow \text{DMHg}$) being ~6 times higher than rates applied in current
353 biogeochemical models [8,9]. The important formation of DMHg raises questions about the stability of
354 DMHg influencing its fate in seawater. Unlike particle-reactive MMHg (and Hg(II)), which can be
355 scavenged and exported to deeper waters and sediments, DMHg, as a neutral dissolved gas, and may
356 persist in the water column [89]. Early studies suggested that DMHg is highly stable in the deep ocean
357 [20], while the photolytic degradation of DMHg [21,60], demethylation in surface waters [87], and
358 evasion to the atmosphere [86,90] are important loss mechanisms. There is a lack of experimentally
359 determined *in situ* rates but stability experiments indicated that DMHg remained stable over a period
360 of at least 20 days [91] to weeks [22].

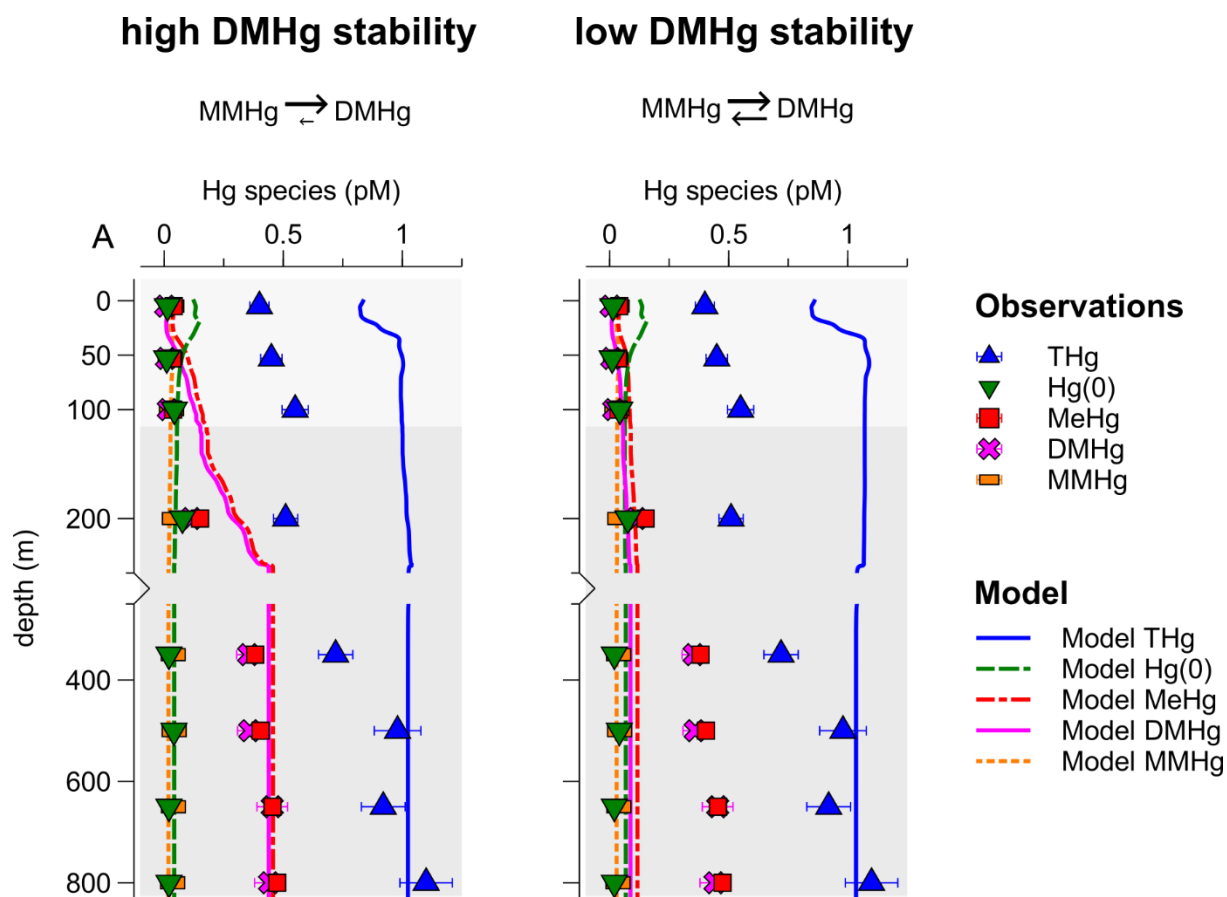
361 Our experimental set-up was not designed to assess the stability of DMHg. Based on the importance
362 of DMHg within the ambient MeHg pool, we hypothesize that both the formation and stability of DMHg
363 are key to explain MeHg maxima. To test this hypothesis and the plausibility of our rates, we modeled
364 ambient Hg species along a vertical profile for the MED station.

365 We included two DMHg demethylation rates in our model runs, previously applied in coupled
366 biogeochemical models [8,9,49] a low rate of $2.2 \times 10^{-9} \text{ s}^{-1}$ (high DMHg stability) and a high rate of 1.9
367 $\times 10^{-8} \text{ s}^{-1}$ (low DMHg stability) while keeping our fastest observed DMHg formation rate ($5.71 \times 10^{-8} \text{ s}^{-1}$
368 at +20°C). Reduction, oxidation, methylation of Hg(II) to MMHg and demethylation of MMHg were
369 kept constant for both model scenarios (Table SI 5).

370 Overall the agreement between modeled THg and observational data was good, within a factor of 2
371 (see Figure SI 9), with better agreement in deep waters (>101 m) than for surface waters (0 – 101 m),
372 where THg was overestimated by ~110 % (Figure 4). Modeled Hg(0) deviated from observations, with
373 a good fit in the surface compared to our (Figure SI 10) and previous observations at the same station
374 (Figure SI 11, Figure SI 12) [29].

375 For MeHg species, subsurface observations for this and a previous study, could only be reproduced
376 under the high DMHg stability scenario (Figure 4A, Figure SI 11). The slight underestimation of MMHg
377 (<30 %, average) may be attributed to an underestimation of MMHg formation rates or its stability.

378 The 1D water column model supports the plausibility of our high DMHg formation rates, and indicates
379 that DMHg must be very stable. High DMHg stability mediates high DMHg concentrations, even if
380 methylation of Hg(II) to MMHg is slower than the demethylation of MMHg to Hg(II).



381 Figure 4. Illustrates model output for Hg species and observations (error bars represent
 382 measurement uncertainties at $k = 2$) for the MED station. The results are presented in pM for the A)
 383 high DMHg stability and B) low DMHg stability.

384 3.6. Environmental Implications

385 Our study highlights the important role of DMHg in the marine biogeochemical cycle of MeHg. We
386 demonstrate the potential for formation of DMHg in deep waters of two distinct environments,
387 consistent with the dominance of DMHg within the MeHg pool. Under our experimental conditions,
388 the formation of both MMHg and DMHg was limited to the subsurface waters and appeared to be
389 biotically mediated, as it was exclusively detected in the presence of particles and living cells.

390 Our modeling exercise suggests that both, the formation of MMHg and DMHg, as well as their stability,
391 are key to explain ambient MeHg concentrations. Our study indicates that DMHg formation rates
392 applied in current coupled biogeochemical models may be underestimated. In addition, current
393 models may underestimate the stability of DMHg [8,9]. Both methylation (of Hg(II) and MMHg) and
394 demethylation rates (of MMHg and DMHg) were kept constant in our model, and reproduced MeHg
395 observations well. However, it is likely that these rates exhibit a seasonal variability [11] driving
396 ambient seasonal MeHg variations in the MED [13] and elsewhere [88,92]. Future work should include
397 more MMHg and DMHg observations and further investigate seasonal changes, along with MMHg and
398 DMHg formation rates. We anticipate that systematically integrating microbial diversity and activity
399 data, with Hg species transformation rates, will help to better understand the marine Hg cycling which
400 is needed to update current models guiding future Hg mitigation strategies in the frame of the
401 Minamata Convention on Mercury.

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434

435 Supporting Information

436 Additional details on the study sites, experimental setup, and model configuration, as well as a

437 summary of literature-reported rates for methylation and demethylation, are provided in the

438 supporting information. The supporting information also includes results from microbial community

439 analyses (16S rDNA), reductive demethylation experiments, and tables summarizing reaction rates and

440 modeling data.

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745 TOC Graphic

