1 # Effect of elevated pCO$_2$ on trace gas production during an

2 # ocean acidification mesocosm experiment

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31 **Abstract**

32 A mesocosm experiment was conducted in Wuyuan Bay (Xiamen), China to investigate the effects of elevated

33 pCO$_2$ on phytoplankton species and production of dimethylsulfide (DMS), dimethylsulfoniopropionate (DMSP)

34 and DMSP-consuming bacteria (DCB) as well as four halocarbon compounds (CHBrCl$_2$, CH$_3$Br, CH$_2$Br$_2$, and

35 CH$_3$I). Over a period of 5 weeks, *Phaeodactylum tricornuntum* outcompeted *Thalassiosira weissflogii* and

36 *Emiliania huxleyi*, comprising more than 99% of the final biomass. During the logarithmic growth phase (phase I),

37 DMS concentrations in high pCO$_2$ mesocosms (HC, 1000 μatm) were 28% lower than those in low pCO$_2$

38 mesocosms (LC, 400 μatm). Elevated pCO$_2$ led to a delay in DCB concentrations attached to *Thalassiosira*

39 *weissflogii* and *Phaeodactylum tricornutum* and finally resulted in the delay of DMS concentration in the HC

40 treatment. Unlike DMS, the elevated pCO$_2$ did not affect DMSP production ability of *Thalassiosira weissflogii* or

41 *Phaeodactylum tricornuntum* throughout the 5 weeks culture. A positive relationship was detected between CH$_3$I

42 and *Thalassiosira weissflogii* and *Phaeodactylum tricornuntum* during the experiment, and there was a 40%

43 reduction in mean CH$_3$I concentrations in the HC mesocosms. CHBrCl$_2$, CH$_3$Br, and CH$_2$Br$_2$ concentrations did

44 not increase with elevated chlorophyll *a* (Chl *a*) concentrations compared with DMS(P) and CH$_3$I, and there were

45 no major peaks both in the HC or LC mesocosms. In addition, no effect of elevated pCO$_2$ was identified for any of

46 the three bromocarbons.

47 **Keywords:** ocean acidification, dimethylsulfide (DMS), dimethylsulfoniopropionate (DMSP), halocarbons,

48 phytoplankton, bacteria

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1. Introduction

Anthropogenic emissions have increased the fugacity of atmospheric carbon dioxide (pCO$_2$) from the pre-industrial value of 280 µatm to the present-day value of over 400 µatm, and these values will further increase to 800–1000 µatm by the end of this century (Gattuso et al., 2015). The dissolution of this excess CO_2 into the surface of the ocean directly affects the carbonate system and has lowered the pH by 0.1 units, from 8.21 to 8.10 over the last 250 years. Further decreases of 0.3–0.4 pH units are predicted by the end of this century (Doney et al., 2009; Orr et al., 2005; Gattuso et al., 2015), which is commonly referred to as ocean acidification (OA). The physiological and ecological aspects of the phytoplankton response to this changing environment can potentially alter marine phytoplankton community composition, community biomass, and feedback to biogeochemical cycles (Boyd and Doney, 2002). These changes simultaneously have an impact on some volatile organic compounds produced by marine phytoplankton (Liss et al., 2014; Liu et al., 2017), including the climatically important trace gas dimethylsulfide (DMS) and a number of volatile halocarbon compounds.

DMS is the most important volatile sulfur compound produced from dimethylsulfoniopropionate (DMSP), which is ubiquitous in marine environments, mainly synthesized by marine microalgae (Stefels et al., 2007), a few angiosperms, some corals (Raina et al., 2016), and several heterotrophic bacteria (Curson et al., 2017) through complex biological interactions in marine ecosystems. Although it remains controversial, DMS and its by-products, such as methanesulfonic acid and non-sea-salt sulfate, are suspected to have a prominent part in climate feedback (Charlson et al., 1987; Quinn and Bates, 2011). The conversion of DMSP to DMS is facilitated by several enzymes, including DMSP-lyase and acyl CoA transferase

74 (Kirkwood et al., 2010; Todd et al., 2007); these enzymes are mainly found in phytoplankton,

75 macroalgae, *Symbiodinium*, bacteria and fungi (de Souza and Yoch, 1995; Stefels and Dijkhuizen,

76 1996; Steinke and Kirst, 1996; Bacic and Yoch, 1998; Yost and Mitchelmore, 2009). Several

77 studies have shown a negative impact of decreasing pH on DMS-production capability (Hopkins

78 et al., 2010; Avgoustidi et al., 2012; Archer et al., 2013; Webb et al., 2016), while others have

79 found either no effect or a positive effect (Vogt et al., 2008; Hopkins and Archer, 2014). Several

80 assumptions have been presented to explain these contrasting results and attributed the

81 pH-induced variation in DMS-production capability to altered physiology of the algae cells or of

82 bacterial DMSP degradation (Vogt et al., 2008; Hopkins et al., 2010, Avgoustidi et al., 2012;

83 Archer et al., 2013; Hopkins and Archer, 2014; Webb et al., 2015).

84   Halocarbons also play a significant role in the global climate because they are linked to

85 tropospheric and stratospheric ozone depletion and a synergistic effect of chlorine and bromine

86 species has been reported that they may account for approximately 20% of the polar stratospheric

87 ozone depletion (Roy et al., 2011). In addition, iodocarbons can release atomic iodine (I) quickly

88 through photolysis in the atmospheric boundary layer and I atoms are very efficient in the catalytic

89 removal of O_3, which governs the lifetime of many climate relevant gases including methane and

90 DMS (Jenkins et al., 1991). Compared with DMS, limited attention was received about the effect

91 of OA on halocarbon concentrations. Hopkins et al. (2010) and Webb et al. (2015) measured lower

92 concentrations of several iodocarbons, while bromocarbons were unaffected by elevated $p\mathrm{CO_2}$

93 through two acidification experiments. In addition, an additional mesocosm study did not elicit

94 significant differences from any halocarbon compounds at up to 1,400 μatm $p\mathrm{CO_2}$ (Hopkins et al.,

95 2013).

DMS and halocarbons play a significant role in the global climate and perhaps act a greater extent in the future. Meanwhile, the combined picture arising from existing studies is that the response of communities to OA is not predictable and further studies were required. Based on the controversial results about OA on DMS and halocarbons production, a mesocosm experiment was conducted in Wu Yuan Bay, Xiamen. The aim of this study was to investigate the influence of elevated pCO$_2$ on diatoms and coccolithophores and to further understand how the productions of DMS and halocarbons respond to OA.

2. Experimental method

2.1 General experimental device

The mesocosm experiments were carried out on a floating platform at the Facility for Ocean Acidification Impacts Study of Xiamen University (FOANIC-XMU, 24.52 °N, 117.18 °E) (for full technical details of the mesocosms, see Liu et al. 2017). Six cylindrical transparent thermoplastic polyurethane bags with domes were deployed along the south side of the platform. The width and depth of each mesocosm bag was 1.5 m and 3 m, respectively. Filtered (0.01 μm, achieved using an ultrafiltration water purifier, MU801-4T, Midea, Guangdong, China) *in situ* seawater was pumped into the six bags simultaneously within 24 h. A known amount of NaCl solution was added to each bag to calculate the exact volume of seawater in the bags, according to a comparison of the salinity before and after adding salt (Czerny et al., 2013). The initial *in situ* pCO$_2$ was about 650 μatm. To set the low and high pCO$_2$ levels, we added Na$_2$CO$_3$ solution and CO$_2$ saturated seawater to the mesocosm bags to alter total alkalinity and dissolved inorganic carbon (Gattuso et al., 2010; Riebesell et al., 2013). Subsequently, during the whole experimental process, air at the ambient (400 μatm) and elevated pCO$_2$ (1000 μatm) concentrations was

118 continuously bubbled into the mesocosm bags using a CO_2 Enricher (CE-100B, Wuhan Ruihua

119 Instrument & Equipment Ltd., Wuhan, China). Because the seawater in the mesocosm was filtered,

120 the algae in the coastal environment and their attached bacteria were removed and the trace gases

121 produced in the environment did not influence the mesocosm trace gas concentrations after the

122 bags were sealed.

123 *2.2 Algal strains*

124 *Emiliania huxleyi* (CS-369), *Phaeodactylum tricornuntum* (CCMA 106), and *Thalassiosira*

125 *weissflogii* (CCMA 102) were inoculated into the mesocosm bags, with an initial

126 diatom/coccolithophorid cell ratio of 1:1. The initial concentrations of *Phaeodactylum*

127 *tricornuntum*, *Thalassiosira weissflogii*, and *Emiliania huxleyi* inoculated into the mesocosm were

128 10, 10, and 20 cells mL^{-1}, respectively. *Phaeodactylum tricornuntum* and *Thalassiosira*

129 *weissflogii* were obtained from the Center for Collections of Marine Bacteria and Phytoplankton

130 of the State Key Laboratory of Marine Environmental Science (Xiamen University).

131 *Phaeodactylum tricornuntum* was originally isolated from the South China Sea in 2004 and

132 *Thalassiosira weissflogii* was isolated from Daya Bay in the coastal South China Sea. *Emiliania*

133 *huxleyi* was originally isolated in 1992 from the field station of the University of Bergen

134 (Raunefjorden; 60°18'N, 05°15'E). Before being introduced into the mesocosms, the three

135 phytoplankton species were cultured in autoclaved, pre-filtered seawater from Wuyuan Bay at

136 16 ℃ (similar to the in situ temperature of Wuyuan Bay) without any addition of nutrients.

137 Cultures were continuously aerated with filtered ambient air containing 400 µatm of CO_2 within

138 plant chambers (HP1000G-D, Wuhan Ruihua Instrument & Equipment, China) at a constant

139 bubbling rate of 300 mL min^{-1}. The culture medium was renewed every 24 h to maintain the cells

140 of each phytoplankton species in exponential growth. Meanwhile, no meaningful numbers of

141 bacteria were counted by flow cytometer in the pre-filtered seawater before the inoculations.

142 *2.3 Sampling for DMS(P) and halocarbons*

143 DMS(P) and halocarbons samples were generally obtained from six mesocosms at 9 a.m., then all

144 collected samples were transported into a dark cool box back to the laboratory onshore for

145 analysis within 1 h. For DMS analysis, 2 mL sample was gently filtered through a 25 mm GF/F

146 (glass fiber) filter and transferred to a purge and trap system linked to a Shimadzu GC-2014 gas

147 chromatograph (Tokyo, Japan) equipped with a glass column packed with 10% DEGS on

148 Chromosorb W-AW-DMCS (3 m $\times$ 3 mm) and a flame photometric detector (FPD) (Zhang et al.,

149 2014). For total DMSP analysis, 10 mL water sample was fixed using 50 μL of 50 % H_2SO_4 and

150 sealed (Kiene and Slezak, 2006). After > 1 d preservation, DMSP samples were hydrolysed for 24

151 h with a pellet of KOH (final pH > 13) to fully convert DMSP to DMS. Then, 2 mL hydrolysed

152 sample was carefully transferred to the purge and trap system mentioned above for extraction of

153 DMS. For halocarbons, 100 mL sample was purged at 40 ℃ with pure nitrogen at a flow rate of

154 100 mL min^{-1} for 12 min using another purge and trap system coupled to an Agilent 6890 gas

155 chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with an electron capture

156 detector (ECD) as well as a 60 m DB-624 capillary column (0.53 mm ID; film thickness, 3 μm)

157 (Yang et al., 2010). The analytical precision for duplicate measurements of DMS(P) and

158 halocarbons was > 10%.

159 *2.4 Measurements of chlorophyll a*

160 Chlorophyll *a* (Chl *a*) was measured in water samples (200–1,000 mL) collected every 2 d at 9

161 a.m. by filtering onto Whatman GF/F filters (25 mm). The filters were placed in 5 mL 100%

162 methanol overnight at 4 ℃ and centrifuged at 5000 r min^{-1} for 10 min. The absorbance of the

163 supernatant (2.5 mL) was measured from 250 to 800 nm using a scanning spectrophotometer (DU

164 800, Beckman Coulter Inc., Brea, CA, USA). Chl *a* concentration was calculated according to the

165 equation reported by Porra (2002).

166 *2.5 Enumeration of DMSP-consuming bacteria (DCB)*

167 The number of DMSP-consuming bacteria (DCB) was estimated using the most probable number

168 (MPN) methodology. The MPN medium consisted of a mixture (1:1 v/v) of sterile artificial sea

169 water (ASW) and mineral medium (Visscher et al., 1991), 3 mL of which was dispensed in 6 mL

170 test tubes, which were closed off by an over-sized cap, allowing gas exchange. Triplicate dilution

171 series were set up. All test tubes contained 1 mmol L^{-1} DMSP as the sole organic carbon source

172 and were kept at 30 ℃ in the dark. After 2 weeks, the presence/absence of bacteria in the tubes

173 was verified by DAPI staining (Porter and Feig, 1980). Three tubes containing 3 mL ASW

174 without substrate were used as controls.

175 *2.6 Statistical analysis*

176 One-way analysis of variance (ANOVA), Tukey's test, and the two-sample *t*-test were carried out

177 to demonstrate the differences between treatments. A *p*-value < 0.05 was considered significant.

178 Relationships between DMS(P), halocarbons and a range of other parameters were detected using

179 Pearson's correlation analysis via SPSS 22.0 for Windows (SPSS Inc., Chicago, IL, USA).

180 **3. Results and Discussion**

181 *3.1 Temporal changes in pH, Chl a, Phaeodactylum tricornuntum, Thalassiosira weissflogii, and*

182 *Emiliania huxleyi during the experiment*

183 During the experiment, the seawater in each mesocosm was well combined, and the temperature

184 and salinity were well controlled, with a mean of 16 $^{\circ}$C and 29 in all mesocosms, respectively.

185 Meanwhile, we observed significant differences in pH levels between the two CO_2 treatments on

186 days 0–11, but the differences disappeared with subsequent phytoplankton growth (Fig. 1). The

187 phytoplankton growth process was divided into three phases in terms of variations in Chl *a*

188 concentrations in the mesocosm experiments as described in Liu et al. (2017): i) the logarithmic

189 growth phase (phase I, days 0–13), ii) a plateau phase (phase II, days 13–23, bloom period), and iii)

190 a secondary plateau phase (phase III, days 23–33) attained after a decline in biomass from a

191 maximum in phase II. The initial chemical parameters of the mesocosm experiment are shown in

192 Table 1. The initial mean dissolved nitrate (including NO_3^- and NO_2^-), NH_4^+, PO_4^{3-} and silicate

193 (SiO_3^{2-}) concentrations were 54, 20, 2.6 and 41 μmol L^{-1} for the low pCO$_2$ (LC) treatment and 52,

194 21, 2.4 and 38 μmol L^{-1} for the high pCO$_2$ (HC) treatment, respectively. The nutrient

195 concentrations (NO_3^-, NO_2^-, NH_4^+ and phosphate) during phase I were consumed rapidly and

196 their concentrations were below or close to the detection limit during phase II (Table 1). In

197 addition, although dissolved inorganic nitrogen (NH_4^+, NO_3^-, and NO_2^-) and phosphate were

198 depleted, Chl *a* concentration in both treatments (biomass dominated by *Phaeodactylum*

199 *tricornuntum*) remained constant over days 12–22, and then declined over subsequent days (Liu et

200 al., 2017). *Emiliania huxleyi* was only found in phase I and its maximal concentration reached 310

201 cells mL^{-1} according to the results of microscopic inspection. *Thalassiosira weissflogii* was found

202 throughout the entire period in each bag, but the maximum concentration was 8,120 cells mL^{-1},

203 which was far less than the concentration of *Phaeodactylum tricornutum* with a maximum density

204 of about 1.5 million cells mL^{-1} (Liu et al., 2017).

205 *3.2 Impact of elevated p*CO$_2$ *on DMS and DMSP production*

At the beginning of the experiment, the mean DMS, DMSP and DCB concentrations were all low in both treatments due to the low concentrations of DMS, DMSP and DCB in the original fjord water and possible loss during the filtration procedure (Fig. 2). With the growth of phytoplankton, DMS, DMSP and DCB showed slightly different trends during the mesocosm experiment. The DMSP concentrations in the HC and LC treatments increased significantly along with the increase of Chl a concentrations and algal cells, and stayed relatively constant over the following days. A significant positive relationship was observed between DMSP and phytoplankton in the experiment (r = 0.961, $p < 0.01$ for *Phaeodactylum tricornuntum*, r = 0.617, $p < 0.01$ for *Thalassiosira weissflogii* in the LC treatment, table 2; r = 0.954, $p < 0.01$ for *Phaeodactylum tricornuntum*, r = 0.743, $p < 0.01$ for *Thalassiosira weissflogii* in the HC treatment, table 3). Compared with DMSP, DMS and DCB concentrations showed similar trends during the mesocosm experiment. DMS concentrations in the LC and HC treatments were 1.03 and 0.74 nmol L^{-1}, respectively, while DCB concentrations in the LC and HC treatments were 0.20×10^6 and 0.16×10^6 cells mL^{-1}. DMS and DCB concentrations did not increase significantly during phase I, but began to increase rapidly on day 15. DCB concentrations in the LC and HC treatments peaked on days 21 (11.65×10^6 cells mL^{-1}) and 23 (10.70×10^6 cells mL^{-1}), while DMS concentrations in the LC and HC treatments peaked on days 25 (112.1 nmol L^{-1}) and 30 (101.9 nmol L^{-1}). Both DMS and DCB concentrations began to decrease obviously during phase III. Meanwhile, a significant positive relationship was also observed between DMS and *Phaeodactylum tricornuntum* (r = 0.560, $p < 0.05$ in the LC treatment; r = 0.635, $p < 0.01$ in the HC treatment), while no relationship was observed between DMS and *Thalassiosira weissflogii* (table 2 and table 3) during the experiment.

228   In this study, no difference in mean DMSP concentrations was observed between the two

229   treatments, indicating that elevated pCO$_2$ had no significant influence on DMSP production in

230   *Phaeodactylum tricornuntum* and *Thalassiosira weissflogii* throughout this study. However, a

231   significant 29% reduction in DMS concentrations was detected in the HC treatment compared

232   with the LC treatment (p = 0.016), though no statistical difference for DCB concentrations was

233   found between the LC and HC treatments during phase I. This reduction in DMS concentrations

234   may be attributed to greater consumption of DMS and conversion to DMSO (Webb et al., 2015).

235   In addition, the peak DMS concentration in the HC treatment was delayed 5 days relative to that in

236   the LC treatment during phase II (Fig. 2-A). This result has been observed in previous mesocosm

237   experiments and it was attributed to small scale shifts in community composition and succession

238   that could not be identified with only a once-daily measurement regime (Vogt et al., 2008; Webb et

239   al., 2016). However, this phenomenon can be explained in another straightforward way during this

240   study. Previous studies have showed that marine bacteria play a key role in DMS production and the

241   efficiency of bacteria converting DMSP to DMS may vary from 2 to 100% depending on the

242   nutrient status of the bacteria and the quantity of dissolved organic matter (Simó et al., 2002, 2009;

243   Kiene et al., 1999, 2000). In addition, a significant positive relationship was also observed

244   between DMS and DCB (r = 0.643, p < 0.01 in the LC treatment; r = 0.544, p < 0.01 in the HC

245   treatment) during this experiment. All of these observations point to the importance of bacteria in

246   DMS and DMSP dynamics. During the present mesocosm experiment, DMSP concentrations in

247   the LC treatment decreased slightly on day 23, while the slight decrease appeared on day 29 in the

248   HC treatment (Fig. 2-B). In addition, the time that the DMSP concentration began to decrease was

249   very close to the time when the highest DMS concentration occurred in both treatments. Moreover,

250 DCB peaked on days 21 (11.65×10^6 cells mL^{-1}) and 23 (10.70×10^6 cells mL^{-1}) in the LC and

251 HC treatments, respectively, as shown in Fig. 2-C. Similar to DMS, DCB was also delayed in the

252 HC mesocosm compared to that in the LC mesocosm. Taken together, we inferred that the

253 elevated pCO$_2$ first delayed growth of DCB in the mesocosm, then the delayed DCB postponed

254 the DMSP degradation process, and eventually delayed the DMS concentration in the HC

255 treatment. In addition, considering that the algae and their attached bacteria were removed through

256 a filtering process before the experiment and the unattached bacteria were maintained in a

257 relatively constant concentration during this mesocosm experiment (Huang et al., 2018), we

258 further concluded that the elevated pCO$_2$ controlled DMS concentrations mainly by affecting DCB

259 attached to *Thalassiosira weissflogii* and *Phaeodactylum tricornuntum*.

260 *3.3 Impact of elevated pCO$_2$ on halocarbon compounds*

261 The temporal development in CHBrCl$_2$, CH$_3$Br, and CH$_2$Br$_2$ concentrations is shown in Fig. 3

262 (A–C) and the temporal changes of their concentrations were substantially different from those of

263 DMS, DMSP, *Phaeodactylum tricornuntum* and *Thalassiosira weissflogii*. The mean

264 concentrations of CHBrCl$_2$, CH$_3$Br and CH$_2$Br$_2$ for the entire experiment were 8.58, 7.85, and 5.13

265 pmol L^{-1} in the LC treatment and 8.81, 9.73, and 6.27 pmol L^{-1} in the HC treatment. The

266 concentrations of CHBrCl$_2$, CH$_3$Br, and CH$_2$Br$_2$ did not increase with the Chl *a* concentration

267 compared with those of DMS and DMSP, and no major peaks were detected in the mesocosms. In

268 addition, no effect of elevated pCO$_2$ was identified for any of the three bromocarbons, which

269 compared well with previous mesocosm findings (Hopkins et al., 2010, 2013; Webb, et al., 2016).

270 No clear correlation was observed between the three bromocarbons and any of the measured algal

271 groups (table 2 and table 3), indicating that *Phaeodactylum tricornuntum* and *Thalassiosira*

272   *weissflogii* did not primarily release these three bromocarbons during the mesocosm experiment.

273   Previous studies have reported that large-size cyanobacteria, such as *Aphanizomenon flos*-aquae,

274   produce bromocarbons (Karlsson et al. 2008) and significant correlations between cyanobacterium

275   abundance and several bromocarbons have been reported in the Arabian Sea (Roy et al., 2011).

276   However, the filtration procedure led to the loss of cyanobacterium in the mesocosms and finally

277   resulted in low bromocarbon concentrations during the experiment, although *Phaeodactylum*

278   *tricornuntum* and *Thalassiosira weissflogii* abundances were high.

279   The temporal dynamics of CH_3I in the HC and LC treatments are shown in Fig. 3-D. The CH_3I

280   concentrations in the LC treatment varied from 0.38 to 12.61 pmol L^{-1}, with a mean of 4.76 pmol

281   L^{-1}. The CH_3I concentrations in the HC treatment ranged between 0.44 and 8.78 pmol L^{-1}, with a

282   mean of 2.88 pmol L^{-1}. The maximum CH_3I concentrations in the HC and LC treatments were

283   both observed on day 23. The range of CH_3I concentrations during this experiment was similar to

284   that measured in the mesocosm experiment (< 1~10 pmol L^{-1}) in Kongsfjorden conducted by

285   Hopkins et al. (2013). In addition, the mean CH_3I concentration in the LC treatment was similar to

286   that measured in the East China Sea, with an average of 5.34 pmol L^{-1} in winter and 5.74 pmol L^{-1}

287   in summer (Yuan et al., 2015). Meanwhile, a positive relationship was detected between CH_3I and

288   Chl *a*, *Phaeodactylum tricornuntum* and *Thalassiosira weissflogii* (r = 0.588, *p* < 0.01 in the LC

289   treatment; r = 0.834, *p* < 0.01 in the LC treatment for *Phaeodactylum tricornuntum*; r = 0.680 *p* <

290   0.01 in the LC treatment; r = 0.690, *p* < 0.01 in the HC treatment for *Thalassiosira weissflogii*; r =

291   0.717, *p* < 0.01 in the LC treatment; r = 0.741, *p* < 0.01 in the HC treatment for Chl *a*). This result

292   agrees with previous mesocosm (Hopkins et al., 2013) and laboratory experiments (Hughes et al.,

293   2013; Manley and De La Cuesta, 1997) identifying diatoms as significant producers of CH_3I.

294   Moreover, similar to DMS, the maximum CH_3I concentration also occurred after the maxima of

295   *Phaeodactylum tricornuntum* and *Thalassiosira weissflogii*, at about 4 d (Fig. 3-D). This was

296   similar to iodocarbon gases measured in a Norway mesocosm conducted by Hopkins et al. (2010)

297   and chloroiodomethane (CH_2ClI) concentrations measured in another Norway mesocosm

298   conducted by Wingenter et al. (2007). Furthermore, the CH_3I concentrations measured in the HC

299   treatment were significantly lower than those measured in the LC treatment during the mesocosm,

300   which is in accord with the discoveries of Hopkins et al. (2010) and Webb et al. (2015) but in

301   contrast to the findings of Hopkins et al. (2013) and Webb et al. (2016). Throughout the mesocosm

302   experiment, there was a 40.2% reduction in the HC mesocosm compared to the LC mesocosm.

303   Considering that the phytoplankton species did not show significant differences in the HC and LC

304   treatments during the experiment, this reduction in the HC treatment was likely not caused by

305   phytoplankton. Apart from direct biological production via methyl transferase enzyme activity by

306   both phytoplankton and bacteria (Amachi et al., 2001), CH_3I is produced from the breakdown of

307   higher molecular weight iodine-containing organic matter (Fenical, 1982) through photochemical

308   reactions between organic matter and light (Richter and Wallace, 2004). Both bacterial methyl

309   transferase enzyme activity and a photochemical reaction may have reduced the CH_3I

310   concentrations in the HC treatment but further experiments are needed to verify this result.

311   **4. Conclusions**

312   In this study, the effects of increased levels of $p\text{CO}_2$ on marine DMS(P) and halocarbons release

313   were studied in a controlled mesocosm facility. A 28.2% reduction during the logarithmic growth

314   phase and a 5 d delay in DMS concentration was observed in the HC treatment due to the effect of

315   elevated $p\text{CO}_2$. Because the seawater in the mesocosm was filtered, the algae in the coastal

316 environment and their attached bacteria were removed and the trace gases produced in the

317 environment did not influence the mesocosm trace gas concentrations after the bags were sealed.

318 Therefore, we attribute this phenomenon to the DMSP-consuming bacteria attached to

319 *Phaeodactylum tricornuntum* and *Thalassiosira weissflogii*. More attention should be paid to the

320 DMSP-consuming bacteria attached to algae under different pH values in future studies. Three

321 bromocarbons compounds were not correlated with a range of biological parameters, as they were

322 affected by the filtration procedure and elevated $p\text{CO}_2$ had no effect on any of the three

323 bromocarbons. The temporal dynamics of CH_3I, combined with strong correlations with biological

324 parameters, indicated biological control of the concentrations of this gas. In addition, the

325 production of CH_3I was sensitive to $p\text{CO}_2$, with a significant increase in CH_3I concentration at

326 higher $p\text{CO}_2$. However, without additional empirical measurements, it is unclear whether this

327 decrease was caused by bacterial methyl transferase enzyme activity or by photochemical

328 degradation at higher $p\text{CO}_2$.

329 Author contribution: Gui-Peng Yang and Kun-Shan Gao designed the experiments. Sheng-Hui

330 Zhang, Juan Yu and Qiong-Yao Ding carried out the experiments and prepared the manuscript.

331 Hong-Hai Zhang and Da-Wei Pan revised the paper.

332 **Acknowledgements**

333 This study was financially supported by the National Natural Science Foundation of China (Grant

334 Nos. 41320104008 and 41576073), the National Key Research and Development Program of

335 China (Grant No. 2016YFA0601300), the National Natural Science Foundation for Creative

336 Research Groups (Grant No. 41521064), and AoShan Talents Program of Qingdao National

Laboratory for Marine Science and Technology (No. 2015 ASTP). We are thankful to Minhan Dai

for the nutrient data and to Bangqin Huang for the bacterial data.

Competing interests: The authors declare that they have no conflict of interest.

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Figure captions

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478 Fig. 1 Temporal changes of pH in the HC (1,000 μatm, solid squares) and LC (400 μatm, white

479 squares) mesocosms (3,000 L). Data are mean $\pm$ standard deviation, n = 3 (triplicate independent

480 mesocosm bags) (Origin 8.0).

481 Fig. 2 Temporal changes in DMS, DMSP and DCB concentrations in the HC (1,000 μatm, black

482 squares) and LC (400 μatm, white squares) mesocosms (3,000 L). Data are mean $\pm$ standard

483 deviation, n = 3 (triplicate independent mesocosm bags).

484 Fig. 3 Temporal changes in $CHBrCl_2$, CH_3Br, CH_2Br_2 and CH_3I concentrations in the HC (1,000

485 μatm, black squares) and LC (400 μatm, white squares) mesocosms (3,000 L). Data are mean $\pm$

486 standard deviation, n = 3 (triplicate independent mesocosm bags).

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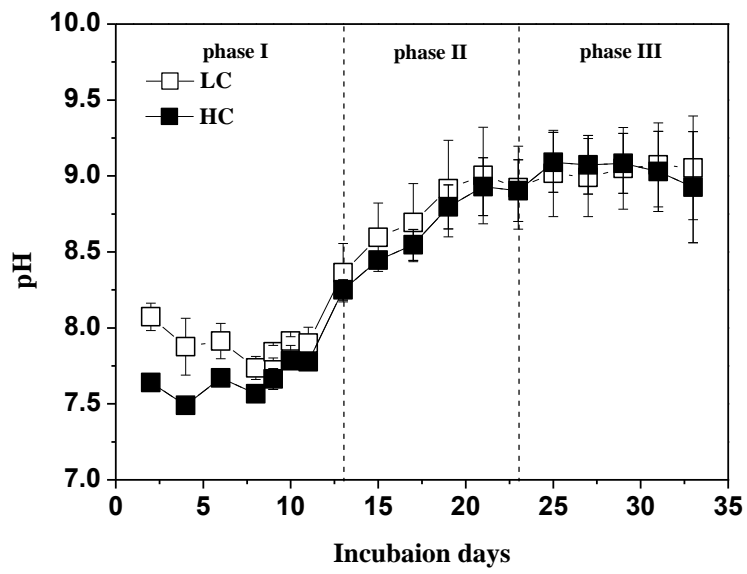
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496   **Fig. 1.** Temporal changes of pH in the HC (1,000 μatm, solid squares) and LC (400 μatm, white squares)

497   mesocosms (3,000 L). Data are mean ± standard deviation, n = 3 (triplicate independent mesocosm bags) (Origin

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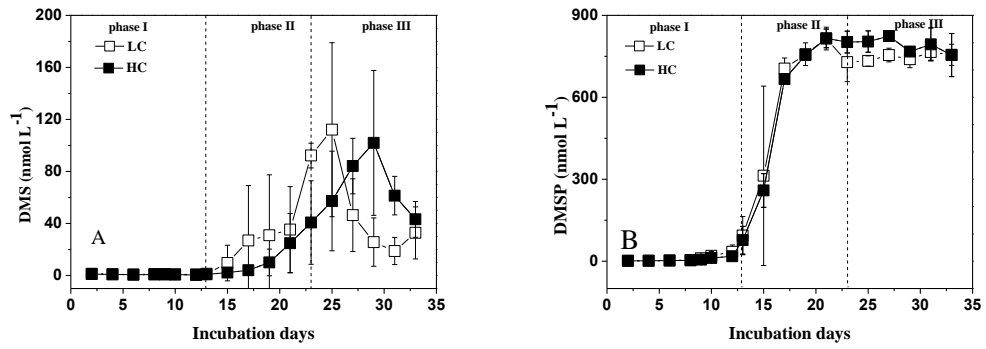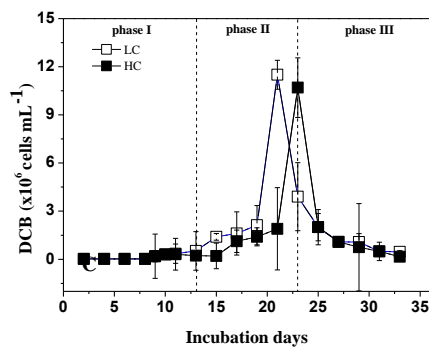
Fig. 2 Temporal changes in DMS (A), DMSP (B), DCB (C) concentrations in the HC (1,000 μatm, black squares)

and LC (400 μatm, white squares) mesocosms (3,000 L). Data are mean ± standard deviation, n = 3 (triplicate

independent mesocosm bags) (Origin 8.0).

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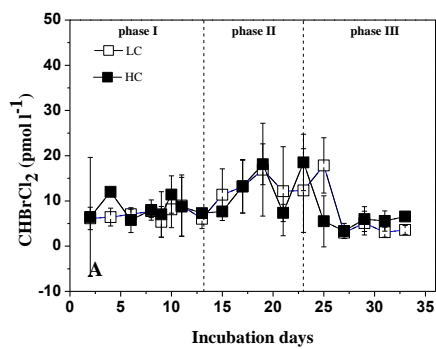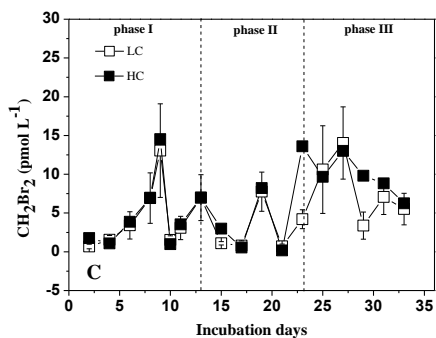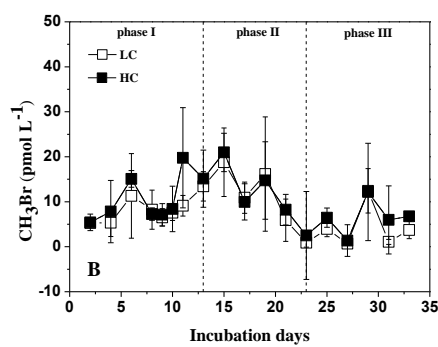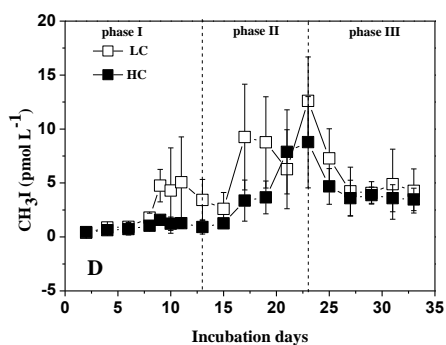
Fig. 3 Temporal changes in CHBrCl$_2$ (A), CH$_3$Br (B), CH$_2$Br$_2$ (C) and CH$_3$I (D) concentrations in the HC (1,000

μatm, black squares) and LC (400 μatm, white squares) mesocosms (3,000 L). Data are mean ± standard deviation,

n = 3 (triplicate independent mesocosm bags) (Origin 8.0).

516

517   **Table 1**. The conditions of DIC, pH_T, pCO_2 and nutrient concentrations in the mesocosm experiments. "-" means

518   that the values were below the detection limit.

		pH_T	DIC ($\mu mol\ kg^{-1}$)	pCO_2 (μatm)	$NO_3^-+NO_2^-$ ($\mu mol\ L^{-1}$)	NH_4^+ ($\mu mol\ L^{-1}$)	PO_4^{3-} ($\mu mol\ L^{-1}$)	SiO_3^{2-} ($\mu mol\ L^{-1}$)
day 0	LC	8.0±0.1	2181±29	1170~1284	52~56	19~23	2.6±0.2	38~40
	HC	7.5±0.1	2333±34	340~413	51~55	19~23	2.5±0.2	38~39
PhaseI	LC	7.9~8.4	1825~2178	373~888	15~52	1.6~20	0.5~2.6	31~38
	HC	7.4~8.2	2029~2338	1295~1396	47~54	0.2~21	0.7~2.5	34~39
Phase II	LC	8.4~8.5	1706~1745	46~749	-~ 15.9	-	0.1~0.5	10~24
	HC	8.4~8.6	1740~1891	59~1164	1.1~25	-	-~0.1	29~30
Phase III	LC	8.5~8.8	1673~1706	30~43	-	-	-	10~16
	HC	8.6~8.7	1616~1740	34~110	-	-	-~0.3	24~25

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520 **Table 2**. Relationships between DMS, DMSP, Chl a, $CHBrCl_2$, CH_3Br, CH_2Br_2, CH_3I, DCB, *Thalassiosira weissflogii* (*T. weissflogii*) and *Phaeodactylum tricornutum* (*P. tricornutum*)

521 concentrations in the LC treatments.

	DMS (nmol L^{-1})	DMSP (nmol L^{-1})	Chl a (μg L^{-1})	$CHBrCl_2$ (pmol L^{-1})	CH_3Br (pmol L^{-1})	CH_2Br_2 (pmol L^{-1})	CH_3I (pmol L^{-1})	DCB ($\times10^6$ cells mL^{-1})	*T. weissflogii* ($\times10^3$ cells mL^{-1})	*P. tricornutum* (cells mL^{-1})
DMS	1									
DMSP	0.701**	1								
Chl a	0.597**	0.792**	1							
$CHBrCl_2$	0.526	0.280	0.559	1						
CH_3Br	-0.413	-0.230	0.196	0.313	1					
CH_2Br_2	0.310	0.180	0.001	-0.136	-0.308	1				
CH_3I	0.694**	0.654**	0.717**	0.596*	-0.151	0.129	1			
DCB	0.643**	0.520*	0.522*	0.394	-0.268	-0.038	0.762**	1		
T. weissflogii	0.410	0.617**	0.899**	0.301	0.322	0.028	0.680**	0.399	1	
P. tricornutum	0.560*	0.961**	0.821**	0.528	-0.032	0.162	0.588**	0.334	0.685**	1

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Table 3. Relationships between DMS, DMSP, Chl *a*, CHBrCl$_2$, CH$_3$Br, CH$_2$Br$_2$, CH$_3$I, DCB, *Thalassiosira weissflogii* (*T. weissflogii*) and *Phaeodactylum tricornutum* (*P. tricornutum*)

concentrations in the HC treatments.

	DMS (nmol L^{-1})	DMSP (nmol L^{-1})	Chl *a* (µg L^{-1})	CHBrCl$_2$ (pmol L^{-1})	CH$_3$Br (pmol L^{-1})	CH$_2$Br$_2$ (pmol L^{-1})	CH$_3$I (pmol L^{-1})	DCB (×10^6 cells mL^{-1})	*T. weissflogii* (×10^3 cells mL^{-1})	*P. tricornutum* (cells mL^{-1})
DMS	1									
DMSP	0.752[**]	1								
Chl *a*	0.318[*]	0.738[**]	1							
CHBrCl$_2$	0.324	0.094	0.326	1						
CH$_3$Br	-0.410	-0.349	0.065	0.076	1					
CH$_2$Br$_2$	0.540[*]	0.352	0.142	0.233	-0.377	1				
CH$_3$I	0.694[**]	0.816[**]	0.741[**]	0.690[*]	-0.407	0.316	1			
DCB	0.544[*]	0.522	0.549[*]	0.532	-0.311	0.368	0.851[*]	1		
T. weissflogii	0.355	0.743[**]	0.930[**]	0.304	0.076	0.233	0.690[**]	0.567	1	
P. tricornutum	0.635[**]	0.954[**]	0.803[**]	0.143	-0.257	0.267	0.834[**]	0.559	0.820[**]	1

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