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1 **Effect of ocean acidification and elevated $f\text{CO}_2$ on trace gas**
2 **production by a Baltic Sea summer phytoplankton community**

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21

22 **Abstract**

23 **The Baltic Sea is a unique environment as the largest body of brackish water in the world.**
24 **Acidification of the surface oceans due to absorption of anthropogenic CO_2 emissions is an**
25 **additional stressor facing the pelagic community of the already challenging Baltic Sea. To**
26 **investigate its impact on trace gas biogeochemistry, a large-scale mesocosm experiment was**
27 **performed off Tvärminne Research Station, Finland in summer 2012. During the second half of**
28 **the experiment, dimethylsulphide (DMS) concentrations in the highest $f\text{CO}_2$ mesocosms (1075 -**



29 1333 μatm) were 34% lower than at ambient CO_2 (350 μatm). However the net production (as
30 measured by concentration change) of seven halocarbons analysed was not significantly affected
31 by even the highest CO_2 levels after 5 weeks exposure. Methyl iodide (CH_3I) and diiodomethane
32 (CH_2I_2) showed 15% and 57% increases in mean mesocosm concentration ($3.8 \pm 0.6 \text{ pmol L}^{-1}$
33 increasing to $4.3 \pm 0.4 \text{ pmol L}^{-1}$ and $87.4 \pm 14.9 \text{ pmol L}^{-1}$ increasing to $134.4 \pm 24.1 \text{ pmol L}^{-1}$
34 respectively) during Phase II of the experiment, which were unrelated to CO_2 and corresponded
35 to 30% lower *Chl-a* concentrations compared to Phase I. No other iodocarbons increased or
36 showed a peak, with mean chloriodomethane (CH_2ClI) concentrations measured at $5.3 (\pm 0.9)$
37 pmol L^{-1} and iodoethane ($\text{C}_2\text{H}_5\text{I}$) at $0.5 (\pm 0.1) \text{ pmol L}^{-1}$. Of the concentrations of bromoform
38 (CHBr_3 ; mean $88.1 \pm 13.2 \text{ pmol L}^{-1}$), dibromomethane (CH_2Br_2 ; mean $5.3 \pm 0.8 \text{ pmol L}^{-1}$) and
39 dibromochloromethane (CHBr_2Cl , mean $3.0 \pm 0.5 \text{ pmol L}^{-1}$), only CH_2Br_2 showed a decrease of
40 17% between Phases I and II, with CHBr_3 and CHBr_2Cl showing similar mean concentrations in
41 both Phases. Outside the mesocosms, an upwelling event was responsible for bringing colder,
42 high CO_2 , low pH water to the surface starting on day *t*16 of the experiment; this variable CO_2
43 system with frequent upwelling events implies the community of the Baltic Sea is acclimated to
44 regular significant declines in pH caused by up to 800 $\mu\text{atm } f\text{CO}_2$. After this upwelling, DMS
45 concentrations declined, but halocarbon concentrations remained similar or increased compared
46 to measurements prior to the change in conditions. Based on our findings, with future
47 acidification of Baltic Sea waters, biogenic halocarbon emissions are likely to remain at similar
48 values to today, however emissions of biogenic sulphur could significantly decrease from this
49 region.

50

51 1 Introduction

52 Anthropogenic activity has increased the fugacity of atmospheric carbon dioxide ($f\text{CO}_2$) from 280
53 μatm (pre-Industrial Revolution) to over 400 μatm today (Hartmann *et al.*, 2013). The IPCC AR5
54 long-term projections for atmospheric $p\text{CO}_2$ and associated changes to the climate have been
55 established for a variety of scenarios of anthropogenic activity until the year 2300. As the largest
56 global sink for atmospheric CO_2 , the global oceans have absorbed an estimated 30% of excess CO_2
57 produced (Canadell *et al.*, 2007). With atmospheric $p\text{CO}_2$ projected to possibly exceed 2000 μatm by
58 the year 2300 (Collins *et al.*, 2013; Cubasch *et al.*, 2013), the ocean will take up increasing amounts of
59 CO_2 , with a potential lowering of surface ocean pH by over 0.8 units (Raven *et al.*, 2005). The overall
60 effect of acidification on the biogeochemistry of surface ocean ecosystems is unknown and currently



61 unquantifiable, with a wide range of potential positive and negative impacts (Doney *et al.*, 2009;
62 Hofmann *et al.*, 2010; Ross *et al.*, 2011).

63 A number of volatile organic compounds are produced by marine phytoplankton (Liss *et al.*, 2014),
64 including the climatically important trace gas dimethylsulphide (DMS, C₂H₆S) and a number of
65 halogen-containing organic compounds (halocarbons) including methyl iodide (CH₃I) and bromoform
66 (CHBr₃). These trace gases are a source of sulphate particles and halide radicals when oxidised in the
67 atmosphere, and have important roles as ozone catalysts in the troposphere and stratosphere (O'Dowd
68 *et al.*, 2002; Solomon *et al.*, 1994) and as cloud condensation nuclei (CCNs; Charlson *et al.*, 1987).

69 DMS is found globally in surface waters originating from the algal-produced precursor
70 dimethylsulphonioacetate (DMSP, C₅H₁₀O₂S). Both DMS and DMSP are major routes of sulphur
71 and carbon flux through the marine microbial food web, and can provide up to 100% of the bacterial
72 (Simó *et al.*, 2009) and phytoplanktonic (Vila-Costa *et al.*, 2006a) sulphur demand. DMS is also a
73 volatile compound which readily passes through the marine boundary layer to the troposphere, where
74 oxidation results in a number of sulphur-containing particles important for atmospheric climate
75 feedbacks (Charlson *et al.*, 1987; Quinn and Bates, 2011); for this reason, any change in the production
76 of DMS may have significant implications for climate regulation. Several previous acidification
77 experiments have shown differing responses of both compounds (e.g. Avgoustidi *et al.*, 2012; Hopkins
78 *et al.*, 2010; Webb *et al.*, 2015), while others have shown delayed or more rapid responses as a direct
79 effect of CO₂ (e.g. Archer *et al.*, 2013; Vogt *et al.*, 2008). Further, some laboratory incubations of
80 coastal microbial communities showed increased DMS production with increased *f*CO₂ (Hopkins and
81 Archer, 2014), but lower DMSP production. The combined picture arising from existing studies is that
82 the response of communities to *f*CO₂ perturbation is not predictable and requires further study.
83 Previous studies measuring DMS in the Baltic Sea measured concentrations up to 100 nmol L⁻¹ during
84 the summer bloom, making the Baltic Sea a significant source of DMS (Orlikowska and Schulz-Bull,
85 2009).

86 In surface waters, halocarbons such as methyl iodide (CH₃I), chloriodomethane (CH₂ClI) and
87 bromoform (CHBr₃) are produced by biological and photochemical processes: many marine microbes
88 (for example cyanobacteria; Hughes *et al.*, 2011, diatoms; Manley and De La Cuesta, 1997 and
89 haptophytes; Scarratt and Moore, 1998) and macroalgae (e.g. brown-algal *Fucus* species; Chance *et al.*,
90 2009 and red algae; Leedham *et al.*, 2013) utilise halides from seawater and emit a range of
91 organic and inorganic halogenated compounds. This production can lead to significant flux to the
92 marine boundary layer in the order of 10 Tg iodine-containing compounds ('iodocarbons'; O'Dowd *et al.*,
93 2002) and 1 Tg bromine-containing compounds ('bromocarbons'; Goodwin *et al.*, 1997) into the



94 atmosphere. The effect of acidification on halocarbon concentrations has received limited attention,
95 but two acidification experiments measured lower concentrations of several iodocarbons while
96 bromocarbons were unaffected by $f\text{CO}_2$ up to 3000 μatm (Hopkins *et al.*, 2010; Webb, 2015), whereas
97 an additional mesocosm study did not elicit significant differences from any compound up to 1400
98 $\mu\text{atm } f\text{CO}_2$ (Hopkins *et al.*, 2013).

99 Measurements of the trace gases within the Baltic Sea are limited, with no prior study of DMSP
100 concentrations in the region. The Baltic Sea is the largest body of brackish water in the world, and
101 salinity ranges from 1 to 15. Furthermore, seasonal temperature variations of over 20 °C are common.
102 A permanent halocline at 50-80 m separates CO_2 -rich, bottom waters from fresher, lower CO_2 surface
103 waters, and a summer thermocline at 20 m separates warmer surface waters from those below 4°C
104 (Janssen *et al.*, 1999). Upwelling of bottom waters from below the summer thermocline is a common
105 summer occurrence, replenishing the surface nutrients while simultaneously lowering surface
106 temperature and pH (Brutemark *et al.*, 2011). Baltic organisms are required to adapt to significant
107 variations in environmental conditions. The species assemblage in the Baltic Sea is different to those
108 studied during previous mesocosm experiments in the Arctic, North Sea and Korea (Brussaard *et al.*,
109 2013; Engel *et al.*, 2008; Kim *et al.*, 2010), and are largely unstudied in terms of their community trace
110 gas production during the summer bloom. Post-spring bloom (July-August), a low dissolved inorganic
111 nitrogen (DIN) to dissolved inorganic phosphorous (DIP) ratio combines with high temperatures and
112 light intensities to encourage the growth of heterocystous cyanobacteria, (Niemisto *et al.*, 1989;
113 Raateoja *et al.*, 2011), in preference to nitrate-dependent groups.

114 Here we report the concentrations of DMS, DMSP and halocarbons from the 2012 summer season
115 mesocosm experiment aimed to assess the impact of elevated $f\text{CO}_2$ on the microbial community and
116 trace gas production in the Baltic Sea. Our objective was to assess how changes in the microbial
117 community driven by changes in $f\text{CO}_2$ impacted DMS and halocarbon concentrations. It is anticipated
118 that any effect of CO_2 on the growth of different groups within the phytoplankton assemblage will
119 result in an associated change in trace gas concentrations measured in the mesocosms as $f\text{CO}_2$
120 increases, which can potentially be used to predict future halocarbon and sulphur emissions from the
121 Baltic Sea region.

122



123 2 Methods

124 2.1 Mesocosm design and deployment

125 Nine mesocosms were deployed on the 10th June 2012 (day $t-10$; days are numbered negative prior to
126 CO_2 addition and positive afterward) and moored near Tvärminne Zoological Station ($59^\circ 51.5' \text{ N}$, 23°
127 $15.5' \text{ E}$) in Tvärminne Storfjärden in the Baltic Sea. Each mesocosm comprised a thermoplastic
128 polyurethane (TPU) enclosure of 17 m depth, containing approximately 54,000 L of seawater,
129 supported by an 8m tall floating frame capped with a polyvinyl hood. For full technical details of the
130 mesocosms see Czerny *et al.* (2013) and Riebesell *et al.* (2013). The mesocosm bags were filled by
131 lowering through the stratified water column until fully submerged, with the opening at both ends
132 covered by 3 mm mesh to exclude organisms larger than 3 mm such as fish. The mesocosms were then
133 left for 3 days ($t-10$ to $t-7$) with the mesh in position to allow exchange with the external water masses
134 and ensure the mesocosm contents were representative of the phytoplankton community in the
135 Storfjärden. On $t-7$ the bottom of the mesocosm was sealed with a sediment trap and the upper opening
136 was raised to approximately 1.5 m above the water surface. Stratification within the mesocosm bags
137 was broken up on $t-5$ by the use of compressed air for three and a half minutes to homogenise the
138 water column and ensure an even distribution of inorganic nutrients at all depths. Unlike in previous
139 experiments, there was no addition of inorganic nutrients to the mesocosms at any time during the
140 experiment; mean inorganic nitrate, inorganic phosphate and ammonium concentrations measured
141 across all mesocosms at the start of the experiment were $37.2 (\pm 18.8 \text{ s.d.}) \text{ nmol L}^{-1}$, $323.9 (\pm 19.4 \text{ s.d.})$
142 nmol L^{-1} and $413.8 (\pm 319.5 \text{ s.d.}) \text{ nmol L}^{-1}$ respectively.

143 To obtain mesocosms with different $f\text{CO}_2$, the carbonate chemistry of the mesocosms was altered by
144 the addition of different volumes of 50 μm filtered, CO_2 -enriched Baltic Sea water (sourced from
145 outside the mesocosms), to each mesocosm over a four day period, with the first day of addition being
146 defined as day t_0 . Addition of the enriched CO_2 water was by the use of a bespoke dispersal apparatus
147 ('Spider') lowered through the bags to ensure even distribution throughout the water column (further
148 details are in Riebesell *et al.* 2013). Measurements of salinity in the mesocosms throughout the
149 experiment determined that three of the mesocosms were not fully sealed, and had undergone
150 unquantifiable water exchange with the surrounding waters. These three mesocosms (M2, M4 and M9)
151 were excluded from the analysis. Two mesocosms were designated as controls (M1 and M5) and
152 received only filtered seawater via the Spider; four mesocosms received addition of CO_2 -enriched
153 waters, with the range of target $f\text{CO}_2$ levels between 600 and 1650 μatm (M7, 600 μatm ; M6, 950
154 μatm ; M3, 1300 μatm ; M8 1650 μatm). Mesocosms were randomly allocated a target $f\text{CO}_2$; a



155 noticeable decrease in $f\text{CO}_2$ was identified in the three highest $f\text{CO}_2$ mesocosms (M6, M3 and M8)
156 over the first half of the experiment, which required the addition of more CO_2 enriched water on $t15$ to
157 bring the $f\text{CO}_2$ back up to maximum concentrations (Fig. 1a; Paul *et al.*, 2015). A summary of the
158 $f\text{CO}_2$ in the mesocosms can be seen in Table 1. At the same time as this further CO_2 addition on $t15$,
159 the walls of the mesocosms were cleaned using a bespoke wiper apparatus (See Riebesell *et al.*, 2013
160 for more information), followed by weekly cleaning to remove aggregations on the film which would
161 block incoming light. Light measurements showed that over 95% of the photosynthetically active
162 radiation (PAR) was transmitted by the clean TPU and PVC materials with 100% absorbance of UV
163 light (Riebesell *et al.*, 2013). Samples for most parameters were collected from the mesocosms at the
164 same time every morning from $t-3$, and analysed daily or every other day.

165 2.2 Trace gas extraction and analysis

166 2.2.1 DMS and halocarbons

167 A depth-integrated water sampler (IWS, HYDRO-BIOS, Kiel, Germany) was used to sample the entire
168 17 m water column daily or alternative daily. As analysis of Chlorophyll-*a* (Chl-*a*) showed it to be
169 predominantly produced in the first 10 m of the water column; trace gas analysis was conducted on
170 only integrated samples collected from the surface 10 m, with all corresponding community parameter
171 analyses with the exception of pigment analysis performed also to this depth. Water samples for trace
172 gas analysis were taken from the first IWS from each mesocosm to minimise the disturbance and
173 bubble entrainment from taking multiple samples in the surface waters. As in Hughes *et al.* (2009),
174 samples were collected in 250 mL amber glass bottles in a laminar flow with minimal disturbance to
175 the water sample, using Tygon tubing from the outlet of the IWS. Bottles were rinsed twice before
176 being carefully filled from the bottom with minimal stirring, and allowed to overflow the volume of
177 the bottle approximately three times before sealing with a glass stopper to prevent bubble formation
178 and atmospheric contact. Samples were stored below 10°C in the dark for 2 hours prior to analysis.
179 Each day, a single sample was taken from each mesocosm, with two additional samples taken from
180 one randomly selected mesocosm to evaluate the precision of the analysis.

181 On return to the laboratory, 40 mL of water was injected into a purge and cryotrap system (Chuck *et al.*
182 *et al.*, 2005), filtered through a 25 mm Whatman glass fibre filter (GF/F; GE Healthcare Life Sciences,
183 Little Chalfont, England) and purged with oxygen-free nitrogen (OFN) at 80 mL min⁻¹ for 10 minutes.
184 Each gas sample passed through a glass wool trap to remove particles and aerosols, before a dual
185 nafion counterflow drier (180 mL min⁻¹ OFN) removed water vapour from the gas stream. The gas
186 sample was trapped in a stainless steel loop held at -150 °C in the headspace of a liquid nitrogen-filled



187 dewar. The sample was injected by immersion of the sample loop in boiling water into an Agilent 6890
188 gas chromatograph equipped with a 60 m DB-VRX capillary column (0.32 mm ID, 1.8 μm film
189 thickness, Agilent J&W Ltd) according to the programme outlined by Hopkins *et al.* (2010). Analysis
190 was performed by an Agilent 5973 quadrupole mass spectrometer operated in electron ionisation,
191 single ion mode. Liquid standards of CH_3I , diiodomethane (CH_2I_2), CH_2ClI , iodoethane ($\text{C}_2\text{H}_5\text{I}$),
192 iodopropane ($\text{C}_3\text{H}_7\text{I}$), CHBr_3 , dibromoethane (CH_2Br_2), dibromochloromethane (CHBr_2Cl),
193 bromiodomethane (CH_2BrI) and DMS (Standards supplied by Sigma Aldrich Ltd, UK) were
194 gravimetrically prepared by dilution in HPLC-grade methanol (Table 2) and used for calibration. The
195 relative standard error was expressed as a percentage of the mean for the sample analysis, calculated
196 for each compound using triplicate analysis each day from a single mesocosm, and was $<7\%$ for all
197 compounds. GC-MS instrument drift was corrected by the use of a surrogate analyte standard in every
198 sample, comprising deuterated DMS ($\text{D}_6\text{-DMS}$), deuterated methyl iodide (CD_3I) and ^{13}C
199 dibromoethane ($^{13}\text{C}_2\text{H}_4\text{Br}_2$) via the method described in Hughes *et al.* (2006) and Martino *et al.* (2005).
200 Five-point calibrations were performed weekly for each compound with the addition of the surrogate
201 analyte, with a single standard analysed daily to check for instrument drift; linear regression from
202 calibrations typically produced $r^2 > 0.98$. All samples measured within the mesocosms were within the
203 concentration ranges of the calibrations (Table 2).

204 2.2.2 DMSP

205 Samples for total DMSP (DMSP_T) were collected and stored for later analysis by the acidification
206 method of Curran *et al.* (1998). A 7 mL sub-sample was collected from the amber glass bottle into an 8
207 mL glass sample vial (Labhut, Churcham, UK), into which 0.35 μL of 50% H_2SO_4 was added, before
208 storage at ambient temperature. Particulate DMSP (DMSP_P) samples were prepared by the gravity
209 filtration of 20 mL of sample through a 47 mm GF/F in a glass filter unit, before careful removal and
210 folding of the GF/F into a 7 mL sample vial filled with 7 mL of Milli-Q water and 0.35 μL of H_2SO_4
211 before storage at ambient temperature. Samples were stored for approximately 8 weeks prior to
212 analysis. DMSP samples (total and particulate) were analysed on a PTFE purge and cryotrap system
213 using 2 mL of the sample purged with 1 mL of 10M NaOH for 5 minutes at 80 mL min^{-1} . The sample
214 gas stream passed through a glass wool trap and Nafion counterflow (Permapure) drier before being
215 trapped in a PTFE sample loop kept at $-150\text{ }^\circ\text{C}$ by suspension in the headspace of a liquid nitrogen-
216 filled dewar and controlled by feedback from a thermocouple. Immersion in boiling water rapidly re-
217 volatilised the sample for injection into a Shimadzu GC2010 gas chromatograph with a Varian
218 Chrompack CP-Sil-5CB column (30 m, 0.53 mm ID) and flame photometric detector (FPD). The GC
219 oven was operated isothermally at $60\text{ }^\circ\text{C}$ which resulted in DMS eluting at 2.1 minutes. Liquid DMSP



220 standards were prepared and purged in the same manner as the sample to provide weekly calibrations
221 of the entire analytical system. Involvement in the 2013 AQA 12-23 international DMS analysis
222 proficiency test (National Measurement Institute of Australia, 2013) in February 2013 demonstrated
223 excellent agreement between our method of DMSP analysis and the mean from thirteen laboratories
224 measuring DMS using different methods, with a measurement error of 5%.

225 DMSP was not detected in any of the samples (total or particulate) collected and stored during the
226 experiment, and it was considered likely that this was due to an unresolved issue regarding acidifying
227 the samples for later DMSP analysis. It was considered unlikely that rates of bacterial DMSP turnover
228 through demethylation rather than through cleavage to produce DMS (Curson *et al.*, 2011) were
229 sufficiently high in the Baltic Sea to remove all detectable DMSP, yet still produce measureable DMS
230 concentrations. Also, rapid turnover of DMSP_D in surface waters being the cause of low DMSP_T
231 concentrations does not explain the lack of intracellular particulate-phase DMSP. Although production
232 of DMS is possible from alternate sources, it is highly unlikely that there was a total absence of
233 DMSP-producing phytoplankton within the mesocosms or Baltic Sea surface waters around
234 Tvärminne; DMSP has been measured in surface waters of the Southern Baltic Sea at 22.2 nmol L⁻¹ in
235 2012, indicating that DMSP-producing species are present within the Baltic Sea (Cathleen Zindler,
236 GEOMAR, Pers. Comm.).

237 A previous study by del Valle *et al.* (2011) highlighted up to 94% loss of DMSP from acidified
238 samples of colonial *Phaeocystis globosa* culture, and field samples dominated by colonial *Phaeocystis*
239 *antarctica*. Despite filamentous, colonial cyanobacteria in the samples from Tvärminne mesocosms
240 potentially undergoing the same process, these species did not dominate the community at only 6.6%
241 of the total Chl-*a*, implying that the acidification method for DMSP fixation also failed for unicellular
242 phytoplankton species. This suggests that the acidification method is unreliable in the Baltic Sea, and
243 should be considered inadequate as the sole method of DMSP fixation in future experiments in the
244 region. The question of its applicability in other marine waters also needs further investigation.

245

246 **2.3 Measurement of community dynamics**

247 Water samples were collected from the 10m and 17m IWS on a daily basis and analysed for carbonate
248 chemistry, fluorometric Chl-*a*, phytoplankton pigments (17m IWS only) and cell abundance to analyse
249 the community structure and dynamics during the experiment. The carbonate system was analysed
250 through a suite of measurements (Paul *et al.*, 2015), including potentiometric titration for total
251 alkalinity (TA), infrared absorption for dissolved inorganic carbon (DIC) and spectrophotometric



252 determination for pH. For Chl-*a* analysis and pigment determination, 500 mL sub-samples were
253 filtered through a GF/F and stored frozen (-20 °C for two hours for Chl-*a* and -80 °C for up to 6
254 months for pigments), before homogenisation in 90 % acetone with glass beads. After centrifuging
255 (10 minutes at 800 x g at 4 °C) the Chl-*a* concentrations were determined using a Turner AU-10
256 fluorometer by the methods of Welschmeyer (1994), and the phytoplankton pigment concentrations
257 by reverse phase high performance liquid chromatography (WATERS HPLC with a Varian Microsorb-
258 MV 100-3 C8 column) as described by Barlow *et al.* (1997). Phytoplankton community composition
259 was determined by the use of the CHEMTAX algorithm to convert the concentrations of marker
260 pigments to Chl-*a* equivalents (Mackey *et al.*, 1996; Schulz *et al.*, 2013). Microbes were enumerated
261 using a Becton Dickinson FACSCalibur flow cytometer (FCM) equipped with a 488 nm argon laser
262 (Crawford *et al.*, 2015) and counts of phytoplankton cells >20 µm were made on concentrated (50 mL)
263 sample water, fixed with acidic Lugol's iodine solution with an inverted microscope. Filamentous
264 cyanobacteria were counted in 50 µm length units.

265 2.4 Statistical Analysis

266 All statistical analysis was performed using Minitab V16. In analysis of the measurements between
267 mesocosms, one-way ANOVA was used with Tukey's post-hoc analysis test to determine the effect of
268 different $f\text{CO}_2$ on concentrations measured in the mesocosms and the Baltic Sea. Spearman's Rank
269 Correlation Coefficients were calculated to compare the relationships between trace gas
270 concentrations, $f\text{CO}_2$, and a number of biological parameters, and the resulting p -values for each
271 correlation are given in Supplementary table S1 for the mesocosms and S2 for the Baltic Sea data.

272

273 3 Results and Discussion

274 3.1 Biogeochemical changes within the mesocosms

275 The mesocosm experiment was split into three phases based on the temporal variation in Chl-*a* (Fig. 2;
276 Paul *et al.*, 2015) evaluated after the experiment was completed:

- 277 • Phase 0 (days $t-5$ to t_0) – pre- CO_2 addition
- 278 • Phase I (days t_1 to t_{16}) – 'productive phase'
- 279 • Phase II (days t_{17} to t_{30}) – temperature induced autotrophic decline.



280 3.1.1 Physical Parameters

281 $f\text{CO}_2$ decreased over Phase I in the three highest $f\text{CO}_2$ mesocosms, mainly through air-sea gas
282 exchange and carbon fixation by phytoplankton (Fig. 1a). All mesocosms still showed distinct
283 differences in $f\text{CO}_2$ levels throughout the experiment (Table 1), and there was no overlap of mesocosm
284 $f\text{CO}_2$ values on any given day, save for the two controls (M1 and M5). The control mesocosm $f\text{CO}_2$
285 increased through Phase I of the experiment, likely as a result of undersaturation of the water column
286 encouraging dissolution of atmospheric CO_2 (Paul *et al.*, 2015). Salinity in the mesocosms remained
287 constant throughout the experiment at 5.70 ± 0.004 , and showed no variation with depth. It remained
288 similar to salinity in the Baltic Sea surrounding the mesocosms, which was 5.74 ± 0.14 . Water
289 temperature varied from a low of 8.6 ± 0.4 °C during Phase 0 to a high of 15.9 ± 2.2 °C measured on
290 day $t16$, before decreasing once again (Fig. 1b).

291 Summertime upwelling events are common and well described (Gidhagen, 1987; Lehmann and
292 Myrberg, 2008), and induce a significant temperature decrease in surface waters; such an event
293 appears to have commenced around $t16$, as indicated by significantly decreasing temperatures inside
294 and out of the mesocosms (Fig. 1b) and increased salinity in the Baltic Sea from 5.5 to 6.1 over the
295 following 15 days to the end of the experiment. Due to the enclosed nature of the mesocosms, the
296 upwelling affected only the temperature and not pH, $f\text{CO}_2$ or the microbial community. However, the
297 temperature decrease after $t16$ was likely to have had a significant effect on phytoplankton growth,
298 explaining the lower Chl-*a* in Phase II.

299 3.1.2 Community Dynamics

300 Mixing of the mesocosms after closure prior to $t-3$ did not trigger a notable increase in Chl-*a* in Phase
301 0; in previous mesocosm experiments, mixing redistributed nutrients from the deeper stratified layers
302 throughout the water column. During Phase I, light availability, combined with increasing water
303 temperatures favoured the growth of phytoplankton in all mesocosms (Paul *et al.* 2015), and was
304 unlikely to be a direct result of the CO_2 enrichment. Mean Chl-*a* during Phase I was $1.98 (\pm 0.29)$ μg
305 L^{-1} from all mesocosms, decreasing to $1.44 (\pm 0.46)$ μg L^{-1} in Phase II: this decrease was attributed to a
306 temperature induced decreased in phytoplankton growth rates and higher grazing rates as a result of
307 higher zooplankton reproduction rates during Phase I (Lischka *et al.*, 2015; Paul *et al.*, 2015).
308 Mesocosm Chl-*a* decreased until the end of the experiment on $t31$.

309 The largest contributors to Chl-*a* in the mesocosms during the summer of 2012 were the chlorophytes
310 and cryptophytes, with up to 40% and 21% contributions to the Chl-*a* respectively (Table 3; Paul *et al.*,
311 2015). Significant long-term differences in abundance between mesocosms developed as a result of



312 elevated $f\text{CO}_2$ in only two groups: picoeukaryotes I showed higher abundance at high $f\text{CO}_2$ ($F=8.2$,
313 $p<0.01$; Crawford *et al.*, 2016 and Supplementary Fig. S2), as seen in previous mesocosm experiments
314 (Brussaard *et al.*, 2013; Newbold *et al.*, 2012) and picoeukaryotes III the opposite trend ($F=19.6$,
315 $p<0.01$; Crawford *et al.* this issue). Temporal variation in phytoplankton abundance was similar
316 between all mesocosms (Supplementary Fig. S1 and S2).

317 Diazotrophic, filamentous cyanobacterial blooms in the Baltic Sea are an annual event in summer
318 (Finni *et al.*, 2001), and single-celled cyanobacteria have been found to comprise as much as 80% of
319 the cyanobacterial biomass and 50% of the total primary production during the summer in the Baltic
320 Sea (Stal *et al.*, 2003). However, CHEMTAX analysis identified cyanobacteria as contributing less
321 than 10% of the total Chl-*a* in the mesocosms (Crawford *et al.*, 2015; Paul *et al.*, 2015). These
322 observations were backed up by satellite observations showing reduced cyanobacterial abundance
323 throughout the Baltic Sea in 2012 compared to previous and later years (Oberg, 2013). It was proposed
324 that environmental conditions of limited light availability and lower surface water temperatures during
325 the summer of 2012 were sub-optimal for triggering a filamentous cyanobacteria bloom (Wasmund,
326 1997).

327

328 **3.2 DMS and DMSP**

329 **3.2.1 Mesocosm DMS**

330 A significant 34% reduction in DMS concentrations was detected in the high $f\text{CO}_2$ treatments during
331 Phase II compared to the ambient $f\text{CO}_2$ mesocosms ($F=31.7$, $p<0.01$). Mean DMS concentrations of
332 $5.0 (\pm 0.8; \text{range } 3.5 - 6.8) \text{ nmol L}^{-1}$ in the ambient treatments compared to $3.3 (\pm 0.3; \text{range } 2.9 - 3.9)$
333 nmol L^{-1} in the 1333 and 1075 μatm mesocosms (Fig. 3a). The primary differences identified were
334 apparent from the start of Phase II on $t17$, after which maximum concentrations were observed in the
335 ambient mesocosms on $t21$. The relationship between DMS and increasing $f\text{CO}_2$ during Phase II was
336 found to be linear (Fig. 3b), a finding also identified in previous mesocosm experiments (Archer *et al.*,
337 2013; Webb *et al.*, 2015). Furthermore, increases in DMS concentrations under high $f\text{CO}_2$ were
338 delayed by three days relative to the ambient and medium $f\text{CO}_2$ treatments, a situation which has been
339 observed in a previous mesocosm experiment. This was attributed to small-scale shifts in community
340 composition and succession which could not be identified with only a once-daily measurement regime
341 (Vogt *et al.*, 2008). DMS measured in all mesocosms fell within the range 2.7 to 6.8 nmol L^{-1} across
342 the course of the experiment. During Phase I, no difference was identified in DMS concentrations



343 between $f\text{CO}_2$ treatments with the mean of all mesocosms $3.1 (\pm 0.2) \text{ nmol L}^{-1}$. Concentrations in all
344 mesocosms gradually declined from $t21$ until the end of DMS measurements on $t31$. DMS
345 concentrations measured in the mesocosms and Baltic Sea were comparable to those measured in
346 temperate coastal conditions in the North Sea (Turner *et al.*, 1988), the Mauritanian upwelling
347 (Franklin *et al.*, 2009; Zindler *et al.*, 2012) and South Pacific (Lee *et al.*, 2010).

348 Although the majority of DMS production is presumed to be from DMSP, an alternative production
349 route for DMS is available through the methylation of methanethiol (Drotar *et al.*, 1987; Kiene and
350 Hines, 1995; Stets *et al.*, 2004) predominantly identified in anaerobic environments such as freshwater
351 lake sediments (Lomans *et al.*, 1997), saltmarsh sediments (Kiene and Visscher, 1987) and microbial
352 mats (Visscher *et al.*, 2003; Zinder *et al.*, 1977). However, recent studies have identified this pathway
353 of DMS production from *Pseudomonas deceptionensis* in an aerobic environment (Carrión *et al.*,
354 2015), where *P. deceptionensis* was unable to synthesis or catabolise DMSP, but was able to
355 enzymatically mediate DMS production from methanethiol (MeSH). The same enzyme has also been
356 identified in a wide range of other bacterial taxa, including the cyanobacterial *Pseudanabaena*, which
357 was identified in the Baltic Sea during this and previous investigations (Stuhr, pers. comm.; Kangro *et al.*,
358 2007; Nausch *et al.*, 2009). Correlations between DMS and the cyanobacterial equivalent Chl-*a*
359 ($\rho=0.42$, $p<0.01$) indicate that the methylation pathway may be a potential source of DMS within the
360 Baltic Sea community. In addition to the methylation pathway, DMS production has been identified
361 from S-methylmethionine (Bentley and Chasteen, 2004), as well as from the reduction of
362 dimethylsulphoxide (DMSO) in both surface and deep waters by bacterial metabolism (Hatton *et al.*,
363 2004). As these compounds were not measured in the mesocosms, it is impossible to determine if they
364 were significant sources of DMS.

365 **3.2.2 DMS and Community Interactions**

366 Throughout Phase I, DMS showed no correlation with any measured variables of biological activity or
367 cell abundance, and was unaffected by elevated $f\text{CO}_2$, indicating DMS net production was not directly
368 related to the perturbation of the system and associated cellular stress (Sunda *et al.*, 2002). During
369 Phase II, DMS was negatively correlated with Chl-*a* in the ambient and medium $f\text{CO}_2$ mesocosms ($\rho=-$
370 0.60, $p<0.01$). During Phase II, a significant correlation was seen between DMS and single-celled
371 cyanobacteria identified as *Synechococcus* ($\rho=0.53$, $p<0.01$; Crawford *et al.* 2016 and supplementary
372 table S1) and picoeukaryotes III ($\rho=0.75$, $p<0.01$). The peak in DMS concentrations is unlikely to be a
373 delayed response to the increased Chl-*a* on $t16$.



374 In previous mesocosm experiments (Archer *et al.*, 2013; Hopkins *et al.*, 2010; Webb *et al.*, 2015),
375 DMS has shown poor correlations with many of the indicators of primary production and
376 phytoplankton abundance, as well as showing the same trend of decreased concentrations in high $f\text{CO}_2$
377 mesocosms compared to ambient. DMS production is often uncoupled from measurements of primary
378 production in open waters (Lana *et al.*, 2012), and also often from production of its precursor DMSP
379 (Archer *et al.*, 2009).. DMS and DMSP are important sources of sulphur and carbon in the microbial
380 food web for both bacteria and algae (Simó *et al.*, 2002, 2009), and since microbial turnover of DMSP
381 and DMS play a significant role in net DMS production, it is unsurprising that DMS concentrations
382 have shown poor correlation with DMSP-producing phytoplankton groups in past experiments and
383 open waters.

384 DMS concentrations have been reported lower under conditions of elevated $f\text{CO}_2$ compared to ambient
385 controls, in both mesocosm experiments (Table 4) and phytoplankton monocultures (Arnold *et al.*,
386 2013; Avgoustidi *et al.*, 2012). However, these experiments limit our ability to generalise the response
387 of algal production of DMS and DMSP in all situations due to the characteristic community dynamics
388 of each experiment in specific geographical areas and temporal periods. Previous experiments in the
389 temperate Raunefjord of Bergen, Norway, showed lower abundance of DMSP-producing algal species,
390 and subsequently DMSP-dependent DMS concentrations (Avgoustidi *et al.*, 2012; Hopkins *et al.*,
391 2010; Vogt *et al.*, 2008; Webb *et al.*, 2015). In contrast mesocosm experiments in the Arctic and Korea
392 have shown increased abundance of DMSP producers (Archer *et al.*, 2013; Kim *et al.*, 2010) but lower
393 DMS concentrations, while incubation experiments by Hopkins and Archer (2014) showed lower
394 DMSP production but higher DMS concentrations at high $f\text{CO}_2$. However, in all previous experiments
395 with DMSP as the primary precursor of DMS, elevated $f\text{CO}_2$ had a less marked effect on measured
396 DMSP concentrations than on measured DMS concentrations. Hopkins *et al.* (2010) suggested that
397 ‘the perturbation of the system has a greater effect on the processes that control the conversion of
398 DMSP to DMS rather than the initial production of DMSP itself’. This is relevant even for the current
399 experiment, where DMSP was not identified, since processes controlling DMS concentrations were
400 likely more affected by the change in $f\text{CO}_2$ than the production of precursors.

401 Previous mesocosm experiments have suggested significant links between increased bacterial
402 production through greater availability of organic substrates at high $f\text{CO}_2$ (Engel *et al.*, 2013; Piontek
403 *et al.*, 2013). Further, Endres *et al.* (2014) identified significant enhanced enzymatic hydrolysis of
404 organic matter with increasing $f\text{CO}_2$, with higher bacterial abundance. Higher bacterial abundance will
405 likely result in greater bacterial demand for sulphur, and therefore greater consumption of DMS and
406 conversion to DMSO. This was suggested as a significant sink for DMS in a previous experiment



407 (Webb *et al.*, 2015), but during the present experiment, both bacterial abundance and bacterial
408 production were lower at high $f\text{CO}_2$ (Hornick *et al.*, 2015). However, as it has been proposed that only
409 specialist bacterial groups are DMS consumers (Vila-Costa *et al.*, 2006b), and there is no
410 determination of the DMS consumption characteristics of the bacterial community in the Baltic Sea,
411 this is still a potential stimulated DMS loss pathway at high $f\text{CO}_2$. *Synechococcus* has been identified
412 as a DMS consumer in the open ocean, but abundance of this group was negatively correlated with
413 $f\text{CO}_2$, implying that DMS consumption by this group would have been lower as $f\text{CO}_2$ increased.

414 3.3 Iodocarbons in the mesocosms and relationships with community composition

415 Elevated $f\text{CO}_2$ did not affect the concentration of iodocarbons in the mesocosms significantly at any
416 time during the experiment, which is in agreement with the findings of Hopkins *et al.* (2013) in the
417 Arctic, but in contrast to Hopkins *et al.* (2010) and Webb (2015), where iodocarbons were measured
418 significantly lower under elevated $f\text{CO}_2$ (Table 4). Concentrations of all iodocarbons measured in the
419 mesocosms and the Baltic Sea fall within the range of those measured previously in the region (Table
420 5). Mesocosm concentrations of CH_3I (Fig. 4a) and $\text{C}_2\text{H}_5\text{I}$ (Fig. 4b) showed concentration ranges of
421 2.91 to 6.25 and 0.23 to 0.76 pmol L^{-1} respectively. CH_3I showed a slight increase in all mesocosms
422 during Phase I, peaking on *t*16 which corresponded with higher Chl-*a* concentrations, and correlated
423 throughout the entire experiment with picoeukaryote groups II ($\rho=0.59$, $p<0.01$) and III ($\rho=0.23$,
424 $p<0.01$; Crawford *et al.* this issue) and nanoeukaryotes I ($\rho=0.37$, $p<0.01$). Significant differences
425 identified between mesocosms for CH_3I were unrelated to elevated $f\text{CO}_2$ ($F=3.1$, $p<0.05$), but
426 concentrations were on average 15% higher in Phase II than Phase I. $\text{C}_2\text{H}_5\text{I}$ decreased slightly during
427 Phases I and II, although concentrations of this halocarbon were close to its detection limit (0.2 pmol
428 L^{-1}), remaining below 1 pmol L^{-1} at all times. As this compound showed no significant effect of
429 elevated $f\text{CO}_2$, and was identified by Orlikowska and Schulz-Bull (2009) as having extremely low
430 concentrations in the Baltic Sea (Table 5), it will not be discussed further.

431 No correlation was found between CH_3I and Chl-*a* at any phase, and the only correlation of any
432 phytoplankton grouping was with nanoeukaryotes II ($\rho=0.88$, $p<0.01$; Crawford *et al.*, 2015). These
433 CH_3I concentrations compare well to the 7.5 pmol L^{-1} measured by Karlsson *et al.* (2008) during a
434 cyanobacterial bloom in the Baltic Sea (Table 5), and the summer maximum of 16 pmol L^{-1} identified
435 by Orlikowska and Schulz-Bull (2009).

436 Karlsson *et al.* (2008) showed Baltic Sea halocarbon production occurring predominately during
437 daylight hours, with concentrations at night decreasing by 70% compared to late afternoon. Light
438 dependent production of CH_3I has been shown to take place through abiotic processes, including



439 radical recombination of CH_3 and I (Moore and Zafiriou, 1994). However since samples were
440 integrated over the surface 10m of the water column, it was impossible to determine if photochemistry
441 was affecting iodocarbon concentrations near the surface where some UV light was able to pass
442 between the top of the mesocosm film material and the cover. For the same reason, photodegradation
443 of halocarbons (Zika *et al.*, 1984) within the mesocosms was also likely to have been significantly
444 restricted. Thus, as photochemical production was expected to be minimal, biogenic production was
445 likely to have been the dominant source of these compounds. Karlsson *et al.* (2008) identified
446 *Pseudanabaena* as a key producer of CH_3I in the Baltic Sea. However the abundance of
447 *Pseudanabaena* was highest during Phase I of the experiment (A. Stühr, Pers. Comm.) when CH_3I
448 concentrations were lower, and as discussed previously, the abundance of these species constituted
449 only a very small proportion of the community. Previous investigations in the laboratory have
450 identified diatoms as significant producers of CH_3I (Hughes *et al.*, 2013; Manley and De La Cuesta,
451 1997), and the low, steady-state abundance of the diatom populations in the mesocosms could have
452 produced the same relatively steady-state trends in the iodocarbon concentrations.

453 Measured in the range $57.2 - 202.2 \text{ pmol L}^{-1}$ in the mesocosms, CH_2I_2 (Fig. 4c) showed the clearest
454 increase in concentration during Phase II, when it peaked on *t*21 in all mesocosms, with a maximum of
455 $202.2 \text{ pmol L}^{-1}$ in M5 (348 μatm). During Phase II, concentrations of CH_2I_2 were 57% higher than
456 Phase I, and were therefore negatively correlated with Chl-*a*. The peak on *t*21 corresponds with the
457 peak identified in DMS on *t*21, and concentrations through all three phases correlate with
458 picoeukaryotes II ($\rho=0.62$, $p<0.01$) and III ($\rho=0.47$, $p<0.01$) and nanoeukaryotes I ($\rho=0.88$, $p<0.01$;
459 Crawford *et al.*, 2015). CH_2ClI (Fig. 4d) showed no peaks during either Phase I or Phase II, remaining
460 within the range 3.81 to 8.03 pmol L^{-1} , and again correlated with picoeukaryotes groups II ($\rho=0.34$,
461 $p<0.01$) and III ($\rho=0.38$, $p<0.01$). These results may suggest that these groups possessed halo-
462 peroxidase enzymes able to oxidise I, most likely as an anti-oxidant mechanism within the cell to
463 remove H_2O_2 (Butler and Carter-Franklin, 2004; Pedersen *et al.*, 1996; Theiler *et al.*, 1978). However,
464 given the lack of response of these compounds to elevated $f\text{CO}_2$ ($F=1.7$, $p<0.01$), it is unlikely that
465 production was increased in relation to elevated $f\text{CO}_2$. Production of all iodocarbons increased during
466 Phase II when total Chl-*a* decreased, particularly after the walls of the mesocosms were cleaned for the
467 first time, releasing significant volumes of organic aggregates into the water column. Aggregates have
468 been suggested as a source of CH_3I and $\text{C}_2\text{H}_5\text{I}$ (Hughes *et al.*, 2008), likely through the alkylation of
469 inorganic iodide (Urhahn and Ballschmiter, 1998) or through the breakdown of organic matter by
470 microbial activity to supply the precursors required for iodocarbon production (Smith *et al.*, 1992).
471 Hughes *et al.* (2008) did not identify this route as a pathway for CH_2I_2 or CH_2ClI production, but



472 Carpenter *et al.* (2005) suggested a production pathway for these compounds through the reaction of
473 HOI with aggregated organic materials.

474 **3.4 Bromocarbons in the mesocosms and the relationships with community** 475 **composition**

476 No effect of elevated $f\text{CO}_2$ was identified for any of the three bromocarbons, which compared with the
477 findings from previous mesocosms where bromocarbons were studied (Hopkins *et al.*, 2010, 2013;
478 Webb, 2015; Table 4). Measured concentrations were comparable to those of Orlikowska and Schulz-
479 Bull (2009) and Karlsson *et al.* (2008) measured in the Southern part of the Baltic Sea (Table 3). The
480 concentrations of CHBr_3 , CH_2Br_2 and CHBr_2Cl showed no major peaks of production in the
481 mesocosms. CHBr_3 (Fig. 5a) decreased rapidly in all mesocosms over Phase 0 from a maximum
482 measured concentration of $147.5 \text{ pmol L}^{-1}$ in M1 (mean of $138.3 \text{ pmol L}^{-1}$ in all mesocosms) to a mean
483 of $85.7 (\pm 8.2 \text{ s.d.}) \text{ pmol L}^{-1}$ in all mesocosms for the period t_0 to t_{31} (Phases I and II). The steady-state
484 CHBr_3 concentrations indicated a production source, however there was no clear correlation with any
485 measured algal groups. CH_2Br_2 concentrations (Fig. 5b) decreased steadily in all mesocosms from t_3
486 through to t_{31} , over the range 4.0 to 7.7 pmol L^{-1} , and CHBr_2Cl followed a similar trend in the range
487 1.7 to 4.7 pmol L^{-1} (Fig. 5c). Of the three bromocarbons, only CH_2Br_2 showed correlation with total
488 Chl-*a* ($\rho=0.52$, $p<0.01$), and with cryptophyte ($\rho=0.86$, $p<0.01$) and dinoflagellate ($\rho=0.65$, $p<0.01$)
489 derived Chl-*a*. Concentrations of CH_2BrI were below detection limit for the entire experiment.

490 CH_2Br_2 showed positive correlation with Chl-*a* ($\rho=0.52$, $p<0.01$), nanoeukaryotes II ($\rho=0.34$, $p<0.01$)
491 and cryptophytes ($\rho=0.86$, $p<0.01$; see supplementary material), whereas CHBr_3 and CHBr_2Cl showed
492 very weak or no correlation with any indicators of primary production. Schall *et al.* (1997) have
493 proposed that CHBr_2Cl is produced in seawater by the nucleophilic substitution of bromide by chloride
494 in CHBr_3 , which given the steady-state concentrations of CHBr_3 would explain the similar distribution
495 of CHBr_2Cl concentrations. Production of all three bromocarbons was identified from large-size
496 cyanobacteria such as *Aphanizomenon flos-aquae* by Karlsson *et al.* (2008), and in addition, significant
497 correlations were found in the Arabian Sea between the abundance of the cyanobacterium
498 *Trichodesmium* and several bromocarbons (Roy *et al.*, 2011), and the low abundance of such bacteria
499 in the mesocosms would explain the low variation in bromocarbon concentrations through the
500 experiment.

501 Halocarbon loss processes such as nucleophilic substitution (Moore, 2006), hydrolysis (Elliott and
502 Rowland, 1995), sea-air exchange and microbial degradation are suggested as of greater importance
503 than production of these compounds by specific algal groups, particularly given the relatively low



504 growth rates and total Chl-*a*. Hughes *et al.* (2013) identified bacterial inhibition of CHBr₃ production
505 in laboratory cultures of *Thalassiosira* diatoms, but that it was not subject to bacterial breakdown;
506 which could explain the relative steady state of CHBr₃ concentrations in the mesocosms. In contrast,
507 significant bacterial degradation of CH₂Br₂ in the same experiments could explain the steady decrease
508 in CH₂Br₂ concentrations seen in the mesocosms. Bacterial oxidation was also identified by Goodwin
509 *et al.* (1998) as a significant sink for CH₂Br₂. As discussed for the iodocarbons, photolysis was
510 unlikely due to the UV absorption of the mesocosm film, and limited UV exposure of the surface
511 waters within the mesocosm due to the mesocosm cover. The ratio of CH₂Br₂ to CHBr₃ was also
512 unaffected by increased *f*CO₂, staying within the range 0.04 to 0.08. This range in ratios is consistent
513 with that calculated by Hughes *et al.* (2009) in the surface waters of an Antarctic depth profile, and
514 attributed to higher sea-air flux of CHBr₃ than CH₂Br₂ due to a greater concentrations gradient, despite
515 the similar transfer velocities of the two compounds (Quack *et al.*, 2007). Using cluster analysis in a
516 time-series in the Baltic Sea, Orlikowska and Schulz-Bull (2009) identified both these compounds as
517 originating from different sources and different pathways of production.

518 Macroalgal production would not have influenced the mesocosm concentrations due to the isolation
519 from the coastal environment, however the higher bromocarbon concentrations identified in the
520 mesocosms during Phase 0 may have originated from macroalgal sources (Klick, 1992; Leedham *et al.*,
521 2013; Moore and Tokarczyk, 1993) prior to mesocosm closure, with concentrations decreasing
522 through turnover and transfer to the atmosphere.

523

524 **3.5 Natural variations in Baltic Sea *f*CO₂ and the effect on biogenic trace gases**

525 **3.5.1 Physical variation and community dynamics**

526 Baltic Sea deep waters have high *f*CO₂ and subsequently lower pH (Schneider *et al.*, 2002), and the
527 influx to the surface waters surrounding the mesocosms resulted in *f*CO₂ increasing to 725 µatm on
528 *t*31, close to the average *f*CO₂ of the third highest mesocosm (M6: 868 µatm). These conditions imply
529 that pelagic communities in the Baltic Sea are regularly exposed to rapid changes in *f*CO₂ and the
530 associated pH, as well as having communities associated with the elevated *f*CO₂ conditions.

531 Chl-*a* followed the pattern of the mesocosms until *t*4, after which concentrations were significantly
532 higher than any mesocosm, peaking at 6.48 µg L⁻¹ on *t*16, corresponding to the maximum Chl-*a* peak
533 in the mesocosms and the maximum peak of temperature. As upwelled water intruded into the surface
534 waters, the surface Chl-*a* was diluted with low Chl-*a* deep water: Chl-*a* in the surface 10m decreased



535 from around t_{16} at the start of the upwelling until t_{31} when concentrations were once again equivalent
536 to those found in the mesocosms at $1.30 \mu\text{g L}^{-1}$. In addition there was potential introduction of different
537 algal groups to the surface, but chlorophytes and cryptophytes were the major contributors to the Chl-*a*
538 in the Baltic Sea, as in the mesocosms. Cyanobacteria contributed less than 2% of the total Chl-*a* in the
539 Baltic Sea (Crawford *et al.*, 2015; Paul *et al.*, 2015).

540 Temporal community dynamics in the Baltic Sea were very different to that in the mesocosms across
541 the experiment, with euglenophytes, chlorophytes, diatoms and prasinophytes all showing distinct
542 peaks at the start of Phase II, with these same peaks identified in the nanoeukaryotes I and II, and
543 picoeukaryotes II (Crawford *et al.*, 2016; Paul *et al.*, 2015; Supplementary Figs. S1 and S2). The
544 decrease in abundance of many groups during Phase II was attributed to the decrease in temperature
545 and dilution with low-abundance deep waters.

546 3.5.2 DMS in the Baltic Sea

547 The input of upwelled water into the region mid-way through the experiment significantly altered the
548 biogeochemical properties of the waters surrounding the mesocosms, and as a result it is inappropriate
549 to directly compare the community structure and trace gas production of the Baltic Sea and the
550 mesocosms. The Baltic Sea samples gave a mean DMS concentration of $4.6 \pm 2.6 \text{ nmol L}^{-1}$ but peaked
551 at 11.2 nmol L^{-1} on t_{16} , and were within the range of previous measurements for the region (Table 5).
552 Strong correlations were seen between DMS and Chl-*a* ($\rho=0.84$, $p<0.01$), with the ratio of DMS: Chl-*a*
553 at $1.6 (\pm 0.3) \text{ nmol } \mu\text{g}^{-1}$. Other strong correlations were seen with euglenophytes ($\rho=0.89$, $p<0.01$),
554 dinoflagellates ($\rho=0.61$, $p<0.05$) and nanoeukaryotes II ($\rho=0.88$, $p<0.01$), but no correlation was found
555 between DMS and cyanobacterial abundance, or with picoeukaryotes III which was identified in the
556 mesocosms, suggesting that DMS had a different origin in the Baltic Sea community than in the
557 mesocosms. Once again, there was no DMSP detected in the samples.

558 As CO_2 levels increased during Phase II, the DMS concentration measured in the Baltic Sea decreased,
559 from the peak on t_{16} to the lowest recorded sample of the entire experiment at 1.85 nmol L^{-1} . As with
560 Chl-*a*, DMS concentrations in the surface of the Baltic Sea may have been diluted with low-DMS deep
561 water, however, the inverse relationship of DMS with CO_2 shown in the mesocosms may suggest that
562 this decrease in DMS is attributed to the increase in CO_2 levels. Bacterial abundance was similar in the
563 Baltic Sea as in the mesocosms (Hornick *et al.*, 2015), however the injection of high CO_2 water may
564 have stimulated bacterial consumption of DMS during the upwelling, which combined with the
565 dilution of DMS-rich surface water could have resulted in the rapid decrease in DMS concentrations.
566 As no discernible decrease in total bacterial abundance was identified during the upwelling, it is also



567 possible that the upwelled water contained a different microbial community, and may potentially have
568 introduced a higher abundance of DMS-consuming microbes. No breakdown of bacterial distributions
569 was available with which to test this hypothesis.

570 **3.5.3 Halocarbon concentrations in the Baltic Sea**

571 Outside the mesocosms in the Baltic Sea, CH₃I was measured at a maximum concentration of 8.65
572 pmol L⁻¹, during Phase II, and showed limited effect of the upwelling event. Both CH₂I₂ and CH₂CII
573 showed higher concentrations in the Baltic Sea samples than the mesocosms (CH₂I₂: 373.9 pmol L⁻¹
574 and CH₂CII: 18.1 pmol L⁻¹), and were correlated with the euglenophytes (CH₂I₂; $\rho=0.63$, $p<0.05$ and
575 CH₂CII; $\rho=0.68$, $p<0.01$) and nanoeukaryotes II (CH₂I₂; $\rho=0.53$, $p<0.01$ and CH₂CII; $\rho=0.58$, $p<0.01$),
576 but no correlation with Chl-*a*. Both polyiodinated compounds showed correlation with picoeukaryote
577 groups II and III, indicating that production was not limited to a single source. These concentrations of
578 CH₂I₂ and CH₂CII compared well to those measured over a macroalgal bed in the higher saline waters
579 of the Kattegat by Klick and Abrahamsson (1992), suggesting that macroalgae were a significant
580 iodocarbon source in the Baltic Sea.

581 As with the iodocarbons, the Baltic Sea showed significantly higher concentrations of CHBr₃ ($F=28.1$,
582 $p<0.01$), CH₂Br₂ ($F=208.8$, $p<0.01$) and CHBr₂Cl ($F=23.5$, $p<0.01$) than the mesocosms, with
583 maximum concentrations 191.6 pmol L⁻¹, 10.0 pmol L⁻¹ and 5.0 pmol L⁻¹ respectively. In the Baltic
584 Sea, only CHBr₃ was correlated with Chl-*a* ($\rho=0.65$, $p<0.05$), cyanobacteria ($\rho=0.61$, $p<0.01$; Paul *et al.*,
585 2015) and nanoeukaryotes II ($\rho=0.56$, $p<0.01$; Crawford *et al.*, 2015), with the other two
586 bromocarbons showing little to no correlations with any parameter of community activity. Production
587 of bromocarbons from macroalgal sources (Laternus *et al.*, 2000; Leedham *et al.*, 2013; Manley *et al.*,
588 1992) was likely a significant contributor to the concentrations detected in the Baltic Sea; over the
589 macroalgal beds in the Kattegat, Klick (1992) measured concentrations an order of magnitude higher
590 than seen in this experiment for CH₂Br₂ and CHBr₂Cl.

591

592 **4 The Baltic Sea as a natural analogue to future ocean acidification?**

593 Mesocosm experiments are a highly valuable tool in assessing the potential impacts of elevated CO₂
594 on complex marine communities, however they are limited in that the rapid change in $f\text{CO}_2$
595 experienced by the community may not be representative of changes in the future ocean (Passow and
596 Riebesell, 2005). This inherent problem with mesocosm experiments can be overcome through using
597 naturally low pH/ high CO₂ areas such as upwelling regions or vent sites (Hall-Spencer *et al.*, 2008),
598 which can give an insight into populations already living and adapted to high CO₂ regimes by exposure



599 over timescales measured in years. This mesocosm experiment was performed at such a location with a
600 relatively low $f\text{CO}_2$ excursion compared to some sites (800 μatm compared to $>2000 \mu\text{atm}$; Hall-
601 Spencer et al., 2008), and it was clear through the minimal variation in Chl-*a* between all mesocosms
602 that the community was relatively unaffected by elevated $f\text{CO}_2$, although variation could be identified
603 in some phytoplankton groups and some shifts in community composition. The upwelling event
604 occurring mid-way through our experiment allowed comparison of the mesocosm findings with a
605 natural analogue of the system, as well as showing the extent to which the system perturbation can
606 occur (up to 800 μatm). However, it is very difficult to determine where and when an upwelling will
607 occur, and therefore hard to utilise these events as natural high CO_2 analogues.

608 In this paper, we described the temporal changes in concentrations of DMS and halocarbons in natural
609 Baltic phytoplankton communities exposed to elevated $f\text{CO}_2$ treatments. In contrast to the halocarbons,
610 concentrations of DMS were significantly lower in the highest $f\text{CO}_2$ treatments compared to the
611 control. Despite very different physicochemical and biological characteristics of the Baltic Sea (e.g.
612 salinity, community composition and nutrient concentrations), this is a very similar outcome to that
613 seen in several other high $f\text{CO}_2$ experiments. The Baltic Sea trace gas samples give a good record of
614 trace gas production during the injection of high $f\text{CO}_2$ deep water into the surface community during
615 upwelling events. For the concentrations of halocarbons, no response was shown to the upwelling
616 event in the Baltic Sea, which may indicate that emissions of organic iodine and bromine are unlikely
617 to change with future acidification of the Baltic Sea. However, production of organic sulphur within
618 the Baltic Sea region is likely to decrease with an acidified future ocean scenario, despite the possible
619 acclimation of the microbial community to elevated $f\text{CO}_2$. This will potentially impact the flux of
620 DMS to the atmosphere over Northern Europe, and could have significant impacts on the local climate
621 through the reduction of atmospheric sulphur aerosols. Data from a previous mesocosm experiment
622 has been used to estimate future global changes in DMS production, and predicted that global warming
623 would be amplified (Six *et al.*, 2013); utilising the data from this experiment combined with those of
624 other mesocosm, field and laboratory experiments and associated modelling provide the basis for a
625 better understanding of the future changes in global DMS production and their climatic impacts.

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931 Table 1. Summary of $f\text{CO}_2$ and pH_T (total scale) during phases 0, 1 and 2 of the mesocosm experiment.

	Target	Whole Experiment							
		/ $t-3$ to $t31$			Phase 0 / $t-3$ to $t0$		Phase I / $t1-t16$		Phase II / $t16-t31$
Mesocosm ^a	$f\text{CO}_2 / \mu\text{atm}$	Mean $f\text{CO}_2 / \mu\text{atm}$	Mean pH_T	Mean $f\text{CO}_2 / \mu\text{atm}$	Mean pH_T	Mean $f\text{CO}_2 / \mu\text{atm}$	Mean pH_T	Mean $f\text{CO}_2 / \mu\text{atm}$	Mean pH_T
M1	Control	331	7.91	231	8.00	328	7.95	399	7.86
M5	Control	334	7.91	244	7.98	329	7.94	399	7.52
M7	390	458	7.80	239	7.99	494	7.81	532	7.76
M6	840	773	7.63	236	7.99	932	7.59	855	7.59
M3	1120	950	7.56	243	7.98	1176	7.51	1027	7.52
M8	1400	1166	7.49	232	8.00	1481	7.43	1243	7.45
Baltic Sea	380	350	7.91	298	7.91	277	7.98	436	7.86

932 ^a listed in order of increasing $f\text{CO}_2$

933



934 Table 2. Calibration ranges and calculated percentage mean relative standard error for the trace gases
 935 measured in the mesocosms.

Compound	Calibration range / pmol L^{-1}	% Mean relative standard error
DMS	600 – 29300*	6.33
DMSP	2030 – 405900*	
CH ₃ I	0.11 – 11.2	4.62
CH ₂ I ₂	5.61 – 561.0	4.98
C ₂ H ₅ I	0.10 – 4.91	5.61
CH ₂ ClI	1.98 – 99.0	3.64
CHBr ₃	8.61 – 816.0	4.03
CH ₂ Br ₂	0.21 – 20.9	5.30
CHBr ₂ Cl	0.07 – 7.00	7.20

936 * throughout the rest of this paper, these measurements are given in nmol L^{-1} .

937



938 Table 3. Abundance and contributions of different phytoplankton groups to the total phytoplankton
 939 community assemblage, showing the range of measurements from total Chl-*a* (Paul *et al.*, 2015),
 940 CHEMTAX analysis of derived Chl-*a* (Paul *et al.*, 2015) and phytoplankton abundance (Crawford *et*
 941 *al.*, 2015). Data are split into the range of all the mesocosm measurements and those from the Baltic
 942 Sea.

	Mesocosm			Baltic Sea		
	Range Integrated 10 m	Range Integrated 17 m	% Contribution to Chl- <i>a</i>	Range Integrated 10 m	Range Integrated 17 m	% Contribution to Chl- <i>a</i>
Chl-<i>a</i>	0.9 – 2.9	0.9 – 2.6	100	1.3 – 6.5	1.12 – 5.5	100
Phytoplankton Taxonomy / Equivalent Chlorophyll $\mu\text{g L}^{-1}$						
Cyanobacteria		0.01 – 0.4	8		0.0 – 0.1	1
Prasinophytes		0.04 – 0.3	7		0.01 – 0.3	4
Euglenophytes		0.0 – 1.6	15		0.0 – 2.6	21
Dinoflagellates		0.0 – 0.3	3		0.04 – 0.6	9
Diatoms		0.1 – 0.3	7		0.04 – 0.9	9
Chlorophytes		0.3 – 2.0	40		0.28 – 3.1	41
Cryptophytes		0.1 – 1.4	21		0.1 – 1.0	15
Small Phytoplankton (<10 μm) abundance / cells mL^{-1}						
Cyanobacteria	55000 – 380000	65000 – 470000		30000 – 180000	30000 – 250000	
Picoeukaryotes I	15000 – 100000	17000 – 111000		5000 – 70000	6100 – 78000	
Picoeukaryotes II	700 – 4000	600 – 4000		400 – 3000	460 – 3700	
Picoeukaryotes III	1000 – 9000	1100 – 8500		1000 – 6000	950 – 7500	
Nanoeukaryotes I	400 – 1400	270 – 1500		200 – 4000	210 – 4100	
Nanoeukaryotes II	0 – 400	4 – 400		100 – 1100	60 – 1300	

943



944 Table 4. Concentration ranges of trace gases measured in the mesocosms compared to other open
 945 water ocean acidification experiments, showing the range of concentrations for each gas and the
 946 percentage change between the control and the highest $f\text{CO}_2$ treatment.

	Range $f\text{CO}_2$		DMS	CH_3I	CH_2I_2	CH_2ClI	CHBr_3	CH_2Br_2	$\text{CH}_2\text{Br}_2\text{Cl}$
	/ μatm		/ nmol L^{-1}	/ pmol L^{-1}					
SOPRAN Tvärminne Mesocosm (this study)	346 – 1333	Range	2.7-6.8	2.9-6.4	57-202	3.8-8.0	69-148	4.0-7.7	1.7-3.1
		% change	-34	-0.3	1.3	-11	-9	-3	-4
SOPRAN Bergen 2011 (Webb <i>et al.</i> , 2015)	280 – 3000	Range	0.1-4.9	4.9-32	5.8-321	9.0-123	64-306	6.3-30.8	3.9-14
		% change	-60	-37	-48	-27	-2	-4	-6
NERC Microbial Metagenomics Experiment, Bergen 2006 (Hopkins <i>et al.</i> , 2010)	300 - 750	Range	ND-50	2.0-25	ND-750	ND-700	5.0-80	ND-5.5	0.2-1.2
		% change	-57	-41	-33	-28	13	8	22
EPOCA Svalbard 2010 (Archer <i>et al.</i> , 2013; Hopkins <i>et al.</i> , 2013)	180 - 1420	Range	ND-14	0.04-10	0.01-2.5	0.3-1.6	35-151	6.3-33.3	1.6-4.7
		% change	-60	NS		NS	NS	NS	NS
UKOA European Shelf 2011 (Hopkins and Archer, 2014)	340 - 1000	Range	0.5-12						
		% change	225						
Korean Mesocosm Experiment 2012 (Park <i>et al.</i> , 2014)	160 - 830	Range	1.0-100						
		% change	-82						

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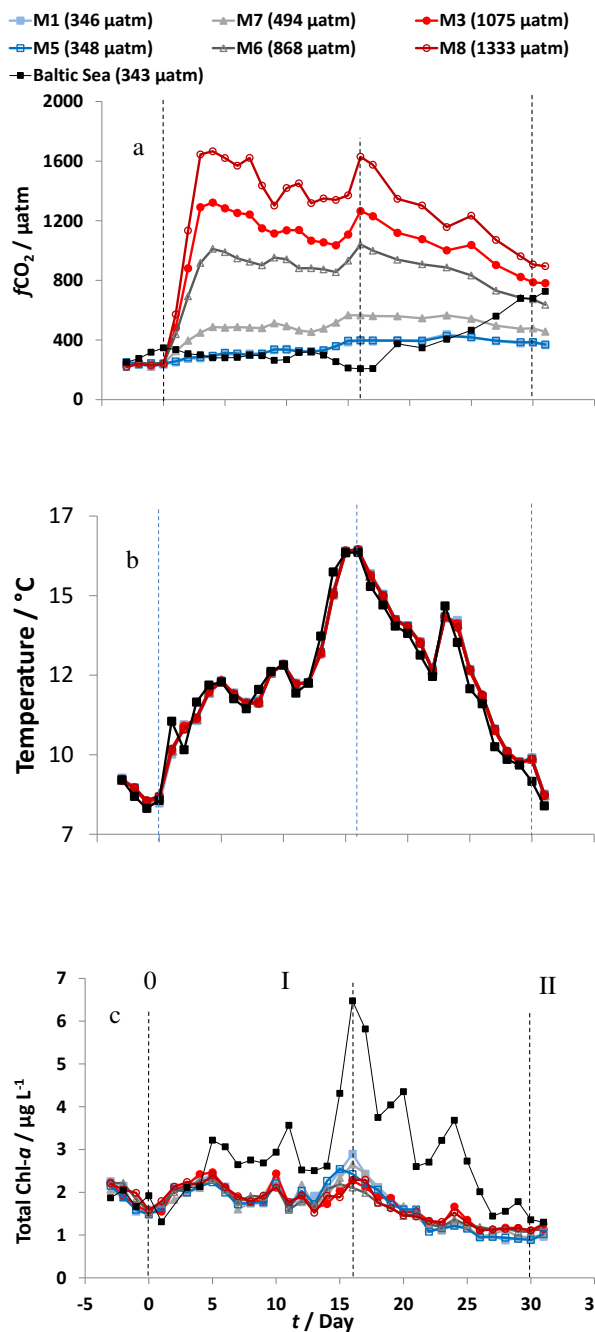


949 Table 5. Concentration ranges of trace gases measured in the Baltic Sea compared to concentrations
 950 measured in the literature. ND – Not Detected.

Study	DMS concentration range / nmol L ⁻¹	Halocarbon concentration range / pmol L ⁻¹						
		CH ₃ I	CH ₂ I ₂	C ₂ H ₃ I	CH ₂ ClI	CHBr ₃	CH ₂ Br ₂	CH ₂ Br ₂ Cl
SOPRAN Tvärminne Baltic Sea (This Study)	1.9-11	4.3-8.6	66.9-374	0.6 – 1.0	7.0-18	93-192	7.1-10	3.3-5.0
Orlikowska and Schulz- BullS(2009)	0.3-120	1-16	0.85	0.4 – 1.2	5-50	5.0-40	2.0-10	0.8-2.5
Karlsson <i>et al.</i> (2008)		3.0-7.5				35-60	4.0-7.0	2.0-6.5
Klick and Abrahamsson (1992)			15-709		11-74	14-585		
Klick (1992)			ND-243		ND-57	40-790	ND-86	ND-29
Leck and Rodhe (1991)	0.4-2.8							
Leck <i>et al.</i> (1990)	ND-3.2							

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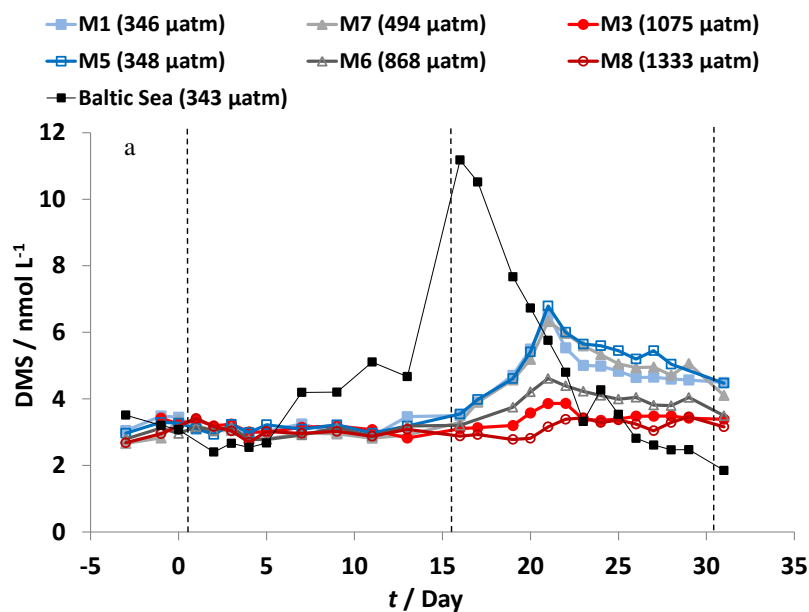
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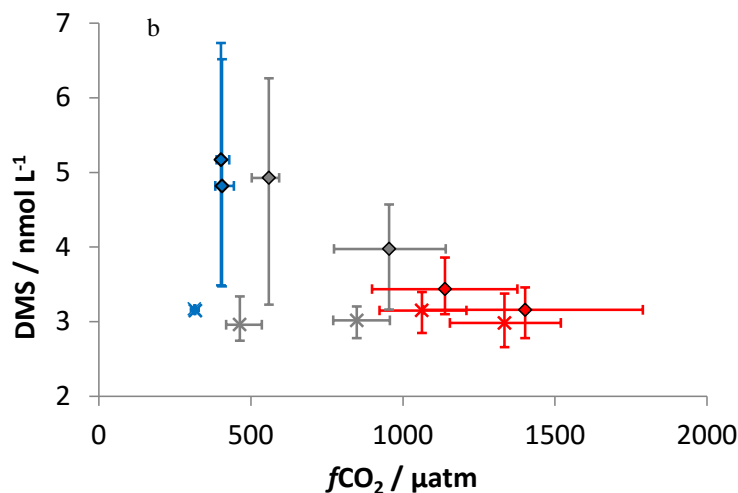
956 Figure 1. Daily measurements of (a) $f\text{CO}_2$, (b) mean temperature and (c) total Chlorophyll- a in the
 957 mesocosms and surrounding Baltic Sea waters. Dashed lines represent the three Phases of the
 958 experiment, based on the Chl- a data.



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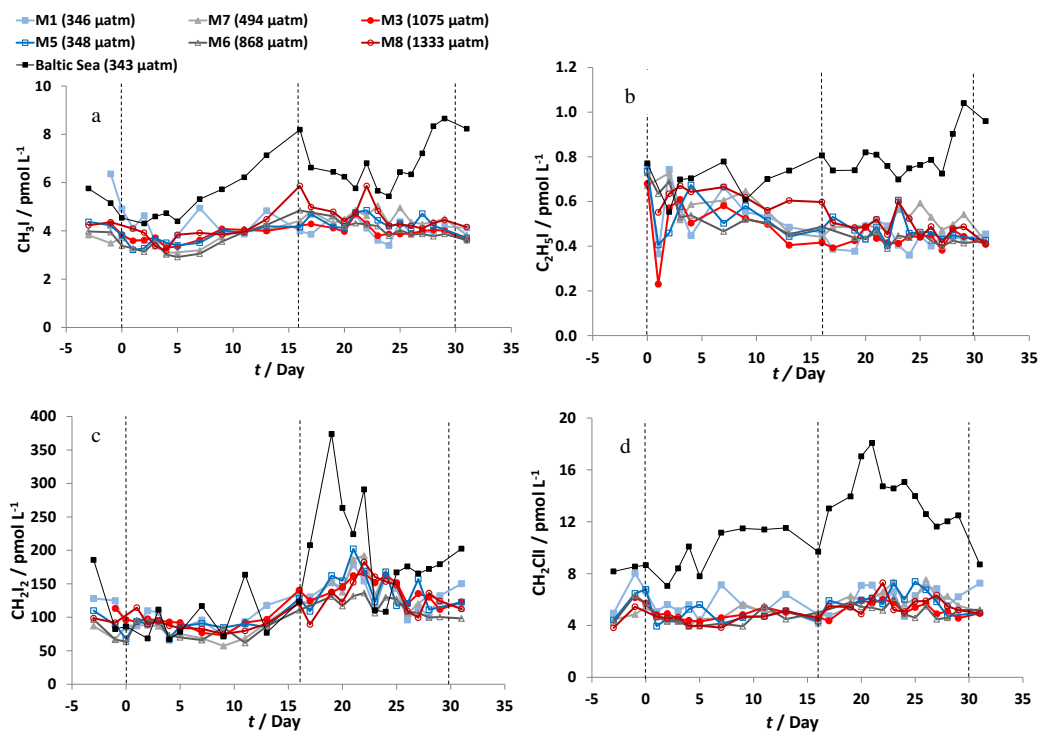


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962 Figure 3. (a) Integrated DMS concentrations measured daily in the mesocosms and Baltic Sea from the
 963 surface 10 m and (b) mean DMS concentrations from each mesocosm during Phase I (crosses) and
 964 Phase II (diamonds), for ambient (blue), medium (grey) and high $f\text{CO}_2$ (red), with error bars showing
 965 the range of both the DMS and $f\text{CO}_2$. Dashed lines show the Phases of the experiment as given in Fig.
 966 2, $f\text{CO}_2$ shown in the legend are mean $f\text{CO}_2$ across the duration of the experiment.

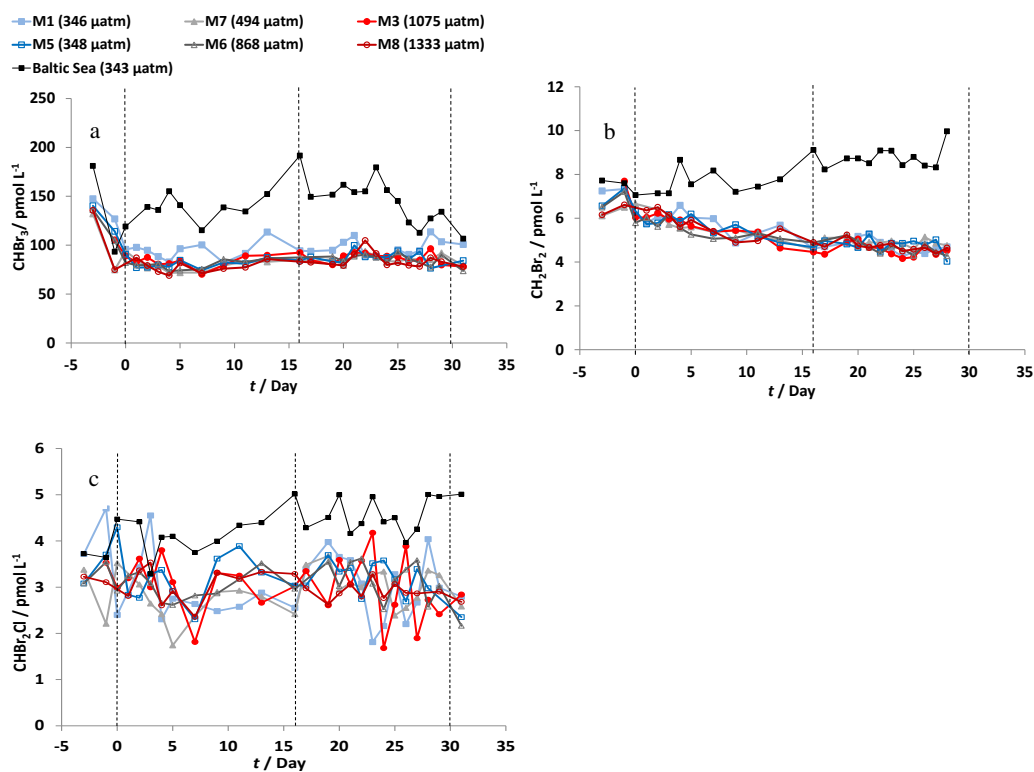


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969 Figure 4. Concentrations (pmol L⁻¹) of (a) CH₃I, (b) C₂H₅I, (c) CH₂I₂ and (d) CH₂ClI. Dashed lines
970 indicate the Phases of the experiment, as given in Fig. 2. *f*CO₂ shown in the legend are mean *f*CO₂
971 across the duration of the experiment.

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975 Figure 5. Concentrations (pmol L⁻¹) of (a) CHBr₃, (b) CH₂Br₂ and (c) CHBr₂Cl. Dashed lines indicate
976 the phases of the experiment as defined in Fig. 2, *f*CO₂ shown in the legend are mean *f*CO₂ across the
977 duration of the experiment.

978