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Effect of ocean acidification and elevated fCO_2 on trace gas production by a Baltic Sea summer phytoplankton community

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Abstract

The Baltic Sea is a unique environment as the largest body of brackish water in the world. Acidification of the surface oceans due to absorption of anthropogenic CO_2 emissions is an additional stressor facing the pelagic community of the already challenging Baltic Sea. To investigate its impact on trace gas biogeochemistry, a large-scale mesocosm experiment was performed off Tvärminne Research Station, Finland in summer 2012. During the second half of the experiment, dimethylsulphide (DMS) concentrations in the highest fCO_2 mesocosms (1075 -

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1333 µatm) were 34% lower than at ambient CO_2 (350 µatm). However the net production (as measured by concentration change) of seven halocarbons analysed was not significantly affected by even the highest CO_2 levels after 5 weeks exposure. Methyl iodide (CH_3I) and diiodomethane (CH_2I_2) showed 15% and 57% increases in mean mesocosm concentration (3.8 ± 0.6 pmol L^{-1} increasing to 4.3 ± 0.4 pmol L^{-1} and 87.4 ± 14.9 pmol L^{-1} increasing to 134.4 ± 24.1 pmol L^{-1} respectively) during Phase II of the experiment, which were unrelated to CO_2 and corresponded to 30% lower Chl-*a* concentrations compared to Phase I. No other iodocarbons increased or showed a peak, with mean chloroiodomethane (CH_2ClI) concentrations measured at 5.3 (± 0.9) pmol L^{-1} and iodoethane (C_2H_5I) at 0.5 (± 0.1) pmol L^{-1}. Of the concentrations of bromoform ($CHBr_3$; mean 88.1 ± 13.2 pmol L^{-1}), dibromomethane (CH_2Br_2; mean 5.3 ± 0.8 pmol L^{-1}) and dibromochloromethane ($CHBr_2Cl$, mean 3.0 ± 0.5 pmol L^{-1}), only CH_2Br_2 showed a decrease of 17% between Phases I and II, with $CHBr_3$ and $CHBr_2Cl$ showing similar mean concentrations in both Phases. Outside the mesocosms, an upwelling event was responsible for bringing colder, high CO_2, low pH water to the surface starting on day *t*16 of the experiment; this variable CO_2 system with frequent upwelling events implies the community of the Baltic Sea is acclimated to regular significant declines in pH caused by up to 800 µatm fCO_2. After this upwelling, DMS concentrations declined, but halocarbon concentrations remained similar or increased compared to measurements prior to the change in conditions. Based on our findings, with future acidification of Baltic Sea waters, biogenic halocarbon emissions are likely to remain at similar values to today, however emissions of biogenic sulphur could significantly decrease from this region.

1 Introduction

Anthropogenic activity has increased the fugacity of atmospheric carbon dioxide (fCO_2) from 280 µatm (pre-Industrial Revolution) to over 400 µatm today (Hartmann *et al.*, 2013). The IPCC AR5 long-term projections for atmospheric pCO_2 and associated changes to the climate have been established for a variety of scenarios of anthropogenic activity until the year 2300. As the largest global sink for atmospheric CO_2, the global oceans have absorbed an estimated 30% of excess CO_2 produced (Canadell *et al.*, 2007). With atmospheric pCO_2 projected to possibly exceed 2000 µatm by the year 2300 (Collins *et al.*, 2013; Cubasch *et al.*, 2013), the ocean will take up increasing amounts of CO_2, with a potential lowering of surface ocean pH by over 0.8 units (Raven *et al.*, 2005). The overall effect of acidification on the biogeochemistry of surface ocean ecosystems is unknown and currently

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

A number of volatile organic compounds are produced by marine phytoplankton (Liss *et al.*, 2014), including the climatically important trace gas dimethylsulphide (DMS, C_2H_6S) and a number of halogen-containing organic compounds (halocarbons) including methyl iodide (CH_3I) and bromoform ($CHBr_3$). These trace gases are a source of sulphate particles and halide radicals when oxidised in the atmosphere, and have important roles as ozone catalysts in the troposphere and stratosphere (O'Dowd *et al.*, 2002; Solomon *et al.*, 1994) and as cloud condensation nuclei (CCNs; Charlson *et al.*, 1987).

DMS is found globally in surface waters originating from the algal-produced precursor dimethylsulphoniopropionate (DMSP, $C_5H_{10}O_2S$). Both DMS and DMSP are major routes of sulphur and carbon flux through the marine microbial food web, and can provide up to 100% of the bacterial (Simó *et al.*, 2009) and phytoplanktonic (Vila-Costa *et al.*, 2006a) sulphur demand. DMS is also a volatile compound which readily passes through the marine boundary layer to the troposphere, where oxidation results in a number of sulphur-containing particles important for atmospheric climate feedbacks (Charlson *et al.*, 1987; Quinn and Bates, 2011); for this reason, any change in the production of DMS may have significant implications for climate regulation. Several previous acidification experiments have shown differing responses of both compounds (e.g. Avgoustidi *et al.*, 2012; Hopkins *et al.*, 2010; Webb *et al.*, 2015), while others have shown delayed or more rapid responses as a direct effect of CO_2 (e.g. Archer *et al.*, 2013; Vogt *et al.*, 2008). Further, some laboratory incubations of coastal microbial communities showed increased DMS production with increased fCO_2 (Hopkins and Archer, 2014), but lower DMSP production. The combined picture arising from existing studies is that the response of communities to fCO_2 perturbation is not predictable and requires further study. Previous studies measuring DMS in the Baltic Sea measured concentrations up to 100 nmol L^{-1} during the summer bloom, making the Baltic Sea a significant source of DMS (Orlikowska and Schulz-Bull, 2009).

In surface waters, halocarbons such as methyl iodide (CH_3I), chloroiodomethane (CH_2ClI) and bromoform ($CHBr_3$) are produced by biological and photochemical processes: many marine microbes (for example cyanobacteria; Hughes *et al.*, 2011, diatoms; Manley and De La Cuesta, 1997 and haptophytes; Scarratt and Moore, 1998) and macroalgae (e.g. brown-algal *Fucus* species; Chance *et al.*, 2009 and red algae; Leedham *et al.*, 2013) utilise halides from seawater and emit a range of organic and inorganic halogenated compounds. This production can lead to significant flux to the marine boundary layer in the order of 10 Tg iodine-containing compounds ('iodocarbons'; O'Dowd *et al.*, 2002) and 1 Tg bromine-containing compounds ('bromocarbons'; Goodwin *et al.*, 1997) into the

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atmosphere. The effect of acidification on halocarbon concentrations has received limited attention, but two acidification experiments measured lower concentrations of several iodocarbons while bromocarbons were unaffected by fCO_2 up to 3000 µatm (Hopkins *et al.*, 2010; Webb, 2015), whereas an additional mesocosm study did not elicit significant differences from any compound up to 1400 µatm fCO_2 (Hopkins *et al.*, 2013).

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

Here we report the concentrations of DMS, DMSP and halocarbons from the 2012 summer season mesocosm experiment aimed to assess the impact of elevated fCO_2 on the microbial community and trace gas production in the Baltic Sea. Our objective was to assess how changes in the microbial community driven by changes in fCO_2 impacted DMS and halocarbon concentrations. It is anticipated that any effect of CO_2 on the growth of different groups within the phytoplankton assemblage will result in an associated change in trace gas concentrations measured in the mesocosms as fCO_2 increases, which can potentially be used to predict future halocarbon and sulphur emissions from the Baltic Sea region.

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2 Methods

2.1 Mesocosm design and deployment

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

To obtain mesocosms with different fCO_2, the carbonate chemistry of the mesocosms was altered by the addition of different volumes of 50 µm filtered, CO_2-enriched Baltic Sea water (sourced from outside the mesocosms), to each mesocosm over a four day period, with the first day of addition being defined as day *t*0. Addition of the enriched CO_2 water was by the use of a bespoke dispersal apparatus ('Spider') lowered through the bags to ensure even distribution throughout the water column (further details are in Riebesell *et al.* 2013). Measurements of salinity in the mesocosms throughout the experiment determined that three of the mesocosms were not fully sealed, and had undergone unquantifiable water exchange with the surrounding waters. These three mesocosms (M2, M4 and M9) were excluded from the analysis. Two mesocosms were designated as controls (M1 and M5) and received only filtered seawater via the Spider; four mesocosms received addition of CO_2-enriched waters, with the range of target fCO_2 levels between 600 and 1650 µatm (M7, 600 µatm; M6, 950 µatm; M3, 1300 µatm; M8 1650 µatm). Mesocosms were randomly allocated a target fCO_2; a

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noticeable decrease in fCO_2 was identified in the three highest fCO_2 mesocosms (M6, M3 and M8) over the first half of the experiment, which required the addition of more CO_2 enriched water on *t*15 to bring the fCO_2 back up to maximum concentrations (Fig. 1a; Paul *et al*., 2015). A summary of the fCO_2 in the mesocosms can be seen in Table 1. At the same time as this further CO_2 addition on *t*15, the walls of the mesocosms were cleaned using a bespoke wiper apparatus (See Riebesell *et al*., 2013 for more information), followed by weekly cleaning to remove aggregations on the film which would block incoming light. Light measurements showed that over 95% of the photosynthetically active radiation (PAR) was transmitted by the clean TPU and PVC materials with 100% absorbance of UV light (Riebesell *et al.*, 2013). Samples for most parameters were collected from the mesocosms at the same time every morning from *t*-3, and analysed daily or every other day.

2.2 Trace gas extraction and analysis

2.2.1 DMS and halocarbons

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

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

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dewar. The sample was injected by immersion of the sample loop in boiling water into an Agilent 6890 gas chromatograph equipped with a 60 m DB-VRX capillary column (0.32 mm ID, 1.8 µm film thickness, Agilent J&W Ltd) according to the programme outlined by Hopkins *et al.* (2010). Analysis was performed by an Agilent 5973 quadrupole mass spectrometer operated in electron ionisation, single ion mode. Liquid standards of CH_3I, diiodomethane (CH_2I_2), CH_2ClI, iodoethane (C_2H_5I), iodopropane (C_3H_7I), $CHBr_3$, dibromoethane (CH_2Br_2), dibromochloromethane ($CHBr_2Cl$), bromoiodomethane (CH_2BrI) and DMS (Standards supplied by Sigma Aldrich Ltd, UK) were gravimetrically prepared by dilution in HPLC-grade methanol (Table 2) and used for calibration. The relative standard error was expressed as a percentage of the mean for the sample analysis, calculated for each compound using triplicate analysis each day from a single mesocosm, and was <7% for all compounds. GC-MS instrument drift was corrected by the use of a surrogate analyte standard in every sample, comprising deuterated DMS (D_6-DMS), deuterated methyl iodide (CD_3I) and ^{13}C dibromoethane ($^{13}C_2H_4Br_2$) via the method described in Hughes *et al.* (2006) and Martino *et al.* (2005). Five-point calibrations were performed weekly for each compound with the addition of the surrogate analyte, with a single standard analysed daily to check for instrument drift; linear regression from calibrations typically produced $r^2>0.98$. All samples measured within the mesocosms were within the concentration ranges of the calibrations (Table 2).

2.2.2 DMSP

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

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

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

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

2.3 Measurement of community dynamics

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

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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 (Crawfurd *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 fCO_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, fCO_2, and a number of biological parameters, and the resulting ρ-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.

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3.1.1 Physical Parameters

fCO_2 decreased over Phase I in the three highest fCO_2 mesocosms, mainly through air-sea gas exchange and carbon fixation by phytoplankton (Fig. 1a). All mesocosms still showed distinct differences in fCO_2 levels throughout the experiment (Table 1), and there was no overlap of mesocosm fCO_2 values on any given day, save for the two controls (M1 and M5). The control mesocosm fCO_2 increased through Phase I of the experiment, likely as a result of undersaturation of the water column encouraging dissolution of atmospheric CO_2 (Paul *et al.*, 2015). Salinity in the mesocosms remained constant throughout the experiment at 5.70 ± 0.004, and showed no variation with depth. It remained similar to salinity in the Baltic Sea surrounding the mesocosms, which was 5.74 ± 0.14. Water 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 day *t*16, before decreasing once again (Fig. 1b).

Summertime upwelling events are common and well described (Gidhagen, 1987; Lehmann and Myrberg, 2008), and induce a significant temperature decrease in surface waters; such an event appears to have commenced around *t*16, as indicated by significantly decreasing temperatures inside and out of the mesocosms (Fig. 1b) and increased salinity in the Baltic Sea from 5.5 to 6.1 over the following 15 days to the end of the experiment. Due to the enclosed nature of the mesocosms, the upwelling affected only the temperature and not pH, fCO_2 or the microbial community. However, the temperature decrease after *t*16 was likely to have had a significant effect on phytoplankton growth, explaining the lower Chl-*a* in Phase II.

3.1.2 Community Dynamics

Mixing of the mesocosms after closure prior to *t*-3 did not trigger a notable increase in Chl-*a* in Phase 0; in previous mesocosm experiments, mixing redistributed nutrients from the deeper stratified layers throughout the water column. During Phase I, light availability, combined with increasing water temperatures favoured the growth of phytoplankton in all mesocosms (Paul *et al.* 2015), and was unlikely to be a direct result of the CO_2 enrichment. Mean Chl-*a* during Phase I was 1.98 (± 0.29) µg L^{-1} from all mesocosms, decreasing to 1.44 (± 0.46) µg L^{-1} in Phase II: this decrease was attributed to a temperature induced decreased in phytoplankton growth rates and higher grazing rates as a result of higher zooplankton reproduction rates during Phase I (Lischka *et al.*, 2015; Paul *et al.*, 2015). Mesocosm Chl-*a* decreased until the end of the experiment on *t*31.

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

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elevated fCO_2 in only two groups: picoeukaryotes I showed higher abundance at high fCO_2 ($F=8.2$, $p<0.01$; Crawfurd *et al.*, 2016 and Supplementary Fig. S2), as seen in previous mesocosm experiments (Brussaard *et al.*, 2013; Newbold *et al.*, 2012) and picoeukaryotes III the opposite trend ($F=19.6$, $p<0.01$; Crawfurd *et al.* this issue). Temporal variation in phytoplankton abundance was similar between all mesocosms (Supplementary Fig. S1 and S2).

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

3.2 DMS and DMSP

3.2.1 Mesocosm DMS

A significant 34% reduction in DMS concentrations was detected in the high fCO_2 treatments during Phase II compared to the ambient fCO_2 mesocosms ($F=31.7$, $p<0.01$). Mean DMS concentrations of 5.0 (± 0.8; range 3.5 – 6.8) nmol L^{-1} in the ambient treatments compared to 3.3 (± 0.3; range 2.9 – 3.9) nmol L^{-1} in the 1333 and 1075 µatm mesocosms (Fig. 3a). The primary differences identified were apparent from the start of Phase II on *t*17, after which maximum concentrations were observed in the ambient mesocosms on *t*21. The relationship between DMS and increasing fCO_2 during Phase II was found to be linear (Fig. 3b), a finding also identified in previous mesocosm experiments (Archer *et al.*, 2013; Webb *et al.*, 2015). Furthermore, increases in DMS concentrations under high fCO_2 were delayed by three days relative to the ambient and medium fCO_2 treatments, a situation which has been observed in a previous mesocosm experiment. This was attributed to small-scale shifts in community composition and succession which could not be identified with only a once-daily measurement regime (Vogt *et al.*, 2008). DMS measured in all mesocosms fell within the range 2.7 to 6.8 nmol L^{-1} across the course of the experiment. During Phase I, no difference was identified in DMS concentrations

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between fCO_2 treatments with the mean of all mesocosms 3.1 (± 0.2) nmol L^{-1}. Concentrations in all mesocosms gradually declined from *t*21 until the end of DMS measurements on *t*31. DMS concentrations measured in the mesocosms and Baltic Sea were comparable to those measured in temperate coastal conditions in the North Sea (Turner *et al.*, 1988), the Mauritanian upwelling (Franklin *et al.*, 2009; Zindler *et al.*, 2012) and South Pacific (Lee *et al.*, 2010).

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

3.2.2 DMS and Community Interactions

Throughout Phase I, DMS showed no correlation with any measured variables of biological activity or cell abundance, and was unaffected by elevated fCO_2, indicating DMS net production was not directly related to the perturbation of the system and associated cellular stress (Sunda *et al.*, 2002). During Phase II, DMS was negatively correlated with Chl-*a* in the ambient and medium fCO_2 mesocosms (ρ=-0.60, p<0.01). During Phase II, a significant correlation was seen between DMS and single-celled cyanobacteria identified as *Synechococcus* (ρ=0.53, p<0.01; Crawfurd *et al.* 2016 and supplementary table S1) and picoeukaryotes III (ρ=0.75, p<0.01). The peak in DMS concentrations is unlikely to be a delayed response to the increased Chl-*a* on *t*16.

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In previous mesocosm experiments (Archer *et al.*, 2013; Hopkins *et al.*, 2010; Webb *et al.*, 2015), DMS has shown poor correlations with many of the indicators of primary production and phytoplankton abundance, as well as showing the same trend of decreased concentrations in high fCO_2 mesocosms compared to ambient. DMS production is often uncoupled from measurements of primary production in open waters (Lana *et al.*, 2012), and also often from production of its precursor DMSP (Archer *et al.*, 2009).. DMS and DMSP are important sources of sulphur and carbon in the microbial food web for both bacteria and algae (Simó *et al.*, 2002, 2009), and since microbial turnover of DMSP and DMS play a significant role in net DMS production, it is unsurprising that DMS concentrations have shown poor correlation with DMSP-producing phytoplankton groups in past experiments and open waters.

DMS concentrations have been reported lower under conditions of elevated fCO_2 compared to ambient controls, in both mesocosm experiments (Table 4) and phytoplankton monocultures (Arnold *et al.*, 2013; Avgoustidi *et al.*, 2012). However, these experiments limit our ability to generalise the response of algal production of DMS and DMSP in all situations due to the characteristic community dynamics of each experiment in specific geographical areas and temporal periods. Previous experiments in the temperate Raunefjord of Bergen, Norway, showed lower abundance of DMSP-producing algal species, and subsequently DMSP-dependent DMS concentrations (Avgoustidi *et al.*, 2012; Hopkins *et al.*, 2010; Vogt *et al.*, 2008; Webb *et al.*, 2015). In contrast mesocosm experiments in the Arctic and Korea have shown increased abundance of DMSP producers (Archer *et al.*, 2013; Kim *et al.*, 2010) but lower DMS concentrations, while incubation experiments by Hopkins and Archer (2014) showed lower DMSP production but higher DMS concentrations at high fCO_2. However, in all previous experiments with DMSP as the primary precursor of DMS, elevated fCO_2 had a less marked effect on measured DMSP concentrations than on measured DMS concentrations. Hopkins *et al.* (2010) suggested that 'the perturbation of the system has a greater effect on the processes that control the conversion of DMSP to DMS rather than the initial production of DMSP itself'. This is relevant even for the current experiment, where DMSP was not identified, since processes controlling DMS concentrations were likely more affected by the change in fCO_2 than the production of precursors.

Previous mesocosm experiments have suggested significant links between increased bacterial production through greater availability of organic substrates at high fCO_2 (Engel *et al.*, 2013; Piontek *et al.*, 2013). Further, Endres *et al.* (2014) identified significant enhanced enzymatic hydrolysis of organic matter with increasing fCO_2, with higher bacterial abundance. Higher bacterial abundance will likely result in greater bacterial demand for sulphur, and therefore greater consumption of DMS and conversion to DMSO. This was suggested as a significant sink for DMS in a previous experiment

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(Webb *et al.*, 2015), but during the present experiment, both bacterial abundance and bacterial production were lower at high fCO_2 (Hornick *et al.*, 2015). However, as it has been proposed that only specialist bacterial groups are DMS consumers (Vila-Costa *et al.*, 2006b), and there is no determination of the DMS consumption characteristics of the bacterial community in the Baltic Sea, this is still a potential stimulated DMS loss pathway at high fCO_2. *Synechococcus* has been identified as a DMS consumer in the open ocean, but abundance of this group was negatively correlated with fCO_2, implying that DMS consumption by this group would have been lower as fCO_2 increased.

3.3 Iodocarbons in the mesocosms and relationships with community composition

Elevated fCO_2 did not affect the concentration of iodocarbons in the mesocosms significantly at any time during the experiment, which is in agreement with the findings of Hopkins *et al.* (2013) in the Arctic, but in contrast to Hopkins *et al*. (2010) and Webb (2015), where iodocarbons were measured significantly lower under elevated fCO_2 (Table 4). Concentrations of all iodocarbons measured in the mesocosms and the Baltic Sea fall within the range of those measured previously in the region (Table 5). Mesocosm concentrations of CH_3I (Fig. 4a) and C_2H_5I (Fig. 4b) showed concentration ranges of 2.91 to 6.25 and 0.23 to 0.76 pmol L^{-1} respectively. CH_3I showed a slight increase in all mesocosms during Phase I, peaking on *t*16 which corresponded with higher Chl-*a* concentrations, and correlated throughout the entire experiment with picoeukaryote groups II (ρ=0.59, p<0.01) and III (ρ=0.23, p<0.01; Crawfurd *et al.* this issue) and nanoeukaryotes I (ρ=0.37, p<0.01). Significant differences identified between mesocosms for CH_3I were unrelated to elevated fCO_2 (F=3.1, p<0.05), but concentrations were on average 15% higher in Phase II than Phase I. C_2H_5I decreased slightly during Phases I and II, although concentrations of this halocarbon were close to its detection limit (0.2 pmol L^{-1}), remaining below 1 pmol L^{-1} at all times. As this compound showed no significant effect of elevated fCO_2, and was identified by Orlikowska and Schulz-Bull (2009) as having extremely low concentrations in the Baltic Sea (Table 5), it will not be discussed further.

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

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

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

Measured in the range 57.2 – 202.2 pmol L^{-1} in the mesocosms, CH_2I_2 (Fig. 4c) showed the clearest increase in concentration during Phase II, when it peaked on *t*21 in all mesocosms, with a maximum of 202.2 pmol L^{-1} in M5 (348 µatm). During Phase II, concentrations of CH_2I_2 were 57% higher than Phase I, and were therefore negatively correlated with Chl-*a*. The peak on *t*21 corresponds with the peak identified in DMS on *t*21, and concentrations through all three phases correlate with picoeukaryotes II (ρ=0.62, p<0.01) and III (ρ=0.47, p<0.01) and nanoeukaryotes I (ρ=0.88, p<0.01; Crawfurd *et al.*, 2015). CH_2ClI (Fig. 4d) showed no peaks during either Phase I or Phase II, remaining within the range 3.81 to 8.03 pmol L^{-1}, and again correlated with picoeukaryotes groups II (ρ=0.34, p<0.01) and III (ρ=0.38, p<0.01). These results may suggest that these groups possessed halo-peroxidase enzymes able to oxidise I^-, most likely as an anti-oxidant mechanism within the cell to remove H_2O_2 (Butler and Carter-Franklin, 2004; Pedersen *et al.*, 1996; Theiler *et al.*, 1978). However, given the lack of response of these compounds to elevated fCO_2 (F=1.7, p<0.01), it is unlikely that production was increased in relation to elevated fCO_2. Production of all iodocarbons increased during Phase II when total Chl-*a* decreased, particularly after the walls of the mesocosms were cleaned for the first time, releasing significant volumes of organic aggregates into the water column. Aggregates have been suggested as a source of CH_3I and C_2H_5I (Hughes *et al.*, 2008), likely through the alkylation of inorganic iodide (Urhahn and Ballschmiter, 1998) or through the breakdown of organic matter by microbial activity to supply the precursors required for iodocarbon production (Smith *et al.*, 1992). Hughes *et al.* (2008) did not identify this route as a pathway for CH_2I_2 or CH_2ClI production, but

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

3.4 Bromocarbons in the mesocosms and the relationships with community composition

No effect of elevated fCO_2 was identified for any of the three bromocarbons, which compared with the findings from previous mesocosms where bromocarbons were studied (Hopkins *et al.*, 2010, 2013; Webb, 2015; Table 4). Measured concentrations were comparable to those of Orlikowska and Schulz-Bull (2009) and Karlsson *et al.* (2008) measured in the Southern part of the Baltic Sea (Table 3). The concentrations of $CHBr_3$, CH_2Br_2 and $CHBr_2Cl$ showed no major peaks of production in the mesocosms. $CHBr_3$ (Fig. 5a) decreased rapidly in all mesocosms over Phase 0 from a maximum measured concentration of 147.5 pmol L^{-1} in M1 (mean of 138.3 pmol L^{-1} in all mesocosms) to a mean of 85.7 (±8.2 s.d.) pmol L^{-1} in all mesocosms for the period *t*0 to *t*31 (Phases I and II). The steady-state $CHBr_3$ concentrations indicated a production source, however there was no clear correlation with any measured algal groups. CH_2Br_2 concentrations (Fig. 5b) decreased steadily in all mesocosms from *t*-3 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 1.7 to 4.7 pmol L^{-1} (Fig. 5c). Of the three bromocarbons, only CH_2Br_2 showed correlation with total Chl-*a* (ρ=0.52, p<0.01), and with cryptophyte (ρ=0.86, p<0.01) and dinoflagellate (ρ=0.65, p<0.01) derived Chl-*a*. Concentrations of CH_2BrI were below detection limit for the entire experiment.

CH_2Br_2 showed positive correlation with Chl-*a* (ρ=0.52, p<0.01), nanoeukaryotes II (ρ=0.34, p<0.01) and cryptophytes (ρ=0.86, p<0.01; see supplementary material), whereas $CHBr_3$ and $CHBr_2Cl$ showed very weak or no correlation with any indicators of primary production. Schall *et al.* (1997) have proposed that $CHBr_2Cl$ is produced in seawater by the nucleophilic substitution of bromide by chloride in $CHBr_3$, which given the steady-state concentrations of $CHBr_3$ would explain the similar distribution of CHBr2Cl concentrations. Production of all three bromocarbons was identified from large-size cyanobacteria such as *Aphanizomenon flos-aquae* by Karlsson *et al.* (2008), and in addition, significant correlations were found in the Arabian Sea between the abundance of the cyanobacterium *Trichodesmium* and several bromocarbons (Roy *et al.*, 2011), and the low abundance of such bacteria in the mesocosms would explain the low variation in bromocarbon concentrations through the experiment.

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

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504 growth rates and total Chl-*a*. Hughes *et al.* (2013) identified bacterial inhibition of $CHBr_3$ 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 $CHBr_3$ concentrations in the mesocosms. In contrast,
507 significant bacterial degradation of CH_2Br_2 in the same experiments could explain the steady decrease
508 in CH_2Br_2 concentrations seen in the mesocosms. Bacterial oxidation was also identified by Goodwin
509 *et al.* (1998) as a significant sink for CH_2Br_2. 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 CH_2Br_2 to $CHBr_3$ was also
512 unaffected by increased fCO_2, 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 $CHBr_3$ than CH_2Br_2 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*
521 *al.*, 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 fCO_2 and the effect on biogenic trace gases

525 #### 3.5.1 Physical variation and community dynamics

526 Baltic Sea deep waters have high fCO_2 and subsequently lower pH (Schneider *et al.*, 2002), and the
527 influx to the surface waters surrounding the mesocosms resulted in fCO_2 increasing to 725 µatm on
528 *t*31, close to the average fCO_2 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 fCO_2 and the
530 associated pH, as well as having communities associated with the elevated fCO_2 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

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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 µg L^{-1}. In addition there was potential introduction of different
537 algal groups to the surface, but chlorophytes and crytophytes 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 (Crawfurd *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 (Crawfurd *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 ± 2.6 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* (ρ=0.84, p<0.01), with the ratio of DMS: Chl-*a*
553 at 1.6 (± 0.3) nmol μg^{-1}. Other strong correlations were seen with euglenophytes (ρ=0.89, p<0.01),
554 dinoflagellates (ρ=0.61, p<0.05) and nanoeukaryotes II (ρ=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

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

3.5.3 Halocarbon concentrations in the Baltic Sea

Outside the mesocosms in the Baltic Sea, CH_3I was measured at a maximum concentration of 8.65 pmol L^{-1}, during Phase II, and showed limited effect of the upwelling event. Both CH_2I_2 and CH_2ClI showed higher concentrations in the Baltic Sea samples than the mesocosms (CH_2I_2: 373.9 pmol L^{-1} and CH_2ClI: 18.1 pmol L^{-1}), and were correlated with the euglenophytes (CH_2I_2; ρ=0.63, p<0.05 and CH_2ClI; ρ=0.68, p<0.01) and nanoeukaryotes II (CH_2I_2; ρ=0.53, p<0.01 and CH_2ClI; ρ=0.58, p<0.01), but no correlation with Chl-*a*. Both polyiodinated compounds showed correlation with picoeukaryote groups II and III, indicating that production was not limited to a single source. These concentrations of CH_2I_2 and CH_2ClI compared well to those measured over a macroalgal bed in the higher saline waters of the Kattegat by Klick and Abrahamsson (1992), suggesting that macroalgae were a significant iodocarbon source in the Baltic Sea.

As with the iodocarbons, the Baltic Sea showed significantly higher concentrations of $CHBr_3$ (F=28.1, p<0.01), CH_2Br_2 (F=208.8, p<0.01) and $CHBr_2Cl$ (F=23.5, p<0.01) than the mesocosms, with maximum concentrations 191.6 pmol L^{-1}, 10.0 pmol L^{-1} and 5.0 pmol L^{-1} respectively. In the Baltic Sea, only $CHBr_3$ was correlated with Chl-*a* (ρ=0.65, p<0.05), cyanobacteria (ρ=0.61, p<0.01; Paul *et al.*, 2015) and nanoeukaryotes II (ρ=0.56, p<0.01; Crawfurd *et al.*, 2015), with the other two bromocarbons showing little to no correlations with any parameter of community activity. Production of bromocarbons from macroalgal sources (Laturnus *et al.*, 2000; Leedham *et al.*, 2013; Manley *et al.*, 1992) was likely a significant contributor to the concentrations detected in the Baltic Sea; over the macroalgal beds in the Kattegat, Klick (1992) measured concentrations an order of magnitude higher than seen in this experiment for CH_2Br_2 and $CHBr_2Cl$.

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

Mesocosm experiments are a highly valuable tool in assessing the potential impacts of elevated CO_2 on complex marine communities, however they are limited in that the rapid change in fCO_2 experienced by the community may not be representative of changes in the future ocean (Passow and Riebesell, 2005). This inherent problem with mesocosm experiments can be overcome through using naturally low pH/ high CO_2 areas such as upwelling regions or vent sites (Hall-Spencer *et al.*, 2008), which can give an insight into populations already living and adapted to high CO_2 regimes by exposure

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599 over timescales measured in years. This mesocosm experiment was performed at such a location with a
600 relatively low fCO_2 excursion compared to some sites (800 µatm compared to >2000 µatm; 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 fCO_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 fCO_2 treatments. In contrast to the halocarbons,
610 concentrations of DMS were significantly lower in the highest fCO_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 fCO_2 experiments. The Baltic Sea trace gas samples give a good record of
614 trace gas production during the injection of high fCO_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 fCO_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 fCO_2 and pH_T (total scale) during phases 0, 1 and 2 of the mesocosm experiment.

		Whole Experiment / *t*-3 to *t*31		**Phase 0 / *t*-3 to *t*0**		**Phase I / *t*1 –*t*16**		**Phase II / *t*16 – *t*31**	
Mesocosm[a]	**Target fCO_2 / µatm**	**Mean fCO_2 / µatm**	**Mean pH / pH_T**	**Mean fCO_2 / µatm**	**Mean pH / pH_T**	**Mean fCO_2 / µatm**	**Mean pH / pH_T**	**Mean fCO_2 / µatm**	**Mean pH / 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 fCO_2

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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_3I	0.11 – 11.2	4.62
CH_2I_2	5.61 – 561.0	4.98
C_2H_5I	0.10 – 4.91	5.61
CH_2ClI	1.98 – 99.0	3.64
$CHBr_3$	8.61 – 816.0	4.03
CH_2Br_2	0.21 – 20.9	5.30
$CHBr_2Cl$	0.07 – 7.00	7.20

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

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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 (Crawfurd *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-*a***	**Range Integrated 10 m**	**Range Integrated 17 m**	**% Contribution to Chl-*a***
Chl-*a*	0.9 – 2.9	0.9 – 2.6	100	1.3 – 6.5	1.12 – 5.5	100
Phytoplankton Taxonomy / Equivalent Chlorophyll µg 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	

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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 fCO_2 treatment.

	Range fCO_2 / µatm		DMS / nmol L^{-1}	CH_3I / pmol L^{-1}	CH_2I_2	CH_2ClI	$CHBr_3$	CH_2Br_2	CH_2Br_2Cl
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 *et al.*, 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 *et al.*, 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 *et al.*, 2013; Hopkins *et al.*, 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 *et al.*, 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_3I	CH_2I_2	C_2H_5I	CH_3ClI	$CHBr_3$	CH_2Br_2	CH_2Br_2Cl
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-Bull5(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 *et al.* (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 *et al.* (1990)	ND-3.2							

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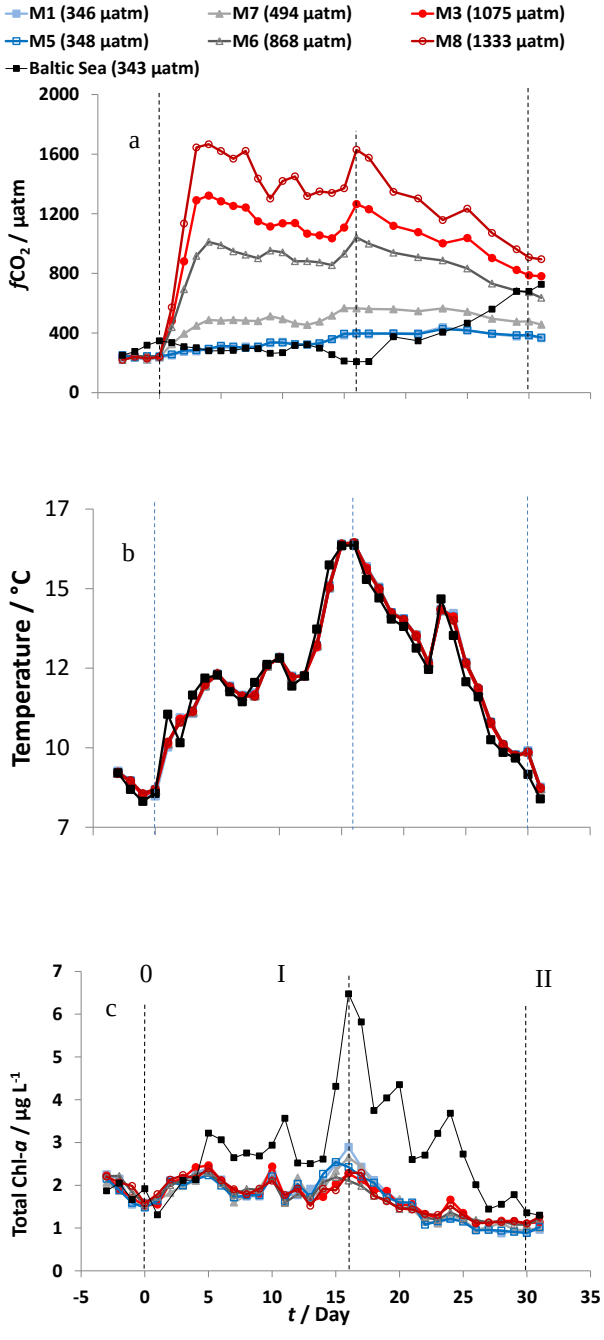

Figure 1. Daily measurements of (a) fCO_2, (b) mean temperature and (c) total Chlorophyll-a in the mesocosms and surrounding Baltic Sea waters. Dashed lines represent the three Phases of the experiment, based on the Chl-*a* data.

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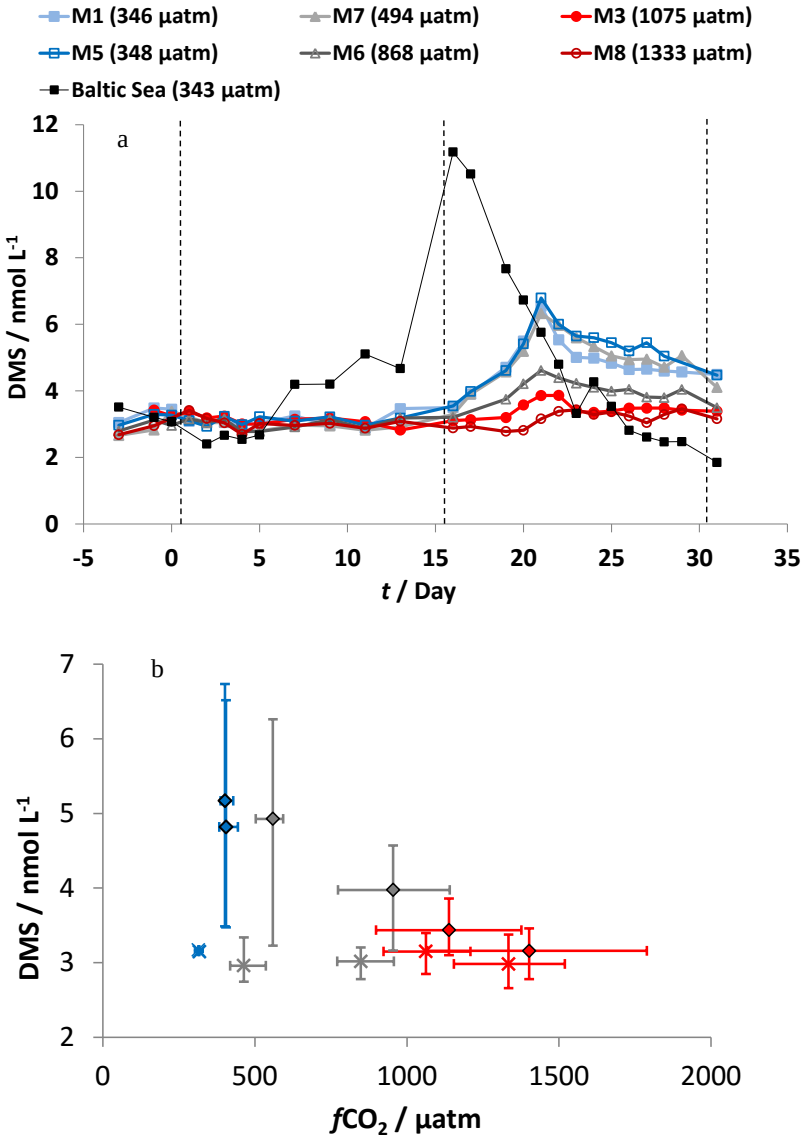

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962 Figure 3. (a) Integrated DMS concentrations measured daily in the mesocosms and Baltic Sea from the
963 surface 10 m and (b) mean DMS concentrations from each mesocosm during Phase I (crosses) and
964 Phase II (diamonds), for ambient (blue), medium (grey) and high fCO_2 (red), with error bars showing
965 the range of both the DMS and fCO_2. Dashed lines show the Phases of the experiment as given in Fig.
966 2, fCO_2 shown in the legend are mean fCO_2 across the duration of the experiment.

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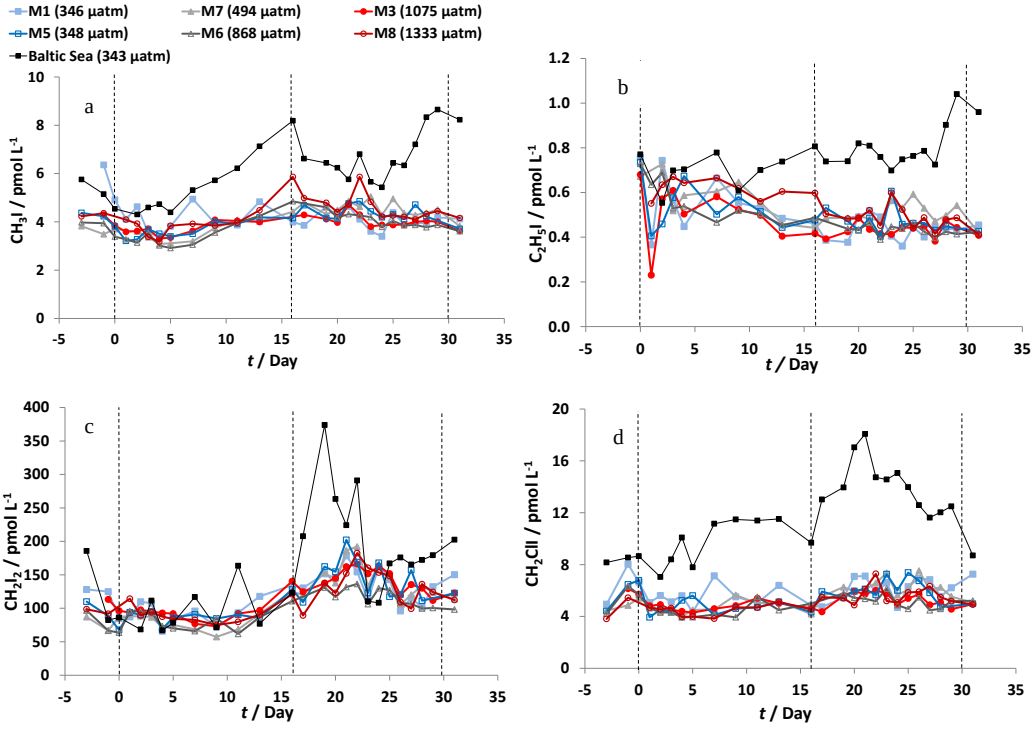

Figure 4. Concentrations (pmol L^{-1}) of (a) CH_3I, (b) C_2H_5I, (c) CH_2I_2 and (d) CH_2ClI. Dashed lines indicate the Phases of the experiment, as given in Fig. 2. fCO_2 shown in the legend are mean fCO_2 across the duration of the experiment.

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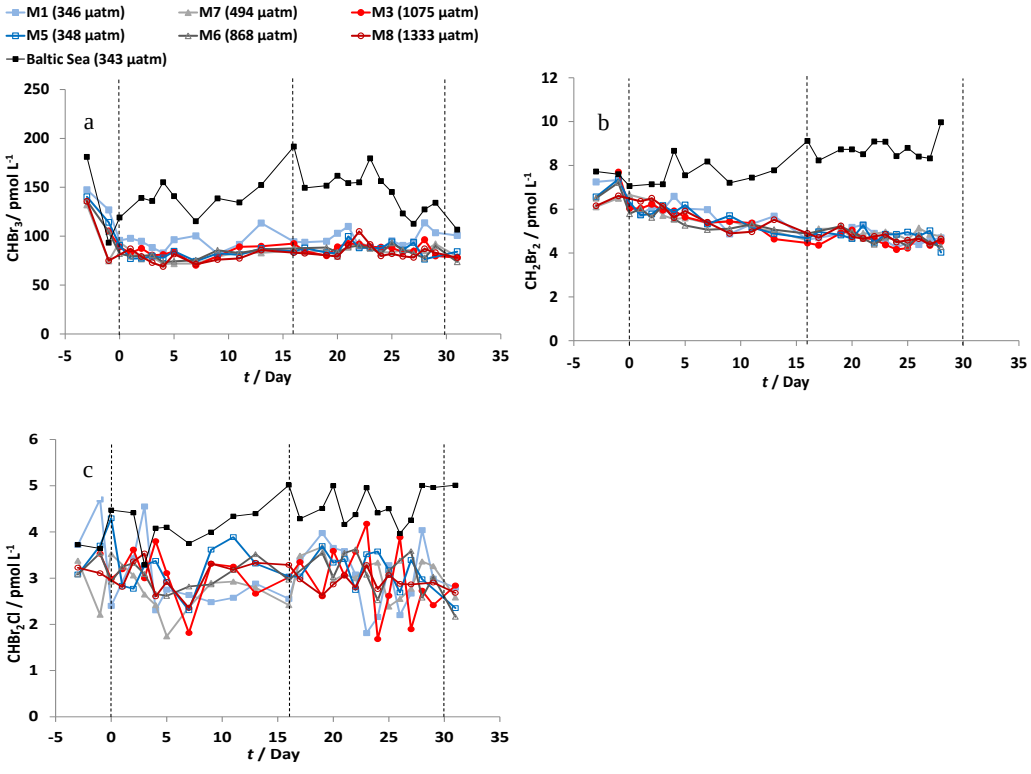

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975 Figure 5. Concentrations (pmol L^{-1}) of (a) $CHBr_3$, (b) CH_2Br_2 and (c) $CHBr_2Cl$. Dashed lines indicate
976 the phases of the experiment as defined in Fig. 2, fCO_2 shown in the legend are mean fCO_2 across the
977 duration of the experiment.

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