Thank you very much to the reviewers and editors for their time on this manuscript. The authors have reviewed the changes suggested in the technical corrections, and have highlighted the changes here. A tracked changes version of the manuscript is included.

Reviewer 1

Line numbers corresponding to the document still including the changes.
Line 93: …annual flux….

Changed

Line 396: 't' needs to be in italics.

Changed

Line 397: …as well as a response to the mesocosm wall cleaning which took place on t16…this part of the sentence does not fit with the beginning of the sentence. Needs to be reworded.

The section about wall cleaning has been put into a second sentence. Now reads 'These higher DMS concentrations were likely connected to a peak in dissolved organic carbon (DOC) on *t*15, as well as increasing bacterial abundance during Phase II (Hornick *et al.*, 2016). It is also likely that DMS concentrations increased as a response to the mesocosm wall cleaning which took place on *t*16.'

Line 441: …vary…Typo

changed

Line 544: …coastal environment. However, …

changed

Line 599: …t17 or t17 as before and just one line below?

CO2 did increase between t16 and t17, but the largest increase was seen after t17. However, as the first increase was seen after t16, and for ease of discussion, this has been changed to t16, as it corresponds with the change in DMS.

Line 651: …hard… I don't think that 'hard' is the appropriate word to use here.

Suggestion: …therefore these upwelling events cannot be considered as natural high CO2 analogues.
But the beginning of this sentence needs to be reworded also.

The section has been reworded to ‘The upwelling event occurring mid-way through our experiment allowed comparison of the mesocosm findings with a natural analogue of the system, as well as showing the extent to which the system perturbation can occur (up to 800 µatm). This event was a fortuitous occurrence during this mesocosm experiment, but as the scale and timing of these upwelling events is difficult to determine, and therefore these upwelling events are extremely challenging to study as natural high CO_2 analogues. ‘

Reviewer 2

The data in this manuscript are important information.
The results show a lack of response of gas concentrations to the experimental design and no linkage to the external conditions due to the outside undergoing its own “experiment”, i.e., upwelling. No rates were measured, concentrations (mostly) remained the same, and the need to have rates of production, consumption, (photo/chem)-degradation or even “net” rates to include in prognostic and predictive models has been emphasized.

I recommend publishing pending changes. For me personally it would be important to have a clearer number agreement for the mean CO2 values.

Could the reviewer clarify what is meant by this, as I do not understand?

Also I think the firm and clearly stated replies to the editor comments under Point 1 and 2 would strengthen the discussion, as they nicely address the criticism that could still emerge.

The section on DMSP has been edited to include the following (TC version)

L 235 This method had been used during a previous mesocosm experiment (Bergen, Norway) and the results correlated well with those measured immediately on a similar GC-FPD system (Webb *et al.* 2015).

L 255 The DMSP acidification method is used worldwide as a simple and effective method of DMSP storage. The findings here, alongside those of del Valle *et al.* (2011) question the applicability of this method in other marine environments, and suggests significant testing prior to reliance on this method as a sole means of DMSP storage.

The section on the Baltic Sea has been amended to include comments from Section 2 of the replies to editors. Specifically (TC version):

L 578 The changes in biological parameters and trace gas concentrations are therefore discussed here separately from the concentrations measured in the mesocosms.

L 581 Given the separation of the waters within the mesocosms, and the movement of water masses within the Baltic Sea, it is expected that phytoplankton population structure could be significantly different inside the mesocosms compared to the external waters.

It could be worth to have a (short, taken from the comments) discussion section on methodological caveats/challenges and reasoning for the way the data is presented.

In terms of this, I believe this comment has been covered in the individual sections mentioned, and to include this recommended section would cause repetition within the manuscript. It is fair to say that the layout of the sections has caused a lot of discussion during the preparation of this manuscript.

L 607 In addition, the community demands of sulphur are likely to be very different in the Baltic Sea compared to the mesocosms, due to differences in community composition and sulphur availability, and therefore direct comparisons with mesocosm concentrations are inappropriate.

L634 Macroalgal production in the Baltic Sea is likely the predominant iodocarbon source, compared to the mesocosms where macroalgae are excluded.

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 - 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 ocean has 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 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~~ provide the basis for 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 (Simó et al., 2009; Vila-Costa et al., 2006a). 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

annual 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 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. Following the 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 post-bloom 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.

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 and large zooplankton. 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 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 (<4%, no further data shown).

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 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 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~~ Baltic Sea samples for later DMSP analysis. This method had been used during a previous mesocosm experiment (Bergen, Norway) and the results correlated well with those measured immediately on a similar GC-FPD system (Webb *et al.* 2015). ~~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 dissolved $DMSP_{~~D~~}$ 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 $DMSP_T$ 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. The findings of this mesocosm study ~~is~~ suggest~~s~~ 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 DMSP acidification method is used worldwide as a simple and effective method of DMSP storage. The findings here, alongside those of del Valle *et al.* (2011) ~~The~~ question ~~of its~~the applicability of this method in other marine

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~~waters~~ environments, and suggests significant testing prior to reliance on this method as a sole means of DMSP storage. ~~also needs further investigation.~~

2.3 Measurement of carbonate chemistry and community dynamics

Water samples were collected from the 10~~b~~ m and 17 m IWS on a daily basis and analysed for carbonate chemistry, fluorometric Chl-*a*, phytoplankton pigments (17 m 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 determination for pH. For Chl-*a* analysis and pigment determination, 500 mL sub-samples were filtered through a GF/F and stored frozen (-20 °C for two hours for Chl-*a* and -80 °C for up to 6 months for pigments), before homogenisation in 90 % acetone with glass beads. After centrifuging (10 minutes at 800 x g at 4 °C) the Chl-*a* concentrations were determined using a Turner AU-10 fluorometer by the methods of Welschmeyer (1994), and the phytoplankton pigment concentrations by reverse phase high performance liquid chromatography (WATERS HPLC with a Varian Microsorb-MV 100-3 C8 column) as described by Barlow *et al.* (1997). Phytoplankton community composition was determined by the use of the CHEMTAX algorithm to convert the concentrations of marker pigments to Chl-*a* equivalents (Mackey *et al.*, 1996; Schulz *et al.*, 2013). Microbes were enumerated using a Becton Dickinson FACSCalibur flow cytometer (FCM) equipped with a 488 nm argon laser (Crawfurd et al., 2016) and counts of phytoplankton cells >20 µm were made on concentrated (50 mL) sample water, fixed with acidic Lugol's iodine solution with an inverted microscope. Filamentous cyanobacteria were counted in 50 µm length units.

2.4 Statistical Analysis

All statistical analysis was performed using Minitab V16. In analysis of the measurements between mesocosms, one-way ANOVA was used with Tukey's post-hoc analysis test to determine the effect of different fCO_2 on concentrations measured in the mesocosms and the Baltic Sea (H_0 assumes no significant difference in the mean concentrations of trace gases measured through the duration of the experiment). Spearman's Rank Correlation Coefficients were calculated to compare the relationships between trace gas concentrations, fCO_2, and a number of biological parameters, and the resulting ρ-values for each correlation are given in Supplementary table S1 for the mesocosms and S2 for the Baltic Sea data.

3 Results and Discussion

3.1 Biogeochemical changes within the mesocosms

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

- Phase 0 (days *t*-5 to *t*0) – pre-CO_2 addition
- Phase I (days *t*1 to *t*16) – 'productive phase'
- Phase II (days *t*17 to *t*30) – temperature induced autotrophic decline.

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 (data not shown but available in Paul *et al.* 2015). 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 (and biogenic gas production), explaining the lower Chl-*a* in Phase II.

3.1.2 Community Dynamics

Mixing of the mesocosms and redistribution of the nutrients throughout the water column after closure (prior to *t*-3) did not trigger a notable increase in total Chl-*a* in Phase 0 as was identified in previous mesocosm experiments~~; 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, as no difference was identified between enriched mesocosms and controls. 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 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.*, 2016~~)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., 2016; 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. 2~~3~~a). 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. ~~3~~2b), 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 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 t~~The majority of DMS production is presumed to be from DMSP. However, 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, r~~Recent studies have also identified this pathway of DMS production from *Pseudomonas deceptionensis* in an aerobic environment (Carrión *et al*., 2015), where *P. deceptionensis* was unable to synthesise 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~~s~~

between DMS and the cyanobacterial equivalent Chl-*a* (ρ=0.42, p<0.01; Supplementary Figure S1g) and DMS and single-celled cyanobacteria (ρ=0.58, p<0.01; Supplementary Figure S2a) ~~indicate~~ suggest 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 measured DMS ~~net production concentrations was~~ were not directly related to the perturbation of the system and associated cellular stress (Sunda *et al.*, 2002). Of the studied phytoplankton groupings, neither the cryptophyes or chlorophyes as the largest contributors of Chl-*a* were identified as significant producers of DMSP. 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 predominantly 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 on *t*21 is unlikely to be a delayed response to the increased Chl-*a* on *t*16 due to the time lag of 7 days. These higher DMS concentrations were likely connected to a peak in dissolved organic carbon (DOC) on *t*15, as well as increasing bacterial abundance during Phase II (Hornick *et al.*, 2016). It is also likely that DMS concentrations increased as a response to the mesocosm wall cleaning which took place on *t*16. The variation in inorganic nutrient concentrations between mesocosms at the start of the experiment did not have an effect on DMS concentrations during Phase I, and by the start of Phase II the variation between mesocosms had decreased.

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

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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, the varying response of the community within each experiment ~~se 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 (Webb *et al.*, 2015), but during the present experiment, both bacterial abundance and bacterial production were lower at high fCO_2 (Hornick *et al.*, 2016). 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, it is not known if this loss pathway is stimulated at ~~this is still a potential stimulated DMS loss pathway at~~ high fCO_2. As microbial DMS yields can vary between 5-40% depending on the sulphur and carbon demand (Kiene and Linn, 2000), a change in the bacterial sulphur requirements could change DMS turnover despite lower abundance. ~~*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. 3~~4~~a) and C_2H_5I (Fig. 3~~4~~b) 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~~2016) 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.*, 201~~5~~6). 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 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. 34c) 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. 34d) 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 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. 4~~5~~a) 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~~4b) 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~~4c). 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 algal biomass~~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 $CHBr_2Cl$ 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

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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 growth rates and low net increase in total Chl-*a*. Hughes *et al.* (2013) identified bacterial inhibition of $CHBr_3$ production in laboratory cultures of *Thalassiosira* diatoms, but that it was not subject to bacterial breakdown; which could explain the relative steady state of $CHBr_3$ concentrations in the mesocosms. In contrast, significant bacterial degradation of CH_2Br_2 in the same experiments could explain the steady decrease in CH_2Br_2 concentrations seen in the mesocosms. Bacterial oxidation was also identified by Goodwin *et al.* (1998) as a significant sink for CH_2Br_2. As discussed for the iodocarbons, photolysis was unlikely due to the UV absorption of the mesocosm film, and limited UV exposure of the surface waters within the mesocosm due to the mesocosm cover. The ratio of CH_2Br_2 to $CHBr_3$ was also unaffected by increased fCO_2, staying within the range 0.04 to 0.08. This range in ratios is consistent with that calculated by Hughes *et al.* (2009) in the surface waters of an Antarctic depth profile, and attributed to higher sea-air flux of $CHBr_3$ than CH_2Br_2 due to a greater concentrations gradient, despite the similar transfer velocities of the two compounds (Quack *et al.*, 2007). Using cluster analysis in a time-series in the Baltic Sea, Orlikowska and Schulz-Bull (2009) identified both these compounds as originating from different sources and different pathways of production.

Macroalgal production would not have influenced the mesocosm concentrations after the bags were sealed due to the isolation from the coastal environment~~,~~. H~~h~~owever macroalgal production into the water column prior to mesocosm installation ~~the higher bromocarbon concentrations identified in the mesocosms during Phase 0 may have originated from macroalgal sources~~ (Klick, 1992; Leedham *et al*., 2013; Moore and Tokarczyk, 1993) ~~prior to mesocosm closure,~~could account for the high initial concentrations with concentrations decreasing through the duration of the experiment via turnover and transfer to the atmosphere.

3.5 Natural variations in Baltic Sea fCO_2 and the effect on biogenic trace gases

3.5.1 Physical variation and community dynamics

Baltic Sea deep waters have high fCO_2 and subsequently lower pH (Schneider *et al.*, 2002), and the influx to the surface waters surrounding the mesocosms resulted in fCO_2 increasing to 725 µatm on *t*31, close to the average fCO_2 of the third highest mesocosm (M6: 868 µatm). The input of upwelled water into the region mid-way through the experiment significantly altered the biogeochemical properties of the waters surrounding the mesocosms, and as a result it is inappropriate to directly compare the community structure and trace gas production of the Baltic Sea and the mesocosms. These conditions imply that pelagic communities in the Baltic Sea are regularly exposed to rapid changes in fCO_2 and the associated pH, as well as having communities associated with the elevated fCO_2 conditions. The changes in biological parameters and trace gas concentrations are therefore discussed here separately from the concentrations measured in the mesocosms.

Given the separation of the waters within the mesocosms, and the movement of water masses within the Baltic Sea, it is expected that phytoplankton population structure could be significantly different inside the mesocosms compared to the external waters. Chl-*a* followed the pattern of the mesocosms until *t*4, after which concentrations were significantly higher than any mesocosm, peaking at 6.48 µg L^{-1} on *t*16, corresponding to the maximum Chl-*a* peak in the mesocosms and the maximum peak of temperature. As upwelled water intruded into the surface waters, the surface Chl-*a* was diluted with low Chl-*a* deep water: Chl-*a* in the surface 10m decreased from around *t*16 at the start of the upwelling until *t*31 when concentrations were once again equivalent to those found in the mesocosms at 1.30 µg L^{-1}. In addition, there was potential introduction of different algal groups to the surface, but chlorophytes and cryptophytes were the major contributors to the Chl-*a* in the Baltic Sea, as in the mesocosms. Cyanobacteria contributed less than 2% of the total Chl-*a* in the Baltic Sea (Crawfurd et al., 2016; Paul et al., 2015).

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

3.5.2 DMS in the Baltic Sea

The Baltic Sea samples gave a mean DMS concentration of 4.6 ± 2.6 nmol L^{-1}~~.~~but peaked at 11.2 nmol L^{-1} on *t*16, and were within the range of previous measurements for the region (Table 5). Strong correlations were seen between DMS and Chl-*a* (ρ=0.84, p<0.01), with the ratio of DMS: Chl-*a* at 1.6 (± 0.3) nmol μg^{-1}. Other strong correlations were seen with euglenophytes (ρ=0.89, p<0.01), dinoflagellates (ρ=0.61, p<0.05) and nanoeukaryotes II (ρ=0.88, p<0.01), but no correlation was found between DMS and cyanobacterial abundance, or with picoeukaryotes III which was identified in the mesocosms, suggesting that DMS had a different origin in the Baltic Sea community than in the mesocosms. In addition, the community demands of sulphur are likely to be very different in the Baltic Sea compared to the mesocosms, due to differences in community composition and sulphur availability, and therefore direct comparisons with mesocosm concentrations are inappropriate. ~~Once again, there was no DMSP detected in the samples.~~

As CO_2 levels increased after t16 ~~during Phase II,~~ the DMS concentration measured in the Baltic Sea decreased, from the peak on *t*16 to the lowest recorded sample of the entire experiment at 1.85 nmol L^{-1} on *t*31.~~.~~ As with Chl-*a*, DMS concentrations in the surface of the Baltic Sea may have been diluted with low-DMS deep water~~, however, the inverse relationship of DMS with CO_2 shown in the mesocosms may suggest that this decrease in DMS is attributed to the increase in CO_2 levels. Bacterial abundance was similar in the Baltic Sea as in the mesocosms (Hornick *et al.*, 2015), however the injection of high CO_2 water may have stimulated bacterial consumption of DMS during the upwelling, which combined with the dilution of DMS-rich surface water could have resulted in the rapid decrease in DMS concentrations. As no discernible decrease in total bacterial abundance was identified during the upwelling, it is also 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.~~

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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 polyhalogenated~~iodinated~~ compounds showed

correlation with picoeukaryote groups II and III, indicating that production was probably 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. Macroalgal production in the Baltic Sea is likely the predominant iodocarbon source, compared to the mesocosms where macroalgae are excluded.

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* ($\rho=0.65$, $p<0.05$), cyanobacteria ($\rho=0.61$, $p<0.01$; Paul *et al.*, 2015) and nanoeukaryotes II ($\rho=0.56$, $p<0.01$; Crawfurd *et al.*, 2016~~5~~), 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 $CHBr_2Cl$. There was only a slight increase in bromocarbon concentrations as a result of the upwelling, indicating that the upwelled water had similar concentrations to the surface waters. These data from the Baltic Sea are presented as an important time-series of halocarbon measurements during the summer of 2012, which are expected to add to existing Baltic Sea trace gas datasets.

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~~ acclimated to high CO_2 regimes by exposure over timescales measured in years. This mesocosm experiment was performed at such a location with a relatively ~~low~~ high fCO_2 excursion, however still low compared to some sites (800 µatm compared to >2000 µatm; Hall-Spencer et al., 2008), and it was clear through the minimal variation in Chl-*a* between all mesocosms that the community was relatively

unaffected by elevated fCO_2, although variation could be identified in some phytoplankton groups and some shifts in community composition. The upwelling event occurring mid-way through our experiment allowed comparison of the mesocosm findings with a natural analogue of the system, as well as showing the extent to which the system perturbation can occur (up to 800 µatm). This event was a fortuitous occurrence during this mesocosm experiment, but as the scale and timing of these upwelling events is difficult to determine, ~~. However, it is very difficult to determine where and when an upwelling will occur,~~ and therefore these upwelling events are extremely challenging to study as natural high CO_2 analogues. ~~hard to utilise these events as natural high CO_2 analogues.~~

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In this paper, we described the temporal changes in concentrations of DMS and halocarbons in natural Baltic phytoplankton communities exposed to elevated fCO_2 treatments. In contrast to the halocarbons, concentrations of DMS were significantly lower in the highest fCO_2 treatments compared to the control. Despite very different physicochemical and biological characteristics of the Baltic Sea (e.g. salinity, community composition and nutrient concentrations), this is a very similar outcome to that seen in several other high fCO_2 experiments. The Baltic Sea trace gas samples give a good record of trace gas ~~production~~ cycling during the injection of high fCO_2 deep water into the surface community during upwelling events. For the concentrations of halocarbons, ~~no response~~the measured concentrations did not change during ~~was shown to~~ the upwelling event in the Baltic Sea, which may indicate that emissions of organic iodine and bromine are unlikely to change with future acidification of the Baltic Sea without significant alteration to the meteorological conditions. Further studies of these compounds are important to determine rates of production and consumption to include in prognostic and predictive models. However, net production of organic sulphur within the Baltic Sea region is likely to decrease with an acidified future ocean scenario, despite the possible acclimation of the microbial community to elevated fCO_2. This will potentially impact the flux of DMS to the atmosphere over Northern Europe, and could have significant impacts on the local climate through the reduction of atmospheric sulphur aerosols. Data from a previous mesocosm experiment has been used to estimate future global changes in DMS production, and predicted that global warming would be amplified (Six *et al.*, 2013); utilising the data from this experiment combined with those of other mesocosm, field and laboratory experiments and associated modelling provide the basis for a better understanding of the future changes in global DMS production and their climatic impacts.

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1031 Table 1. Summary of fCO_2 and pH_T (total scale) during phases 0, 1 and 2 of the mesocosm
1032 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_T**	**Mean fCO_2 (µatm)**	**Mean pH_T**	**Mean fCO_2 (µatm)**	**Mean pH_T**	**Mean fCO_2 (µatm)**	**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

1033 [a] listed in order of increasing fCO_2

1034

1035 Table 2. Calibration ranges and calculated percentage mean relative standard error for the trace
1036 gases 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

1037 * throughout the rest of this paper, these measurements are given in nmol L^{-1}.

1038

Table 3. Abundance and contributions of different phytoplankton groups to the total phytoplankton community assemblage, showing the range of measurements from total Chl-*a* (Paul *et al.*, 2015), CHEMTAX analysis of derived Chl-*a* (Paul *et al.*, 2015) and phytoplankton abundance (Crawfurd et al., 2016). Data are split into the range of all the mesocosm measurements and those from the Baltic 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	

Table 4. Concentration ranges of trace gases measured in the mesocosms compared to other open water ocean acidification experiments, showing the range of concentrations for each gas and the percentage change between the control and the highest fCO_2 treatment.

	Range fCO_2		**DMS**	**CH_3I**	**CH_2I_2**	**CH_2ClI**	**$CHBr_3$**	**CH_2Br_2**	**CH_2Br_2Cl**
	(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 *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						

Table 5. Concentration ranges of trace gases measured in the Baltic Sea compared to concentrations 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-Bull (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							

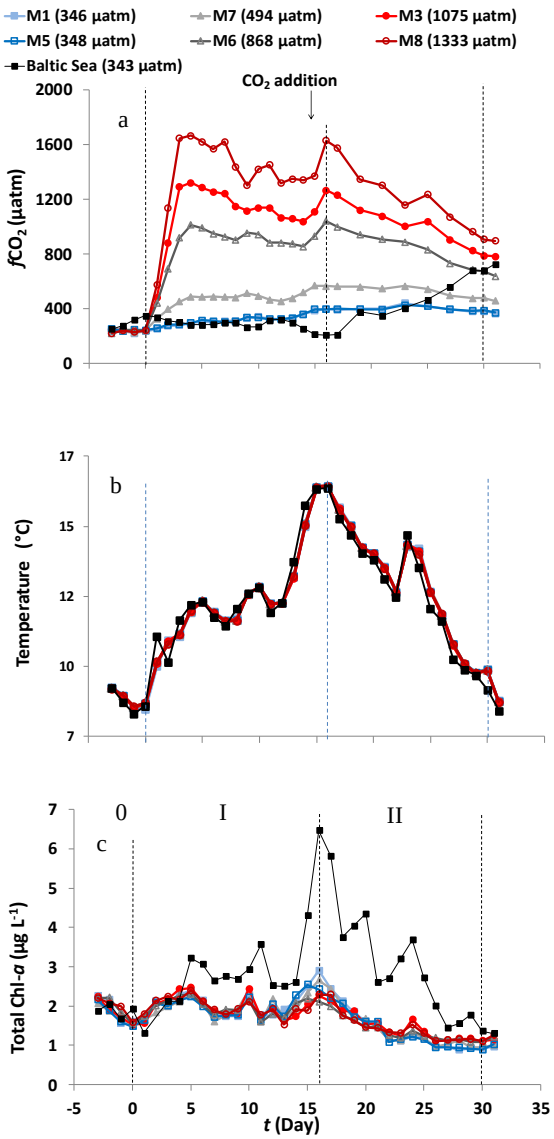

Figure 1. Daily measurements of (a) fCO_2, (b) mean temperature and (c) total Chlorophyll-*a* in the mesocosms and surrounding Baltic Sea waters. Dashed lines represent the three Phases of the experiment, based on the Chl-*a* data.

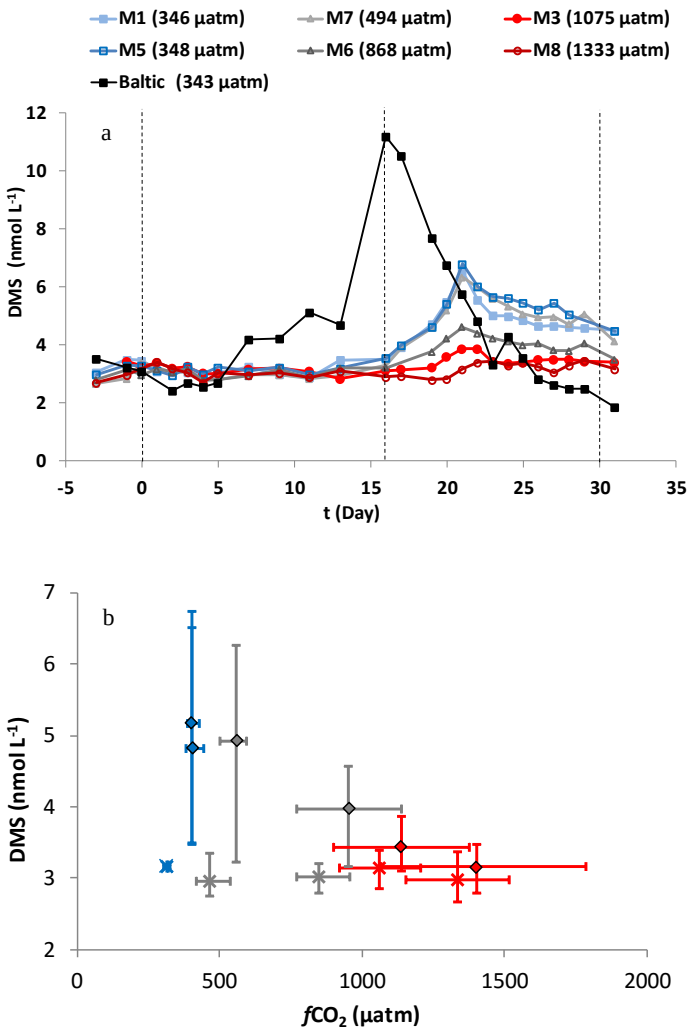

Figure ~~3~~2. (a) Mean DMS concentrations measured daily in the mesocosms and Baltic Sea from an integrated water sample of the surface 10m~~integrated from the surface 10 m~~. Dashed lines show the Phases of the experiment as given in Fig. 1~~2~~, fCO_2 shown in the legend are mean fCO_2 across the duration of the experiment. (b) Mean DMS concentrations from each mesocosm during Phase I (crosses) and Phase II (diamonds), for ambient (blue), medium (grey) and high fCO_2 (red), with error bars showing the range of both the DMS and fCO_2.

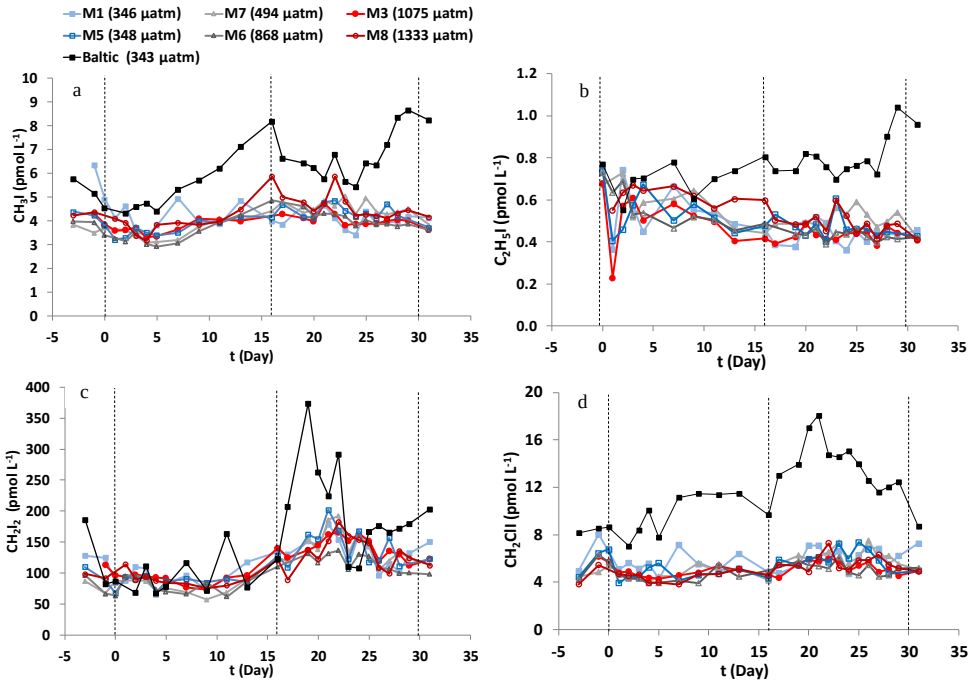

Figure 3. Mean ~~C~~concentrations (pmol L^{-1}) of (a) CH_3I, (b) C_2H_5I, (c) CH_2I_2 and (d) CH_2ClI taken from a water sample integrated from the surface 10m. Dashed lines indicate the Phases of the experiment, as given in Fig. 2. fCO_2 shown in the legend are mean fCO_2 across the duration of the experiment.

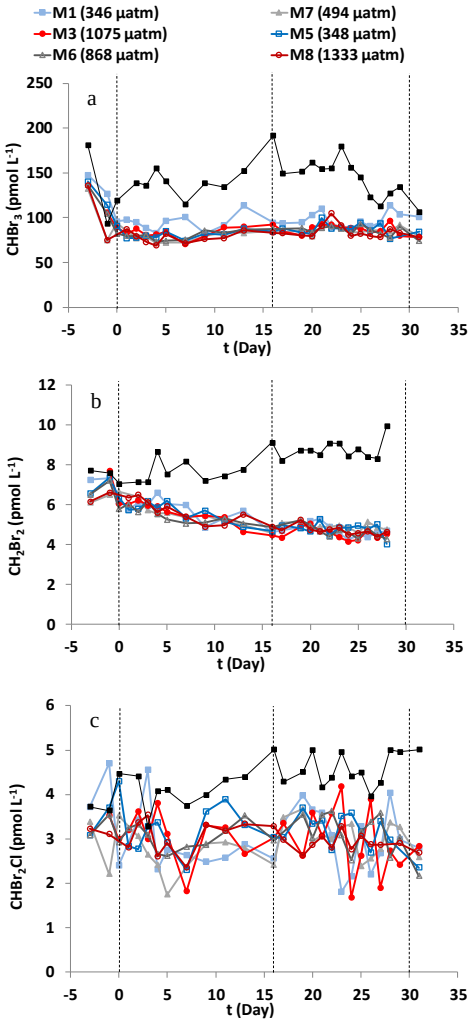

Figure ~~5~~4. Mean c~~C~~oncentrations (pmol L^{-1}) of (a) $CHBr_3$, (b) CH_2Br_2 and (c) $CHBr_2Cl$ taken from a water sample integrated from the surface 10m. Dashed lines indicate the phases of the experiment as defined in Fig. 2, fCO_2 shown in the legend are mean fCO_2 across the duration of the experiment.