Emission of iodine containing volatiles by selected microalgae species

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Abstract

In this study we present the results of an emission study of different phytoplankton samples in aqueous media treated with elevated ozone levels. Halocarbon measurements show that the samples tested released bromoform and different iodocarbons including iodomethane, iodochloromethane and diiodomethane. Iodide and iodate levels in the liquid phase were representative of concentrations of surface water in a natural environment. Measurement of volatile iodine (I_2) emissions from two diatom samples (*Mediopyxis helysia* and *Porosira glacialis*) and the background sample (F/2-medium from filtered natural seawater), showed that the quantity of I_2 evolved depends on the ozone concentration in the air. This behaviour was assumed to be caused by the oxidation reaction mechanism of iodide with ozone. The I_2 emission flux agrees with model calculations at different iodide concentrations. The I_2 emission of a natural plankton concentrate sample was, however, very low compared to other samples and showed no dependence on ozone. The reason for this was shown to be the low iodide concentration in the algal suspension, which seems to be the limiting factor in the oxidative formation of I_2.

Introduction

Iodine chemistry plays an essential role in the marine boundary layer (MBL) due to its effect on the destruction of tropospheric ozone, perturbation of the HO_x/NO_x cycle and the formation of new particles and cloud condensation nuclei, thereby leading to changes in the global radiative forcing (Hoffmann et al., 2001; von Glasow and Crutzen, 2003; O'Dowd and Hoffmann, 2005; Bloss et al., 2005; Huang et al., 2010a, b). This essential role of iodine and of other activated halogens is shown in field measurements in the marine boundary layer (MBL), laboratory chamber experiments or incubation experiments of different algae and in atmospheric models (Carpenter, 2003; Küpper et al., 2008; Kundel et al., 2012; McFiggans et al., 2000). The biogeochemical cycle of iodine is controlled by large iodine exchanges from the oceans to the atmosphere, driven by marine biotic and abiotic production (Schall et al., 1997). Volatilized species are photolabile iodocarbons like CH_2I_2, CH_3I, C_2H_5I, CH_2ICl, CH_2IBr and molecular iodine (I_2). Marine species like macroalgae and microalgae play a dominant role in the emission of these compounds (Carpenter et al., 1999, Huang et al., 2013, Saiz-Lopez and Plane, 2004).

Since molecular iodine and iodocarbons are photochemically unstable (lifetimes between about some tens of seconds for I_2 and a few days for CH_3I) they are photolysed under UV-visible light to form I・ atoms, which are then instantly oxidised by ozone to form the iodine monoxide radical IO (g) (Hoffmann et al., 2001; Saiz-Lopez et al., 2006). Further oxidation reactions of IO in the gas phase then can form low volatile iodine oxides (I_xO_y) which may nucleate under certain conditions and form new particles.

Recently it was proposed that the ozone loss over the tropical Atlantic Ocean was higher than calculated from global atmospheric models, and that this additional ozone destruction is induced by halogens such as bromine and iodine (Read et al., 2008). Biogenic emissions, such as the already studied iodocarbon emissions by phytoplankton species, e.g. coccolithophorids, diatoms and chlorophytes, (Colomb et al. 2008) are too low to explain the differences in model calculations and observations (Mahajan et al. 2010), therefore additional sources of the reactive iodine species are discussed, one of them being the surface reaction of ozone with seawater.

Garland and Curtis first discovered that the emission of molecular iodine from the surface of artificial and natural seawater is proportional to the ozone concentration at the air/water interface (Garland and Curtis, 1981). Sakamoto and co-workers examined the reaction mechanism of the iodide oxidation by ozone at the air/water interface, resulting in the formation of the intermediates $IOOO^-$ and HOI and the emission products IO and I_2 (Sakamoto et al., 2009). Further laboratory experiments show that different organics affect the reaction of iodide with ozone, e.g. fulvic acid enhances the I_2 formation, but not the formation of IO (Hayase et al., 2010, 2012).

Since the formation of I_2 and IO from the air/water interface is dependent on the iodide concentration in seawater, the reaction path found by Garland and Curtis may explain elevated iodine emissions in areas of higher phytoplankton activity (Garland and Curtis, 1981). The ability of different phytoplankton, e.g diatoms, to reduce iodate, which is ubiquitous in the open ocean, to iodide was shown for natural and elevated iodate concentrations (Wong et al. 2002; Chance et al. 2007) and for the different growth states (Bluhm et al. 2010) of the phytoplankton cultures. A correlation of iodine species in the particle phase and average chlorophyll exposure of air masses along back trajectories was found by Lai et al, 2011, indicating the link between phytoplankton activity and emission of atmospheric iodine.

Since the formation of I_2 and IO is correlated to the iodide concentration (Sakamoto et al. 2009) and the iodide concentration of surface waters is correlated to phytoplankton (Bluhm et al. 2010), this study investigates links between iodide concentrations in microalgae-containing seawater and abiotic formation and emission of I_2, utilising laboratory experiments of the reaction of the seawater surface with ozone.

Materials and Methods

Experimental set-up

Two diatom cultures (*M. helysia, Porosyra glacialis* both from the Alfred Wegener Institut/Sylt), were kept in F/2 seawater medium for growing. These media were prepared from filtered natural seawater from the shores of Sylt and additional nutrients which the diatoms need to grow (0.88 mmol NO_3^-, 0.04 mmol PO_4^{3-} and 0.01 mmol SiO_3^{2-}) and which is a common used medium as described by Guillard et al., 1975 and Kraberg et al. 2012. Both cultures were incubated in the F/2 medium at 16°C with 12-h-light-12-h-dark cycling (LUMILUX Plus Eco daylight lamp; approx.. 40 µmol PAR) for 4 weeks prior the experiment. Just before the emission experiment, the algal suspensions were diluted in a 2:1 ratio in F/2 medium and homogenised by stirring. In addition to the diatom cultures, a plankton concentrate was collected from the North Sea (55°01.562N; 8°27.113E) on May 24th 2012 using a 80 µm and 200 µm Apstein plankton net and diluted using the same medium as for the diatom cultures. Microscopic observations showed that the plankton concentrate sample was dominated by colonies of the haptophyte *Phaeocystis sp.* and only a low amount of diatoms were present.

For each experiment 1.5 L of the sample (i.e. diatom suspension, natural plankton concentrate or background (F/2 medium)) was introduced into a glass chamber tube (10 L), shown in Figure 1, and three magnetic stirrers were switched on immediately. A continuous flow of synthetic air (3.4 L min^{-1}) was channelled over the stirred algae suspension in the first experiment with no ozone and in the second experiment with elevated ozone levels of 100 ppb. The ozone was generated using an UV radiation source and the resulting ozone levels were measured using an ozone analyzer (Dasibi Environmental Corp. Model 1008-RS, Glendale, USA). To measure the emission of I_2 and halocarbons, α-cyclodextrin-coated denuders (Huang and Hoffmann, 2009; Huang et al., 2010c) and adsorption tubes (Kundel et al. 2012) were mounted at the other end of the tube chamber together with the ozone monitor. The chamber outflow was sampled using two membrane pumps, one with 0.50 L min^{-1} for the denuders and the other using 0.15 L min^{-1} for the adsorption tubes. To assure an overpressure over the sampling time a U-shaped tube filled with ultra-pure water was mounted in the centre exit of the glass chamber to measure the overpressure hydrostatically. The whole set-up was wrapped with aluminium foil to prevent photolysis of I_2 and halocarbon compounds. Potential wall losses of I_2 and halocarbons were investigated using diffusion (I_2) and permeation (halocarbons) test gas sources; no wall losses were observed within the precision of the measurements using the stated gas flows.

To monitor the emissions of I_2 and halocarbons from the liquid samples, an evaporation standard was added to the microalgal suspension in order to highlight any problems related to air sampling. This standard was 1,3-dibromopropane diluted in ultrapure water (500 µl of 0.94 µg L^{-1} which was then diluted with the sample to 1.5 L). The standard was chosen given the results from a first set of experiments with *M. helysia* and *Coscinodiscus wailesii* which show no detectable traces of this compound. We decided not to add any iodine containing compounds to prevent interferences with the I_2 emission.

Halocarbon measurements

Air samples of 6.75 L sampling volume were pre-concentrated at a flow rate of 150 ml min^{-1} on thermal desorption tubes filled with 100 mg Tenax TA 60/80 and 150 mg Carbotrap^{TM} 20/40 both provided by Supelco (Bellefonte, PA, USA). The samples were analysed using a self-made thermal desorption device mounted on a gas chromatograph (TraceGC, Thermo Scientific, Dreieich Germany) - mass spectrometer (PolarisQ, Thermo Scientific, Dreieich, Germany). During the desorption period of 6 minutes the cryotrap was cooled to -160 °C. Afterwards the cryotrap was rapidly heated to 270 °C for injection. The analytes were separated on a DB624 Durabond column (60 m; 0,32 mm; 1,8 µm FT) using helium as carrier gas with a constant pre-column pressure of 0.5 bar. The temperature program was: 55 °C (4 min), ramp with 5 °C min^{-1} to 120 °C (4 min) and ramp with 8 °C min^{-1} to 200 °C (4 min). Halocarbons were detected using a mass spectrometer in NCI mode with methane as reagent gas (2.5 ml min^{-1}), the primary electron energy was set to 120 eV and an emission current of 50 mA in single ion monitoring mode (SIM) was used. Iodinated compounds (CH_3I, C_2H_5I, CH_2ICl, CH_2IBr, CH_2I_2, 1-C_3H_7I, 2-C_3H_7I, 1-nC_4H_9I, 2-nC_4H_9I, 1-iso-C_4H_9I) were quantified using *m/z* 127 and brominated compounds (CH_2Br_2, CH_3Br, 1,3-$C_3H_6Br_2$) were quantified using *m/z* 79 and 81 at a 1:1 ratio. A five point calibration was done in the range between 0.01 ng and 1 ng using the continuously diluted output of a permeation test gas source (Thorenz et al. 2012). The detection limits for the individual iodocarbons were 0.003-0.088 ppt and for the bromocarbons were 0.004 – 0.009 ppt. For each series of measurements, the calibration was done in triplicate (precision of method 3-13%).

I_2, Iodide and Iodate measurements

Sampling of gaseous I_2 was performed using the denuder technique described by Huang and Hoffmann, 2009. Brown glass denuder tubes (6 mm i.d., 50 cm length) were coated using a α-cyclodextrin suspension (2.5 mg mL^{-1} in methanol) and sealed with polypropylene caps. Before sampling the denuders were stored in a fridge. For sampling the denuders were mounted vertically with a glass tube of 15 cm upstream to achieve laminar flow. The sampling flow was 500 mL min^{-1} for 45 min. After sampling the denuders were sealed and stored in a fridge until derivatization. For derivatization the α-cyclodextrine coating was eluted with ultrapure water (20 mL), then 25 µL N,N-dimethylaniline (1 µg mL^{-1} in methanol), 500 µL phosphate buffer (pH 6.4) and 500 µL 2-iodosobenzoate (4 mg mL^{-1}) were added, the mixture was shaken for 2 hours. After adding 3 ml sodium acetate the sample was extracted with 100 µL cyclohexane and 100µL 2,4,6-tribromoaniline (internal standard: IS) in cyclohexane (250ppb).

Iodide and iodate were derivatized from seawater to form the same product as described for I_2. Iodide was oxidized to form I_2 by using iodosobenzoate and iodate was reduced first to iodide and then oxidized to form I_2. 10 mL aliquots of seawater were analysed for iodide and for total iodine, iodate was calculated by difference. The method for iodide derivatization was slightly changed from the one described by Mishra et al. (2000). The use of sodium hydrogen sulfite as an agent to reduce iodate to iodide is described by Schwehr and Santschi (2003).

$I_{seawater} = I^- + IO_3^-$

To measure iodide, 10 mL seawater were mixed with 1 ml ethylenediaminetetraacetic acid solution (0.5%), 500 µL phosphate buffer, 500 µL N,N-dimethylaniline, 500 µL iodosobenzoate and shaken. After adding 3 ml sodium acetate the sample was extracted with 100 µL cyclohexane and 100 µL 2,4,6-tribromoaniline (IS) in cyclohexane (250 ppb).

To measure iodate an aliquot of 10 mL seawater was mixed with 1 mL ethylenediaminetetraacetic acid solution (0.5%), 1 mL hydrochloric acid (3.7%) and 500 µL sodium hydrogen sulfite solution (283.9 µmol L^{-1}) to reduce the iodate. Afterwards 500µl sodium acetate, 4 mL phosphate buffer, 500 µL N,N-dimethylaniline, 500 µL iodosobenzoate were added. After shaking the sample was again extracted with 100 µL cyclohexane and 100µL 2,4,6-tribromoaniline (IS) in cyclohexane (250 ppb).

1 µL of the cyclohexane extract was injected to the GC-MS System (6850 GC & 5973 MS, Agilent Technologies, Waldbronn, Germany) at a constant flow of 1 mL min^{-1} of helium (99.999%) and, the chromatographic separation was performed using a capillary column FS Supreme 5 MS with a length of 30 m, inner diameter of 0.25 mm and film thickness of 0.25µm (CS Chromatographie Servieve, Langenwehe, Germany) with a temperature program starting at 50°C (for 3 min), then heating up at 30 °C min^{-1} to 220°C (for 3 min). The mass spectrometer measured in electron ionisation mode at 70 eV, the specific fragments of the product 4-iodo-N,N-dimethylaniline was extracted at *m/z* 247 (M+) and of the internal standard 2,4,6-tribromoaniline at *m/z* 329 (M+).

Chlorophyll measurements

The analytical method for chlorophyll α (chl α) measurements is described by Edler et al 1979. An aliquot of 50-100 mL water samples were filtered on glass fibre filters (GF/F-Whatman). The dry filters were put in polypropylene vials and extracted with 7.5 ml acetone. The extract was stored together with the filter in a dark fridge at 3°C overnight and centrifuged the next day (5500 rpm, 7 min) at 5°C. The absorption of the supernatant was measured against acetone using an Uvikon XL double beam spectrophotometer at λ = 750 nm, 663 nm, 645 nm and 630 nm. To calculate the concentration of chl α the equation of Jeffrey and Humphrey, 1975 was used. Chl α can be a good indicator for microalgae biomass (Roy 2010; Bluhm et al. 2010; Colomb et al. 2008), and has been used to calculated emission rates of iodine-containing volatiles from phytoplankton. This calculation was not used here, since the mechanisms of synthesis and release of these iodine containing gases is still unclear. All gaseous compounds in this study are therefore given as measured mixing ratio and the chl α value of the corresponding algae suspension is also given.

Results and Discussion

Halocarbons

The emission rates of the natural halocarbons and the evaporation standard, given in Table 1, were calculated by the amount measured in the adsorption tubes divided by the emission time and the surface area of the suspension sample (pmol min^{-1} m^{-2}). The halocarbon emission rates showed no effect on the different ozone levels; therefore the data for each sample are summarized for high and low ozone conditions. An evaporation standard was added to the different samples to recognize differences in emission rates of the organic compounds from the aqueous phase. The standard was added in a 10 to 100-fold excess compared to natural concentrations of bromocarbons in Atlantic seawater (Carpenter et al. 2000) to reduce the effect of natural 1,3-dibromopropane which may alter the mixing ratio of the evaporation standard measured. In the chosen concentration a natural abundance would change the result only by 1-10% compared to the spike solution. The results of the measurements of 1,3-dibromopropane showed very constant values, as can be seen from the low standard deviation between the different samples and replicates. This result indicates a stable and reliable experimental setup in terms of evaporation of volatile compounds from the water surface and of the mixing of the bulk water.

The measured emission rates of the natural halocarbons show that the brominated compound, $CHBr_3$, is elevated compared to the iodocarbons emission rates. This result fits to observations of the natural abundance of halocarbons in seawater as described in earlier studies (Roy et al. 2011). The emission rate of $CHBr_3$ is higher for the two diatom cultures (*M. helysia* and *P. glacialis)* than for the plankton samples containing *Phaeocystis sp.* and the background. Again, this result matches field and laboratory data showing a link between elevated $CHBr_3$ concentrations in seawater and the simultaneous occurrence of diatoms (Colomb et al. 2008, Quack et al. 2007, Moore et al. 1996).

The iodocarbon emissions in experiments using the background (F/2 medium) and the plankton concentrate were dominated by CH_3I, followed by CH_2ICl and CH_2I_2. However, for the diatom cultures, CH_2I_2 was the dominant iodocarbon emitted with CH_3I and CH_2ICl both showing lower emission rates. The emission of iodocarbons from the F/2 background is not surprising for two reasons; first, the medium was produced from natural shoreline filtered water, which already may contain iodocarbons (Wong and Cheng, 1998). The second reason may be related to iodocarbon-producing bacteria (Amachi et al. 2001; Amachi et al. 2003). These bacteria could have been present and active in the natural seawater water used to produce the F/2 medium, since it was not sterilized prior to use. Additionally, the emission rates of $CH_2I_{2,}$ CH_2ICl and CH_3I in the diatom samples *P. glacialis* and *M. helysia* were significant higher compared to the background (Wilcoxon rank sum test p=0.00032 and p=0.00007, respectively). This increase in emission can be explained by the capability of the diatoms to produce iodocarbons which had already been reported by Moore et al. (1996). To compare the natural plankton concentrate with the cultivated diatom cultures and the background one must keep in mind that chl α concentrations are biomass tracers reflecting the abundance of phytoplankton. The results for the chl α measurement, given in Table 1, clearly show that the natural plankton concentrate contains less biomass than the cultured diatoms. Therefore, we conclude that the lower iodocarbon emissions of the plankton concentrate compared to the diatom cultures is partly due to lower biomass density. The lower iodocarbon emission rates in the natural plankton concentrate could also be related to iodine uptake of natural occurring micro algae (van Bergeijk et al. 2013). The emission flux summed for the three iodocarbons in the four samples' background, plankton concentrate, *P. glacialis* and *M. helysia,* was in the range 0.21 – 1.02 pmol min^{-1} m^{-2}, 0.14 – 0.58 pmol min^{-1} m^{-2}, 0.50 – 1.35 pmol min^{-1} m^{-2} and 0.57 – 1,53 pmol min^{-1} m^{-2}, respectively. We are not aware of emission studies investigating the flux of iodocarbons from micro algae suspensions to directly compare these results. To establish a connection to other experimental observations the results listed above are compared to incubation studies of marine aggregates producing iodocarbons and calculated emission fluxes in coastal, seaweed-rich regions. Hughes et al. (2008) measured the iodocarbon production of different marine aggregates to be within 0.71 to 6.90 pmol h^{-1} L^{-1}. The production rate is difficult to compare to the presented results, since the flux in our study is based on the production by the microalgae species and evaporation from the surface, whereas Hughes et al. (2008) measured the production in the aqueous phase. Jones et al. (2009) calculated iodocarbon emissions at a sampling site surrounded by fields of macro algae in open sea water at Roscoff, France. The flux of iodocarbons was estimated to 85.28 pmol min^{-1} m^{-2}, two orders of magnitude higher than the flux obtained in the present study. Thus it appears that on an areal basis, the natural populations of microalgae studied here are much less prevalent emitters of iodocarbons than seaweeds and marine aggregates.

Iodide and iodate

The concentrations of iodide and iodate in the different samples are shown in Table 1. For each sample, the mean and range for six replicates are shown; no differences in iodide and iodate concentrations where observed under elevated (100 ppb O_3) and low ozone (0 ppb O_3) conditions. The iodate concentrations in the background and in the three plankton samples were in the same range, with mean concentrations between 438 and 448 nmol L^{-1}. These iodate concentrations are in the range measured for the open ocean of 400 to 500 nmol L^{-1} iodate in most oceanic regions (Bluhm et al. 2011). The ubiquity of iodate suggests that its concentration is not a limiting factor.

The iodide concentrations in the two diatom cultures, *P. glacialis* and *M. helysia,* are slightly elevated with mean values of 12.70 nmol L^{-1} and 16.84 nmol L^{-1}, respectively, compared to the background iodide concentration of 10.35 nmol L^{-1} and the plankton concentrate iodide concentration of 6.47 nmol L^{-1}. This enhanced iodide concentration indicates the reduction of iodate by the two diatom cultures, which was also found by Bluhm et al. 2010 and Wong et al. 2002 for different phytoplankton species. Such a reduction of iodate to iodide will result in a decrease in the iodate concentration, however, for the measured iodate concentration in this study the expected decrease falls within the analytical precision of the measurement. The iodide concentrations in all samples are comparable with oceanic surface water concentrations, for example around 10-30 nmol L^{-1} in the Weddel Sea surface water (Bluhm et al. 2011).

The low iodide concentration of the plankton concentrate sample compared to the background sample is surprising, but may be assigned to an overall low level of different nutrients, like phosphate and silicate, in the Wadden Sea of Sylt at springtime (Weisse et al. 1986), although the level of iodate was consistent. Another possible reason for the low iodide concentration in the plankton concentrate could be iodine uptake by microalgae present in the natural plankton sample (van Bergeijk et al. 2013).

Ozone measurements

The results of the ozone measurement for the samples: background, *P. glacialis*, *M. helysia* and the plankton concentrate were normalized against a background measurement obtained using ultra-pure water in the chamber. This was performed in order to account for losses of ozone through wall reactions, losses on the water surface, and losses due to droplet formation from stirring. The ozone consumption was calculated using a Continuous Stirred-Tank Reactor (CSTR) approach with 668 ng min^{-1} ozone (100 ppb) introduced into the chamber (total volume: 10 L, flow: 3.4 L min^{-1} and residence time: 2.94 min). The difference between the introduced ozone flow and measured ozone flow is considered as consumed ozone, due to the oxidation of iodide and other ozone depleting reactions in the samples. To calculate the consumed ozone, the flow rate was summarized over 45 min of the experiment. Ozone consumption was clearly observed for all samples. The background sample showed the weakest ozone consumption of 58 nmol, followed by the sample of *P. glacialis* with 186 nmol and the plankton concentrate with 253 nmol. The highest ozone consumption was shown by *M. helysia* with 335 nmol.

I_2 emissions

The I_2 emission rate was calculated by dividing the amount of I_2 by the sampling time and the suspension surface area. The results for the four samples are shown in Figure 2. The background and the two diatom samples, *M. helysia* and *P. glacialis* show significant higher emission rates when the ozone level is elevated (100 ppb O_3) compared to conditions where no ozone is present (0 ppb O_3). The difference between the high and low ozone conditions is small for the background, increases for the *P. glacialis* sample and is highest for the *M. helysia* sample. The plankton concentrate does not show a significant dependence of the I_2 emission rate on the ozone level. The ozone-dependent increase in the I_2 emission rate of the other samples indicates that iodide, which is present at the air/water interface, is oxidised by ozone to form I_2, which is consistent with the results from artificial and natural seawater (Garland and Curtis, 1981, Sakamoto et al. 2009).

Figure 3 shows the change in I_2 emission rate ([I_2 at 100 ppb ozone] – [I_2 at 0 ppb ozone]) of the different samples as a function of the iodide concentration measured in the bulk water. A linear correlation fits the data well with a Pearson coefficient of $R^2 = 0.998$. This behaviour indicates a direct proportional relationship, which was also seen by Sakamoto et al. 2009 for small iodide concentrations (0 – 5 mmol L^{-1}). Carpenter et al. (2013) also observed that the I_2 emission is dependent on the aqueous iodide concentration. The proposed reaction sequence, as shown in equations (1)-(5), explains the relationship between the iodide concentration in the aqueous phase and the I_2 emissions (Sakamoto et al. 2009).

$$I^-(aq) + O_3\ (g\ or\ interface) \rightarrow IOOO^-\ (interface) \qquad (1)$$

$$IOOO^-\ (interface) \rightarrow IO^-(aq) + O_2(aq) \qquad (2)$$

$$IO^-(aq) + H^+ \rightleftarrows HOI(aq) \qquad (3)$$

$$HOI(aq) + I^-(aq) + H+ \rightleftarrows I_2(aq) + H_2O \qquad (4)$$

$$I_2(aq) \rightarrow I_2(g) \qquad (5)$$

The plankton sample does not show an elevated I_2 emission at 100 ppb ozone compared to zero ozone. This observation indicates that in the plankton sample an additional I_2 loss process takes place. Reactions or partitioning of I_2 in an organic surface layer, which was discussed in Carpenter et al. (2013), would be one possibility to explain these results. In fact the specific microalgae found in the plankton concentrate, *Phaeocystis sp.,* is known to produce high amounts of organic matter (Eberlein et al. 1985). An alternative explanation is the low iodide concentration in the plankton concentrate, which may be related to iodide uptake by the natural occurring plankton communities. The iodide concentrations and ozone mixing ratios in this study represent more likely natural conditions compared to the study of Sakamoto et al. (iodide concentration between 0.01 – 50 mmol L^{-1} and ozone mixing ratio from 2 – 298 ppm). However, the results presented here demonstrate that even under low iodide concentrations, representative of natural conditions of the MBL, a significant formation of I_2 by the ozone driven oxidation of iodide at the air/water interface takes place, until the iodide concentration gets too low.

Comparing the I_2 and iodocarbon emission rates, it is clear that the volatile iodine emissions are dominated by I_2. Therefore I_2 emissions from natural seawater surfaces are more relevant for atmospheric processes than the emission of iodocarbons. At the same time the experiments presented here show that the emission of iodocarbons is not linked to the formation of I_2 at the air/water interface (Martino et al., 2009), since no correlation between I_2 emissions or O_3 mixing ratio and iodocarbon emissions was observed.

Calculated emissions for the background, *P. glacials* and *M. helysia* were 8.32×10^5, 1.47×10^6 and 2.40×10^6 molecules cm^{-2} s^{-1}, respectively. Modelled emissions calculated using the kinetic model of the aqueous interfacial layer by Carpenter et al. (2013) for the iodide concentration measured were 1.16×10^6, 1.67×10^6 and 2.91×10^6 molecules cm^{-2} s^{-1}, respectively. The measured and modelled values agree well, showing that the model is able to predict emissions for natural iodide concentrations.

Figure 4 shows the change in the I_2 emission rate plotted versus the consumed ozone for the four different samples. This was done to see whether ozone depletion in the flow chamber is mainly driven by the iodide or if other factors are important. The graph shows that the ozone depletion correlates with the enhancement in the I_2 emission rate for the two diatom samples and for the background. Therefore, the ratio of the formation of I_2 to the amount of O_3 consumed, calculated as $R(I_2) = n(I_2) / n(O_3)$, with $n(I_2)$ = amount of I_2 formed and $n(O_3)$ = amount of O_3 consumed during the experiment, was used to determine the dependence of I_2 formation on O_3. $R(I_2)$ has a maximum value of 1, which, referring to eqs.1-5, indicates that every molecule of ozone which is consumed produces one molecule of I_2. The formation ratio for the background sample was the highest with $R(I_2)$ = 0.14‰ , followed by the samples of *M. helysia* with $R(I_2)$ = 0.08‰ and *P. glacialis* $R(I_2)$ = 0.07‰. This means that a higher degree of biological activity of the sample decreases the formation ratio. The decrease of I_2 emission in the surface reaction of ozone with iodide was also seen by Carpenter et al. when turning from iodide solutions to sea water, which contains more organic substances (Carpenter et al. 2013).

The plankton concentrate also depletes ozone, although there is no enhancement in I_2 emission. Therefore, another mechanism in ozone depletion must be taking place, possibly induced by other ozone reactive substances formed or excreted from *Phaeocystis sp.*. Another explanation is a reduced release of I_2 and a higher release of HOI, which was not measured in this study. In fact, Carpenter and coworkers observed HOI as the main iodine compound released in their experiments, followed by I_2 (Carpenter et al. 2013).

Conclusions

Different phytoplankton suspensions were treated with high and low ozone levels. Halocarbons including bromoform, iodomethane, iodochloromethane and diiodomethane, were released from the suspensions independent of the ozone level. The use of an evaporation standard in the aqueous phase indicated that the emission rates of all gaseous organics were quite stable. The iodide and iodate concentration in the liquid phase also showed no dependence on the ozone level in the gas phase and were comparable to concentrations in surface water in the open ocean.. The emission flux of the iodocarbons was lower compared to the calculated flux at a coastal, kelp-rich site in Roscoff, France, an observation which emphasize the higher emission of iodocarbons from macroalgae compared to microalgae. The emission rates of iodocarbons were also lower than the emission of I_2, confirming that I_2 emissions from the remote ocean dominate over organic iodine sources for the MBL (Jones et al., 2010; Lawler 2012; Carpenter et al., 2013). The emission of I_2 showed a dependency on the ozone level in the air as well as on the iodide concentration in the sample suspension, as has been found previously (Carpenter et al. 2013 and other refs). For the two diatom samples, *M. helysia* and *P. glacialis,* and the background sample, a correlation was found for the I_2 emission and the ozone consumption during the experiment. The I_2 emissions from the plankton concentrate, taken in the Wadden Sea of Sylt, were lower than the other samples and showed no dependence on the ozone levels. An explanation could be the lower iodide concentration in the plankton sample, since iodide is the limiting factor for the oxidative reaction. Another explanation may be the preferred formation and emission of HOI when organic compounds are present in the liquid phase. The experiments showed that different algae suspensions (*M. helysia* and *P. glaciales*) are capable of emitting I_2 by the reaction of ozone with dissolved iodide at the air/water interface under natural conditions. However, it remains unclear whether iodine emissions from aquatic systems can be fully understood without the simultaneous measurement of HOI.

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Table 1: Halocarbon emission rates, concentrations of chlorophyll α, iodide and iodate in the four different sample suspensions

Sample		F/2 medium background	*P. glacialis*	*M. helysia*	plankton concentrate
		Range (Mean)	Range (Mean)	Range (Mean)	Range (Mean)
CH_3I	pmol min^{-1} m^{-2}	0.17 – 0.72 (0.35)	0.21 – 0.69 (0.45)	0.32 – 0.82 (0.53)	0.08 – 0.37 (0.19)
CH_2ICl	pmol min^{-1} m^{-2}	0.02 – 0.22 (0.11)	0.02 – 0.22 (0.16)	0.04 – 0.22 (0.18)	0.02 – 0.12 (0.07)
CH_2I_2	pmol min^{-1} m^{-2}	0.02 – 0.08 (0.07)	0.27 – 0.44 (0,36)	0.21 – 0.50 (0.37)	0.04 – 0.09 (0.07)
$CHBr_3$	pmol min^{-1} m^{-2}	1.76 – 1.90(1.81)	1.99 – 2.17 (2.09)	1.75 – 2.17 (2.09)	1.75 – 2.33 (1.82)
chl α	µg L^{-1}	n.d.	257.27	926.59	2.53
Iodide	nmol L^{-1}	6.60 - 15.69 (10.35)	7.32 - 19.71 (12.70)	9.90 - 21.94 (16.84)	3.52 - 9.45 (6.47)
Iodate	nmol L^{-1}	402 - 538 (428)	408 - 478 (448)	397 - 499 (446)	424 - 478 (442)
1,3-$C_3H_6Br_2$ *	pmol min^{-1} m^{-2}	7.77 ± 0.04	7.78 ± 0.59	7.77 ± 0.99	7.69 ± 0.07
$\Sigma_{\text{Iodocarbon/chl }\alpha}$	pmol/g	n.d.	19.75	6.06	694.88

* evaporation standard given as

mean ± standard deviation

chl α was measured for each sample once halocarbons, iodide, iodate mean values and ranges are calculated from 6 replicates

$\Sigma_{\text{Iodocarbon/chl }\alpha}$ Iodocarbon emissions were summed for the eperimetntal conditions (time and surface area) and normalized to chla in the watery phase

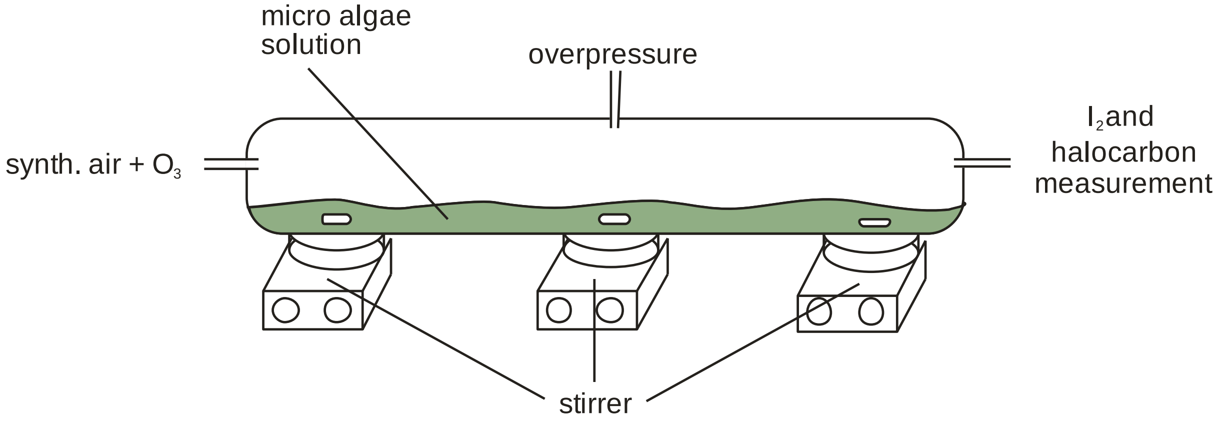

Figure 1: Experimental setup of the chamber with the phytoplankton suspension

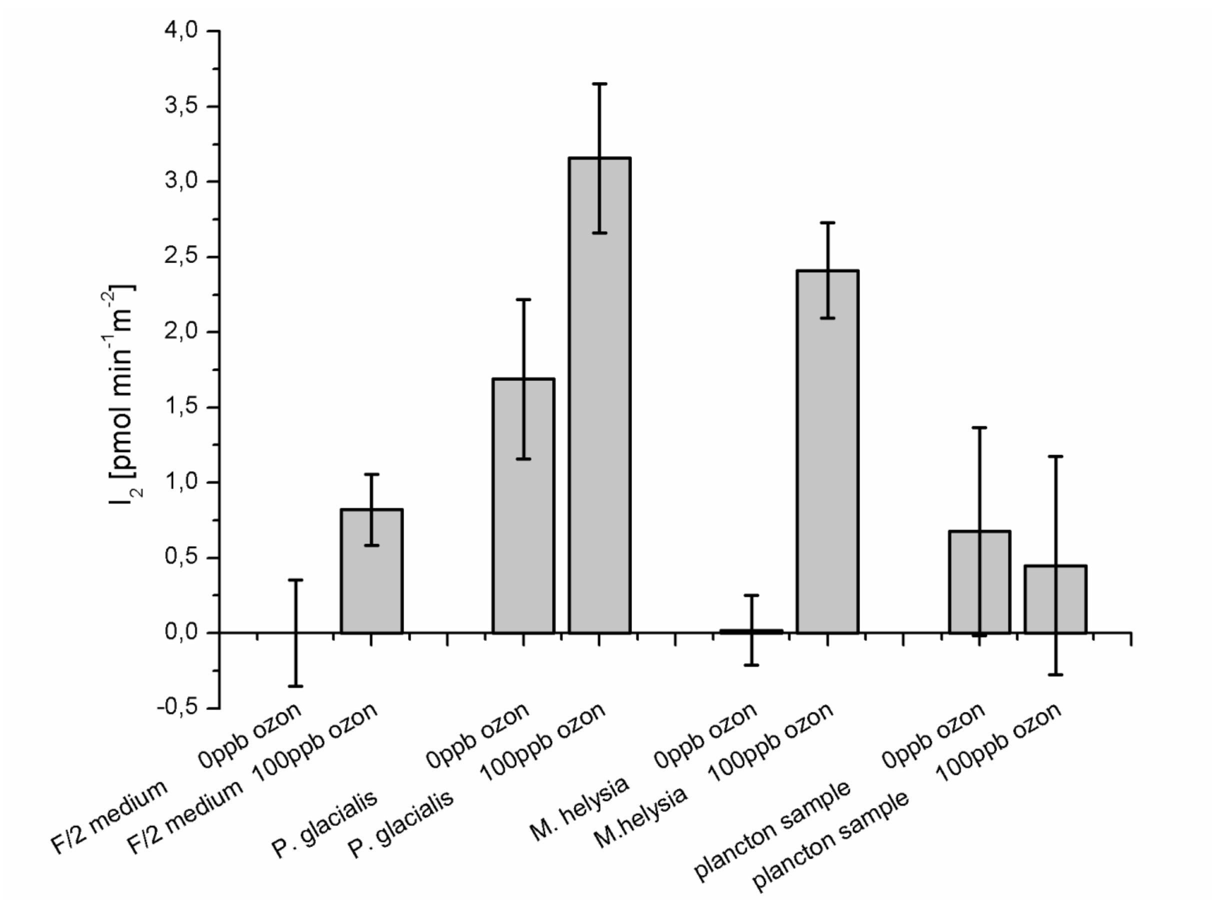

Figure 2: Iodine emission rates normalized for the surface area of the different samples at 0 ppb and 100 ppb ozone. The error bars represent the standard deviation of the three replicates of each experiment.

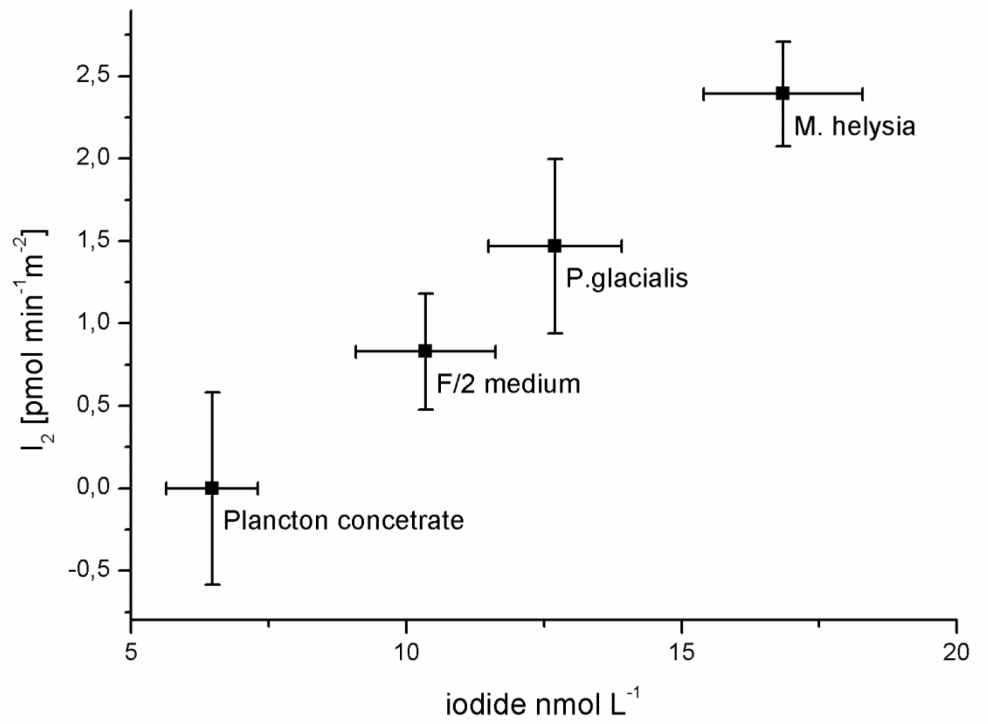

Figure 3: Correlation of the change in the I_2 emission and the iodide concentration in the mikro algae suspension

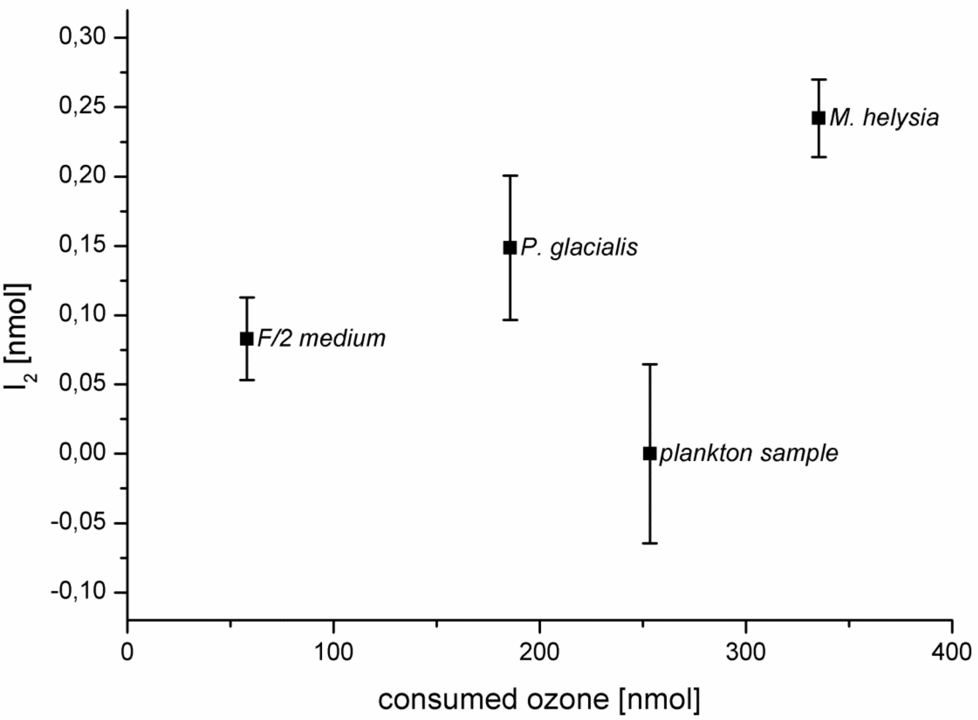

Figure 4: Function of the change in the total I_2 emissions in relation to the amount of consumed ozone