Atmospheric
Chemistry
and Physics
Discussions

Open Access

# Emission of iodine containing volatiles by selected microalgae species

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## Abstract

In this study we present the results of an incubation study of different phytoplankton samples in F/2 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 locally 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 iodine 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 algae suspension, which seems to be the limiting factor in the oxidative formation of $I_2$.

## 1   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 instable (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).

14577

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 phytoplankton, iodide concentrations in seawater and $I_2$ emission, utilising laboratory experiments of the reaction of the seawater surface with ozone.

## 2 Materials and methods

### 2.1 Experimental set-up

Two diatom cultures (*M. helysia, Porosyra glacialis*) were kept in F/2 seawater medium (Guillard, 1975). Both cultures were kept for at least 4 weeks prior the experiment and were then 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°01.562′ N; 8°27.113′ E) on 24 May 2012 using a 80 μm and 200 μm Apstein plankton net and diluted using F/2 medium, the sample was dominated by colonies of the haptophyte *Phaeocystis sp.* and only a low amount of diatoms was present in the sample, as determined by a microscopic analyses.

14578

For each experiment, 1.5 L of the sample was introduced into a glass chamber tube (10 L), shown in Fig. 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, $\alpha$-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.

To monitor the emissions of I$_2$ and halocarbons from the liquid samples, an evaporation standard was added to the microalgae 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.

### 2.2 Halocarbon measurements

Air samples of 6.75 L sampling volume were preconcentrated 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™ 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 min 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$_3$I, C$_2$H$_5$I, CH$_2$ICl, CH$_2$IBr, CH$_2$I$_2$, 1-C$_3$H$_7$I, 2-C$_3$H$_7$I, 1-nC$_4$H$_9$I, 2-nC$_4$H$_9$I, 1-iso-C$_4$H$_9$I) were quantified using $m/z$ 127 and brominated compounds (CH$_2$Br$_2$, CH$_3$Br, 1,3-C$_3$H$_6$Br$_2$) 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 %).

### 2.3 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 $\alpha$-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 $\alpha$-cyclodextrin 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 h.

After adding 3 mL sodium acetate the sample was extracted with 100 µL cyclohexane and 100 µL 2,4,6-tribromoanilin (internal standard: IS) in cyclohexane (250 ppb).

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-tribromoanilin (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 500 µL 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 100 µL 2,4,6-tribromoanilin (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 %), the chromatographic separation was performed using a capillary column FS Supreme 5 MS with length of 30 m, inner diameter of 0.25 mm and film thickness of 0.25 µm (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+).

## 2.4 Chlorophyll measurements

The analytical method for chlorophyll $\alpha$ (chl $\alpha$) 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 $\lambda = 750$ nm, 663 nm, 645 nm and 630 nm. To calculate the concentration of chl $\alpha$ the equation of Jeffrey and Humphrey (1975) was used . Chl $\alpha$ 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 $\alpha$ value of the corresponding algae suspension is listed aside.

## 3 Results and discussion

### 3.1 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 (ng 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 evapora-

tion 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 actually 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 F/2 medium. 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 organoiodine compounds have two different emission patterns regarding the relative abundance of the different iodine containing volatiles: the first one is reflected by the F/2 media background and the plankton concentrate and the other by the two diatom cultures. The abundance of iodocarbons in experiment using the F/2 media background was dominated by $CH_3I$, followed by $CH_2ICl$ and $CH_2I_2$. Whereas for the diatom cultures, $CH_2I_2$ was the dominant iodocarbon emitted and $CH_3I$ and $CH_2ICl$ both showing lower emission rates. Additionally, the iodocarbon emission rates in the diatom samples were elevated compared to the F/2 background, showing that diatoms are capable of producing iodocarbons (Moore et al., 1996). To compare the natural

plankton concentrate with the cultivated diatom cultures one must keep in mind that chl-$\alpha$ concentrations are biomass tracers reflecting the abundance of phytoplankton. The results for the chl-$\alpha$ 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 emission flux summed for the three iodocarbons in the four samples F/2-medium, plankton concentrate, *P. glacialis* and *M. helysia* was in the range of 0.034–0.163 ng min$^{-1}$ m$^{-2}$, 0.025–0.098 ng min$^{-1}$ m$^{-2}$, 0.106–0.264 ng min$^{-1}$ m$^{-2}$ and 0.153–0.288 ng min$^{-1}$ m$^{-2}$, respectively. We are not aware of incubation 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 for open sea water. Hughes et al. (2008) measured the iodocarbon production of different marine aggregates to be within 6 to 66 ng min$^{-1}$ 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 fluxes from seawater and gas phase concentrations. The sampling site was surrounded by fields of macro algae in open sea water at Roscoff, France. The flux of iodocarbons was estimated to 11.281 ng min$^{-1}$ m$^{-2}$, actually two orders of magnitude higher than the flux obtained in the present study. This may be explained by the higher iodocarbon emissions from macro algae exposed to intertidal dryness (Carpenter et al., 1999), compared to micro algae suspensions.

## 3.2 Iodide and iodate

The concentration of iodide and iodate is also shown in Table 1, again the concentrations were not dependent on the ozone concentration and therefore results are summarized for the six replicates of each sample. The iodate concentrations in the

background F/2 medium 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 ubiquitous abundance 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 F/2 medium 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. 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 F/2 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.

## 3.3 Ozone measurements

The results of the ozone measurement for the samples: F/2 medium, *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

14585

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 F/2 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.

## 3.4 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 Fig. 2. The F/2 medium 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 F/2 medium, 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 Reactions (R1)–(R5) explain the relationship between the iodide concentration in the aqueous phase

14586

and the $I_2$ emission (Sakamoto et al., 2009).

$$I^-(aq) + O_3(g \text{ or interface}) \rightarrow IOOO^-(interface) \tag{R1}$$

$$IOOO^-(interface) \rightarrow IO^-(aq) + O_2(aq) \tag{R2}$$

$$IO^-(aq) + H^+ \leftrightarrow HOI(aq) \tag{R3}$$

$$HOI(aq) + I^-(aq) + H^+ \leftrightarrow I_2(aq) + H_2O \tag{R4}$$

$$I_2(aq) \rightarrow I_2(g) \tag{R5}$$

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. 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 show that also at natural conditions 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.

Calculated emissions for the F/2 medium, *P. glacials* and *M. helysia* were $8.32 \times 10^5$, $1.47 \times 10^6$ and $2.40 \times 10^6$ 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 $1.16 \times 10^6$, $1.67 \times 10^6$ and $2.91 \times 10^6$ 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 well.

Figure 4 shows the change in the $I_2$ emission rate plotted vs. 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 F/2 medium. Therefore the formation ratio of $I_2$ in dependence on $O_3$ was calculated by $R(I_2) = n(I_2)/n(O_3)$, with $n(I_2) =$ amount of $I_2$ formed and $n(O_3) =$ amount of $O_3$ consumed during the experiment. $R(I_2)$ has a maximum value of 1, regarding to Reactions (R1)–(R5) if every molecule ozone which is consumed produces one molecule of $I_2$. The formation ratio for the F/2 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 biologic 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 obviously takes 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. Indeed Carpenter and coworkers observed HOI as the main iodine compound released in their experiments, followed by $I_2$ (Carpenter et al., 2013).

## 4 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. The emis-

sion flux of the iodocarbons was lower compared to the calculated flux at a natural site in Roscoff, France, an observation which emphasis the higher emission of iodocarbons from macroalgae compared to microalgae. The iodide and iodate concentration of the investigated samples was comparable to surface water in the open ocean. The emission of $I_2$ showed a dependency on the ozone level in the air as well as from 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 F/2 medium 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, was 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 (*M. helysia* and *P. glaciales*) suspensions are capable to emit $I_2$ by the reaction of ozone with dissolved iodide at the air/water interface. However, it remains unclear whether without the simultaneous measurement of HOI the iodine emission from aquatic systems can be fully understood.

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14593

**Table 1.** Halocarbon emission rates, concentrations of chlorophyll $\alpha$, iodide and iodate in the four different sample suspensions.

| Sample | | F/2 medium background Range (Mean) | *P. glacialis* Range (Mean) | *M. helysia* Range (Mean) | plankton concentrate Range (Mean) |
|---|---|---|---|---|---|
| $CH_3I$ | ng min$^{-1}$ m$^{-2}$ | 0.024–0.102 (0.050) | 0.030–0.098 (0.064) | 0.046–0.116 (0.075) | 0.011–0.053 (0,027) |
| $CH_2ICl$ | ng min$^{-1}$ m$^{-2}$ | 0.004–0.039 (0.019) | 0.003–0.039 (0.028) | 0.05–0.038 (0.031) | 0.003–0.021 (0.013) |
| $CH_2I_2$ | ng min$^{-1}$ m$^{-2}$ | 0.006–0.022 (0.020) | 0.073–0.117 (0,096) | 0.057–0.134 (0.098) | 0.011–0.024 (0.019) |
| $CHBr_3$ | ng min$^{-1}$ m$^{-2}$ | 0.445–0.479 (0.457) | 0.503–0.549 (0.528) | 0.442–0.548 (0.529) | 0.442–0.590 (0.461) |
| chl $\alpha$ | 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-$C_3H_6Br_2$[*] | ng min$^{-1}$ m$^{-2}$ | 1.568 ± 0.009 | 1.570 ± 0.12 | 1.569 ± 0.200 | 1.552 ± 0.014 |

[*] Evaporation standard given as mean ± standard deviation. Chl $\alpha$ was measured for each sample once halocarbons, iodide, iodate mean values and ranges are calculated from 6 replicates.
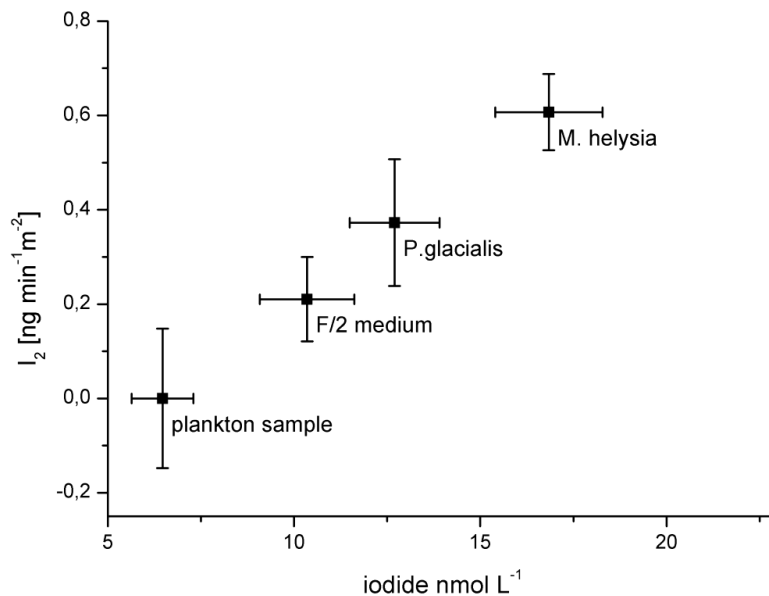
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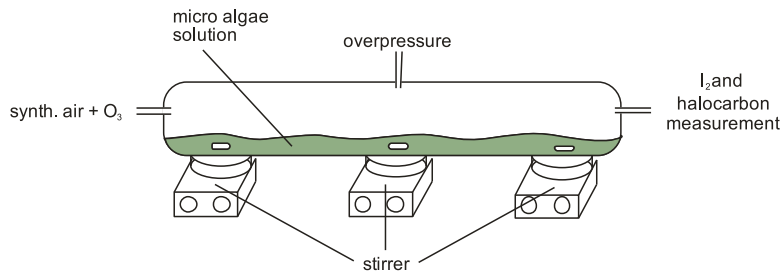
**Figure 1.** Experimental setup of the chamber with the phytoplankton suspension.
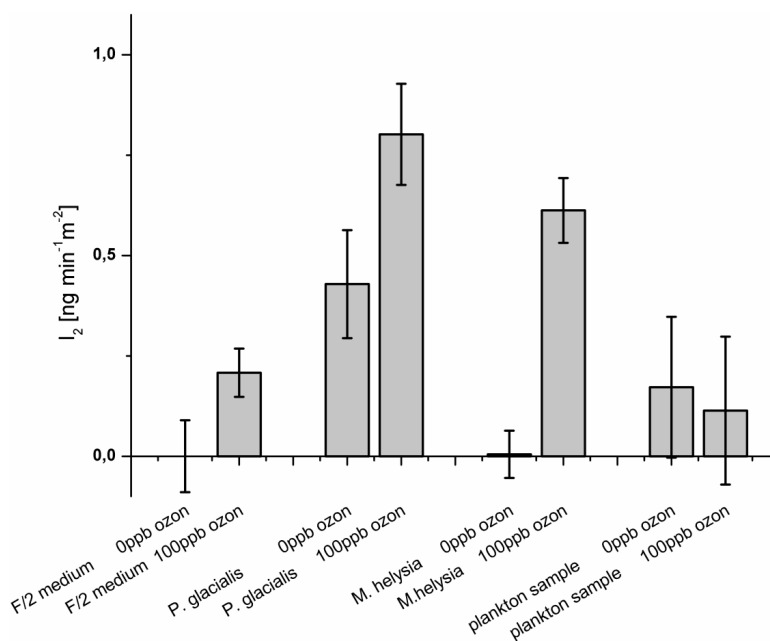
**Figure 2.** Iodine emission rates normalized for the surface area of the different samples at 0 ppb and 100 ppb ozone. The error bars represent the standard deviation of the three replicates of each experiment.

**Figure 3.** Correlation of the change in the $I_2$ emission in dependency on the iodide concentration in the phytoplankton suspension.
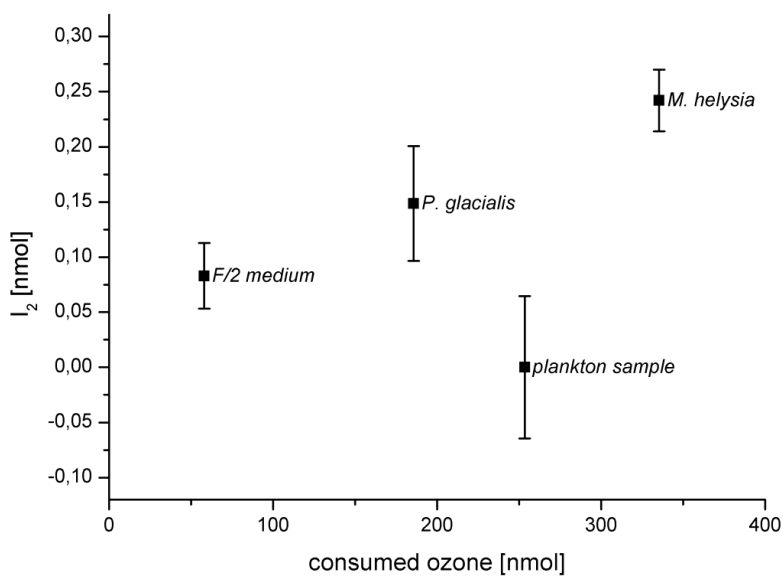
**Figure 4.** Function of the change in the $I_2$ emission rate in dependency of the amount of consumed ozone.