



Emission of iodine containing volatiles by selected microalgae species

U. R. Thorenz et al.

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Emission of iodine containing volatiles by selected microalgae species

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

Emission of iodine containing volatiles by selected microalgal species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emission of iodine containing volatiles by selected microalgae species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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 , $\text{C}_2\text{H}_5\text{I}$, 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 $\text{I}\cdot$ 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).

Emission of iodine containing volatiles by selected microalgal species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 μ m and 200 μ m 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.

Emission of iodine containing volatiles by selected microalgae species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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, 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.

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 ($500 \mu\text{L}$ of $0.94 \mu\text{g L}^{-1}$ 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

Emission of iodine containing volatiles by selected microalgal species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



chromatograph (TraceGC, Thermo Scientific, Dreieich Germany) – mass spectromete-
ter (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 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$ (4 min), ramp with 5 $^{\circ}\text{C min}^{-1}$ to 120 $^{\circ}\text{C}$
(4 min) and ramp with 8 $^{\circ}\text{C min}^{-1}$ to 200 $^{\circ}\text{C}$ (4 min). Halocarbons were detected using
a mass spectrometer in NCI mode with methane as reagent gas (2.5 mL min^{-1}), the pri-
mary 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 , $\text{C}_2\text{H}_5\text{I}$, CH_2ICl , CH_2IBr ,
 CH_2I_2 , 1- $\text{C}_3\text{H}_7\text{I}$, 2- $\text{C}_3\text{H}_7\text{I}$, 1- $\text{nC}_4\text{H}_9\text{I}$, 2- $\text{nC}_4\text{H}_9\text{I}$, 1-iso- $\text{C}_4\text{H}_9\text{I}$) were quantified using m/z
127 and brominated compounds (CH_2Br_2 , CH_3Br , 1,3- $\text{C}_3\text{H}_6\text{Br}_2$) were quantified us-
ing m/z 79 and 81 at a 1 : 1 ratio. A five point calibration was done in the range be-
tween 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 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 derivatiza-
tion the α -cyclodextrin coating was eluted with ultrapure water (20 mL), then 25 μL
 N,N -dimethylaniline (1 $\mu\text{g mL}^{-1}$ 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).

$$I_{\text{seawater}} = \text{I}^- + \text{IO}_3^-$$

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 ($283.9 \mu\text{mol L}^{-1}$) 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 $0.25 \mu\text{m}$ (CS Chromatographie Servieve, Langenwehe, Germany) with a temperature program starting at 50°C (for 3 min), then heating up at $30^\circ\text{C min}^{-1}$ to 220°C (for 3 min). The mass spectrometer measured in electron ionisation mode at 70 eV, the

Emission of iodine containing volatiles by selected microalgae species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emission of iodine containing volatiles by selected microalgae species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



plankton concentrate with the cultivated diatom cultures 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 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

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 I₂ emissions

The I₂ emission rate was calculated by dividing the amount of I₂ 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 O₃) compared to conditions where no ozone is present (0 ppb O₃). 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 I₂ emission rate on the ozone level. The ozone-dependent increase in the I₂ emission rate of the other samples indicates that iodide, which is present at the air/water interface, is oxidised by ozone to form I₂, 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 I₂ emission rate ($[I_2 \text{ at } 100 \text{ ppb ozone}] - [I_2 \text{ at } 0 \text{ ppb ozone}]$) 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 I₂ 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

Emission of iodine containing volatiles by selected microalgal species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emission of iodine containing volatiles by selected microalgal species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 I₂ emission rate for the two diatom samples and for the F/2 medium. Therefore the formation ratio of I₂ in dependence on O₃ was calculated by $R(I_2) = n(I_2)/n(O_3)$, with $n(I_2)$ = amount of I₂ formed and $n(O_3)$ = amount of O₃ 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 I₂. 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 I₂ 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 I₂ 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 I₂ 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 I₂ (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-

Emission of iodine containing volatiles by selected microalgae species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



sion flux of the iodocarbons was lower compared to the calculated flux at a natural site in Roscoff, France, an observation which emphasizes 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. glacialis*) 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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**Emission of iodine
containing volatiles
by selected
microalgal species**

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Emission of iodine
containing volatiles
by selected
microalgae species**

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Hoffmann, T., O'Dowd, C. D., and Seinfeld, J. H.: Iodine oxide homogeneous nucleation: an explanation for coastal new particle production, *Geophys. Res. Lett.*, 28, 1949–1952, 2001.
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**Emission of iodine
containing volatiles
by selected
microalgal species**

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Emission of iodine
containing volatiles
by selected
microalgal species**

U. R. Thorenz et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Emission of iodine containing volatiles by selected microalgal species

U. R. Thorenz et al.

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

Sample		F/2 medium background Range (Mean)	<i>P. glacialis</i> Range (Mean)	<i>M. helysia</i> Range (Mean)	plankton concentrate Range (Mean)
CH ₃ I	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 ₂ ICl	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 ₂ I 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 α	$\mu\text{g L}^{-1}$	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 ₃ H ₆ Br 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 α was measured for each sample once halocarbons, iodide, iodate mean values and ranges are calculated from 6 replicates.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emission of iodine containing volatiles by selected microalgae species

U. R. Thorenz et al.

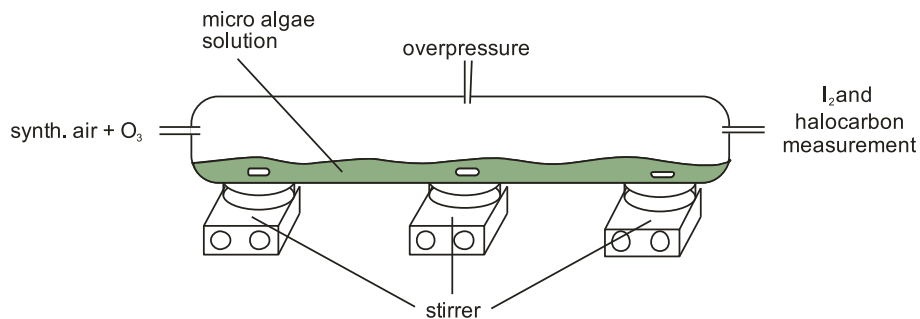


Figure 1. Experimental setup of the chamber with the phytoplankton suspension.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Emission of iodine containing volatiles by selected microalgal species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

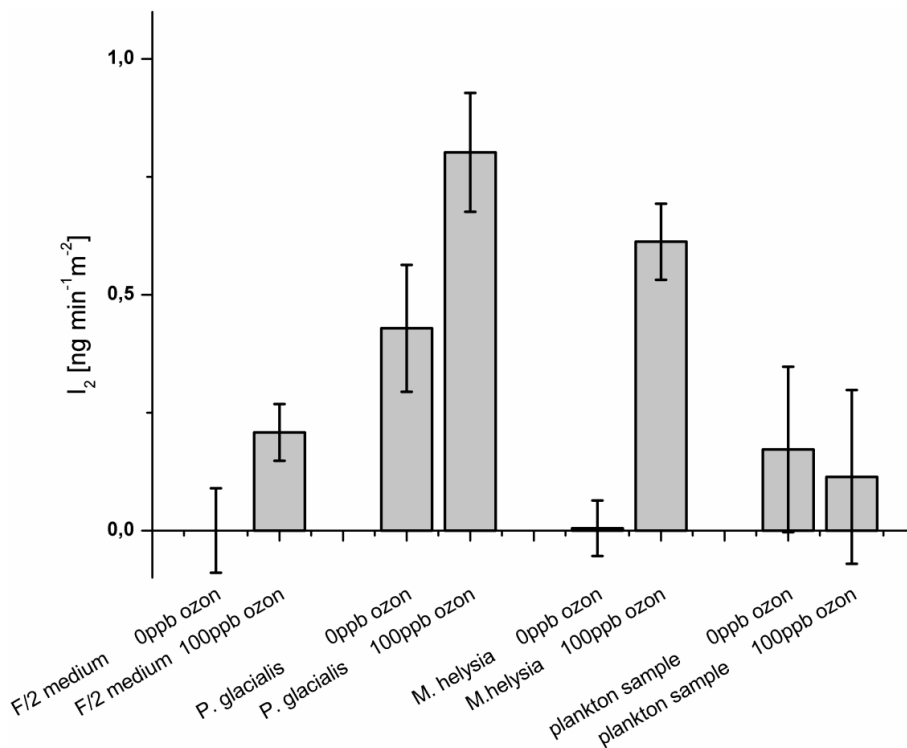


Figure 2. Iodine emission rates normalized for the surface area of the different samples at 0 ppb and 100 ppb ozone. The error bars represent the standard deviation of the three replicates of each experiment.

Emission of iodine containing volatiles by selected microalgae species

U. R. Thorenz et al.

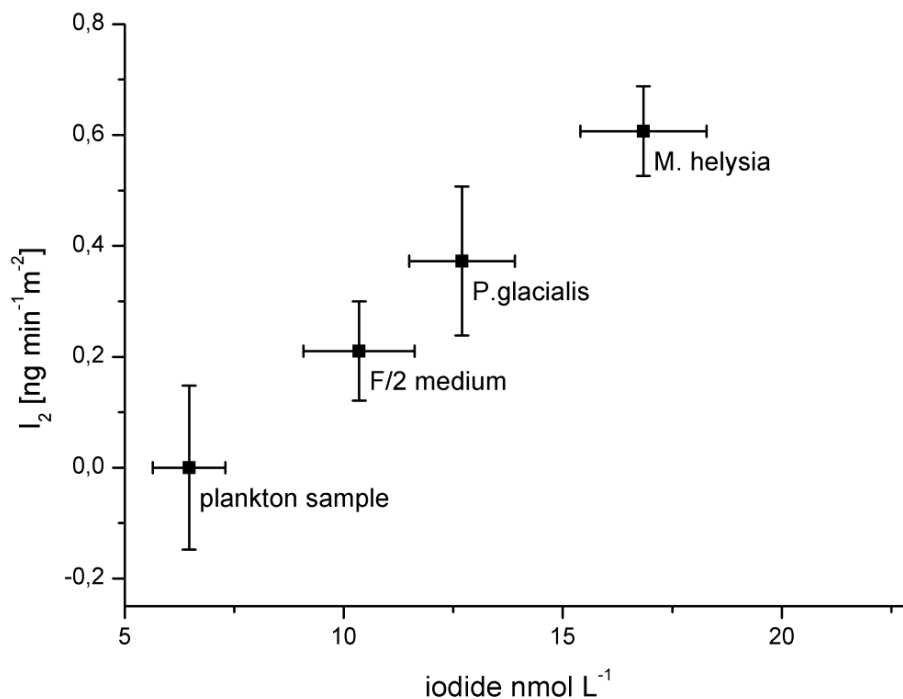


Figure 3. Correlation of the change in the I₂ emission in dependency on the iodide concentration in the phytoplankton suspension.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Emission of iodine containing volatiles by selected microalgae species

U. R. Thorenz et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

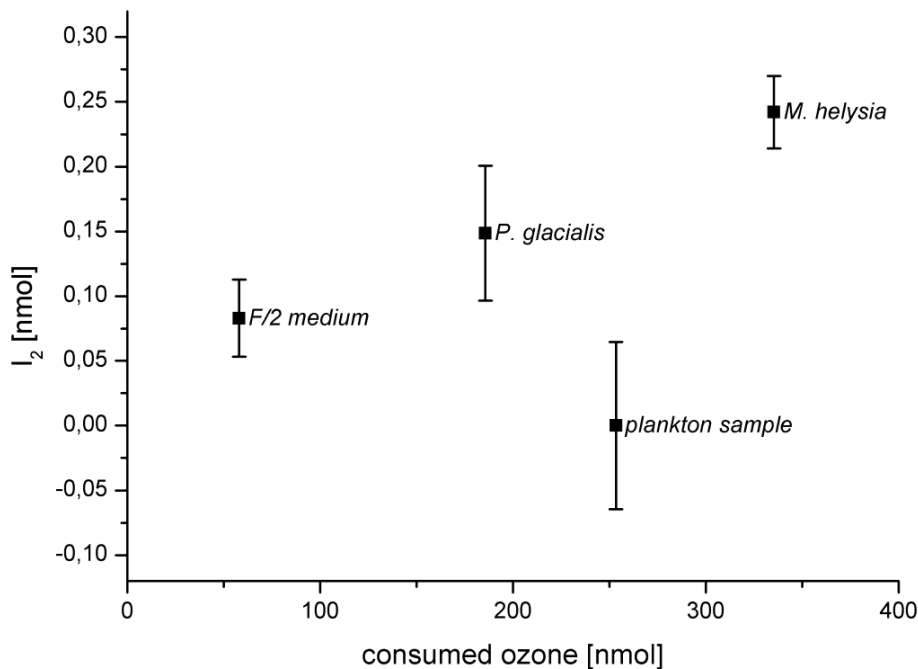


Figure 4. Function of the change in the I_2 emission rate in dependency of the amount of consumed ozone.