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Low-molecular-weight organoiodine and organobromine compounds released by polar macroalgae – The influence of abiotic factors

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Abstract The influence of temperature, light, salinity and nutrient availability on the release of volatile halogenated hydrocarbons was investigated in the Antarctic red macroalgal species *Gymnogongrus antarcticus* Skottsberg. Compared to standard culture condition, an increase in the release rates of iodocompounds was generally found for the exposure of the alga to altered environmental conditions. Macroalgae exhibited higher release rates after adaptation for two months to the changed factors, than after short-term exposure. Monitoring the release rates during a 24 h incubation period (8.25 h light, 15.75 h darkness) showed that changes between light and dark periods had no influence on the release of volatile halocarbons. Compounds like bromoform and 1-iodobutane exhibited constant release rates during the 24 h period. The formation mechanisms and biological role of volatile organohalogens are discussed. Although marine macroalgae are not considered to be the major source of biogenically-produced volatile organohalogens, they contribute significantly to the bromine and iodine cycles in the environment. Under possible environmental changes like global warming and uncontrolled entrophication of the oceans their significance may be increase.

Dedicated to Professor Dr. Klaus G. Heumann on the occasion of his 60th birthday

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Introduction

It is known that several halogenated organic compounds are formed in marine organisms like macroalgae [1], sponges, and worms [2]. For a long time, scientists focused their research only on complex halogenated molecules, their metabolic pathways, and their possible applications [2]. However, since the discovery of a periodical formation of a stratospheric ozone hole over the South polar region in spring (e.g. [3]), interest also shifted to more volatile halogenated hydrocarbons. Halogen radicals, originated after photodissociation from volatile halocarbons and released into the atmosphere, participate in several catalytic atmospheric reaction cycles, including the regulation of the stratospheric and tropospheric ozone layers. Therefore, the identification and investigation of sources and sinks of volatile halogenated organic compounds is of special interest. The oceans have been identified as a major source of these compounds, but terrestrial sources may also have to be considered [4, 39]. In the marine environment, several organisms are implicated in the release of volatile halocarbons, including a wide range of different macroalgal species [5, 6], ice algae [7], and also phytoplankton [8]. However, there may be other hitherto unknown sources contributing to the halocarbon concentrations found in the oceans. Although also some chlorinated hydrocarbons were released by marine macroalgae [5, 9], the major compounds identified were brominated and iodinated hydrocarbons. In contrast to the terrestrial environment, where only very low or no concentrations of volatile brominated and iodinated compounds were found [10], marine organisms seem to be negligible contributors for chlorinated compounds [8, 9]. Whereas in stratospheric photochemical reactions mainly chlorinated and brominated compounds are of interest [11], iodocompounds contribute more significantly to photochemical reactions in the troposphere [12]. In contrast to chloro- and bromocarbons, organic iodinated compounds are more easily photo-dissociated. Estimation of the global cycle of iodine and its contribution to tropospheric reactions re-

Table 1 Environmental conditions during the incubation period

	Light	Nutrients	Salinity	Temperature
Standard culture conditions	15 µmol m^{-2} s^{-1}	Filtered North Sea water (Provasoli enriched)[a]	34‰	0 °C
Short-term exposure[b]	30 µmol m^{-2} s^{-1}	Filtered North Sea water	27‰	10 °C
Long-term exposure[c]	30 µmol m^{-2} s^{-1}	Filtered North Sea water	27‰	10 °C

[a] Wiencke [15]
[b] conditons altered prior to incubation
[c] conditions altered two months before incubation

Table 2 Instrumental detection limit, methodical detection limit, recoveries and purge efficiencies of volatile halocarbons obtained for a 100 mL water sample by GC-ECD on two different analytical columns (BP 624 and PoraPLOT-Q)

	Instrumental detection limit[a] [pmol L^{-1}]		Methodical detection limit[b] [pmol L^{-1}]		Purge efficiency[c] [%]	Recovery[d] [%]
	BP 624	PoraPLOT-Q	BP 624	PoraPLOT-Q		
Iodoethane	0.0040	0.0058	0.045	0.066	88.6 ± 3.3	93.7 ± 1.5
2-Iodopropane	0.012	0.036	0.175	0.444	80.0 ± 13.0	100 ± 0
1-Iodopropane	0.0050	0.0070	0.070	0.098	70.8 ± 2.4	97.5 ± 2.6
Chloroiodomethane	0.0007	0.0018	0.024	0.064	28.3 ± 4.9	54.7 ± 6.8
2-n-Iodobutane	0.0065	–	0.082	–	80.2 ± 11.3	92.0 ± 1.4
Diiodomethane	0.0067	0.089	0.616	8.25	10.8 ± 2.1	24.1 ± 14.8
Bromoform	0.0019	0.024	0.116	1.45	16.4 ± 9.5	34.2 ± 5.0

[a] $D_i = \frac{3\sqrt{2b}}{s}$ s = sensitivity obtained from the gradient of the calibration curve; b = background noise

[b] $D_m = 2\sigma_{n-1}t_{n-1}\sqrt{1+\frac{1}{m}}$ calculated on a 95% confident level (n = 4, m = 2)

[c] $purge-efficiency = \frac{x_1}{\sum_n x_n}100\%$ x_1 = first purging; x_n = n consecutive purging

[d] µL hexane standard (100–200 pg μL^{-1}) added to 100 mL pre-purged seawater sample

quires identification of the volatile forms of iodine and the investigation of its sources. Data about natural sources of iodinated compounds are still scarce. Marine and polar macroalgae form several organoiodine species and release them into the oceans [13, 14], and Antarctic ice algae were also found to contribute to the iodocarbon release into the environment [7]. However, to estimate the significance of the contribution of biogenic sources to atmospheric iodine more detailed investigations are necessary.

In addition to a recent screening study about the release of volatile iodocompounds by polar, temperate and subtropic macroalgae [14], in the present investigation the influence of various abiotic factors like temperature, light, salinity and nutrient availability on the release of volatile iodocompounds is studied using the Antarctic red macroalga *Gymnogongrus antarcticus* Skottsberg.

Experimental

The Antarctic red algal species *Gymnogongrus antarcticus* Skottsberg was chosen due to its ubiquitous occurrence in the Antarctic environment and high release rates of several volatile halogenated compounds. Unialgal cultures of *G. antarcticus*, isolated at King George Island, South Shetlands, were held under temperature conditions similar to the Antarctic habitat (0 ± 1 °C). Cool-white fluorescent neon tubes (Osram L58/W19) were used to simulate photointensity and photoperiods at King George Island. At the time of the investigation, the photoperiod was 8.25 h light and 15.75 h darkness. As culture medium, filtered North Sea water enriched with nutrients was used [15]. A weekly-change of the medium and continuous gassing with filtered air avoided nutrient limitation and low inorganic carbon levels. Using unialgal cultures, sterilized equipment and filtered seawater (filter: 0.2 µm Satorious Sartobran II), contamination of the cultures by microorganisms was minimized.

To investigate the influence of different abiotic factors on formation of organoiodine and organobromine compounds, macroalgae were exposed to variations in temperature, photon fluence rate, salinity and nutrient concentration (see Table 1). The experiments were performed under optimal culture conditions, and under short-term and long-term exposure to varied conditions. For short-term exposure, algal samples held under optimal culture conditions were directly incubated in the incubation vessel at low salinity and nutrient level, and elevated temperature for 24 h. For long-term exposure, the macroalgae were held under the altered conditions two month prior to the incubation.

For the determination of the halocarbon release, duplicates of whole macroalgae plants were held for 24 h in special incubation vessels filled with culture medium. The incubation vessels had a volume of 380 to 420 mL containing a glass grating in the lower part of the vessel. Increasing concentrations of the released compounds and nutrient limitations in close vicinity of the algae were avoided by continuously stirring of the medium during the incubation period. The grating, thereby, avoided injury of the algal sample while stirring the medium. To detect the released compounds, duplicates of 100 mL of the algal medium were taken from each of the incubated macroalgae samples and analyzed by purge-and-trap gas chromatography and electron capture detection (p&t-GC-ECD). The seawater samples (100 mL) were injected into a purging unit covered with aluminium foil to reduce possible decomposition of light-sensitive iodinated compounds. The compounds were removed from the seawater by a helium gas flow (30 min at 45 mL min^{-1}, pre-cleaned by an OMI-2 purifyer, Supelco), trapped on a cryotrap cooled by liquid nitrogen, and, after the purge process was completed, transferred onto a capillary gas chromatographic column by thermodesorption with boiling water.

The cryotrap consisted of a 20 cm stainless steel tube with an inner diameter of 1 mm. Two centimeter of the tube were filled with glass balls (25 µm, treated with DMS) and sealed with small plugs of DMS treated glass wool. Therefore, losses of volatile halocarbons during the purging procedure were avoided, which frequently was observed when using capillary columns or unfilled stainless steel tubes. Before entering the cryotrap, the gas stream passed a glass tube filled with activated potassium carbonate (activated by heating for 5 min with a heating pistol under constant flow with pre-cleaned helium).

Seven different iodinated substances and bromoform were monitored during the experiment (see Fig. 1). The compounds were identified and verified by retention time on two different types of fused silica capillary columns: A. BP-624 (SGE, 30 m × 0.32 mm × 1.8 µm; temperature program: 40 °C held for 20 min, 10 °C min^{-1} to 200 °C, 200 °C held for 9 min), B. PoraPLOT-Q (Chrompack, 25 m × 0.53 mm × 20 µm; temperature program: 60 °C held for 1 min, then raised to 200 °C at 15 °C min^{-1}, 200 °C held for 50 min). Quantification was carried out by comparison with standards of known concentrations of the pure compounds diluted in methanol (standard concentrations between 5 to 900 pg μL^{-1}). The detection limits of the various halocarbons were from 0.024 pmol L^{-1} for chloroiodomethane (CH_2ClI) to 0.62 pmol L^{-1} for diiodomethane (CH_2I_2) with an analytical precision of 2.1 to 13% (n = 4). Purge efficiencies ranged from 11% for diiodomethane to 89% for iodoethane (CH_3CH_2I) (Table 2). The release rates reported were corrected for culture medium blanks and purge efficiencies.

Results and discussion

Analysis of volatile halocarbons

The use of only an ECD for identification contains the risk of misinterpretation of the results due to peak overlapping, especially when analyzing environmental samples for volatile halocarbons. As mass spectrometric identification as the most reliable method is sometimes not available or lacks sensitivity, the use of capillary colums of different properties together with EC detection is an accepted method for verification. Recently, a purge-and-trap method coupled to a GC-MIP-AED was optimized to analyze volatile halocarbons in environmental samples with detection limits for some volatile halocarbons close to those obtained by an ECD [38]. Although the sensitivity of an AED is in general lower compared to an ECD, the method has a higher selectivity due to an element specific detection.

For identification and verification, the samples were analyzed on a BP-624 and a PoraPLOT-Q capillary column. A separation was possible on both columns for iodoethane, 1-iodopropane, 2-iodopropane, 2-iodobutane, chloroiodomethane, diiodomethane, bromoform. Due to peak overlapping, 2-iodobutane was quantified only on the BP-624 column, while 1-iodobutane was quantified only on the PoraPLOT-Q column. For chromatograms on separation of the halocarbons refer to Giese et al. [14]. The determination of allyliodide (CH_2CHCH_2I), 1-iodoethanol (CH_2ICH_2OH), and 2-iodo-2-methylpropane ($CH_3C[CH_3]ICH_3$) was not possible on both columns either due to their thermal instability or due to an insufficient response on the ECD. When measuring 1-chloro-3-iodopropane ($CH_2ClCH_2CH_2I$), severe memory effects were encountered, and consequently, this compound was not determined. In general, compared to the PoraPLOT-Q column, lower detection limits were obtained with the BP-624 column. Especially for less volatile compounds, the difference was about an order of magnitude.

Release of volatile halocarbons by polar macroalgae

Under standard culture conditions (see Table 1), the macroalgae were healthy and fresh with solid branches of a dark-red color. Short-term change of light, temperature, salinity and nutrients had no visible influence on the appearance of the algae. The algal tissues still appeared dark-red with

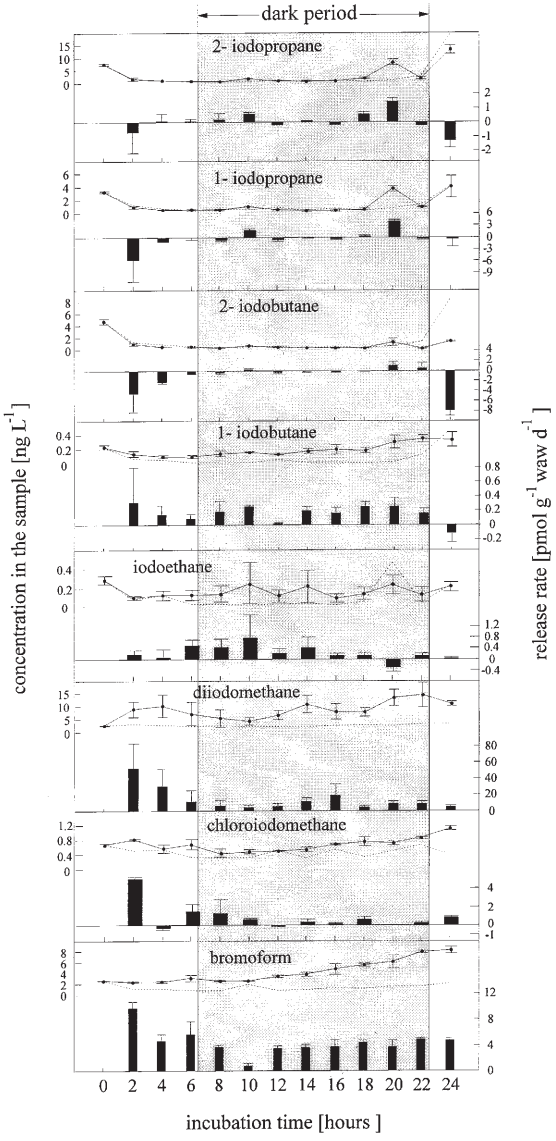

Fig. 1 Release rates of different organohalogen compounds monitored during a 24 h incubation experiment under standard culture conditions. The concentrations of the single compounds detected in the seawater culture medium are given above the release rates. The dotted lines indicate the blank levels in the seawater medium during the incubation period. Error bars are the standard deviation of three samples. waw = wet algal weight

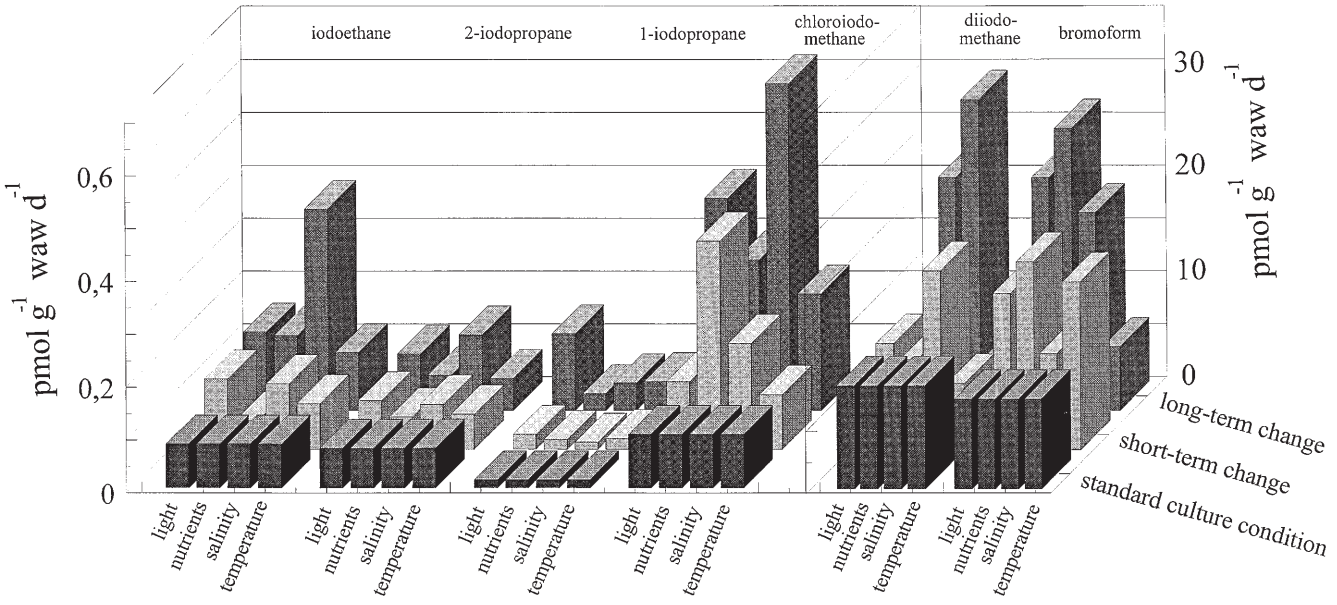

Fig. 2 Variation of the release rates of volatile organohalogens determined under altered environmental conditions. waw = wet algal weight

no sign of the onset of decay. However, algal samples exposed to the altered conditions two months before the incubation showed a slight color change to light brown, but no visible signs of decay. A similar effect was also observed by Laturnus et al. [16] in other macroalgal species exposed to unfavorable growth conditions.

The results of halocarbon release monitored during a 24 h incubation under standard culture conditions are given in Fig. 1. Whereas 1-iodopropane ($CH_3CH_2CH_2I$), 2-iodopropane ($CH_3CH_2ICH_3$) and 2-iodobutane ($CH_3CH_2CHICH_3$), apparently, showed no significant release during the incubation periods, 1-iodobutane ($CH_3CH_2CH_2CH_2I$), iodoethane, diiodomethane and chloroiodomethane exhibited more constant increase and release rates, respectively. Additionally detected bromoform ($CHBr_3$), known as the major released volatile halocarbon and used as a comparison for the brominated compounds, also showed constant release rates during the whole incubation period resulting in a constant increase of the bromoform concentration in the seawater. The change between light and darkness appeared to have no influence on the halocarbon release.

Figure 2 shows the effects of changed conditions on the release of volatile iodinated compounds. Obviously, both short-term and long-term exposure generally led to changed release rates of the compounds compared to the release rates obtained under standard culture conditions. In most cases, algal samples exposed to the altered conditions two months before the incubation, exhibited higher release rates of volatile iodocompounds and bromoform than samples after short-term exposure.

Influence of changed abiotic factors on release of volatile halocarbons

The Antarctic region is known for extreme seasonal variations in climatic conditions with high temperature differences between summer and winter, 24 h of light in summer and 24 h of darkness in winter [17]. However, in the Antarctic marine environment temperature, nutrients and salinity stay almost constant throughout the year and changes may influence only macroalgae occurring in the tidal zone. In contrast, the changes in photon fluence rates and photoperiods effect macroalgae both in the intertidal and subtidal habitat [18]. At present, only the influence of light on release rates of volatile halocarbons has been reported (e.g. [19]). In general, lower release rates were found in macroalgae kept in darkness. Therefore, a photosynthetic formation mechanism was postulated. However, recently a more detailed study of the influence of different light conditions on Antarctic macroalgae using different photoperiods and photon fluence rates showed that algae held in darkness several months, still exhibited considerable release rates of volatile organohalocarbons [16]. Apparently, the formation mechanism may be supported by photosynthesis, but certainly it does not depend on it. These results may be important for the atmospheric photochemical reactions in the Antarctic region. A continuous release and a lack of photodegradation of volatile halocarbons during the long Antarctic winter may lead to an accumulation of these compounds in the sea. After sea ice break-up in spring, they may be a hitherto unknown source of compounds affecting atmospheric photochemical reactions.

Formation of volatile halocarbons in macroalgae

Due to the high variety of different halogenated organic compounds formed by macroalgae [2], the formation

mechanisms of the single compounds are difficult to identify. In general, the formation of organohalogen compounds is based on an enzyme-controlled mechanism [20]. Haloperoxidases, an enzyme group detected in a wide range of marine and terrestial organisms [21, 22] can catalyze the oxidation of halogens in the presence of hydrogen peroxide to form halogenated organic compounds (1).

$$\text{organic matter} + H_2O_2 + X^- + H^+ \xrightarrow[\text{e.g. haloperoxidases}]{\text{enzymic catalyzation}} \text{halogenated compounds} \quad (1)$$

$X^- = Cl^-, Br^-, I^-$

Recently, van Pée [23] reported a novel type of halogenating enzymes called halogenases, which instead of using hydrogen peroxide require NADH (the reduced form of nicotinamide adenine dinucleotide, a co-enzyme involved in biological oxidation-reduction processes). Due to their substrate specificity and regioselectivity, which is lacked by haloperoxidases, halogenases are more likely to be the enzymes involved in halometabolite formation.

Although the halogenation of organic matter in marine macroalgae are basically understood, the formation mechanisms for the variety of halogenated C_1 to C_4 compounds remain poorly known. Metabolic pathways by which volatile halocarbons like bromoform or dibromomethane are synthesized were discussed by several authors [24–26]. Intracellular halogenation of ketones present in marine algae followed by decay *via* the pH dependant haloform reaction can lead to the formation of polyhalogenated methanes like bromoform or dibromomethane. Significant linear correlations between these two compounds were an indication for the occurrence of this mechanism [27]. Another pathway may be the reaction of hypobromeous acid, an extremely reactive species, with organic matter to form volatile halocarbons. Hypobromeous acid can be formed by haloperoxidases located near the macroalgal surface and then released into seawater [28]. Mixed halogenated hydrocarbons like dibromochloromethane or chloroiodomethane probably were also directly formed by macroalgae [25] or by nucleophilic substitution of, e.g., bromoform or diiodomethane with chloride ions present in the seawater [29]. A direct incorporation of chlorine into organic matter may not be possible as chlorinating activity necessary for the enzymic formation of organochlorine compounds was not detected in marine macroalgae [30]. However, Geigert et al. [31] reported the formation of bromochlorocompounds in the presence of bromoperoxidase, an evidence that chloroperoxidases may not be absolutely necessary for the formation of chlorinated compounds. Halogenated C_2 to C_4 hydrocarbons are not available by the haloform reaction. The formation mechanism of these compounds is still unknown. A suggestion is the enzymic halogenation of alkenes [31].

Methyl halides like bromomethane, apparently, were not formed by enzymic reaction *via* haloperoxidases as no correlation between halogenating activity and methyl halide release was found for polar macroalgae [32]. An earlier postulated mechanism involving dimethylsulfoniopropionate (DMSP) as a precursor [33] is unlikely as no correlation between methyl halide releases and DMSP concentrations in the macroalgae was found [32]. At present, a third possibility based on the catalysis *via* a methyltransferase reaction is discussed [34, 35]. A methyltransferring enzyme isolated from marine macroalgae and higher plants catalyzed the S-adenosyl-L-methionine-dependent methylation of the halides Cl^-, Br^-, I^- to the respective methyl halides.

Environmental effects

The results given in Fig. 2 showed that alterations of environmental conditions induced the release of higher rates of volatile halocarbons by macroalgae. For short-term changes, stress may be the reason for observed higher release rates. However, during long-term exposure to altered conditions, stress cannot be the reason, as adaptation of macroalgae to changed conditions like, e.g., light already occurs after 2–4 weeks [36]. Environmental changes like temperature increase discussed as the effect of global warming, and higher nutrient availability due to intensive use of fertilizer in agricultural treatment may influence the formation of volatile halocarbons. The change of abiotic factors led to a variation of the release of volatile organohalogens by macroalgae (Table 3). However, the question still remains how important are marine macroalgae as a source for volatile halocarbons when it comes to a global scale. Estimations of the global emissions of

Table 3 Estimation of the annual atmospheric input of iodine and bromine on a global scale under varied abiotic factors using release rates determined in this study from the long-term incubation, a global algae biomass of 6×10^{13}g [37] and assuming a 100% transfer from the oceans into the atmosphere

	Iodine release [10^6 g yr^{-1}]	Bromine release [10^6 g yr^{-1}]
Standard culture conditions	46.9	41.6
Increasing photon fluence rate	39.8	109.5
Increasing temperature	25.6	29.3
Decreasing salinity	141.3	106.2
Decreasing nutrients	103.6	127.8

Table 4 Estimated global atmospheric emissions of bromine and iodine via organobromine and organoiodine compounds released by marine macroalgae

	Bromine [gr yr^{-1}]	Iodine [gr yr^{-1}]
Marine algae[a, c]	10^8–10^9	10^7–10^8
Marine algae[b, d]	10^8–10^{10}	
Oceans[a]	10^{10}–10^{12}	10^{11}–10^{12}
Anthropogenic[b]	10^{10}–10^{11}	

[a] Giese et al. [14]
[b] Goodwin et al. [19]
[c] polar, temperate, subtropic macroalgae
[d] temperate kelp and non-kelp macroalgae

volatile organohalogens showed that macroalgae contribute significantly to the bromine and iodine cycles (Table 4). Compared to the emissions from the global oceans, marine macroalgae may not be the major source for these compounds. Other marine organisms like icealgae and phytoplankton and yet so far unknown sources may also require consideration. However, their response to variation in environmental factors still has to be seen.

Conclusion

The change of the abiotic factors photon fluence rate, nutrient concentration, temperature and salinity influenced the formation of volatile organoiodine and organobromine compounds by marine macroalgae. However, at present only varying photon fluence rates may significantly effect the release of halocarbons into the environment. Global warming and further uncontrolled eutrophication of the oceans may change the present conditions, probably resulting in the future in an unknown increase of the emission of volatile halocarbons into the global environment.

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