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Release of Volatile Iodinated C_1-C_4 Hydrocarbons by Marine Macroalgae from Various Climate Zones

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Marine macroalgae are known sources of a wide range of volatile brominated hydrocarbons, but before now far less attention was paid to their contribution to the input of volatile organoiodine compounds into the environment. In this work, 29 species of subtropic, temperate, and polar macroalgae were investigated for their release of volatile iodocompounds. Iodoethane, 1-iodopropane, 2-iodopropane, 1-iodo-2-methylpropane, 1-iodobutane, 2-iodobutane, diiodomethane, and chloroiodomethane were identified and their release rates determined. Additionally, release rates of bromoform and dibromomethane were evaluated for comparison with release rates of iodinated compounds. The highest release rates were found for bromoform with up to 253 pmol g^{-1} wet algal weight d^{-1}, followed by diiodomethane and dibromomethane with up to 29.3 and 18.3 pmol g^{-1} wet algal weight d^{-1}, respectively. In contrast to bromoform, which was released in higher rates by subtropic macroalgae as compared to polar macroalgae, all iodinated compounds revealed lower release rates by macroalgae from subtropic regions, possibly due to decreasing stability of iodinated hydrocarbons at higher temperatures. The annual input of iodine into the atmosphere by macroalgae was estimated as 42 ton. Compared to a total global emission of 10^6 ton yr^{-1}, macroalgae apparently participate only in 0.005% of the total iodine emission. However, in coastal regions with high macroalgae biomass and in the polar environment, macroalgae may significantly contribute to the local input of iodine into the atmosphere.

Introduction

Since the discovery of the ozone hole over Antarctica more than 10 years ago, the atmospheric chemistry of volatile halogenated hydrocarbons has gained considerable scientific and public interest due to their role as a major source for halogen radicals in the atmosphere (*1*−*3*). Research on stratospheric ozone depletion has mainly concentrated on chlorine and bromine compounds (*4, 5*), whereas studies on tropospheric ozone also considered iodine chemistry (*6*). Chameides and Davis (*7*) suggested a significant role for iodine in tropospheric photochemistry because organic iodine compounds photodissociate more easily than the corresponding chlorine and bromine compounds. For example, iodine atoms are formed in the troposphere by dissociation of iodomethane (CH_3I). These iodine radicals are very reactive and can initiate several catalytic cycles, e.g., the destruction of troposheric ozone. Despite their short lifetime in the troposphere of less than 10 days (*8*), organic iodine compounds may also be transported into the stratosphere by convective clouds (*6*).

Beside industrially (anthropogenically) produced hydrocarbons, such as freons and halons, several biogenically formed compounds represent a source of halogen radicals in the atmosphere. In contrast to the anthropogenic input, which can be derived from industrial production data, estimations of the biogenic input are rather difficult, especially since natural sources are still poorly known. It is assumed that iodinated compounds are exclusively of biogenic origin, as no significant anthropogenic sources are known (*9*). The oceans are believed to be a main source of iodinated compounds (*10*−*16*). However, at present, information on their origin in the oceans is sparse. Lovelock (*10*) identified iodomethane as the first iodine species to be found in the atmosphere and in seawater. During his investigations, he discovered a 1000-fold higher concentration in algal beds of southwest Ireland as compared to open-ocean concentrations (*17*). From these data, he suggested that macroalgae may be a natural source of iodomethane in the oceans.

Further investigations showed the release of volatile halogenated hydrocarbons by macroalgae from various climate regions (*18*−*25*). For a long time, iodomethane was believed to be the only carrier of iodine into the atmosphere (*11*). However, recent studies showed that other iodinated compounds, such as iodoethane (CH_3CH_2I), 1-iodopropane ($CH_3CH_2CH_2I$), 2-iodopropane (CH_3CHICH_3), 1-iodobutane ($CH_3CH_2CH_2CH_2I$), 2-iodobutane ($CH_3CH_2CHICH_3$), diiodomethane (CH_2I_2), and chloroiodomethane (CH_2ClI), may also contribute to the biogeochemical cycle of iodine (*15, 26*−*28*). These compounds were detected in seawater, in air samples, and as release products of some marine macroalgae (*25, 29, 30*) and ice algae (*31*).

Since data on the production and release of these compounds by macroalgae are rather limited, the significance of algae as a natural source for atmospheric iodine is difficult to estimate. The aim of this study was to investigate the release of volatile iodinated hydrocarbons by macroalgae from various climatic regions to provide a more detailed view over a wider range of different macroalgae species. Emphasis was given to the investigation of macroalgae from polar regions because information on these regions are scarce. Furthermore, in the polar environment the released compounds can have a locally limited but more direct impact on the troposheric and stratospheric ozone layers.

Methods and Techniques

Twenty-nine macroalgae species from polar, temperate, and subtropic regions were investigated for their release of volatile iodinated hydrocarbons (Table 1). All algae were cultivated at the Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, in 1-L beakers at temperatures of 0 (polar), 10 (temperate), or 23 °C (subtropic) as described by Wiencke (*32*). Sterile water from the North Sea (34‰, filtered through a Sartorious Sartobran II 0.2-μm filter) enriched with nutrients

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TABLE 1. Species of Polar, Temperate, and Subtropic Macroalgae Used in This Study

algal species	collection site
Polar Macroalgae	
brown algal species	
Alaria esculenta (L.) Greville	Iceland
Adenoscystis utricularis (Bory) Skottsberg	Puerto William, Chile
green algal species	
Lambia antarctica (Skottsberg) Delepine	King George Island, Antarctica
Enteromorpha compressa (L.) Nees	Spitsbergen, Norway
red algal species	
Phyllophora appenticulata Skottsberg	King George Island, Antarctica
Pantoneura plocamiodes Kylin	King George Island, Antarctica
Delesseria lancifolia (J.D. Hooker) J. Agardh	King George Island, Antarctica
Neuroglossum ligulatum (Reinsch) Skottsberg	Signy Island, Antarctica
Ballia callitricha (J. Agardh) Kuetzing	King George Island, Antarctica
Gigartina skottsbergii (Bory) Setchell and Gardner	King George Island, Antarctica
Phyllophora ahnefeltioides Skottsberg	King George Island, Antarctica
Rhodymenia subantarctica Ricker	King George Island, Antarctica
Georgiella confluens (Reinsch) Kylin	King George Island, Antarctica
Porphyra endivifolium (A. and E.S. Gepp) Chamberlain	King George Island, Antarctica
Plocamium cartilagineum (Linne) Dixon	King George Island, Antarctica
Phycodris quercifolia Skottsberg	King George Island, Antarctica
Gymnogongrus antarcticus Skottsberg	King George Island, Antarctica
Iridea cordata Turner (Bory)	King George Island, Antarctica
Temperate Alga	
green algal species	
Acrosiphonia sp.	Helgoland, North Sea
Subtropic Algae	
green algal species	
Enteromorpha compressa (L.) Nees	Hainan Island, China
Enteromorpha intestinalis (L.) Nees	Hainan Island, China
Ulva fasciata Delile	Hainan Island, China
Ulva conglobata Kjellman	Hainan Island, China
Struvea sp.	Hainan Island, China
red algal species	
Laurencia sp.	Hainan Island, China
Laurencia cartilaginea Yamada	Hainan Island, China
Hypnea spinella (C. Agardh) Kuetzing	Hainan Island, China
Gracilaria changii (Xia and Abott) Abott	Hainan Island, China
Gelidiopsis intricata (Agardh) Vickers	Hainan Island, China

was used as the culture medium and exchanged weekly to avoid nutrient limitations. Natural light conditions were simulated by illumination with cool white fluorescent neon tubes (OSRAM L58/W19) at photon flux rates between 6 and 30 μmol m^{-2} s^{-1} measured in air at the height of the algae samples. For polar macroalgae, photoperiods were adjusted to match the seasonal fluctuations on King George Island, South Shetlands, Antarctica. At time of the study, photoperiods corresponded to 5.75 h (June, Antarctic winter). Photoperiods for temperate and subtropic algae were fixed at 16 and 12 h, respectively.

The release rates of halogenated hydrocarbons were determined according to a method described by Laturnus (*24*). The wet weight of the algae samples was determined after carefully blotting with paper tissue. Duplicates of whole plants of each algae species were placed in two incubation glass vessels filled with culture medium and stored for 48 h under culture conditions. To avoid nutrient limitation and increasing concentrations of released substances in close vicinity of the algae, the medium was stirred continuously during the incubation. Two water samples were taken from each of the incubated algae samples and stored in the dark at 4 °C prior to analysis within the following 4 weeks.

Volatile halogenated hydrocarbons were measured by a purge-and-trap system coupled to a gas chromatograph (Hewlett-Packard 5890A series II) with electron capture detection (ECD). Seawater samples (100 mL) were injected into the purging unit, which was covered with aluminum foil to reduce possible decomposition of light-sensitive iodinated compounds. The compounds were purged from the sample by a helium gas flow of 45 mL min^{-1} for 30 min. Water was removed from the purge gas by passing through a glass tube filled with predried potassium carbonate. The analytes were collected on a cryotrap cooled by liquid nitrogen. After the purge process was completed, the analytes were injected onto a high-resolution gas chromatographic column by thermodesorption with boiling water. Separation of the volatile halogenated hydrocarbons was carried out on a BP-624 column (SGE, 30 m × 0.32 mm × 1.8 μm). The temperature was maintained at 40 °C for 20 min, then raised at 10 °C min^{-1} to a final temperature of 200 °C, and held for 9 min. For verification, half of the sample was analyzed on a PoraPLOT-Q column (Chrompack, 22.5 m × 0.53 mm × 20 μm). The temperature was kept at 60 °C for 1 min, then raised at 15 °C min^{-1} to a final temperature of 200 °C, and held for 50 min. Retention times of standard dilutions of commercially available iodinated and brominated compounds prepared in methanol were used for peak identification.

The method allowed separation on both columns of the following volatile halogenated hydrocarbons (Figure 1A,B): CH_3CH_2I, $CH_3CH_2CH_2I$, CH_3CHICH_3, CH_2ClI, CH_2I_2, $CH_2ClCH_2CH_2I$ (1-chloro-3-iodopropane), and $CHBr_3$. Due to peak overlapping, $CH_3CH_2CHICH_3$, $CH_3CH(CH_3)CH_2I$ (1-iodo-2-methylpropane), and CH_2Br_2 were quantified only on the BP-624 column (Figure 1A), while CH_3I and $CH_3CH_2CH_2CH_2I$ were quantified only on the PoraPLOT-Q column (Figure 1B). Determination of CH_2CHCH_2I (allyliodide), CH_2ICH_2OH (1-iodoethanol), and $CH_3C(CH_3)ICH_3$ (2-iodo-2-methylpropane) was not possible either due to their thermal instability or to an insufficient response on the ECD. When

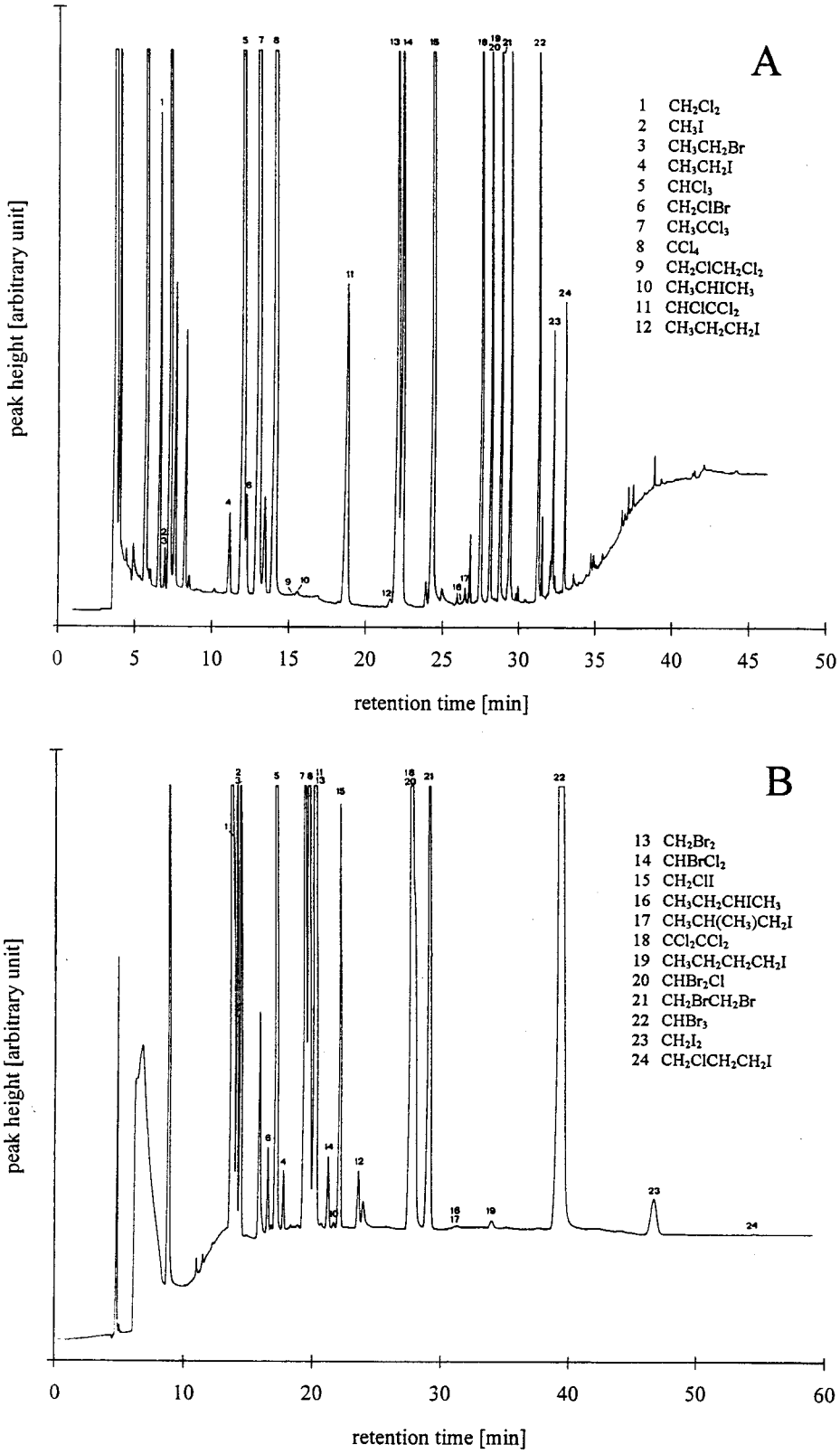

FIGURE 1. Chromatogram of various volatile halocarbons separated from culture medium after the incubation of the subtropic green maroalgae *Ulva conglobata*. Separation was done on a BP-624 column (A) and a PoraPLOT-Q column (B).

measuring $CH_2ClCH_2CH_2I$, severe memory effects were encountered, and consequently, this compound was not determined during this study.

Detection limits were in the range of 0.012 pmol L^{-1} for CH_3I to 0.62 pmol L^{-1} for CH_2I_2. In general, lower detection limits were obtained with the BP-624 column as compared to the PoraPLOT-Q column. Especially for less volatile compounds such as CH_2I_2 and $CHBr_3$, the difference was about an order of magnitude. The analytical precision was 1.4−14.8% ($n = 4$).

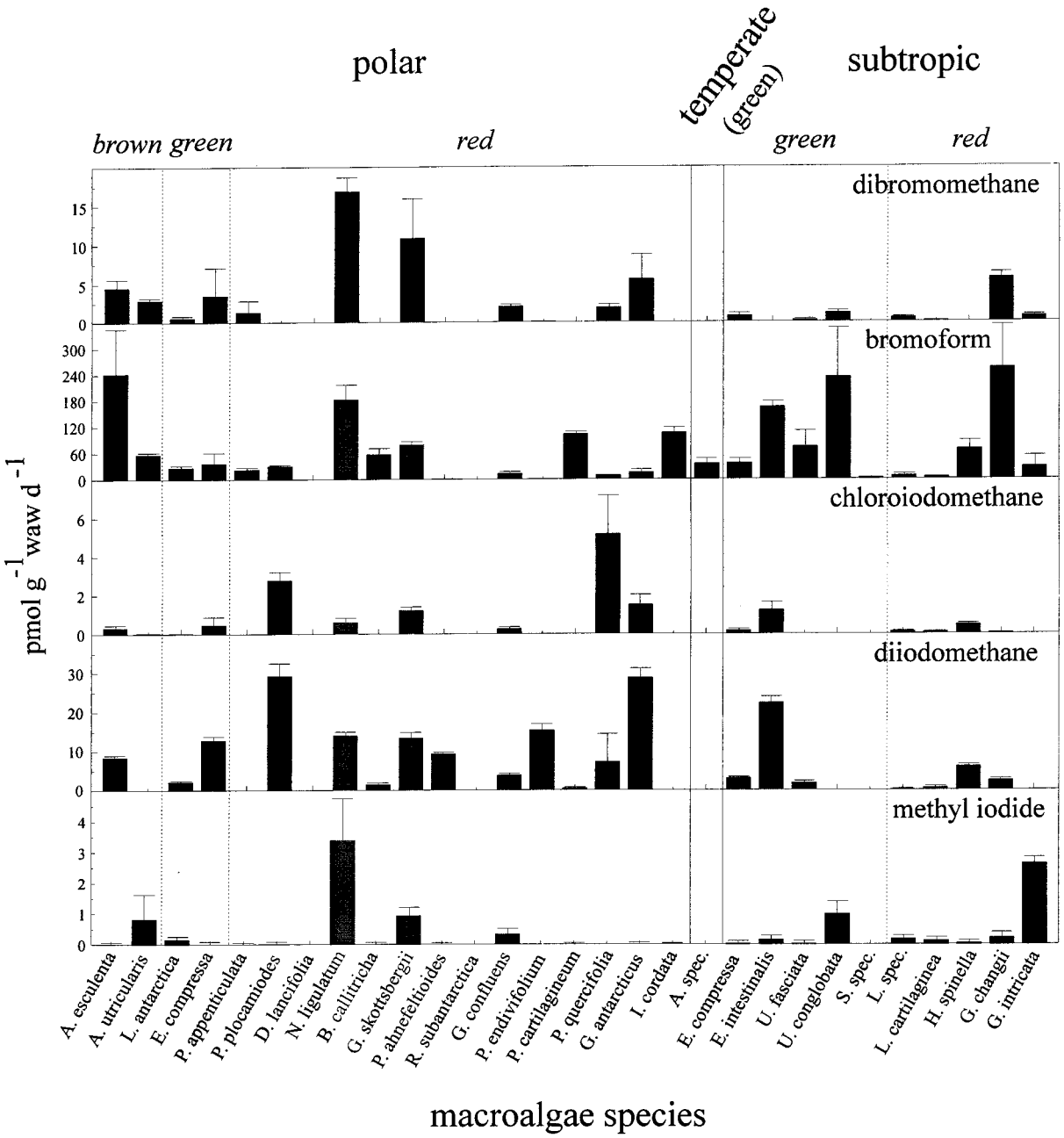

FIGURE 2. Release rates of CH_3I, CH_2I_2, CH_2ClI, $CHBr_3$, and CH_2Br_2 detected from polar and subtropic macroalgae. Error bars indicate the variation of replicates.

Results and Discussion

Eighteen polar, one temperate, and 10 subtropic macroalgae were investigated for their release of volatile iodocompounds (Table 1). The temperate green macroalga *Acrosiphonia* sp. released only $CHBr_3$ and $CH_3CH_2CH_2I$ but none of the other compounds. Thus, this species was not included in any further discussion. The highest release rates (Figure 2) were found for $CHBr_3$ with up to 253 pmol g^{-1} wet algal weight-(waw) d^{-1} for the subtropic red alga *Gracilaria changii*, followed by CH_2I_2 with up to 29.3 pmol g^{-1} waw d^{-1} for the polar red alga *Pantoneura plocamiodes*, and CH_2Br_2 with up to 18.3 pmol g^{-1} waw d^{-1} for the polar red alga *Neuroglossum ligulatum*. Lower release rates were detected for CH_3CH_2-CH_2I, CH_3CHICH_3, CH_3CH_2I, CH_3I, CH_2ClI, and $CH_3CH_2CH_2$-CH_2I (Figures 2 and 3). The lowest release rates were found for $CH_3CH_2CH_2ICH_3$ and $CH_3CH(CH_3)CH_2I$ with concentrations close to the detection limits. To the best of our knowledge, this is the first time a branched halogenated hydrocarbon ($CH_3CH(CH_3)CH_2I$) has been identified as a release product of macroalgae. The wide range of iodinated hydrocarbons released by macroalgae indicates that these compounds need to be taken into account when estimating the global iodine budget.

Macroalgal species differed in their release rates of volatile halogenated hydrocarbons. While the polar red algae *N. ligulatum* and *P. plocamiodes* generally released these compounds at high rates, the polar red alga *Delessaria lancifolia* was only a poor producer. The release rates of most substances detected showed no conspicuous variations between polar brown, green, and red algae, although higher release rates were determined for CH_3CH_2I and CH_3CHICH_3 from brown and green macroalgae as compared to red algae. However, as only a limited number of green and brown algal species were investigated, this result contains some uncertainty. With regards to subtropic macroalgae, CH_2I_2, the iodopropanes, and the iodobutanes were preferably released

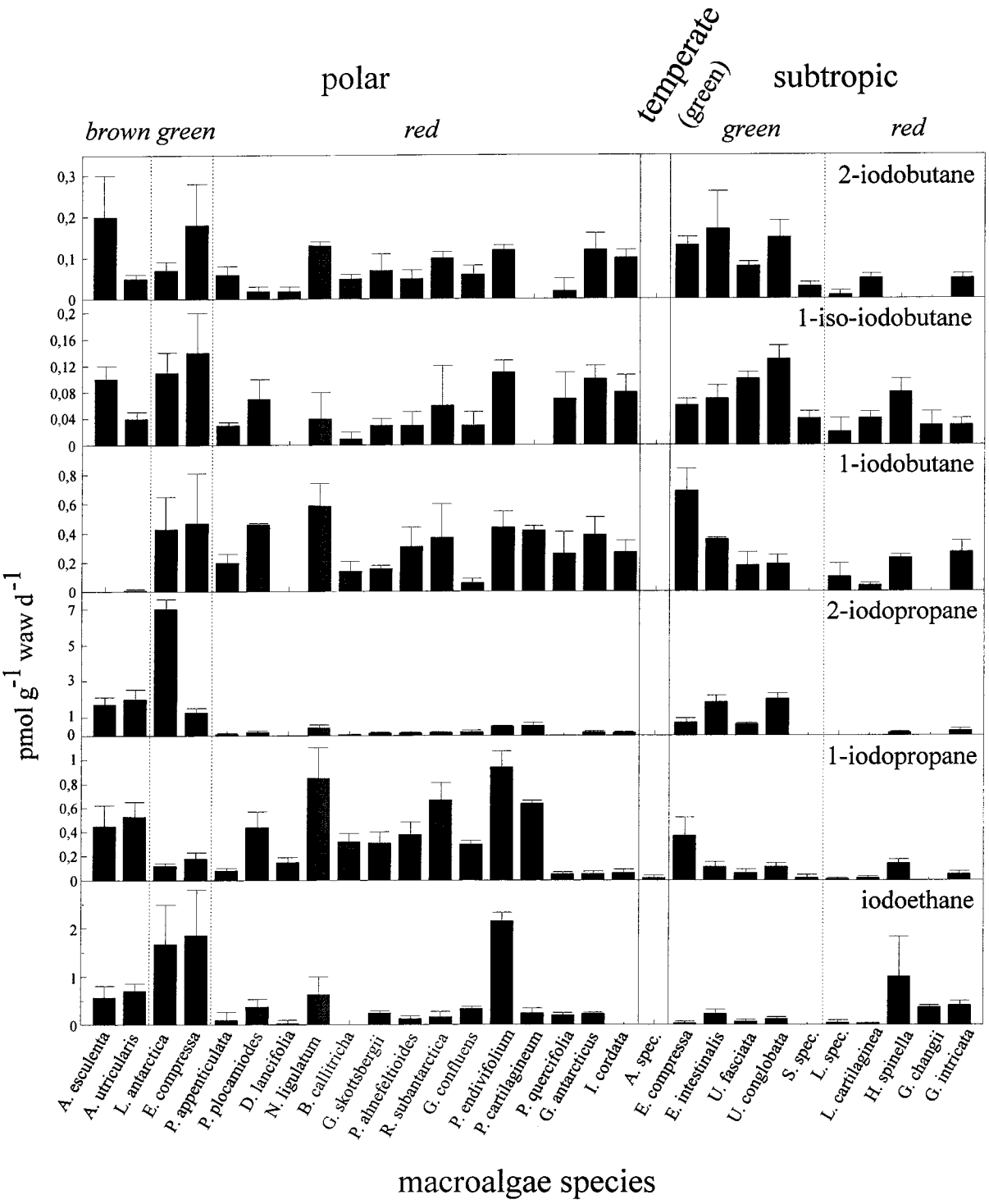

FIGURE 3. Release rates of CH_3CH_2I, $CH_3CH_2CH_2I$, CH_3CHICH_3, $CH_3CH_2CH_2CH_2I$, $CH_3CH(CH_3)CH_2I$, and $CH_3CH_2CHICH_3$ detected from polar and subtropic macroalgae. Error bars indicate the variation of replicates.

by green algae rather than by red algae. While a reverse behavior was observed for CH_3CH_2I, there was no difference between release rates of green and red algae for CH_2ClI and both brominated compounds.

Several authors have reported the release of CH_3I by marine macroalgae (*10, 29*). In our study, all subtropic algae showed a release of CH_3I, but only 5 of the 18 polar macroalgae investigated showed detectable release rates (Figure 2). For these five polar macroalgae species, however, relatively high release rates comparable to the release rates of subtropic algae species were measured. The highest value was 3.41 pmol g^{-1} waw d^{-1} for *N. ligulatum*. Interestingly, in some cases the concentration of CH_3I in the culture medium dropped during the incubation of macroalgae (Table 2). Apparently, some macroalgae or associated bacteria on the surface of the macroalgae can reduce the concentration of CH_3I in seawater. Similar results have been found for the release of methyl bromide (CH_3Br) by polar macroalgae (Laturnus, unpublished data). While to date research has concentrated on the ocean as a source of halogenated hydrocarbons, our results indicate that some polar macroalgae species possibly act as a sink for CH_3I. It should be

TABLE 2. Detected Concentrations of Selected Volatile Halocarbons in the Culture Medium before and after the Incubation of Macroalgae[a]

		concentration (pmol L^{-1})			
		CH_3I	$CH_3CH_2CH_2I$	CH_2I_2	$CHBr_3$
		Polar Algae			
	seawater control	1.42 ± 0.14	<0.07	8.6 ± 1.0	11.6 ± 1.1
brown algae	*Alaria esculenta*	1.35; 0.44	2.12; 1.84	12.9; 26.8	1660; 381
	Adenocystis utricularis	5.92; 31	5.09; 12.6	nd; 10.1	1152; 1096
green algae	*Lambia antarctica*	4.47; 3.88	2.00; 1.84	40.2; 39.5	347; 375
	Enteromorpha compressa	0.55; 0.62	0.91; 0.62	72.1; 48.2	204; 118
red algae	*Neuroglossum ligulatum*	9.71; 10.2	2.17; 2.09	61.1; 53.2	553; 388
	Porphyra endivifolium	0.34; 0.67	4.36; 4.11	93.5; 47.8	15.6; 14.1
	Phycodris quercifolia	0.44; 0.51	0.51; 0.28	49.7; 48.2	89.5; 117
		Subtropic Algae			
	seawater control	1.04 ± 0.07	<0.07	11.0 ± 1.1	7.1 ± 0.8
green algae	*Enteromorpha compressa*	1.01; 1.26	0.37; 4.36	26.2; 30.1	162; 274
	Ulva conglobata	7.91; 11.1	0.78; 0.99	17.4; 7.70	2010; 1952
red algae	*Laurencia cartilaginea*	2.85; 2.30	0.22; 0.22	17.9; 17.4	87.3; 66.8
	Gelidiopsis intricata	16.8; 8.55	0.36; 0.21	10.5; 3.42	250; 76.9

[a] The values for the seawater controls are average concentrations ± standard deviation ($n = 4$). The concentrations after incubation are average values of two measurements for two separate incubations.

TABLE 3. Average Rates (pmol g^{-1} waw d^{-1}) of Various Iodinated and Brominated Hydrocarbons Released from Polar and Subtropic Macroalgae

	polar algae				subtropic algae			
compound	brown	green	red	all	green	red	all	all
CH_3I	0.27	0.02	0.23	0.22	0.23	0.64	0.44	0.30
CH_3CH_2I	0.64	1.8	0.35	0.54	0.10	0.37	0.24	0.43
CH_3CHICH_3	1.9	4.1	0.21	0.83	1.0	0.08	0.56	0.73
$CH_3CH_2CH_2I$	0.49	0.15	0.37	0.36	0.13	0.04	0.09	0.26
CH_2ClI	0.12	0.45	0.65	0.58	0.23	0.08	0.16	0.43
$CH_3CH_2CHICH_3$	0.12	0.12	0.07	0.08	0.11	0.02	0.07	0.08
$CH_3CH(CH_3)CH_2I$	0.07	0.12	0.05	0.06	0.08	0.04	0.06	0.06
$CH_3CH_2CH_2CH_2I$	0.00	0.45	0.29	0.27	0.28	0.12	0.20	0.25
CH_2I_2	4.3	7.5	8.8	8.2	5.4	1.9	3.7	6.6
CH_2Br_2	3.7	2.1	4.1	3.8	1.2	2.4	1.8	3.1
$CHBr_3$	150	32	45	55	102	102	102	71

noted that only the conditions prevailing during the polar winter were simulated in this investigation. Different behavior might be observed at longer day lengths.

Average release rates of the various iodinated and brominated compounds from polar and subtropic macroalgae measured in this study are listed in Table 3. Except for CH_3I, all iodinated compounds had lower release rates from subtropic macroalgae. It is interesting that for *Enteromorpha compressa*, which occurs in both climatic regions, the subtropic species released about 95% less iodinated hydrocarbons than the polar. Mehrtens and Laturnus (*33*) found increasing halogenating activity at higher temperatures for the Arctic population of the brown macroalga *Laminaria saccharina* (L.) Lamour. If this result is valid for other algae species too, the lower release rates found for subtropic algae cannot be explained by a lower production rate of iodinated compounds. However, lower release rates may be caused by a reduced stability of iodinated hydrocarbons at subtropic temperatures. Zika et al. (*34*) found that for organoiodine compounds the half-life ($t_{1/2}$) with regard to the halogen exchange reaction with chloride ions decreased significantly when passing from polar to tropic waters. In consequence, if CH_2ClI is formed by halogen substitution of CH_2I_2 with chloride, an increased formation rate of CH_2ClI may be expected for the subtropic population of *E. compressa*. However, as such an increase was not observed, CH_2ClI may not be formed by halogen exchange but by enzymatic reaction with haloperoxidases as assumed for most volatile halocarbons (*33*). Haloperoxidases, an enzyme group that has been detected in a wide range of marine and terrestrial organisms (*35*−*38*), can catalyze the oxidation of halogens in the presence of hydrogen peroxide to form halogenated organic compounds (*39*). Metabolic pathways by which volatile halocarbons such as bromoform are synthesized have been discussed by several authors (*40*−*42*). Intracellular halogenation of ketones present in marine algae followed by decay via the haloform reaction can lead to the formation of polyhalogenated methanes such as bromoform and dibromomethane (*42, 43*). Another pathway may be the reaction of hypobromous acid, an extremely reactive species, with organic matter to form volatile halocarbons. Hypobromous acid can be formed by haloperoxidases located near the macroalgae surface and then released into seawater (*37*). Although the sites of high halogenating activity correlated well with the release sites of high quantities of halocarbons (*24, 33*), i.e., the formation of volatile halocarbons is clearly connected to the enzyme activity, the exact formation mechanisms of most of the volatile halogenated C_1−C_4 hydrocarbons remain unknown. Furthermore, nothing can be said yet about the function of volatile halocarbons in algal life. Fenical (*41*) pointed out that they may be a chemical defense against microorganisms or herbivores, and Gibson et al. (*44*) described the narcotic effects of bromoform on marine organisms. However, it is possible that these small molecules have no particular function and, perhaps, are only decomposition products in algal metabolism.

CH_3I and $CHBr_3$ were the only compounds for which higher release rates were measured from subtropic mac-

TABLE 4. Global Annual Atmospheric Input of Iodinated and Brominated Hydrocarbons into the Atmosphere Due to Release by Macroalgae

compound	atmospheric input: based on av release rates (10^6 g yr^{-1})	atmospheric input: based on max release rates (10^6 g yr^{-1})
CH_3I	0.92	11
CH_3CH_2I	1.5	6.4
CH_3CHICH_3	2.7	26
$CH_3CH_2CH_2I$	0.98	3.5
CH_2CII	1.7	20
$CH_3CH_2CHICH_3$	0.3	0.70
$CH_3CH(CH_3)CH_2I$	0.24	3.0
$CH_3CH_2CH_2CH_2I$	0.99	2.8
CH_2I_2	39	172.3
iodine (total)	**42**	**210.4**
CH_2Br_2	12	39
$CHBr_3$	397	1404
bromine (total)	**387**	**1363**

roalgae as compared to polar macroalgae. Average release rates of $CHBr_3$ from subtropic algae were found to be twice as high as from polar macroalgae. However, no subtropic brown algae were included in this study. As brown macroalgae were the strongest emitters of $CHBr_3$ among the polar algae (see also ref *25*), the difference in release rates with respect to the climatic region may be even higher. Considering only green and red macroalgae species, the release rates of volatile halocarbons determined for subtropic algae were three times as high.

On the basis of average release rates determined for iodinated and brominated compounds from all macroalgae studied (Table 3), the relevance of the halogen input into the atmosphere by macroalgae via volatile organohalogens was estimated assuming a global algae biomass of 6×10^{13} g (*45*) and a transfer of 100% of the released compounds from the oceans into the atmosphere (Table 4). From the results, an annual atmospheric input of 4.2×10^7g iodine was calculated. CH_2I_2 contributed for 80% of this input, while CH_3I, which has long been considered the main species for the transport of iodine from the ocean into the atmosphere (*11*), contributed only 5%. Our results for the iodine input from volatile iodocarbons lie within the range determined by Schall et al. (*29*) and slightly below the values reported by Gschwend et al. (*18*). However, such estimations have to be considered carefully since the global algae biomass can only be estimated very roughly. Furthermore, the average release rates used in the calculations are dependent on the macroalgae species investigated as the release rates determined in this study ranged from 0 to 253 pmol g^{-1} waw d^{-1}. Independent of these uncertainties, it is rather unlikely that macroalgae are the main source for atmospheric iodine. The estimated 10^{11}–10^{12} g yr^{-1} of iodine transported from the ocean into the atmosphere (*14*, *46*–*48*) is 4–5 orders of magnitude higher than the amount estimated as release from macroalgae. Even if the highest release rates determined in this study were employed, the estimated total input would be 2.1×10^8 g of iodine yr^{-1} only (Table 4). This is still lower than the presumed oceanic flow into the atmosphere. Therefore, other stronger biogenic sources must be available in the ocean. Possible candidates may be phytoplankton, which has been reported to release CH_3I and other volatile halogenated compounds (*49*–*51*), and microalgae, which were found to release a variety of different iodinated C_1–C_4 hydrocarbons (*31*). Due to their higher biomass as compared to macroalgae, phytoplankton and microalage may contribute more to the marine production of organic iodinated compounds.

From the release rates obtained for $CHBr_3$ and CH_2Br_2, an annual global release of 4×10^8 g of bromine by macroalgae was calculated. This value is in the range of results reported by Schall et al. (*29*), who found an input of 0.1×10^9–1.6×10^9 g of bromine yr^{-1}. However, the annual emission of bromine from the ocean is estimated as 10^{10}–10^{12} g (*15*, *52*, *53*). Therefore, brominated compounds may also not be formed primarily by macroalgae.

Considering the estimated annual global input of iodine from the ocean into the atmosphere, marine macroalgae may not be the main source for biogenic iodine. However, they may have a considerable local influence on atmospheric concentrations of iodine. In the polar regions and coastal areas, where macroalgae occurred down to considerable depth (>30m) along thousands of kilometers of coastlines (*54*), higher concentrations of volatile halocarbons were detected as compared to the open oceans (*13*, *14*, *17*, *24*).

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