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17. The other source of interocean exchange that could balance NADW export from the Atlantic is the eastward flow of cold water in the Drake Passage. Since the contrast in temperature of that water with NADW is small, a large NADW production rate is required to support the northward heat flux in the South Atlantic.
18. The Ajax bottle data is supplied by J. Reid of Scripps Institute of Oceanography, prior to its complete processing. Similar θ/S structure is displayed in the Geochemical Ocean Sections Study (GEOSECS) data [A. E. Bainbridge, *GEOSECS Atlantic Expedition*, vol. 1, *Hydrographic Data, 1972–1973* (Government Printing Office, Washington, D.C., 1981]. The GEOSECS Indian Ocean data are from R. F. Weiss, W. S. Broecker, H. Craig, and D. Spencer [*GEOSECS Indian Ocean Expedition*, vol. 5, *Hydrographic Data, 1977–1978* (Government Printing Office, Washington, D.C., 1983)].
19. At these stations the 10°C isotherm is at similar depths. The thermal structure differs significantly only in the upper 300 m.
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Volatile Halogenated Organic Compounds Released to Seawater from Temperate Marine Macroalgae

Abstract. *Volatile halogenated organic compounds synthesized by various industrial processes are troublesome pollutants because they are persistent in terrestrial ecosystems and because they may be present in sufficient quantities to alter the natural atmospheric cycles of the halogens. Certain of these compounds, including polybromomethanes and several previously unobserved alkyl monohalides and dihalides, appear to be natural products of the marine environment. A variety of temperate marine macroalgae (the brown algae* Ascophyllum nodosum *and* Fucus vesiculosis, *the green algae* Enteromorpha linza *and* Ulva lacta, *and the red alga* Gigartina stellata*) not only contain volatile halogenated organic compounds but also release them to seawater at rates of nanograms to micrograms of each compound per gram of dry algae per day. The macroalgae may be an important source of bromine-containing material released to the atmosphere.*

Volatile halogenated organic compounds (VHOC), including haloforms in drinking water (*1*), chlorinated solvents in ground water (*2*), and halogen-containing methanes, ethanes, and ethylenes in the atmosphere (*3*), have proven to be very bothersome pollutants. Such chemicals are biologically recalcitrant in terrestrial ecosystems, presumably because terrestrial organisms have not evolved with these or related organic compounds as common metabolites; thus their hazardous impacts are very slow to diminish. Furthermore, these halogenated volatiles may be dispersed globally in sufficient quantities to alter the natural geochemical cycles of halogens. If we are to appreciate the impact of such synthetic chemicals, they must be evaluated in the context of related natural compounds and processes, which are still poorly characterized for VHOC (*4*). Although it is recognized that various marine macrophytes (primarily tropical and subtropical rhodophytes) synthesize certain VHOC (*5,6*), the release of VHOC to seawater from such biological sources has not been assessed. If this marine capability is widespread, natural inputs of VHOC to the marine environment through the millennia may (i) have led to the development of marine, microbially mediated degradation pathways of VHOC and (ii) have contributed enormous quantities of volatile, organically bound halogens to the atmosphere, which would have important ramifications for the chemistry of transient species such as ozone and the hydroxyl radical.

In this report we demonstrate that a variety of temperate marine macroalgae (the brown algae *Ascophyllum nodosum* and *Fucus vesiculosis*, the green algae *Enteromorpha linza* and *Ulva lacta*, and a red alga, *Gigartina stellata*) not only contain VHOC (tens to hundreds of nanograms of VHOC per gram of dry weight) but also release these compounds to seawater at rates of nanograms to micrograms of each compound per gram of dry algae per day.

Intertidal macroalgae were collected between August 1983 and January 1984 from three sites around Cape Cod, Massachusetts. Heavily epiphytized plants were avoided, but it was not possible to exclude closely associated microscopic organisms. The algae were incubated for 1 day either in situ in 4-liter jars with Teflon-lined screw-cap lids or in a 34-liter laboratory aquarium maintained without headspace, with natural photoperiods, at the temperature of the water at the collection site. After incubation, a 2-liter sample of water was withdrawn, and the VHOC were concentrated by closed-loop stripping (*7*), with Tenax traps used to collect the VHOC. Our stripping and trapping parameters precluded recovery of extremely volatile compounds such as CH_3Cl and CH_3Br or relatively involatile compounds such as CBr_4 or CHI_3. We identified and quantified the VHOC on the Tenax traps using an HP 5995B benchtop gas chromatograph–mass spectrometer system (GCMS). Seawater and abiotic natural substrates collected at the same sites as the algae and used for controls showed no detectable VHOC production. After the incubations, we froze the algae with liquid nitrogen to disrupt the algal cells and then vacuum-extracted them at 30°C for 3 hours while trapping the released volatiles in a liquid-nitrogen trap (*8*). The VHOC recoveries were compared with and without tissue freezing; the polyhalomethanes were recovered at reduced levels (~20 percent) in the frozen specimens as compared with the fresh algae, whereas the monohalo compounds were recovered slightly more effectively (120 percent) after freezing. The VHOC concentrate was transferred to Tenax traps for GCMS analysis, and dry weights were determined (80°C) on the algal debris.

Five out of six temperate-zone representatives of the Phaeophyta, Chlorophyta, and Rhodophyta exhibited VHOC production and release (Table 1). In light

Table 1. Mean (and range) rates of release of the three major VHOC to seawater by temperate macroalgae (in nanograms per gram of dry algae per day); ND, not detected.

Algal species (Number of samples)	$CHBr_3$	$CHBr_2Cl$	CH_2Br_2
	Brown algae		
Ascophyllum nodosum (8)	4,500 (150–12,500)	1,100 (ND–3,000)	680 (ND–2,100)
Fucus vesiculosis (7)	2,200 (140–4,700)	150 (ND–820)	84 (ND–590)
	Green algae		
Enteromorpha linza (2)	(ND; 850)	(ND; ND)	(ND; 300)
Ulva lacta (2)	(1,700; 14,000)	(590; 4,300)	(ND; 250)
	Red algae		
Chondrus crispus (2)	ND	ND	ND
Gigartina stellata (3)	(ND; 320; 2,100)	(ND; ND; 3,000)	(ND; ND; ND)

of the preponderance of literature demonstrating halogenation in the tropical and subtropical red algae (*5, 6*), it was ironic that a temperate rhodophyte, *Chondrus crispus*, was the only species examined that did not demonstrate VHOC release to seawater. Three bromine-containing volatiles, tribromomethane ($CHBr_3$), dibromochloromethane ($CHBr_2Cl$), and dibromomethane (CH_2Br_2), were consistently released by the algae to the seawater at the greatest rates, approximately 1 μg of each compound per gram of dry algae per day (Table 1). Replicate incubations, carried out on different plants, yielded release rates of $CHBr_3$, $CHBr_2Cl$, and CH_2Br_2 that were within a factor of 2; thus we infer that the variations in release rates for algal species examined repeatedly over several months were due to environmental factors. Maximal release of the polybromomethanes by the two brown algal species occurred in October and November.

Several other compounds were frequently recovered from the water at lower abundances after algal incubations, including iodoalkanes (methyl-, ethyl-, isopropyl-, and *n*-propyl iodide) and dihalomethanes (chloroiodomethane, bromoiodomethane, and diiodomethane). Monochloro and dichloro compounds were not observed in any instance (dichloromethane blanks precluded detection of algal production of this compound at concentrations below 100 ng per gram per day). This apparent discrimination against chlorine in the production of VHOC must reflect enzyme specificities, since chloride is by far the most abundant halide in seawater.

We also examined the VHOC content of the algal tissues (Table 2). Because of variability in our recoveries, we do not report methyl iodide contents in Table 2, although this compound was consistently present. In addition to the chemicals recovered from seawater, we observed 1-iodopentane, propyl bromide, and pentyl bromide in some of the algal tissues. Methyl iodide and pentyl bromide have been observed (*6, 9*), but the other alkyl monohalides have not. The alkyl bromides were not formed by nucleophilic substitution reactions of Br^- with the corresponding alkyl iodides, since we did not find the alkyl chlorides which should be produced at the same time (*10*). Although haloperoxidase enzymes capable of forming trihalomethanes are known from a variety of macroalgae (*9, 11*), the metabolic pathways that produce the mono- and dihaloaliphatic compounds are not clear. Theiler *et al.* (*9*) proposed that these VHOC are produced by the hydrolysis of monohalo- and dihalo-oxo-fatty acids.

Comparison of the amount of VHOC present within algal tissues with that released to seawater suggests that there is an important difference between the formation of the polybromomethanes and the alkyl monohalides. The three bromomethanes released in the greatest abundance occurred at relatively low concentrations in the tissues, even if we assume as much as 90 percent loss on freezing with liquid nitrogen. Therefore, these bromine-containing compounds are either produced and transported to the outside of the algal thallus extremely rapidly (about ten turnovers each day) or perhaps are synthesized near the plant surface or by associated epiphytes and never stored. The partial loss of these VHOC on rapid freezing supports the contention that they occur predominantly in an exposed location such as near the outside of the algae. Iodide oxygenase has been reported to occur only in the outermost cells of some brown algae (*12*); this enzyme may be responsible for

Table 2. Mean (and range) VHOC in algal tissues (in nanograms per gram of dry weight); ND, not detected. The $CHBr_3$, $CHBr_2Cl$, and CH_2Br_2 tissue concentrations reported here have not been corrected for poor recoveries due to freezing.

Compound	Algal species (No. of samples)				
	Ascophyllum nodosum (6)	*Fucus vesiculosis* (4)	*Enteromorpha linza* (2)	*Ulva lacta* (2)	*Gigartina stellata* (3)
$CHBr_3$	120 (28–520)	41 (24–62)	ND, 8	19, 43	9 (3–19)
$CHBr_2Cl$	280 (14–550)	470 (ND–890)	150, 460	ND, 590	160 (ND–330)
$CHBrCl_2$	7 (ND–13)	18 (ND–33)	10, 7	7, 22	9 (5–13)
CH_2Br_2	18 (ND–98)	ND	ND	ND	ND
CH_2I_2	4 (ND–11)	ND	ND	ND	22 (14–28)
Ethyl iodide	18 (1–31)	83 (57–100)	13, 5	45, 41	22 (6–46)
Isopropyl iodide	25 (6–59)	140 (79–160)	ND	20, 10	ND
1-Iodopropane	240 (74–570)	550 (440–730)	ND	3, ND	3 (2–4)
1-Iodobutane	3 (ND–7)	7 (ND–10)	ND	9, ND	9 (2–23)
1-Iodopentane	25 (5–66)	82 (11–140)	ND	38, ND	ND
1-Bromopropane	7 (ND–18)	15 (12–20)	9, 5	ND, 9	1 (ND–3)
1-Bromopentane	ND	7 (ND–28)	ND	ND	ND

Table 3. Estimated annual global inputs of organobromides and organoiodides to the atmosphere.

Sources	Bromine or iodine (g/year)
Organobromides	
Macroalgae*	
(10^{13} g algae) (1 to 10 μg Br per gram per day) (365 days per year)	$\sim 10^{10}$
Industrial products†	
CH_3Br (fumigant)	$\sim 5 \times 10^{10}$
BrCH=CHBr (fumigant and gasoline additive)	$\leq 10^{11}$
CF_3Br (flame retardant)	$\leq 10^{9}$
Chlorination‡	
Seawater (6×10^{10} g Cl per year) (1 percent organobromides)	6×10^{8}
Freshwater (4×10^{12} g Cl per year) (0.1 percent organobromides)	4×10^{9}
Organoiodides	
Macroalgae*	
(10^{13} g algae) (10 to 100 ng I per gram per day) (365 days per year)	$\sim 10^{8}$
Phytoplankton-derived CH_3I§	$\sim 10^{12}$

*Global algal biomass estimate from (*19*), on the assumption that 100 percent of the algal release is lost to the atmosphere. †Data from (*18*). ‡Assuming that the global chlorine usage is twice that of the United States (*21*); formation efficiency of volatile bromine species after (*22*). §Estimates from (*23*).

the formation of BrI or Br_2 (in addition to I_2), which subsequently reacts with organic compounds in the vicinity of the algal thallus to form these bromomethanes.

The concentrations of iodine-containing VHOC present in the algal tissues suggest much lower slower turnover for the iodinated compounds (about once every 10 days). Freezing the algal tissues enhanced the recoveries of the iodine-containing VHOC. We have found, however, that the iodine-containing VHOC appear to be released at greater rates when the plants are stressed (for example, under nutrient-limited conditions or at elevated temperatures). A similar finding has been reported concerning methyl iodide production in phytoplankton cultures (*13*).

If we are considering whether the oceanic and atmospheric chemistry is being changed by the biosynthesis of these halocarbons, it is not important whether the algae themselves or their associated microflora, or both, are the actual source of these compounds. Nonetheless, the question of the responsible organism or organisms should be examined. We have several lines of evidence supporting the conclusion that the algae are primarily responsible. First, numerous studies have now demonstrated haloperoxidase enzyme activities in many red, green, and brown algal species (*9, 11*). Second, one common subset of the attached community is microalgae, and at no time have we or others (*14*) observed VHOC, other than CH_3I, produced and released in diatom, dinoflagellate, or blue-green algal cultures. In several experiments designed to magnify or limit the effects of epiphytes, we have seen no evidence suggesting that the microflora produce VHOC. For example, natural rocks covered with attached microflora do not show VHOC production; heavily epiphytized plants after incubation do not show greater production of VHOC than their cleaner counterparts; and algae scraped clean with a paper towel either show enhanced VHOC release or no significant difference from untreated plants. Third, using the *Ascophyllum nodosum* fouling data of Chan and McManus (*15*), we can estimate a microbial biomass of about a microgram of dry epiphytes per gram of dry algal tissue (assuming 10^{-12} g per dry bacteria). In light of our data on tissue contents (total VHOC approaching 1 μg per gram of dry algae), it appears that this microbial biomass is just too low to support these mass reservoirs. Thus we believe that the macroalgae themselves are primarily responsible for VHOC synthesis. However, we cannot completely rule out epiphytic involvement in VHOC production. Indeed, if VHOC production and release is in some way related to epiphytes, these microorganisms must be host-specific if we are to account for the different VHOC release rates that we observe for various algae.

The function of these unusual compounds in the algae is unknown. One possibility is that the VHOC are formed by side reactions of relatively nondiscriminating haloperoxidases or other oxidases (*6*). On the other hand, these substances may provide protection from herbivore feeding or may have antimicrobial benefits (*5, 6*). In an earlier study (*16*), CH_2I_2 was found in some algal species avoided by the herbivore *Littorina littorea* (periwinkle). Addition of this compound to agar containing macerated algae deterred feeding by this snail. Interestingly, $CHBr_3$ was released at comparable concentrations by plants both preferred and avoided by the snail and did not affect feeding in the amended agar experiments. Finally, it has been suggested that the seasonal variation in epiphytic microflora abundance on *Ascophyllum nodosum* may be related to algal metabolism (*15, 17*). Since many VHOC exhibit antibiotic properties, one may speculate that these chemicals may be involved in epiphytic control.

The VHOC produced by macroalgae may be important in the global cycling of gaseous organohalogen species, if these compounds are efficiently transferred to the atmosphere. The natural oceanic sources of volatile bromine and iodine compounds are poorly known (*4, 18*). We have used the macroalgal release rates of volatile bromine- and iodine-containing compounds reported here and global estimates of macroalgal biomass (*19*) to calculate the potential for organobromine and organoiodine transmission from the coastal oceans to the atmosphere. This estimate for volatile bromine-containing compounds may be particularly justified since there are no known major mechanisms for their removal from the sea other than exchange into the atmosphere; however, alkyl iodides are known to react with chlorine in seawater (*10*). Table 3 compares these estimates with reported major anthropogenic and natural atmospheric inputs for volatile organobromides and iodides (*18*). It is very possible that the macroalgae are a major source of volatile organobromine to the atmosphere ($\sim 10^{10}$ g/year); volatile iodine compounds do not appear to come primarily from the macroalgae. Both of these potential organohalide fluxes to the atmosphere appear small relative to the estimated (*20*) inputs of methyl chloride (5×10^{12} g/year).

PHILIP M. GSCHWEND
JOHN K. MACFARLANE
KATHLEEN A. NEWMAN
Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge 02139

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