

Marine Sources of Volatile Organohalogens

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The ocean is a massive reservoir of the halogens, elements which play important roles in the atmosphere, most notably in their catalysis of ozone decomposition. While ionic halides are emitted to the atmosphere as sea salt particles, it is the much smaller fluxes of halogenated organic gases that can provide a pathway for halogens to reach the upper atmosphere. This chapter reviews what is known about the processes, mainly biological, that effect the conversion of seawater halides to volatile halogenated gases. Particular attention is given to the methyl halides, which have become the best-studied group of compounds, in part as a result of studies focussed on natural sources of methyl bromide. Since the ultimate contribution of marine processes to atmospheric halogens depends on the net fluxes to or from the atmosphere, a glimpse is provided of marine sinks: those processes that are consuming halogenated gases in the ocean.

Keywords. Volatile organohalogens, Marine production

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1 Introduction

Of the vast array of naturally-produced halogenated compounds, this chapter will focus on a small subset comprising those for which there is evidence of significant marine sources, and which are sufficiently volatile to be emitted to the atmosphere. A major reason for interest in these compounds stems from the now well-known involvement of halogen chemistry in the control of stratospheric ozone levels. The role of naturally-produced methyl chloride as a source of stratospheric chlorine was first reported by Lovelock in 1975 [1]. With co-workers he had already suggested [2] that methyl iodide is produced in the sea, and that marine algae were a source. Bromine and iodine also subsequently received attention as potential contributors to stratospheric ozone loss [3–5]. In this context the importance of organohalogen compounds lies in their ability to transfer halogen from the Earth's surface reservoirs, of which the ocean is the most important, to the lower and upper atmosphere. For transport to the upper atmosphere, it is essential that the halogen should be in a form that has low aqueous solubility so that it can avoid rapid return to the surface in precipitation. It is for this reason that organohalogens are much more important to upper atmosphere chemistry than the vastly greater quantity of particulate sea salt that enters the atmosphere, this material being quickly washed from the atmosphere. The proportion of a compound that mixes into the stratosphere increases with its tropospheric lifetime. In the case of methyl chloride, for example, which has an atmospheric lifetime of ~1.4 years, about 5% will mix into the stratosphere where the halogen can enter catalytic ozone-destroying reactions. However, it has been shown that even very short-lived compounds can be locally lofted to the lower stratosphere by intense convection in the atmosphere [6]; this is relevant to possible involvement of iodinated and polybrominated compounds in stratospheric ozone regulation [4]. Furthermore, Dvortsov et al. [5] have recently re-evaluated the significance of short-lived bromine compounds, particularly bromoform, to the supply of reactive bromine to the lower stratosphere, a region in which current models have had difficulty in accounting for observed ozone loss.

After it was recognised that synergistic interactions between chlorine and bromine were important [7] and could account for ~20% of polar stratospheric ozone depletion [8], the problem of apportioning methyl bromide releases to natural and anthropogenic sources stimulated much research into its natural sources in both terrestrial and marine environments [9–16]. In parallel, studies have been made of the marine natural sources of atmospheric chlorine and iodine, namely methyl chloride [17, 18] and methyl iodide [19–22]. Halogenated compounds are significant to tropospheric as well as stratospheric chemistry. Natural organobromine compounds have been studied in the Arctic as possible sources of bromine atoms that could initiate catalytic reactions leading to the sudden loss of tropospheric ozone that has been observed in springtime [23], though subsequently the bromine source has been considered to be inorganic sea salt bromide [24].

Efforts have been made to quantify the total emission of reactive chlorine to the atmosphere and to map the emissions on a global grid [25]. Since there are

relatively good estimates of the atmospheric lifetimes of these compounds, together with sometimes uncertain measurements of their atmospheric abundance, it has been possible to calculate the size of the annual atmospheric sinks. Then, from best estimates of industrial production and release, it has also been possible to estimate the natural sources such that a balance exists between sources and sinks. For some compounds (e. g. chloroform) this points to important natural sources among which the ocean may be numbered. Such exercises are, however, subject to many uncertainties, and it will be shown that apparent imbalances between sources and sinks are not always matched by good evidence for marine production.

This chapter will look at possible marine sources of volatile organohalogen compounds, and then show how estimates are made of the global source strength to the atmosphere. While its primary aim is to focus on sources, it will be shown that marine sinks commonly coexist with sources, so what is known of these sinks will be briefly reviewed. Some of the best studied compounds, individually or as groups, will then be discussed.

2 Source Types

2.1 Macroalgal

Macroalgal sources of volatile, as well as non-volatile, compounds are the best understood. This is probably largely due to the greater ease with which significant quantities of individual species of macroalga, in contrast with microalga, may be harvested from the ocean and studied. This facilitates the measurement of release rates of halogenated compounds, and also the biochemical studies that are needed to identify the production mechanisms.

A 1979 review [26] of halogenated compounds present in marine red algae of the family Bonnemaisoniaceae revealed an extremely wide variety of halogenated metabolites present within these macrophytes including, among the C1 compounds, methyl iodide, chloroiodomethane, trihalomethanes including CHBr_3 , CHCl_3 , CHBr_2Cl , CHBr_2I , CHBrCl_2 , and fully-halogenated species, CBr_4 and CCl_4 . The release into seawater of these and similar compounds by various red, brown and green algae was studied by Gschwend et al. [27]. Their findings included release rates of the brominated species CHBr_3 , CHBr_2Cl and CH_2Br_2 , which were not only high, but also large in proportion to the concentrations within tissues, suggesting either rapid transport from the tissue, or synthesis near the plant surface. They reported the presence of a number of alkyl iodides, including ethyl iodide, isopropyl iodide, 1-iodopropane, 1-iodobutane, 1-iodopentane, within the tissues of some macrophyte species. Also identified at lower abundances were the dihalomethanes, chloroiodomethane, bromoiodomethane, and diiodomethane. The work provided evidence for seasonal variations in release of polybromomethanes. Based on estimates of global algal biomass, calculations were made of the potential total organobromine and organoiodine releases to the atmosphere; these suggested an important

bromine source, but a minor source of iodinated compounds. Recent work [28] has added the compounds 1,2-dibromoethylene and tribromoethylene to the list of macrophyte products; they were released by the *Falkenbergia* stages of the red alga, *Asparagopsis taxiformis*.

From field studies, there are reports of elevated levels of various organohalogenes, including bromoform and methyl iodide in coastal waters and in seaweed beds [1, 29, 30]. Nightingale et al. [31] have measured halocarbon release rates from 11 common species of macroalgae in laboratory experiments, and reported broad agreement with in situ measurements in a rock pool. Among the compounds showing significant release rates was CHCl_3 , which they proposed was a product of chloroperoxidase activity. A subsequent rock pool study by Baker et al. [32] provided confirmation of natural production of 1,2-dibromoethylene, and also the first measurements showing production of dichloromethane.

Estimates of the global contributions of volatile organohalogenes made by macroalgae are for most compounds insignificant [19, 32], the primary reason being that the coastal zone which they occupy accounts for a small area, equivalent to only 0.3% of the global ocean.

2.2

Microalgal Sources

Early observations that macrophytes are frequently producers of halogenated compounds led to an interest in whether microalgae might also prove to be a source. Such organisms are potentially very much more important than macrophytes since they differ by having an ocean-wide distribution and could consequently make a much larger contribution to ocean-atmosphere fluxes. Furthermore, early reports [33–35] of elevated concentrations or supersaturations of various halogenated compounds in offshore waters suggested a non-macrophyte source. Sturges et al. [36] demonstrated that Arctic ice algae (mainly pennate diatoms) were a source of bromoform. Laboratory studies of unialgal phytoplankton cultures have been of value in determining whether selected species phytoplankton can produce organohalogenes. It should be noted that, in many of these studies, both methyl halides and trihalomethanes have not been measured; this reflects both analytical limitations and, in many cases, a focus on a particular compound, for example methyl bromide or bromoform. Also, it should be noted that cold-water diatoms have received more attention than warm-water species on account of early interest in sources of Arctic bromine [23] that might lead to surface ozone loss.

A survey of ten species of warm- and cold-water phytoplankton by Tokarczyk and Moore [37] revealed two species that produced organohalogenes from the suite measured that comprised CH_2Br_2 , CHBr_3 , CHBr_2Cl and CH_2ClI . Each of the cold-water marine diatoms, *Nitzschia* (CCMP 580) and *Porosira glacialis* produced the four measured organohalogenes, while two other *Nitzschia* species produced none. A comparison was made of the release rates of bromoform per unit biomass of microalgae and macrophytes using results reported by Manley et al. [30]. This showed that, although the phytoplankton releases were 10–100 times lower, these microorganisms had the potential to be an important source of

volatile organohalogens because they occupy an ocean area about 200 times greater than that occupied by macrophytes.

A follow-up laboratory study [38] which included the same halocarbon-producing Arctic diatoms showed that *Nitzschia* sp. CCMP 580 and *Nitzschia arctica* produced CHBr_3 , CH_2Br_2 , CH_2I_2 and CH_2ClI (*Nitzschia seriata* produced none of these compounds). *Porosira glacialis* produced the same compounds except for CH_2I_2 and CH_2ClI . Two species (*Nitzschia* sp. CCMP 580 and *Navicula* sp. CCMP 545) were then grown in bulk and tested for haloperoxidases. The *Nitzschia* was found to contain a bromoperoxidase, probably heme-containing, while the *Navicula* contained an iodoperoxidase which was not characterized.

Separate studies have shown marine phytoplankton to be sources of methyl halides. Methyl chloride production was demonstrated in all of seven species of cultured phytoplankton, which included both cold-water (diatoms: *Porosira glacialis*, *Nitzschia seriata*, *Nitzschia* sp. CCMP 580), and warm-water species (diatoms: *Odontella mobiliensis*, *Phaeodactylum tricorutum*, *Thalassiosira weissflogii*; prymnesiophyte: *Isochrysis galbana*) [39]. A subsequent study [12] showed that three species of phytoplankton grown in culture (*Phaeodactylum tricorutum*, *Thalassiosira weissflogii* and *Phaeocystis* sp.) all produced methyl bromide as well as methyl chloride, with the *Phaeocystis* giving the highest production rate for both compounds. It was found that the production was generally unaffected by limitation of either carbon or nitrogen, by the presence or absence of bacteria, by darkness, or by poisoning with sodium azide. It was concluded that production of these two compounds might be the result of an autolytic process rather than a direct product of cell metabolism. An observed lack of influence of light on the methyl chloride and bromide production is in marked contrast with studies of the production of bromoform by either microalgae [38, 40, 41] and is consistent with distinctly different production mechanisms for the two classes of compound [42]. A further study [14] of a wider selection of phytoplankton comprising nine species, illustrated the widespread production of methyl chloride (all species produced this compound) and methyl bromide (produced by all but two). There was a rather constant ratio (average 7.4, $\text{CH}_3\text{Cl}:\text{CH}_3\text{Br}$) in the production rates of these two methyl halides, and an attempted global extrapolation using the rates from the most productive species (*Phaeocystis*) suggested that they could account for 40–130% of the estimated ocean-to-atmosphere flux of CH_3Cl [18] and 30% of the global CH_3Br estimated by Lobert et al. [10]. However, since these estimates are upper limits based on *Phaeocystis* production, the work suggested that to account for reported ocean production of methyl halides, other marine sources might exist, possibly zooplankton or fungi.

A study of CH_3Br production in cultured marine phytoplankton [43] showed that 13 of 19 species tested produced methyl bromide, with producers amongst all of the six taxonomic classes represented in the experiments. No trend with respect to temperature was apparent in CH_3Br concentrations normalised to chlorophyll for these species that were grown at temperatures of 4–22 °C. It was observed that CH_3Br increased most rapidly in the stationary and senescent phases of culture growth. Bacterial growth that occurred in most of the cultures may play a role in CH_3Br production or release from cells, and it is also possible that it could be responsible for some removal of methyl bromide so that the mea-

sured release rates represent minimum values. It appeared that production rates were of the right order of magnitude to account for estimated global ocean production [10]. It was significant that again the ubiquitous, bloom-forming prymnesiophyte, *Phaeocystis*, showed the highest rate of production normalised to chlorophyll *a*.

A survey [20] of methyl iodide production by 15 species of cultured marine phytoplankton revealed production in five. Bacteria were present in most of the cultures, but the CH_3I production in three diatom cultures was probably attributable to the algae rather than bacteria, since its rate slowed with the algal growth while bacterial numbers increased. Based on these measurements, it was estimated that phytoplankton could make an insignificant contribution to the ocean production of the gas. A study of the red microalga *Porphyridium purpureum* [44] showed CH_3I production about 40 times faster than that found by Manley and de la Cuesta [20] for *Porosira glacialis*. It is noteworthy that *Porphyridium purpureum* also produced CHCl_3 (though not CH_2Cl_2). However, its restricted distribution makes it unlikely to be a globally important producer of either compound.

Although experiments of the kind described above have been of value in demonstrating the ability of phytoplankton to produce various volatile organohalogenes, there are nevertheless major limitations associated with these laboratory studies. First, the algae that grow easily in the laboratory are not representative of what is abundant in the open ocean, indeed relatively few phytoplankton have been successfully grown in the laboratory. Second, the growth conditions that are appropriate to laboratory experiments are very unlike natural conditions. To ensure the presence of sufficient biomass, the culture is grown with high concentrations of nutrients. Because the aim is to pinpoint the production of organohalogenes, the laboratory cultures are, whenever possible, monocultures grown in the absence of bacteria. In contrast, marine phytoplankton grow in a complex community of algae, bacteria and grazing organisms. While such a system is difficult to study and quantify, field measurements are essential to our understanding of marine organohalogen production.

Field incubations [45] of microalgal communities inhabiting the lower surface of sea ice have shown that CHBr_3 , CH_2Br_2 , and CHBr_2Cl are being actively produced, the CHBr_3 at a rate 30–100 times greater than the other two compounds. The diatom communities were dominated by species of *Nitzschia* and *Navicula*. It has been shown by experiments with metabolic inhibitors [36] that ice algae rather than bacteria are responsible for bromoform production.

The iodinated C1–C4 hydrocarbons, methyl, ethyl, 1- and 2-propyl iodides have been found [46] associated with Antarctic ice algae. In that study, brominated compounds were not elevated in comparison with the underlying water.

Marine microalgal production of a volatile compound can lead to a characteristic vertical concentration profile in the water column. This shows a concentration maximum within the upper 100 m or so. Lower concentrations at shallower depths are primarily due to loss to the atmosphere, while the lower concentrations at greater depths are due to a combination of declining production with depth, downward mixing of the compound, and necessarily a loss process. Such distributions are commonplace for methyl chloride, bromide and

iodide, all of which are likely to have lifetimes of days to months in the upper water column.

In spite of the growing body of evidence for microalgal production of methyl halides, little is known about the production mechanism or about the reason for their production. Itoh et al. [47], in a study of methyl bromide and iodide production by both macro- and microalgae, identified a relatively prolific source from the marine phytoplankton species, *Pavlova gyrans*. Identified in this organism was a halide ion methyl transferase which catalysed the methylation of bromide and iodide ions by *S*-adenosyl-L-methionine (SAM). This enzyme was inactive to chloride ions, and in this respect it differs from a methyltransferase that had been detected [48] in a marine red macroalga (*Endocladia muricata*) which catalysed methylation of chloride, bromide and iodide by SAM.

2.3

Chemical Sources

The most obvious of the possible chemical sources is, perhaps, the interconversion of halocarbons, for example the conversion of methyl iodide or bromide to methyl chloride by nucleophilic substitution [49]. While this does not assist in the search for primary mechanisms for methyl halide production, it is of some consequence for marine methyl chloride. It has been estimated [22] from a Pacific Ocean data set that a CH_3I source could account for about 15% of the CH_3Cl flux to the atmosphere.

The contribution of the CH_3Br reaction may be estimated from data given by Butler and Rodriguez [50] on the total loss of CH_3Br in the ocean and the proportion of it lost by reaction with chloride ion. This yields 1.5×10^9 moles year^{-1} , or about 20% of the CH_3Cl flux to the atmosphere.

Since abundant sources of bromoform and dibromomethane have been identified in macro and microalgae, it may be presumed that there is some progressive conversion of these compounds through chlorobromo compounds, finally yielding chloroform and dichloromethane. Experiments done by Geen [51] indicated a very slow reaction of CHBr_3 with seawater, such that its half-life in seawater was estimated as 18.5 years at 25°C , the temperature of the experiments, and therefore longer at typical ocean water temperatures. An interesting photochemically-mediated conversion has been reported for diiodomethane [52] in seawater to yield chloriodomethane. This probably occurs with the mediation of an iodinated cation that then reacts with a chloride ion. Field measurements support the occurrence of this reaction [35].

It has been proposed that methyl halides should be formed by a nucleophilic substitution reaction between dimethyl sulfonium propionate (DMSP) and halide ions in seawater [53]. DMSP is an algal osmolyte present in many species of prymnesiophytes, dinoflagellates and chrysophytes; its concentration within cell fluids may reach $0.2 - 0.4$ moles L^{-1} [54]. Dissolved DMSP is found in ocean waters at concentration around 10 nM and, in coastal waters, it has been measured at levels up to 200 nM [55]. An environmentally important decomposition pathway is cleavage into dimethyl sulfide and acrylic acid. It has been shown that reaction with bromide ion yields CH_3Br [53] and with iodide yields CH_3I [56]. A

kinetic study [57] of the reactions between DMSP and Cl^- , Br^- and I^- , led to the conclusion that, unless catalysed, the rates of these reactions are too slow to result in significant production of the corresponding methyl halides in seawater.

Moore and Zafiriou [58] reported photochemical production of CH_3I in laboratory experiments with seawater. It was proposed that the mechanism involved combination of methyl radicals originating from photolysis of humic substances and iodine atoms formed by reaction of iodide with photochemically-produced oxidants. This is not expected to be an efficient process, since the main fate of methyl radicals in water would be reaction with the vastly more abundant oxygen that is normally present, particularly in sunlit surface waters. No field experiments designed to investigate the importance of this process have been reported. A complicating factor in investigating this process in the field is that methyl iodide, according to many studies, does have a marine biological source being produced by various species of seaweeds and phytoplankton. Therefore, experiments on photochemical production must ensure that biological production is either prevented or otherwise accounted for. Happell and Wallace [59] have argued that their field measurements of methyl iodide do support a photochemical source; light intensity was found to explain significant variance in methyl iodide saturation anomalies that they measured in the Greenland and Norwegian Seas. It could be questioned whether light intensity played a role through biology rather than direct photochemistry.

There are a number of interconversions between organohalogenes in addition to those mentioned above. For example, it has been suggested by Tanhua et al. [60] that when CCl_4 is reduced in waters that are anoxic or suboxic, CHCl_3 is an intermediate. In their Black Sea study, the authors acknowledge the lesser possibility that the CHCl_3 feature referred to could be algal in origin. Dehydrohalogenation of 1,1,2,2-tetrachloroethane and of pentachloroethane has been shown to rapidly produce trichloroethylene and tetrachloroethylene respectively in laboratory experiments [61]. Whether this is significant in the oceans is unknown.

3 Determination of Fluxes

As pointed out above, much of the interest in marine volatile organohalogenes has come from the field of atmospheric chemistry. From that viewpoint what is required is quantification of the net flux of the compound from ocean to atmosphere, preferably with information on both regional and seasonal variations. The way in which the flux estimates are made is using an equation of the form, $\text{Flux} = K \Delta C$, where ΔC represents the concentration difference across a stagnant microlayer at the ocean surface, and K is an exchange coefficient [62]. ΔC is given by the difference between the concentration of the compound that would be at equilibrium with the atmosphere (i.e. the concentration assumed to exist at the top of the microlayer) and the measured concentration in the top few meters of the water column which is presumed to be well mixed (this therefore represents the concentration at the base of the microlayer). The equilibrium concentration of the compound is commonly determined from its concentration in the atmosphere above the water, and its solubility in seawater. Much effort continues to be

devoted to satisfactory estimation of the exchange velocity (K), which is a function of a number of factors amongst which wind speed and temperature are important. At present it is likely that uncertainties in K alone could result in an uncertainty in flux by as much as a factor of two. Even larger contributors to the uncertainty in net fluxes of any specific compound are the usually woefully inadequate spatial and temporal sampling of the concentrations. In the case of some compounds that have a transitory existence in the atmosphere (such as methyl iodide), the simplification can sometimes be made that the concentration corresponding to equilibrium with the atmosphere is zero in comparison with the measured concentration (C_w) in the upper water column. The local flux is then the product of the exchange velocity and C_w .

Where the focus of marine organohalogen studies is determining the flux to the atmosphere, only surface ocean measurements are needed. If the total ocean production is required, information on the concentrations of the compound throughout the water column is needed as well as knowledge of the rates of all of the loss processes. A summary will be given of our state of knowledge of fluxes of some compounds that are of particular interest from the viewpoint of atmospheric chemistry.

4 Methyl Halides

4.1 Methyl Chloride

Methyl chloride has been of special interest amongst naturally-produced halocarbons, as it is the largest natural contributor to atmospheric chlorine. Its atmospheric abundance of about 550 ppt and its lifetime of 1.4 years with respect to loss by reaction with OH radical alone require an annual supply of around 3.7×10^6 t year⁻¹ [63], although, as pointed out by Harper [64], the existence of various other sinks, particularly soils, would increase the required source. While an early report based on very limited data indicated that the ocean was the major source [65], it became apparent that the ocean is not supersaturated everywhere in methyl chloride [18], and Moore [66] revised the estimate of the ocean source to about 9–11% of the total atmospheric supply.

Vertical profiles (Fig. 1) of its concentration in the water column show near surface maxima consistent with in situ production. Decreasing concentrations deeper in the water column imply in situ removal.

Although laboratory experiments have shown CH₃Cl to have a phytoplankton source, no simple relationship exists between its concentration and the most basic indicator of phytoplankton biomass, the concentration of chlorophyll a [18]. This observation, frequent also for CH₃Br and CH₃I, is consistent with the fact that production rates are dependent on the species of phytoplankton, as seen from laboratory studies, and very likely also dependent on other factors such as the growth stage and level of environmental stress experienced by the producers. As it is difficult to obtain a detailed taxonomic description of water samples, it will become more common for a wider range of photosynthetic pigments to be measured from

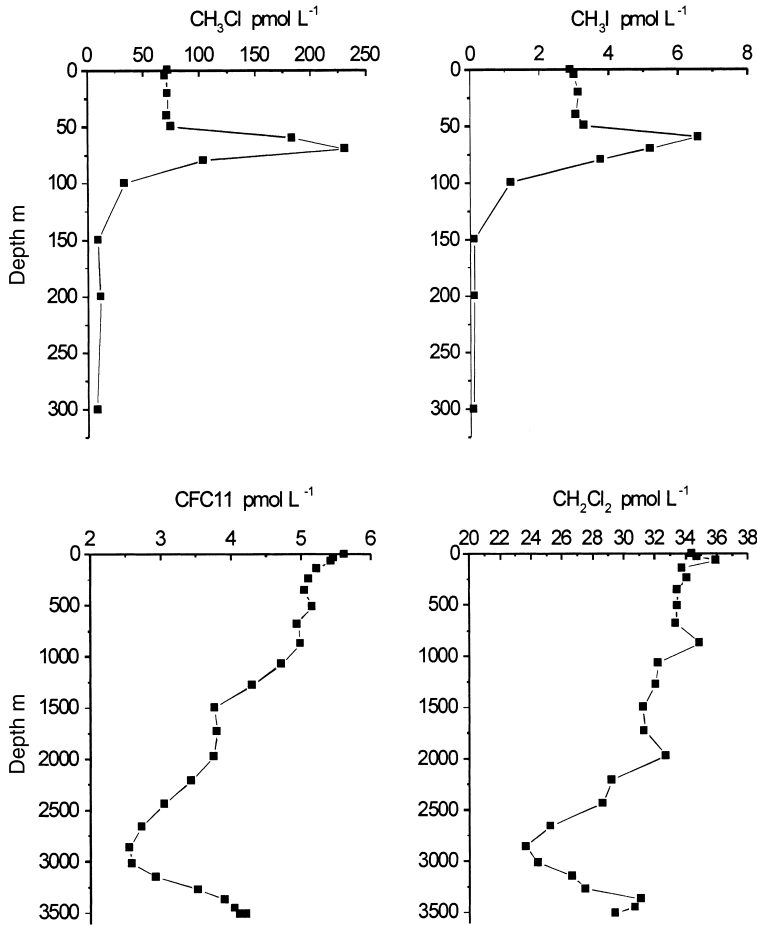


Fig. 1. Typical vertical profiles of methyl chloride (*upper left*) and methyl bromide (*upper right*) concentrations showing well-defined subsurface maxima (Pacific Ocean, 13°41'N 160°W, October 1995); and a comparison of profiles of anthropogenic CFC-11 (*lower left*) and dichloromethane (*lower right*), from the Labrador Sea (59°4'N 49°57'W, June 2000)

which information on the broad classes of algae present can be determined. The surprising contrast between undersaturations observed in productive cold waters to the north of the Gulf Stream and supersaturations in the blue oligotrophic waters to the south may be related also to the vigour of in situ removal mechanisms, but work on this topic, as indicated below, is in its early stages.

4.2 Methyl Bromide

Concern about the possible adverse effects on the ozone layer of increasing anthropogenic releases of fumigant methyl bromide led to a proliferation of re-

search on all aspects of its environmental chemistry, sources and sinks. Although our knowledge of these is far from complete, it is probable that this has become the single best-understood naturally-produced organohalogen. The belief that the ocean was a large net source of methyl bromide to the atmosphere [65] has been replaced by a recognition that the ocean, though a massive producer, represents a net sink of 11–20 Gg year⁻¹ with respect to the atmosphere [67]. That is, while methyl bromide is being produced within the oceans, simultaneous loss processes (outlined below) cause its concentration in some areas, particularly where water temperatures are high, to be below that representing equilibrium with the atmosphere; this undersaturation causes an influx from the atmosphere.

It has been shown above that there is evidence for both macroalgal and phytoplankton sources of methyl bromide in the ocean. Few consistent patterns have emerged for the emissions of the gas to the atmosphere. Some studies have reported higher concentrations in coastal waters than in the open ocean [10], while others have found oceanic concentrations locally as high as coastal sources [67]. Temperature does exert a major influence on concentrations and saturation levels, for example through the rapid reaction with Cl⁻ [68] at high temperatures that contribute to a rapid chemical turnover (8–42% d⁻¹ at 20–30°C [50]) of CH₃Br and tends to lead to undersaturation. The composition of the algal community is expected to be a major factor controlling CH₃Br concentrations. Baker et al. [16] in a North Sea study provided strong evidence that methyl bromide production was related to the growth of the Pymnesiophyte, *Phaeocystis*. In a separate, non-seasonal study in the NE Atlantic, they found good correlation between CH₃Br concentrations in the water and the pigment 19'-hexanoyloxyfucoxanthin that is associated with Pymnesiophytes.

Where there is evidence that organohalogen production in the oceans is a biological process, it may be expected that the rate of production will vary seasonally. Methyl bromide is one of only a few compounds for which evidence for seasonality has been reported; usually data sets are far too sparse to allow such an effect to be confirmed. The yearlong North Sea study by Baker et al. [16] showed that CH₃Br was supersaturated in the North Sea for a three-month period, and that its concentrations showed a similar seasonal trend to chlorophyll a.

4.3

Methyl iodide

Methyl iodide has been of interest as a carrier of this biologically essential element through the atmosphere to the terrestrial environment. Also, it has received attention in connection with the chemistry of iodine in the atmosphere. It should be noted that though methyl iodide is the most widely studied of the marine-produced volatile iodinated compounds, it is not the only one; others include CH₂I₂, CH₂ClI, C₂H₅I and C₃H₇I. Its atmospheric lifetime is so short that its atmospheric concentration is commonly very low, ~1–2.5 ppt. A consequence is that the surface ocean is almost invariably supersaturated unlike the case for CH₃Cl and CH₃Br, though undersaturation has been reported in the Greenland-Norwegian Sea area in the month of November [59]. A recent study [22] of methyl iodide using data from Atlantic and Pacific waters arrived at an estimate for the ocean to

atmosphere flux of $0.9 - 2.5 \times 10^9$ mol year⁻¹. Surface concentrations and vertical profiles were consistent with an average production rate of 0.5 pmol L⁻¹ d⁻¹. In a study made north of the Azores during summer, a number of water samples were incubated on board ship and CH₃I measured with time; four such measurements gave an average production rate of 2.4 pmol L⁻¹ d⁻¹ [69].

5 Polychlorinated Compounds

Whereas the study of the major polybrominated compounds, CHBr₃ and CH₂Br₂, in the ocean has been simplified by the fact that they do not have significant anthropogenic sources, the same is not true of the equivalent chlorinated compounds. In some cases there is undisputed evidence that a compound does have some production within the ocean, for example, chloroform, but in many cases much remains to be done in determining the true magnitude of marine production as well as the source mechanisms.

5.1 Chloroform

From the observed concentration of chloroform in the atmosphere and from its chemical loss rate within the atmosphere it becomes apparent that anthropogenic sources account for only about 15% of the supply [25]. The sole estimate of the ocean to atmosphere flux of chloroform, based on the analysis of only ten samples of ocean water [70] is 0.35 Tg year⁻¹, which would account for about 76% of the atmospheric sink. When combined with an estimated soil emission of 0.2 Tg year⁻¹ and the anthropogenic release of 0.07 Tg year⁻¹, the total emissions are about 37% higher than needed to balance the atmospheric sink (0.46 g year⁻¹). Keene et al. [25] point out that such a large ocean source appears inconsistent with observations that the gas is twice as abundant in the Northern Hemisphere as in the Southern. It seems likely that an excessive exchange velocity has been used to calculate the ocean to atmosphere fluxes [70], so that ocean emissions could be lower by a factor of two.

While a macroalgal source of chloroform has been established [31, 32], its global contribution has been estimated [32] to be insignificant. At present there is only one report of chloroform production by a marine microalga [44], a species that has a restricted distribution in the oceans, being limited primarily to the intertidal and subtidal zones.

A further difficulty that arises in ascertaining the contribution of marine-produced chloroform is the fact that it appears to have a long residence time in the ocean giving a high background concentration throughout the water column. This makes it relatively difficult to identify local production and, as discussed in relation to trichloroethylene and tetrachloroethylene below, could also account for a portion of the ocean supersaturation. Thus, while there is strong evidence that CHCl₃ is largely natural, the magnitude and nature of its marine source are highly uncertain.

5.2

Trichloroethylene and Tetrachloroethylene

There has recently been much interest in the possibility that chlorine atom chemistry is important over the ocean [71]. This has led to some particular interest in sources of atmospheric tetrachloroethylene as it can provide information on the relevance of chlorine atom-initiated oxidation reactions. The reason is that there must be consistency between the observed concentrations of the gas in the atmosphere, its rate of chemical destruction and its rate of supply. The chemical loss rate would be particularly sensitive to Cl atom concentration because the gas reacts at a rate ~ 300 times faster with Cl than with the OH radical [72]. There are reports that tetrachloroethylene and also trichloroethylene are supersaturated in ocean waters [73, 74], and therefore the ocean represents a source of these compounds to the atmosphere. The Reactive Chlorine Emissions Inventory has put the oceanic source at $0.019 \text{ Tg year}^{-1}$, equivalent to about 4% of estimated industrial emissions. There is a mismatch between total sources and sinks of $0.13 \text{ Tg year}^{-1}$, with sinks exceeding known sources. Natural production of both C_2HCl_3 and C_2Cl_4 has been reported [75, 76] in laboratory cultures of both macrophytes and microalgae, with additional evidence from measurements in a tidal pool [77] and, for trichloroethylene, from measurements in the open ocean [78]. In contrast, Marshall et al. [61] did not detect production of either compound in cultures of the same macrophyte, *Falkenbergia*. An independent laboratory study [44] of the red microalga, *Porphyridium purpureum*, found no release of either compound. In their study of halocarbon release by macrophytes, two rock pool studies [31, 32] did not find evidence for production of C_2HCl_3 and C_2Cl_4 . It should be noted that the absence of production of a compound in a particular study cannot prove that it cannot be produced. Marshall et al. [61] pointed out the possibility of production of both C_2HCl_3 and C_2Cl_4 through dehydrohalogenation reactions.

Moore [74] has found that both C_2HCl_3 and C_2Cl_4 have rather unusual oceanic distributions with their concentrations increasing with depth. Such distributions are different from the methyl halides, which have their highest concentration near the surface where they are produced. In part the difference apparently stems from a much longer lifetime of both C_2HCl_3 and C_2Cl_4 in ocean waters. But recent measurements of C_2HCl_3 in the Labrador Sea show similarities between its distribution and that of trichlorofluoromethane (CFC11), which is entirely anthropogenic and is invading the deep ocean from the atmosphere. Their short atmospheric lifetimes cause C_2HCl_3 and C_2Cl_4 to have a strong seasonal variation of their concentrations in high northern latitudes, with concentrations reaching their maxima during winter. Subsurface and deep waters have initially acquired their temperature and atmospheric gas composition through equilibration, or partial equilibration, with the winter atmosphere. It appears that atmospherically-derived C_2HCl_3 and C_2Cl_4 , as well as man-made Freons may be preserved within these waters. Subsequent mixing with surface waters at lower latitudes or in summer months could result in supersaturations of these compounds at the surface. Thus, the observation that supersaturations exist should not lead to the presumption that a compound has been formed within the ocean. If much more ex-

tensive data sets were available, including wintertime distributions, there should be no danger of a compound being incorrectly assigned an oceanic source, for the compensating uptake from the atmosphere would be apparent from the winter measurements.

5.3

Dichloromethane

This compound is relatively abundant in ocean waters and there are plausible mechanisms whereby it could be produced in situ. These include reactions of CH_2Br_2 , CH_2I_2 and CH_2ClI with chloride ion. The possibility exists also for its direct production by mechanisms analogous to those that yield CH_2Br_2 and CH_2I_2 . There is one recent report of its enrichment in a rock pool [32]. Dichloromethane shows a remarkable degree of similarity in North Atlantic concentration profiles with those of CFC11 (Fig. 1). This would be consistent with it having an atmospheric source, though it is possible that it is also related to a slow degradation of CH_2Cl_2 in seawater. Therefore, the ocean inventory of CH_2Cl_2 may have significantly, if not entirely, been derived from anthropogenic emissions. In the presence of a substantial background of manmade CH_2Cl_2 it could be very difficult to identify true marine-derived material.

6

Sinks

Although the focus of this chapter is marine sources of organohalogens, it is commonly the case that we wish to know the net flux of a compound between ocean and atmosphere, or more specifically, we wish to understand the processes that account for the level of saturation of that compound in any water body. This means that we must be concerned with the existence of sinks as well as sources. A good example is provided by oceanic methyl bromide that, while having major marine production, has a net flux from atmosphere to ocean. In some cases, simple chemical reactions such as hydrolysis and nucleophilic substitution can represent important sinks, as in the case of methyl bromide [68]. Chemical loss rates in warm waters of the Caribbean and Pacific have been reported [79] as 0.3 and 0.25 day^{-1} , respectively. Were these the only sinks, it would be expected that major emissions of algal-produced organohalogens would occur in cold, highly productive seas, but in contrast it is found that methyl bromide and chloride are commonly undersaturated in these waters [80, 81]. For methyl bromide an apparently biological sink has been identified in both coastal and ocean waters with the loss appearing from filtration studies to be the result of microbial processes [13, 82, 83]. Tokarczyk and Saltzman [79] report that in the relatively low temperature waters of the N. Atlantic, biological loss accounted for $\sim 35\%$ of the in situ losses of methyl bromide. Recent work has provided evidence for a seasonal cycle in the removal of methyl chloride from seawater, again with an inferred microbial mechanism.

Biological processes have been shown to be responsible for losses of CH_2Br_2 and CHBr_3 in laboratory experiments with *Asparagopsis* [28]. The CH_2Br_2 loss

appeared to be attributable to organisms that occurred on the macrophyte, but which were released to the medium on prolonged incubation (since CH_2Br_2 loss was seen to occur whether or not the macrophyte was removed from the medium, but loss would not occur in a spiked seawater control). Bromoform removal occurred effectively only when the alga was present and was attributed to physical absorption or biochemical conversion within the algal biomass. Goodwin et al. [82, 83] have demonstrated that bacteria are able to oxidize CH_2Br_2 in seawater.

There are a number of reports of halocarbon degradation in low oxygen waters; several refer to CCl_4 [84, 85, 60], but there is evidence also for reduction of chloroform [60] in the Black Sea. Since low oxygen conditions are not common in the open ocean, these processes are probably not significant on a global scale, but they are relevant in environments such as the Black Sea and Baltic Sea, and also in tracer studies which are based on the principle of conservative behaviour of the tracer [84, 85].

7

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