



## Review

# Pattern and sources of naturally produced organohalogenes in the marine environment: biogenic formation of organohalogenes

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**Abstract**

The pattern of organohalogenes found in the marine environment is complex and includes compounds, only assignable to natural (chloromethane) or anthropogenic (hexachlorobenzene, PCBs) sources as well as compounds of a mixed origin (trichloromethane, halogenated methyl phenyl ether).

The chemistry of the formation of natural organohalogenes is summarized. The focus is put on volatile compounds carrying the halogens Cl, Br, and I, respectively. Though marine natural organohalogenes are quite numerous as defined components, they are mostly not produced as major compounds. The most relevant in terms of global annual production is chloromethane (methyl chloride). The global atmospheric mixing ratio requires an annual production of 3.5–5 million tons per year. The chemistry of the group of haloperoxidases is discussed. Incubation experiments reveal that a wide spectrum of unknown compounds is formed in side reactions by haloperoxidases in pathways not yet understood.

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*Keywords:* Organohalogen; Haloperoxidase; Haloform reaction; Methylchloride; Chloroform; Marine atmosphere; Bioproduction

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## 1. Introduction

Halogenated compounds found in the environment can be classified as being:

- biogenic (e.g. CH<sub>3</sub>Cl)
- natural/geogenic (e.g. specific dioxins in clay)
- having anthropogenic non-halogenated precursors (e.g. halogenated phenols formed from phenol)
- having anthropogenic halogenated precursors (e.g. chlorophenols formed from chlorobenzenes, pentachlorophenyl methyl ether formed from pentachlorophenol), or
- anthropogenic (e.g. freons, CH<sub>3</sub>CCl<sub>3</sub>, PCBs, POPs).

Since the identification of 6,6'-dibromoindigotin (Tyrian Purple) in marine snails in 1909, a variety of biogenic carbon-halogen compounds has been detected in algae, fungi, plants and biota. The wide spectrum of natural halogenated compounds has been summarized in the past by several authors (Doonan, 1973; Fenical, 1982; Faulkner, 1984; Neidleman and Geigert, 1986; Grimvall and de Leer, 1995; Gribble, 1996, 1998, 1999).

Recently the group of persistent organic pollutants, the so-called POPs, which are mostly semivolatile chlorinated compounds, have gained wide political visibility thanks to actions of the UN. Ballschmiter summarized the possible spectrum of compounds that have to be discussed in this respect (Ballschmiter et al., 2001).

Polyhalogenated bi-pyrrols identified in the marine environment can be described as natural POPs, persistent organic pollutants. These halogenated 2,2'-bipyrroles, e.g. C<sub>10</sub>H<sub>6</sub>N<sub>2</sub>Br<sub>4</sub>Cl<sub>2</sub>, a 1,1'-dimethyl-tetrabromodichloro-2,2'-bipyrrole accumulate e.g. in fish, birds and marine mammals like the PCBs. (Gribble et al., 1999; Tittlemier et al., 1999, 2002a,b). A C<sub>9</sub>H<sub>3</sub>N<sub>2</sub>Cl<sub>7</sub> compound (Q<sub>1</sub>/U<sub>3</sub>) has also been identified as a bioaccumulating natural product (Weber and Goerke, 1996; Vetter, 1999; Vetter et al., 1999, 2000). The compound C<sub>9</sub>H<sub>3</sub>N<sub>2</sub>Cl<sub>7</sub> (Q<sub>1</sub>/U<sub>3</sub>) is a heptachloro-1'-methyl-1,2'-bipyrrole (Wu et al., 2002).

A similar global spreading through the marine biosphere as it is observed for the PCBs has not been found yet for this natural heptachlorinated 1,2'-bipyrrol (Hackenberg et al., 2001). Vetter also reported a mixed halogenated trichlorodibromo-compound in fish and seal (Vetter et al., 2001). It was tentatively assigned to a monoterpene structure.

The occurrence of natural organohalogen resembling the PCB structure, specifically a broad spectrum of volatile and bioaccumulative organohalogen, has stimulated a renewed interest in the chemistry of formation of natural organohalogen compounds under environmentally conditions. It has been known for long that fungi, for example, produce chlorophenols (Turner, 1971). The higher chlorinated compounds of this group are considered as classical anthropogenic compounds found in the environment. Even the natural formation of dioxins of the 2,3,7,8-type has been reported (Svenson et al., 1989; Hoekstra et al., 1999; Ferrario et al., 2000).

## 2. Biogenic fluorinated compounds

Biogenic formation of fluoro-organic compounds is mainly of theoretical relevance, though the rare organofluorine compounds are more widely spread in nature than originally presumed. F-metabolites have been discovered in bacteria, fungi (*Streptomyces* sp.) and higher plants but not yet in algae (Neidleman and Geigert, 1986; O'Hagan and Harper, 1999; O'Hagan et al., 1999). The toxic monofluoroacetate is found in numerous higher plants at the trace level. Ceylon tea may contain 50–160 ng/g monofluoroacetate, China Green Tea may contain 230 ng/g monofluoroacetate (Vartiainen and Kauranen, 1984; Vartiainen et al., 1995). For CF<sub>4</sub> a geogenic formation in volcanoes has been reported.

O'Hagan and his group recently presented a pathway of biological fluorination involving an S-adenosylmethionine (SAM) as the first acceptor of the fluoride ion

(Murphy et al., 2001; Schaffrath et al., 2001; O'Hagan et al., 2002).

### 3. Volatile organohalogenes in the marine environment

For natural organohalogen compounds found in the marine environment Br mostly dominates over Cl, while for natural organohalogenes found in the terrestrial environment Cl dominates over Br. The volatile organohalogenes like the methane derivatives CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CH<sub>3</sub>I, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>Br<sub>2</sub>, CH<sub>2</sub>I<sub>2</sub>, CH<sub>2</sub>ClBr, CH<sub>2</sub>ClI, CHCl<sub>3</sub>, CHBr<sub>3</sub>, CHBrCl<sub>2</sub>, CHBr<sub>2</sub>Cl, several halogenated ethanes and acetones, and even halogenated methyl-phenyl ethers (anisoles, X<sub>2</sub>C<sub>6</sub>H<sub>5</sub>-(OCH<sub>3</sub>), (X = Br, Cl) can be found worldwide in the marine environment (Table 1) (Lovelock, 1975; Moore, 1977, 1979; Khalil et al., 1983; Kirschmer and Ballschmiter, 1983; Kirschmer et al., 1983; Moore and Tokarczyk, 1993; Führer et al., 1997; Führer and Ballschmiter, 1998).

For the occurrence of some of these compounds, biogenic as well as specific anthropogenic sources such as water chlorination have to be taken into consideration. While the sources of anthropogenic organohalogenes are defined by their industrial production, as well as point source and non-point source applications giving the emission pattern. The sources of biogenic organohalogenes in the environment are widely spread, and spatially and temporarily changing. In the marine environment mostly regional sources, defined by upwelling

water in near shore or off-shore areas, cold water or tropical regions with high primary production rates, including coral reefs, can be given as the generalizing descriptors (Class et al., 1986; Class and Ballschmiter, 1987a,b, 1988).

It has been shown by many authors that macro- and microalgae, particularly the brown algae (Phaeophytae), release dihalo- and trihalomethanes and further brominated and iodinated compounds (Lovelock, 1975; Burreson et al., 1976; McConnell and Fenical, 1976; Moore, 1977; Class and Ballschmiter, 1986; Class et al., 1986; Class and Ballschmiter, 1987a,b; Manley and Dastoor, 1987; Class and Ballschmiter, 1988; Manley et al., 1992; Laturus et al., 1995; Scarratt and Moore, 1999). In the terrestrial environment fungi living in the soils are the major sources of organohalogenes (Turner, 1971; Frank et al., 1989; Asplund et al., 1993; Laturus et al., 1995).

The concentrations of organohalogenes in the troposphere are functions of the strengths of all anthropogenic and natural sources and sinks, and of the mixing by the global wind system, the general circulation (Ballschmiter, 1992). The global sink e.g. for CHCl<sub>3</sub> is mainly degradation by OH radicals in the troposphere. The atmospheric lifetime of CHCl<sub>3</sub> ( $k_{OH} = 10^{-14}$  cm<sup>3</sup> s<sup>-1</sup>) lies between 40 days in the tropics ( $c_{OH}$  about 3 10<sup>6</sup> molecules cm<sup>-3</sup>) and increases to 400 days in the region of the northern and southern westwind belt ( $c_{OH}$  about 0.3 × 10<sup>6</sup> molecules cm<sup>-3</sup>). Knowing the long-time environmental fate of natural volatile organohalogenes can help assess the impact of the anthropogenic portion

Table 1  
Selection of volatile halogenated compounds found in the environment

<i>C<sub>1</sub> compounds</i> H <sub>3</sub> CX, H <sub>2</sub> CX <sub>2</sub> ; HCX <sub>3</sub> , (CX <sub>4</sub> )	X = Cl, Br, J	(and mixed halogenation)
<i>C<sub>2</sub> compounds</i> XCH <sub>2</sub> -CH <sub>2</sub> X X <sub>2</sub> CH-CH <sub>3</sub> Haloacetonitriles Haloacetaldehydes Haloacetic acids	(X = Cl, Br, J) (X = Cl, Br) X <sub>n</sub> CH <sub>(3-n)</sub> CN X <sub>n</sub> CH <sub>(3-n)</sub> CHO ClCH <sub>2</sub> -COOH	(and mixed halogenation) (and mixed halogenation)
<i>C<sub>3</sub> compounds</i> CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> J Haloacetons	(Cl, Br, J in <i>Asparagopsis</i> sp., a red algae)	
<i>Aromatic derivatives</i> Halophenols Halophenylmethyl ether Bromodiphenyl ether	X <sub>n</sub> (Phe)OH X = Cl, Br; X <sub>n</sub> (Phe)OCH <sub>3</sub> X = Cl, Br; Br <sub>3</sub> (Phe)O(Phe)Br <sub>3</sub>	(and mixed halogenation) (and mixed halogenation)

of this group of compounds found in the environment. The role of the naturally occurring bromo-/chloro- and bromomethanes in the atmospheric chemistry of the near surface atmosphere and the stratosphere has stirred wide interest. Ozone depletion periods at polar sunrise in the lower Arctic atmosphere give an inverse correlation to “bromine” linked to the photochemistry of  $\text{CHBr}_3$  (Barrie et al., 1988). The photolytic degradation of  $\text{CHBr}_3$  as a source of Br atoms discussed by Barrie et al. can be extended to further bromo/iodomethanes present in the Arctic atmosphere.

#### 4. Pathways of formation of natural organohalogenes

##### 4.1. Methylation reaction

$\text{CH}_3\text{Cl}$  is by far the most abundant volatile, naturally formed organohalogen. The global atmospheric mixing ratio requires an annual production of 3.5–5 million tons per year of chloromethane (Khalil et al., 1999; Khalil and Rasmussen, 1999a,b; Harper, 2000). The global atmospheric mixing ratio of methyl bromide is substantially lower (Khalil et al., 1993) (Table 2).

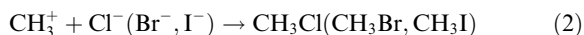
The formation of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$  is mainly through biomethylation of the respective  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  anions. Emissions of chloromethane from terrestrial sources—including tubers of potatoes—have gained an increased importance in the past (Saxena et al., 1998; Watling and Harper, 1998; Harper et al., 1999).

The chemistry of formation of chloromethane, bromomethane, and iodomethane ( $\text{CH}_3\text{X}$ ) by methylation can be explained by assuming that sulfonium compounds act as a formal  $\text{CH}_3^+$  donor for the respective anions (Urhahn and Ballschmiter, 1998). Sulfonium compounds that have to be considered are:

- (a) dimethyl-b-propiothetin (algae, animals)  
 $(\text{CH}_3)_2\text{S}^+\text{CH}_2\text{CH}_2\text{COO}^-$   
 (b) S-adenosyl-L-methionin (SAM)  
 $\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{S}^+(\text{CH}_3)\text{adenosin}$

- (c) methionin methyl sulfonium chloride (MMSCl)  
 $\text{HOOC}(\text{NH}_2)\text{HCH}_2\text{CH}_2\text{S}^+(\text{CH}_3)_2\text{Cl}^-$

These compounds lead to the basic reaction:



Levels of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{I}$  generally do not correlate in the marine boundary layer (MBL). Chloromethane itself acts as methyl-group donor for certain fungi that can live on it as the sole carbon source (Coulter et al., 1999; Studer et al., 2001). It is used in the O-methylation of phenols (Harper et al., 1996).

Methyl-sulfonium compounds react spontaneously in *in vitro* experiments with  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  to  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$ . *In vitro* incubations of methionine methyl sulfonium chloride (MMSCl) plus chloroperoxidases increased the formation of methyl halogenides (Urhahn and Ballschmiter, 1998).

##### 4.2. Radical intermediates

A possible bioformation of  $\text{CCl}_4$  might occur via a radical mechanism though final proof is still open. Radical mechanisms have to be discussed when a light-driven halogen exchange is involved (Urhahn and Ballschmiter, 1998).

Haloamines like *N*-chlorosuccinimide are known to deliver halogen radicals rather than halogen cations.

##### 4.3. Halogen exchange

Exchange of iodine or bromine by chlorine in compounds that are primarily of biogenic origin either by a light-driven radical mechanism or by an ionic  $\text{Br}^-/\text{Cl}^-$  or  $\text{I}^-/\text{Cl}^-$  exchange, will lead to new products e.g.:



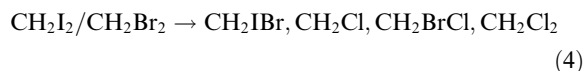
Table 2

Levels of monohalogenated ( $\text{CH}_3\text{X}$ ) and trihalogenated methanes ( $\text{CHX}_3$ ) in the marine background troposphere

Compound	NH (pptv)	SH (pptv)	Tropic (pptv)	Pacific <sup>a</sup>	Global Mio t/year input
<i>(CH<sub>3</sub>X)</i>					
$\text{CH}_3\text{Cl}$	620	620	631		3.5–5 <sup>b</sup>
$\text{CH}_3\text{Br}$	15	11	14		0.8
$\text{CH}_3\text{I}$	2	2	1.1		3
<i>(CHX<sub>3</sub>)</i>					
$\text{CHCl}_3$	21	11	8.5		
$\text{CHBr}_3$	0.9	0.6	1.8		

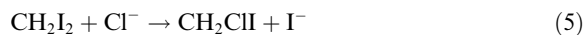
<sup>a</sup> Atlas et al. (1993).

<sup>b</sup> Estimated natural emission in Mio t/year: 4 in total according to the atmospheric load: oceanic: 0.3–2.0—range under discussion, biomass burning: 0.4–1.4; emission by fungi: 0.16 (Watling and Harper, 1998; Harper, 2000).



A photoinduced [ $\lambda > 290$  nm] iodo/bromo/chloro-exchange from the biogenic halomethanes  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{I}_2$ ,  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$  could add to the occurrence of the mixed halomethanes found in marine air and water. Such an exchange has been demonstrated under in vitro conditions (Class and Ballschmiter, 1987a,b).

$\text{CH}_2\text{I}_2$  is released from algae from the Sargasso Sea and has been detected in air samples at coastlines.  $\text{CH}_2\text{ClI}$  could be formed from  $\text{CH}_2\text{I}_2$  via light-induced halogen exchange:



The reaction (5) could be simulated in artificial seawater (salinity 2%) and is induced by light (>290 nm). A formation of  $\text{CH}_2\text{ClI}$  by an  $\text{I}^-/\text{Cl}^-$  exchange has not been observed in the dark. Using light sources with wavelengths shorter than 290 nm generated  $\text{CH}_2\text{BrCl}$  from  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBrCl}_2$  from  $\text{CHBr}_3$  in artificial seawater.  $\text{CH}_2\text{ClI}$ ,  $\text{CH}_2\text{BrCl}$  and  $\text{CHBrCl}_2$  lead to a similar substitution forming  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , respectively (Class and Ballschmiter, 1987a,b).

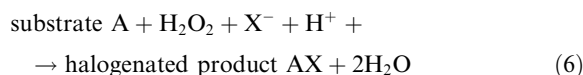
These exchange reactions may also be induced by sunlight and unknown photoreactive chromophores that could photosensitize the halogen-exchange reaction via a radical mechanism in the marine environments. More likely though is the formation of the  $\text{C}_1/\text{C}_2$ -halocarbons via the interaction of haloperoxidases and carbonyl-activated C–H bonds.

#### 4.4. Halogenation of C–H-activated bonds by haloperoxidases

A major production pathway in formation of the C–Hal bond is the reaction of an activated C–H-bond, e.g. in the  $\alpha$ -position to a carbonyl- ( $>\text{C}=\text{O}$ ) or carboxyl-group ( $-\text{COOH}$ ) by haloperoxidases. If it is followed by hydrolysis of the  $(\text{Hal})_x\text{C}-(\text{C}=\text{O})$ -bond, it leads to halomethanes (haloform reaction). Methyl sulfon compounds  $\text{R}-\text{S}(\text{O})_2-\text{CH}_3$  undergo a similar reaction (sulfo-haloform reaction).

A decarboxylation reaction could be involved in the formation of  $\text{CCl}_4$ . Mixed tetrahalomethanes could also be formed this way.  $\text{CCl}_3\text{Br}$  has been observed in the marine atmosphere (Urhahn and Ballschmiter, 2001).

Haloperoxidases are enzymes that are widely distributed throughout nature. They are a subgroup of peroxidases. Every haloperoxidase is a peroxidase, but the reverse is not true. Haloperoxidases are able to carry out a multitude of reactions following the general equation:



In reaction (6) the formation of HOX is considered to be the relevant intermediate step of the halogenation, but a mechanism with an enzyme-bound intermediate, depending on the presence of a substrate and the type of halide ion has also been presented (Colpas et al., 1994, 1996). Chloroperoxidases may also use chlorite ( $\text{ClO}_2^-$ ) instead of  $\text{Cl}^-$  and  $\text{H}_2\text{O}_2$  to form the halogenated product.

Haloperoxidases have been the topic of several reviews (Neidleman and Geigert, 1986; Vanpee, 1990; Butler and Walker, 1993; Franssen, 1994a,b; Butler, 1999; Littlechild, 1999; Almeida et al., 2001).

Haloperoxidases are grouped according to which halide ion they are dominantly able to utilize for the halogenation. Chloroperoxidases (CPO) use  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ ; bromoperoxidases (BPO), e.g. lactoperoxidase (LPO) and horseradish peroxidase (HRP) utilize  $\text{Br}^-$  and  $\text{I}^-$ ; while iodoperoxidases use  $\text{I}^-$  as the halogen source.

Haloperoxidases differ by the metal ion associated with the prosthetic group. Haloperoxidases mostly contain iron (III) as a ferriprotoporphyrin IX. A chloroperoxidase that contains manganese (II) has been isolated from *Caldariomyces fumago*. A haloperoxidase activity of manganese peroxidase has been reported (Sheng and Gold, 1997).

A bromoperoxidase was isolated from brown algae containing vanadium(V) as a prosthetic group. Metal-free haloperoxidases have also been reported (Bongs and Vanpee, 1994; Picard et al., 1997; Kirk and Conrad, 1999).

Synthetic haloperoxidases have been prepared by metal substitution incorporating Co, Ni, Zn, Cu. An oxomanganese(V) porphyrin is reported to mimic a bromo haloperoxidase with enzymatic rates (Jin et al., 2000). In the biosynthesis of halometabolites NADH-dependent halogenases can also be involved (Hohaus et al., 1997).

#### 4.5. Halogenation of the aromatic ring

The direct halogenation of the aromatic system of the anisols or phenols, methylpyrrols and others by haloperoxidases or *N*-halogen systems is observed (Walter and Ballschmiter, 1991b; Hegde et al., 1996; Führer and Ballschmiter, 1998; Tittlemier et al., 2002b).

### 5. In vitro incubations with chloroperoxidase (CPO)

To evaluate the possible formation of volatile halogenated  $\text{C}_1/\text{C}_2$ -hydrocarbons several in vitro incubations with chloroperoxidase (CPO) and horseradish peroxidase (HRP) were carried out with substrate molecules that are common in biochemistry and which possess a carbonyl-activated site (Walter and Ballschmiter, 1991a,b).

The pattern of compounds detected by high resolution capillary gas chromatography and ECD detection is surprisingly high and variable that is formed by different types of haloperoxidases and a variety of normal biochemical precursors ranging from acetic acid and acetyl-CoA to a broad spectrum of biogenic aldehydes, ketones and carboxylic acids including their hydroxy- and amino-substituted derivatives. The full spectrum of products formed by the enzymatic halogenation is not yet elucidated.

The reaction of a glucose oxidase and haloperoxidase has been successfully combined in the production of halocarbons (Walter and Ballschmiter, 1992).

The hydrogen peroxide formed by the first enzymatic reaction was used to drive the halogenation in the second enzymatic step. No external H<sub>2</sub>O<sub>2</sub> was added and only the dissolved oxygen was used by the glucose oxidase. Oxidases are of the two-electron transfer type and react with oxygen as acceptor for hydrogen to form H<sub>2</sub>O<sub>2</sub>. Amino acid oxidases and xanthin oxidases belong to the same group as glucose oxidase. The oxidases lead to  $\alpha$ -ketoacids, thus producing the H<sub>2</sub>O<sub>2</sub> and directly preferred substrates for the haloperoxidase halogenation.

### 5.1. Formation of (Cl, Br) C<sub>2</sub>-alkanes and alkenes in chloroperoxidase experiments

Incubation of acetone with CPO/H<sub>2</sub>O<sub>2</sub>/sea salt leads—besides the expected formation of CHBr<sub>3</sub> and CHBrCl<sub>2</sub> and mixed halogenated volatiles like CHBr<sub>2</sub>Cl—to the formation of CH<sub>2</sub>Br–CH<sub>2</sub>Br, CHCl<sub>2</sub>–CHCl<sub>2</sub>, and CHCl=CCl<sub>2</sub>, CCl<sub>2</sub>=CCl<sub>2</sub> and further not yet identified volatile compounds (Walter and Ballschmiter, 1991a,b). Assuming halogenated cyclopropanones as intermediates in a Favorskii rearrangement may explain the formation of the C<sub>2</sub> alkanes and alkenes. The production of halogenated methanes by bromoperoxidase and iodoperoxidase have been studied in marine diatom cultures (Moore et al., 1996). Next to the CPO/H<sub>2</sub>O<sub>2</sub> driven haloform reaction of carbonyl activated methyl groups, methyl-sulfur compounds—e.g. dimethylsulfoxide, dimethylsulfone, and the sulfur amino acid methionine—also can act as precursors for the biosynthesis of di- and trihalogenated methanes. Moreover there is some but not yet very conclusive evidence for an enzymatic production of tetrahalogenated methanes (Urhahn and Ballschmiter, 1998).

### 5.2. Formation of halogenated acetonitriles and acetaldehydes by chloroperoxidase

In experiments with chloroperoxidase involving further amino acids and complex natural peptide based substrates, dihalogenated acetonitriles and several other volatile halogenated but still unidentified compounds

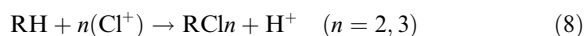
were formed (Urhahn and Ballschmiter, 1998). It appears likely that the biosynthesis of halogenated nitriles occurs in general. Moreover, there should exist a natural atmospheric background for halogenated acetonitriles and halogenated acetaldehydes (Bieber and Trehy, 1984; Peters et al., 1990a,b).

Halogenation of the CN group of acetonitriles bond may lead to halomethanes including CH<sub>3</sub>Cl. Chloroacetonitrile would thus open another way of forming chloromethane while dichloroacetonitrile would lead to dichloromethane.

## 6. Water chlorination chemistry

The similarity of the chemistry discussed above with the basic chemistry of the products formed in water chlorination should be pointed out. In water chlorination as well as in the reaction pathways involving the haloperoxidases, the active species is thought to be HOX (X = Cl, Br, I).

Haloperoxidase reaction: formation of Cl<sup>+</sup>



Water chlorination: formation of Cl<sup>+</sup>



The complete spectrum of the trihalomethanes, furthermore 1,1,1-trichloroacetone, 1,1,1-trichloropropanone, dichloroacetic acid, trichloroacetic acid, and the haloacetonitriles (e.g. dichloroacetonitrile) have been found as part of the total organic halides (TOX) formed from aquatic humic materials in water chlorination (Reckhow et al., 1990).

## 7. Marine areas of high primary production release halomethanes in the Atlantic and the Indian Ocean

Among the volatile halocarbons in the atmosphere the methylhalides CH<sub>3</sub>Cl, CH<sub>3</sub>Br and CH<sub>3</sub>I are known to be mainly of natural origin (Khalil et al., 1993; Khalil and Rasmussen, 1999a,b). The current knowledge of identity and source strength including terrestrial sources explaining the atmospheric concentration of chloromethane has recently been reviewed by Harper (2000).

Table 3  
Concentrations of halomethanes in marine surface water in nanogram/l (Class and Ballschmiter, 1987a,b)

	1 (ng/l)	2 (ng/l)	3 (ng/l)	4 (ng/l)	5 (ng/l)
CH <sub>2</sub> Cl	0.2	1	0.1	0.5	1.2
CH <sub>2</sub> Br <sub>2</sub>	0.3	1	0.3	5	20
CHCl <sub>3</sub>	1.6	1.6	1.5	4	10
CHBr <sub>2</sub> Cl	0.1	2	0.1	2	14
CHBrCl <sub>2</sub>	0.1	1	0.1	3.5	14
CHBr <sub>3</sub>	0.8	6	1.5	22	200

Sampling sites: 1: North Atlantic 31°N, 14°W, 24.3.85; surface water sample (0.5–5 m), (ANT III/4 FS “Polarstern”). 2: North Atlantic near the West African Coast 25°N, 18°W, 23.3.85; surface water sample (0.5–5 m), (ANT III/4 FS “Polarstern”). 3: Indian Ocean, Maldives Islands, 2.3.86; surface water, open sea. 4: Indian Ocean, Lohifushi, Maldives Islands, 7.3.86; surface water from the coral reef, high tide. 5: Indian Ocean, Lohifushi, Maldives Islands, 7.3.86; surface water from the coral reef, low tide.

There has been a long-standing discussion whether CHCl<sub>3</sub> besides its anthropogenic sources, which are not well defined, may have a substantial natural input in the environment (Class and Ballschmiter, 1986; Class and Ballschmiter, 1987a,b, 1988; Khalil and Rasmussen, 1999a,b). This question also may apply to CH<sub>2</sub>Cl<sub>2</sub>.

High concentrations of volatile bromo-, bromo-chloro- and iodomethanes found in marine air mostly correlate with the occurrence of macro algae at the coastlines of islands (Bermuda, The Azores, Tenerife, The Maldives Islands) or to regions of high bioactivity (upwelling water regions at the West African coast). High concentrations of CH<sub>2</sub>Br<sub>2</sub>, CH<sub>2</sub>ClI, CHBr<sub>3</sub>, CHBr<sub>2</sub>Cl, and CHBrCl<sub>2</sub> have been detected in surface water from bioactive regions near the West African coast and in water from a coral reef of the Maldives Islands. Levels of 4–10 ng/l CHCl<sub>3</sub> were found in water samples from the coral island Lohifushi (Maldives) compared to levels of 1.5 ng/l in surface water samples from the North Atlantic and the open Indian Ocean (Male Atoll, Maldives) (Table 3).

Ocean water in the upwelling regions off the coast of West Africa has a high content of chlorophyll a and diatoms. Coral reefs are the most active regions in terms of primary production in the marine environment. Measurements of halomethanes in the water column of the North Atlantic revealed that CHBr<sub>3</sub>, CHBr<sub>2</sub>Cl, CHBrCl<sub>2</sub>, CH<sub>2</sub>Br<sub>2</sub> and CH<sub>3</sub>I showed higher concentrations in coastal waters than in the pelagic zone. CH<sub>2</sub>Cl alone showed higher concentrations in surface open ocean waters. CH<sub>2</sub>I<sub>2</sub> had a strong subsurface maximum at about 50 m while CH<sub>2</sub>Cl concentrations were highest at or near the surface. Both CHBr<sub>2</sub>Cl and CHBrCl<sub>2</sub> showed increases with depth which would be consistent with a slow reaction of surface derived CHBr<sub>3</sub> with chloride ions (Moore and Tokarczyk, 1993).

The natural formation of chlorinated methanes is of major importance for the discussion of the source strengths of CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> in the environment and of the ecotoxicological relevance of very low concentrations of these compounds (Urhahn and Ballschmiter,

1998). In the northern hemisphere atmospheric chloroform levels of 8 pptv (40 ng/N m<sup>3</sup>) at 3500 m above sea level and therefore well above tradewind inversion, of 15 pptv (80 ng/N m<sup>3</sup>) for the MBL of the north east tradewind, and a level of 25 pptv (130 ng/N m<sup>3</sup>) for marine air of the westwind belt, respectively, have been measured in October 1987 at Tenerife, Canary Islands (Class and Ballschmiter, 1987a,b). The global level based on data from 1985 to 1995 is around 18.5 pptv with small mainly seasonal variations (Khalil and Rasmussen, 1999a,b). A substantial latitudinal gradient is observed; there is about 1.7 times as much chloroform in the northern hemisphere as in the southern hemisphere. Earlier studies are summarized in Khalil et al. (1983).

Levels up to 130 pptv (700 ng/N m<sup>3</sup>) have been measured for chloroform in continental air from Central Europe (Class and Ballschmiter, 1986). The natural formation of chloroform and other halomethanes in soil has been reported by several authors (Frank et al., 1989; Hoekstra et al., 1998; Haselmann et al., 2000a,b; Laturus et al., 2000; Hoekstra et al., 2001). The results indicate a substantial natural terrestrial source for chloroform as it is observed in marine areas of high primary production.

## 8. Pattern of global occurrence of halogenated phenyl methyl ether (HMPEs; halogenated anisols) in the marine atmosphere

Chlorophenols are normally considered as anthropogenic compounds. Chlorophenols however have been detected in fungi and soil (Hoekstra et al., 1999). The biosynthesis of chloro-metabolites by fungi has been extensively reviewed by Turner (1971).

Bromophenols are quite often found as chemical repellants in marine biota. Methylation of phenols leads to the quite volatile anisols that can be detected in the marine atmosphere on a global scale (Table 4) (Walter and Ballschmiter, 1991a,b; Führer and Ballschmiter, 1998; Pfeifer, 2002).

Table 4

Levels of chloro- and bromo-phenyl methyl ether (HMPEs) in the marine boundary layer (MBL) of the North- and South Atlantic in picogram/m<sup>3</sup> (Pfeifer, 2002)

Chloro-anisols		pg/m <sup>3</sup>
2,4,6-Trichloro-anisol	(A 14)	2–140
2,3,4,6-Tetrachloro-anisol	(A 17)	0.7–10
Pentachloro-anisol	(A 19)	0.2–12
Bromo-anisols		
2,4-Dibromo-anisol	(A 24)	0.2–7
2,6-Dibromo-anisol	(A 26)	0.4–3.6
2,4,6-Tribromo-anisol	(A 33)	0.5–42

Biogenic and anthropogenic sources of the halogenated phenyl methyl ether can be distinguished. Phenyl methyl ethers of biogenic origin are 2,4-dibromo-phenyl methyl ether (A 24), 2,6-dibromo-phenyl methyl ether (A 26), 2,4,6-tribromo-phenyl methyl ether (A 33), 2,4-dibromo-6-chloro-phenyl methyl ether (A 83), and 2,6-dibromo-4-chloro-phenyl methyl ether (A 87). Highest levels of the bromo-anisols are found close to the equator; levels are than decreasing going south in the South Atlantic.

Phenyl methyl ethers of true anthropogenic origin are 2,4,6-trichloro-phenyl methyl ether (A 14), 2,3,4,6-tetrachloro-phenyl methyl ether (A 17), and pentachloro-phenyl methyl ether pentachloroanisol (PCA) (A 19). The levels of the three chloroanisols decrease in the Northern Hemisphere going south, while their levels are quite low and nearly constant in the South Atlantic.

The 2,4,6-trichloro-, the 2,3,4,6- tetrachloro-, and the pentachloro phenyl methyl ether in air reflect the global pollution of the marine environment by the respective chlorinated phenols used worldwide as fungicides (Führer et al., 1996; Führer and Ballschmiter, 1998).

### 9. Polychlorinated long chain (C<sub>22</sub>/C<sub>24</sub>) hydrocarbons

Unusual hexachlorinated aliphatic C<sub>22</sub> and C<sub>24</sub> compounds (sulfolipids) are found in phytoflagellatae. They contain two CH–OSO<sub>3</sub>– groups, and one CH<sub>2</sub>–CCl<sub>2</sub>–CH<sub>2</sub> moiety, one CH<sub>2</sub>–CHCl–CHCl–CH<sub>2</sub> moiety, and one CH<sub>2</sub>–CHCl–CH<sub>2</sub>–CHCl–CH<sub>2</sub> moiety (Mercer and Davies, 1979). No biochemical pathway of formation of the different (C–Cl) moieties of these polychlorinated C<sub>22</sub>–C<sub>24</sub> sulfolipids can be given yet.

### 10. Formation of halo *n*-(C<sub>1</sub>–C<sub>3</sub>) alkanes by abiotic Fe<sup>3+</sup> oxidation of organic matter—a non-biogenic natural process

Phenolic moieties of natural organic matter containing alkoxy groups can be oxidized without microbial

mediation in the presence of Fe<sup>3+</sup> that is reduced to Fe<sup>2+</sup>. During this process halides are C<sub>1</sub>–C<sub>3</sub> alkylated. Methoxy-, ethoxy-, and propoxy groups of phenolic structures apparently lead to the corresponding methyl-, ethyl-, and *n*-propyl halides (Cl, Br, I) (Keppler et al., 2000). Details of the reaction mechanism are still open.

### 11. Classical anthropogenics as naturally produced organohalogenes?

Tetrachloromethane, as well as tri- and tetrachloroethene, and hexachloroethane are normally considered as classical man-made organic atmospheric pollutants (e.g. Singh et al., 1976; Kirschmer et al., 1983; Fogelqvist, 1985; Class and Ballschmiter, 1986, 1987a,b; Wiedmann et al., 1994; Weifl, 1996; Kleiman and Prinn, 2000). The possible natural formation of tetrahalomethanes may involve a radical mechanism (Gribble, 1996; Urhahn and Ballschmiter, 2001). Tri- and tetrachloroethene have been reported to be released from seaweed; even hexachloroethane is reported to be released by three different algae (Abrahamsson et al., 1995a,b). Ethene as a phytohormon is a major biogenic product. Formation of ethene involves as a precursor the 1-amino-cyclopropane-1-carboxylic acid (ACC). ACC is formed from S-adenosyl-methionine. One might speculate whether a variation of the biochemical pathway leading to ethene may also involve the formation of halogenated ethenes like dichloroethene, trichloroethene, and even tetrachloroethene.

The global distribution of tetrachloroethene has been consistently modeled without the assumption of a biogenic input (Wiedmann et al., 1994). The calculations may have to be re-evaluated to include natural sources. Pre-industrial levels of these polychlorinated volatiles are not known yet, though ice core air bubbles or the analysis of deep-sea water could give the respective information.

### 12. Conclusions

The spectrum of natural volatile organohalogenes seems rather well established in its qualitative aspects, though single new compounds may be found in the future. It is surprising that the detailed reaction pathways of the formation of quite simple volatile organohalogenes often are not known. On the other side, the chemistry of the group of haloperoxidases as seen in incubation experiments reveals that a wide spectrum of unknown compounds is formed in side reactions in pathways not yet understood. Here is a great challenge for the future: learning how simple organohalogenes are synthesized by nature and learning what the full spectrum of the



chemistry of known enzymatic systems like the haloperoxidases is.

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