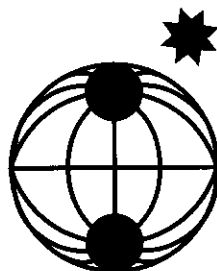
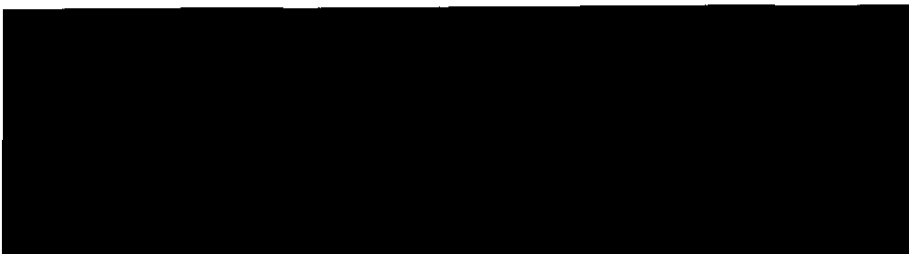


# Berichte

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**The coastal ecosystem of Kongsfjorden, Svalbard.  
Synopsis of biological research performed at the  
Koldewey Station in the years 1991 - 2003**

**Edited by Christian Wiencke**

ALFRED-WEGENER-INSTITUT FÜR POLAR- UND MEERESFORSCHUNG  
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**On the global importance of marine macroalgae as a source for  
volatile organohalogenes – An extrapolation from screening  
studies of macroalgae from Kongsfjorden, Arctic**

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### **The problem of stratospheric ozone depletion**

In 1974, M. Molina and F. S. Rowland published a theoretical paper in Nature suggesting that man-made substances, such as chlorofluorocarbons (CFCs), introduced into the troposphere can be capable of rising unchanged into the stratosphere and can play a major role in the depletion of stratospheric ozone. Almost 10 years had to pass before scientific proof of this hypothesis was obtained through the observation of a massive loss of stratospheric ozone over Antarctica (Farman et al. 1985). The depletion of the stratospheric ozone layer causes an increase of ultraviolet radiation reaching the earth's surface and can lead to many types of damage on organisms and ecosystems (Johanson et al. 1995, Franklin and Forster 1997). To counteract the ongoing ozone depletion, today's effort mainly focus on reducing or omitting industrial emissions of volatile organohalogenes. However, besides the industrial release also a natural input of volatile organohalogenes was identified, whose sources hardly can be controlled by political regulations. Knowledge of the contribution of natural sources to the global emission of volatile organohalogenes is essential to understand nature's part in ozone depletion, and to estimate the effect of global climate changes on the input of naturally produced volatile organohalogenes into the atmosphere.

### **Industrial and natural sources of volatile organohalogenes**

Chlorofluorocarbons (CFCs) and methyl bromide are the first industrially produced volatile organohalogenes under scrutiny. Due to their low chemical reactivity and long atmospheric life time, CFCs and methyl bromide can be transported into the stratosphere and act as a source for halogens involved in ozone destruction. However, other volatile organohalogenes, such as methyl chloride ( $\text{CH}_3\text{Cl}$ ), chloroform ( $\text{CHCl}_3$ ), tetrachloroethene ( $\text{C}_2\text{Cl}_4$ ), trichloroethene ( $\text{C}_2\text{HCl}_3$ ), and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), can be important too for stratospheric ozone chemistry due to the widespread use as industrial solvents, fuel components, and additives to manufactured products (Collins et al. 2001). Other sources are fossil-fuel combustion, incineration, pulp and paper manufacturing, water treatment (Keene et al. 1999), but also biomass burning for agricultural reason, as about 90% of today's biomass burning is induced by humans. Only a minor fraction is considered to be entirely natural, e.g. caused by volcanic eruptions and lightning (Lobert et al. 1999).

A possible natural formation of volatile organohalogenes was first suggested in the mid seventies of the last century (Lovelock 1975). Since then a large variety

of volatile organohalogen was identified to be of natural origin (Gribble 2003). In the marine environment, the oceans are emitting large amounts of volatile organohalogen into the atmosphere (Lovelock 1975). Although only covering 29% of earth's surface, the terrestrial ecosystem equals the marine environment as a source for volatile organohalogen. Among the identified terrestrial sources are wetlands, peat lands, coastal salt marshes, tropical plants, rice fields, soil, termites, volcano and geochemical processes in the earth's crust (Laternus et al. 2002).

### Macroalgae as a source for volatile organohalogen

In the oceans, large amounts of volatile organohalogen were detected in areas with high biological activity (Manley et al. 1992). Lovelock (1975) first proposed that the large kelp *Laminaria* was responsible for high levels of methyl iodide, which he measured in a coastal region of Southwest Ireland. Until today, several macroalgal species from different climate regions were found to emit volatile organohalogen (Manley et al. 1992, Nightingale et al. 1995, Laternus 1996). Screening studies conducted with marine macroalgae collected at Kongsfjorden, Arctic, revealed the emission of a large variety of volatile organohalogen (Laternus 1996). Bromoform is the main compound emitted by macroalgae with up to 20 to 30-fold higher released amounts compared to other mainly released compounds such as methyl chloride and dibromomethane. Besides bromine-containing compounds also iodine and chlorine-containing compounds are released by macroalgae (Laternus 2001). However, the released amounts are much smaller compared to volatile bromine-containing compounds, which in fact is surprising, especially when considering the abundant occurrence of chloride, compared to bromide, in the oceans. Apparently, the metabolism of most marine macroalgal species cannot incorporate chloride, perhaps due to its higher oxidation potential compared to bromide and iodide.

### Global importance of volatile organohalogen emission by macroalgae

The discovery of a natural input of volatile organohalogen raised the question to what extent macroalgae contributes to the input of volatile organohalogen into the atmosphere. A comparison between the atmospheric input of chlorine originating from volatile organohalogen revealed a similar importance of industrial and natural sources (Table 1). Natural sources are even more important with respect to the atmospheric input of bromine and iodine, as the industrial input is negligible or does not exist. From industrial production data, the annual industrial input is estimated to 2500 Gg chlorine and 100 Gg bromine. Global extrapolations of results obtained from single sources investigated, lead to an annual natural emission of 2000 Gg chlorine, 1600 Gg bromine and 400 Gg iodine. Among the natural sources, the terrestrial environment resembles the marine environment in the annual emission of chlorine. In contrast, natural organic bromine and iodine are almost entirely of marine origin. The only so far identified terrestrial sources are insignificant (Laternus 2003).

**Table 1.** Estimated industrial (ind) and natural (nat) emissions of volatile organohalogen.

source	CH <sub>3</sub> Cl [Gg Cl yr <sup>-1</sup> ]		CH <sub>3</sub> Br [Gg Br yr <sup>-1</sup> ]		CH <sub>3</sub> I [Gg I yr <sup>-1</sup> ]		CHBr <sub>3</sub> [Gg Br yr <sup>-1</sup> ]		CHCl <sub>3</sub> [Gg Cl yr <sup>-1</sup> ]		other [Gg Cl yr <sup>-1</sup> ]	reference
	ind	nat	ind	nat	ind	nat	ind	nat	ind	nat		
oceans <sup>c</sup>		460		123		322		1230		303		Nightingale et al. 1995, Gribble 1999, Keene et al. 1999, Lobert et al. 1995, Laternus 2001
biomass burning	640		25						2		62	Keene et al. 1999, Manó and Andrea 1994, Keene et al. 1999
incineration	32											Keene et al. 1999
industry	7		52				24 <sup>a</sup>		62		1567	Keene et al. 1999, Lobert et al. 1999, Itoh and Shinya 1994
fossil-fuel combustion macroalgae <sup>e</sup>	75										5	Keene et al. 1999
		<1		<1		<1		128		1		Laternus 2001, Nightingale et al. 1995
microalgae <sup>b</sup>		3		3		36		66		20		Scarratt and Moore 1998, Gribble 1999, Sæmundsdóttir and Matrai 1998
soil <sup>e</sup>		112								178		Khalil et al. 1999, Keene et al. 1999
termites										89		Khalil et al. 1990
rice fields <sup>f</sup>										20		Khalil et al. 1998
peatland ecosystems forest <sup>d</sup>		4		1		1				4		Dimmer et al. 2001
										4		Haselmann et al. 2000
wetlands		34		4								Varnier et al. 1999
tropical plants		639										Yokouchi et al. 2002
coastal salt marshes		120										Rhew et al. 2000
<b>total (Gg halogen yr<sup>-1</sup>)</b>												
- industrial	754		77		-		24		64		1634	
- natural		1372		131		359		1424		619		

<sup>a</sup>calculated with estimated global macroalgae biomass of  $2.8 \times 10^{14}$  g (Carpenter and Liss 2000) and release rates determined by (Laternus 2001)

<sup>b</sup>calculated with estimated global microalgae biomass of  $1.44 \times 10^{12}$  g chl a (Behrenfeld et al. 2001)

<sup>c</sup>oceanic flux minus emissions from micro and macroalgae

<sup>d</sup>for Northern temperate forests

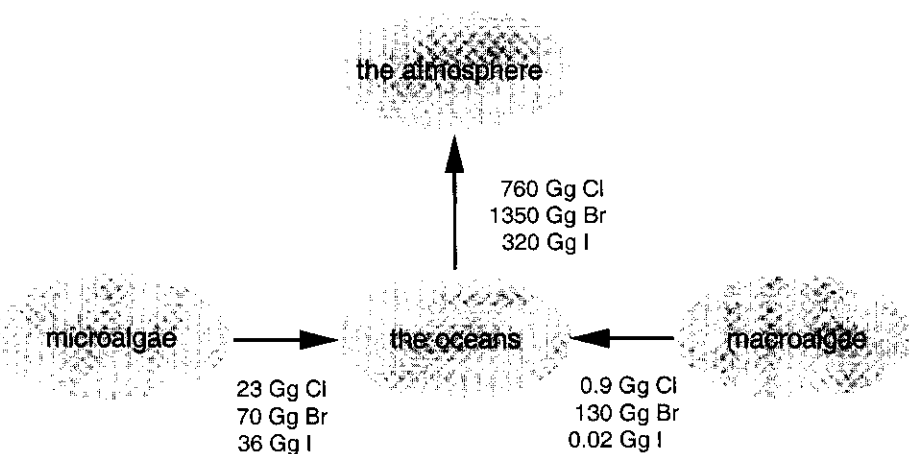
<sup>e</sup>global land area of  $68.5 \times 10^8$  km<sup>2</sup> excluding polar areas

<sup>f</sup>calculated with estimated global rice field area of  $1.45 \times 10^{12}$  m<sup>2</sup> (Redeker et al. 2000)

<sup>g</sup>inland and coastal nuclear power plants, inland fossil fuel burning, desalination, domestic and industrial water (Quack and Wallace 2003)

The oceans are considered to account for around half of the annual natural input of chloroform, methyl chloride and methyl bromide into the atmosphere, and around 90% of the annual natural input of bromoform and methyl iodide into

the atmosphere. An extrapolation using emission studies performed with macroalgae from Kongsfjorden showed that the annual contribution of macroalgae to the global emission of volatile organohalogens is negligible (<0.1%). Only bromoform with approximately 10% is more important (Figure 1). However, recently microalgae have been suggested to be a source for volatile organohalogens too (Baker et al. 1999). On a global scale, microalgae contributed twice as much as macroalgae. However, macroalgae and microalgae together account for less than 10% of the estimated annual emission of volatile organohalogens from the oceans into the atmosphere. In some regions the oceans are acting as a sink for volatile organohalogens (Lobert et al. 1997), but even this cannot explain the missing sources. The transfer, for example, of methyl bromide from the atmosphere into the oceans is estimated to 110 Gg bromine (Lobert et al. 1995). Other unknown sources must exist. Possible sources could be oceanic sediments, bacteria, geochemical processes.



**Figure 1.** Contribution of two at present identified marine sources of volatile organohalogens to the input of organic halogens from the oceans into the atmosphere.

### Influence of global climate changes

The importance of natural sources for the input of volatile organohalogens into the atmosphere may increase in future. Relevant compounds involved in ozone depletion, such as methyl halides, chloroform, bromoform, are emitted in large amounts by natural sources. Different to the industrial emissions, the natural part cannot be controlled by humans, but humans can influence it. Global climate changes as the result of human activities and uncontrolled eutrophication of the environment can effect the natural emission of volatile organohalogens. A study of macroalgae from Kongsfjorden, Arctic, Laturnus *et al.* (2000) revealed abiotic factors, such as temperature and nutrients, to

influence the release of volatile organohalogens by macroalgae. Recently, a study conducted on macroalgae from Kongsfjorden showed that elevated levels of solar ultraviolet radiation lead to an increase in the emission of volatile organohalogens by macroalgae (Laturnus *et al.* 2004). Although the regulations to reduce the input of CFCs and other man-made ozone depleting substance became effective (Tabazadeh and Cordero 2004), other factors like illegal production of ozone depleting substances (Spurgeon 1997) and large scale biomass burning may delay an early recovery of the stratospheric ozone layer. Furthermore, the warming of the troposphere at the same time leads to a cooling of the stratosphere and supports a further depletion of stratospheric ozone. A delay in recovery of the stratospheric ozone layer, however, means that elevated levels of ultraviolet radiation continue to reach the surface of the earth. Therefore, natural sources must be seen in a new light considering their source strength for volatile organohalogens, and must be included into future discussions on global climate changes.

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