

GC determination of volatile organoiodine and organobromine compounds in Arctic seawater and air samples *

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Summary. During September 1992 seawater and air samples were collected on Spitzbergen, Norway, and the concentrations of volatile organoiodine and organobromine compounds of biogenic origin were determined by a GC system supplied with a capillary column and an electron capture detector. A purge and trap technique was used to isolate the organohalogen compounds from the seawater samples, whereas the air samples were collected by an adsorption tube filled with Carbosieve S-III. The iodinated compounds CH_3I , CH_2I_2 , CH_2I , $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ and $\text{CH}_3\text{CHICH}_3$ were determined in Arctic seawater and air samples with mean concentrations in the range of (0.3–6.2) ng/l and (0.7–2) pptv, respectively. This is the first time that 1- and 2-propyl iodide could be analysed both in atmospheric samples and in seawater samples of the Arctic. CH_2Br_2 , CHBr_3 , CH_2BrCl , CHBrCl_2 and CHBr_2Cl were determined as biogenic brominated methanes in mean concentrations of (0.1–164) ng/l and (0.1–0.5) pptv in seawater and air samples, respectively. The highest concentrations in seawater samples were found for CH_2I_2 and CHBr_3 , respectively, whereas in air samples the most abundant iodinated compound was CH_3I and the most abundant brominated compounds with equal mean concentrations were CH_2Br_2 and CHBr_3 . Significant differences were found in the seawater concentration from the middle of the fjord and the shore site, compared with samples from a field of algae. In all cases the concentration was higher for the samples from the field of algae with an especially high excess by a factor of 4–9 for CH_2I_2 and CHBr_3 . This result shows that algae are an important biological species in the polar region for the production of these halogenated substances. Whereas the brominated compounds in seawater samples correlate well with each other, CH_3I or any other iodinated compound does not correlate with the bromomethanes. This indicates a different biogenic mechanism for their formation. Under certain preconditions the annual flux from the Arctic Ocean to the atmosphere could be calculated for CH_3I to be 4×10^9 g, for CHBr_3 to be 5.4×10^{10} g, which is an essential contribution to the total global budget of these important atmospheric trace gases.

Introduction

Whereas many investigations have been carried out in the past on anthropogenic halogenated organic compounds such as Freons and hazardous toxic organic substances in the environment [1, 2], only relatively little is known on the biogenic halogenated hydrocarbons. Because of their high biological production rates the polar oceans should produce an essential portion of the total global amount of biogenic organoiodine and organobromine compounds emitted into the atmosphere. In the atmosphere, iodine and bromine radicals can be formed by photodissociation, which makes these halogenated compounds important substances for atmospheric reactions. For example, an influence on the tropospheric ozone concentration may be possible and also a partial influence on the stratospheric ozone cannot be totally excluded [3, 4]. Most of the investigations on iodinated organic compounds deal with CH_3I [4–7], although CH_2I and CH_2I_2 have also been detected, for example, at a few locations in the Atlantic Ocean and its corresponding atmosphere by Class et al. [8, 9] and by Reifenhäuser and Heumann in the Antarctic Ocean [4]. Many more investigations have been carried out up to now on the bromomethanes in different parts of the marine atmosphere and the corresponding seawater than on iodinated compounds [8–11]. Although the mechanism of formation is not quite clear for the discussed halogenated substances, it was found that phytoplankton and macroalgae are able to produce these compounds and to release them into the seawater [12–14].

Experimental

Sampling and sample treatment

34 seawater and 17 air samples were collected around Ny Ålesund (79° 93' N, 11° 95' E) on Spitzbergen, Norway, from September 1st to September 25th, 1992. Seawater samples were taken from the sea surface of the Kongsfjord at Ny Ålesund directly at the shore and in the middle of the fjord about 1 km away from the sampling point of shore site. Additionally, seawater samples from a field of algae near the coast line were also collected 0.5 m above the sea bottom and (2–6) m under sea level. The air samples were always collected about 15 m easterly of the German Station Koldey (against the normal wind direction), which is located at a distance of about 100 m from the Kongsfjord.

*Dedicated to Professor Dr. Wilhelm Fresenius on the occasion of his 80th birthday

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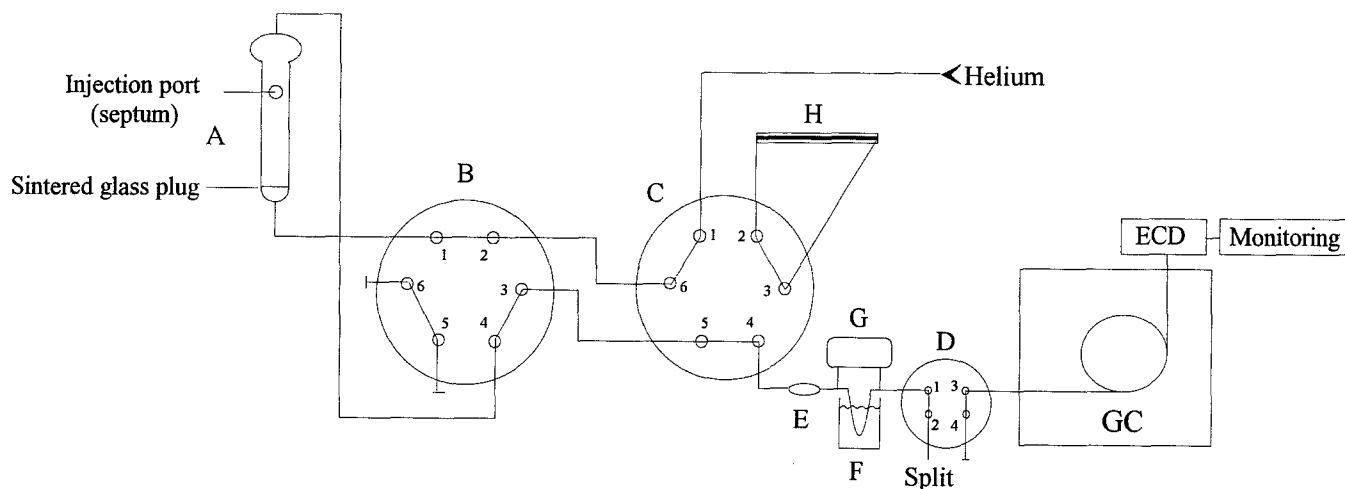


Fig. 1. Schematic figure of the sample treatment/GC system for the determination of volatile halogenated hydrocarbons in seawater and air samples. (A) Purging unit; (B, C, D) valco valve; (E) drying tube (potassium carbonate); (F) cold trap (liquid nitrogen); (G) electrical heating unit for cold trap; (H) adsorbent tube (Carbosieve S-III).

Purging of water samples: B (1-2; 3-4; 5-6); C (1-6; 2-3; 4-5); D (1-2; 3-4). Thermodesorption of air samples: B (1-6; 2-3; 4-5); C (1-2; 3-4; 5-6); D (1-2; 3-4). Analysis of water and air samples: B (1-6; 2-3; 4-5); C (1-6; 2-3; 4-5); D (1-3; 2-4)

All samples were directly analysed in the Arctic in a laboratory of the German Station immediately after sampling. The sample treatment system for seawater samples by a purge and trap unit and for air samples after collection in an adsorption tube, together with the gas chromatographic system is schematically shown in Fig. 1.

An exactly known volume of the seawater sample of about 50 ml was injected into the purging unit (Fig. 1, A) with a syringe through a septum and then degassed for 30 min at room temperature by sucking helium gas through the seawater. The volatile compounds were stripped from the seawater by the helium carrier gas and transferred into a cold trap (F; length 50 cm, inner diameter 1 mm) cooled by liquid nitrogen. During the stripping process the valves B, C, and D were fixed in the following position: B (1-2, 3-4, 5-6), C (1-6, 2-3, 4-5) and D (1-2, 3-4). The steel cold trap was coupled with the gas-chromatographic separation column by a 4-way Valco valve. During degassing, valve D was in the "split" position to achieve a sufficient purge flow of about 60 ml/min. The sintered glass plug at the bottom of the purging unit (A) distributes the gas flow by very small bubbles into the degassing chamber, which increases the degassing efficiency. To prevent the input of moisture into the cold trap (F), a glass tube filled with dried and precleaned potassium carbonate (E) was installed between the purging unit and the cold trap. Potassium carbonate has no effect on the analysed iodine and bromine compounds.

The air samples were collected by sucking (3-8) l of air through an adsorption tube (length 50 cm, inner diameter 4 mm) filled with 400 mg Carbosieve S-III. The adsorption material in the glass tube was fixed by two plugs of silanised glass wool. This arrangement allows flow rates of (80-120) ml/min. After air sampling had been finished, the adsorption tube (H) was connected with the analysing system by Swagelok fittings as shown in Fig. 1. The adsorbed substances were then thermodesorbed by stepwise heating of the tube up to 400 °C within (6-7) min and remaining at this temperature for another 23 min. During thermodesorption the valves were fixed in the following positions: B (1-6, 2-3, 4-5), C (1-2, 3-4, 5-6), and D (1-2, 3-4).

Gas chromatography

After degassing and thermodesorption, respectively, the valves B, C, and D were switched to the "inject" position for the gas-chromatographic analysis: B (1-6, 2-3, 4-5), C (1-6, 2-3, 4-5), and D (1-3, 2-4). The liquid nitrogen was removed from the cold trap and the total cold trap capillary made of steel was then directly heated by a current of 8 A using the electrical heating unit (G). This direct heating of the steel cold trap by an electrical current enables a very fast introduction of the substances into the gas chromatograph with exactly controllable heating rates. On the other hand, every part of the cold trap is heated up both constantly and simultaneously to nearly the same temperature. With this system the disadvantages of other systems are avoided, where a relatively high consumption of liquid nitrogen and difficult handling is necessary [15] or a non-reproducible heating procedure by a hot gun is applied [4, 7]. Other authors, which used hot water for the heating process to avoid the described disadvantages [16] could not increase the temperature above the boiling point of water. This produces peak broadening, especially for non-volatile substances.

The gas-chromatographic analyses were carried out with an instrument from Shimadzu, type GC-9A, equipped with a capillary column from Restek, type Rt_x 502.2 (length 60 m, inner diameter 0.32 mm, film thickness 3 μm) and an electron capture detector (ECD) with a ⁶³Ni source. The temperature program was as follows: 10 min at 40 °C, increase of temperature to 100 °C by a rate of 3 °C/min, 5 min at 100 °C, increase of temperature to 240 °C by 3 °C/min. Afterwards, the temperature was held at 240 °C for 45 min to clean the separation column.

With the method described above the detection limits for the various brominated and iodinated substances in water are in the range of (0.01-0.2) ng/l depending on the substance. CH₃I and CH₂ClI show the highest response and therefore the lowest detection limits. For air samples the detection limits are ranging from 0.004 pptv to 0.08 pptv. External calibration for air samples was carried out by injecting exactly known amounts of gravimetrically produced

standard solutions of the compounds to be analysed in n-nonane into the adsorption tube. Calibration for seawater samples was performed by using standard solutions in ethylene glycol mixed with degassed synthetic seawater. These standard solutions were analysed in the same way as described for real samples.

With the combined sample treatment/gas-chromatographic system shown in Fig. 1 it was possible to analyse both, water and air samples, one after the other one without any time delay. By the used capillary column and the described temperature program it was also possible to separate C_2Cl_4 from $CHBr_2Cl$ and Freon 113 from CH_3I , which cannot easily be done under other conditions.

Results and discussion

Seawater analyses

In Tables 1 and 2 the concentrations of iodinated organic compounds and of brominated methanes, respectively, determined in Arctic seawater samples collected at different locations of the Kongsfjord in Spitzbergen (middle of the fjord, shore site, and in a field of algae) are listed. The given data is the mean of a certain number of samples (fjord 10 samples, shore 13, field of algae 11) collected at the indicated locations during September 1st to September 25th, 1992, and the corresponding concentration ranges. A continuous change in the concentration of the iodinated and brominated organic compounds could not be observed for the investigated time period, although all listed compounds are of bio-

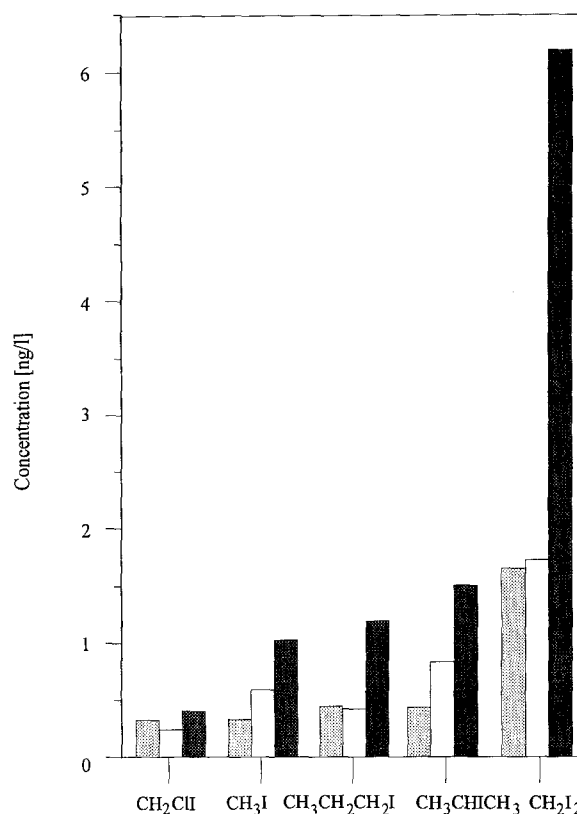


Fig. 2. Concentration of iodinated organic compounds from different locations in Arctic seawater. (▨) Middle of the fjord; (□) shore; (■) field of algae

Table 1. Concentration of iodinated organic compounds in Arctic seawater

Compound	Concentration [ng/l]					
	Fjord (10) ^a		Shore (13) ^a		Field of algae (11) ^a	
	Mean ^b	Range	Mean ^b	Range	Mean ^b	Range
CH_3I	0.33 (10)	0.09 - 0.77	0.59 (10)	<0.01 - 1.50	1.03 (8)	<0.01 - 4.83
CH_2I_2	1.65 (7)	<0.25 - 3.40	1.72 (13)	0.77 - 2.78	6.19 (9)	<0.25 - 12.94
CH_2ClI	0.32 (10)	0.16 - 0.46	0.24 (13)	0.11 - 0.67	0.40 (11)	0.03 - 0.83
$CH_3CH_2CH_2I$	0.44 (8)	<0.06 - 0.94	0.42 (7)	<0.06 - 1.03	1.19 (10)	<0.06 - 3.71
CH_3CHICH_3	0.43 (7)	<0.07 - 1.60	0.83 (7)	<0.07 - 2.14	1.50 (10)	<0.07 - 6.38

^a Number of total samples analysed

^b For calculation of the mean values only concentrations above the detection limit were taken into account. Values in brackets are the number of samples used for the calculation of the mean

Table 2. Concentration of brominated methanes in Arctic seawater

Compound	Concentration [ng/l]					
	Fjord (10) ^a		Shore (13) ^a		Field of algae (11) ^a	
	Mean ^b	Range	Mean ^b	Range	Mean ^b	Range
CH_2Br_2	2.75 (10)	1.26 - 5.24	2.66 (13)	0.74 - 6.77	10.68 (11)	5.81 - 20.44
$CHBr_3$	19.47 (10)	8.70 - 39.90	16.76 (13)	4.68 - 49.80	164.30 (11)	51.41 - 330.88
CH_2BrCl	0.19 (7)	<0.06 - 0.47	0.14 (7)	<0.06 - 0.43	0.51 (9)	<0.06 - 1.17
$CHBrCl_2$	0.17 (10)	0.08 - 0.29	0.23 (13)	0.07 - 0.62	0.55 (11)	0.29 - 1.30
$CHBr_2Cl$	1.07 (10)	0.51 - 1.98	1.05 (12)	<0.03 - 2.37	3.78 (11)	2.20 - 6.25

^a And ^b see Table 1

genic origin. It could be expected that a decreasing duration of daylight would influence the bioactivity in the polar ocean and therefore also the production rate of the organoiodine and organobromine compounds. However, the change in the bioactivity was obviously not high enough in the Arctic from the beginning to the end of September to measure such an effect.

Independent of the location, where sampling took place, CH_2I_2 and CHBr_3 are always found to be the most abundant iodinated and brominated compounds in Arctic seawater samples of the Kongsfjord. The mean CH_2I_2 concentration exceeds the corresponding CH_3I , $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$, and $\text{CH}_3\text{CHICH}_3$ concentrations by a factor of 2–6, whereas the iodinated compound CH_2CII is by a factor of 5–15 lower than CH_2I_2 (Fig. 2). This is the first time that propyl iodide could be detected in Arctic seawater samples. In the past, propyl iodide was only found in a few samples from other regions [17]. It is therefore interesting to mention that we found 1- and 2-propyl iodide in nearly all Arctic seawater samples from the Kongsfjord. Also CH_2CII was measured in all Arctic seawater samples in contrast to comparable investigations in Antarctica, where only a few samples contained detectable CH_2CII amounts [4]. To our knowledge it is also the first time that CH_2I_2 was determined in higher mean concentrations compared with CH_3I .

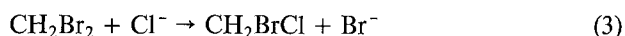
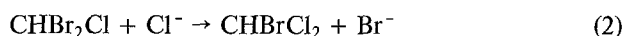
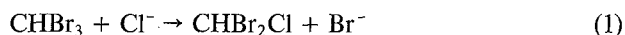
In Antarctic seawater and air samples we always detected methyl iodide as the most abundant iodinated organic compound [4]. In Antarctica the samples were taken not directly at the shore site and in many cases also from the open sea, whereas the samples of the Arctic originate from a fjord. This indicates that different biological species should be responsible for these differences. However, this assumption has to be checked by further investigations because most of the results obtained for iodinated compounds in the past only

deal with CH_3I (Table 3). Our results distinctly show that iodinated biogenic compounds other than CH_3I cannot be neglected in the total iodine budget of the oceans. The mean CH_3I concentration of 0.5 ng/l we found for all surface seawater samples in Spitzbergen is very similar to those observed, for example, in the Atlantic Ocean and in Oregon (Table 3), but it is essentially lower than contents detected during the Antarctic spring time (October–December) around the Antarctic Peninsula.

The bromoform concentrations in the Arctic seawater samples from Spitzbergen exceed the corresponding CH_2Br_2 concentrations by a factor of 6–15, the CHBr_2Cl concentrations by a factor of about 20–40, and the CH_2BrCl and CHBrCl_2 concentrations by a factor of about 100–300 (Table 2). Although the same order in the concentration level was found for the different brominated methanes in other regions, the mean values of CHBr_3 and CH_2Br_2 are distinctly higher for the samples from Spitzbergen than those from the South Atlantic and the Antarctic Peninsula (Table 4). This indicates that during the sampling period in the Arctic especially high production rates of the brominated methanes must have been established by certain biological species. The extremely high mean bromoform concentration of 164 ng/l in samples from a field of algae shows that this type of biological species must be one of the main sources for CHBr_3 . A more detailed picture on the production of halogenated compounds by different types of polar algae is described elsewhere [14]. Although the exact mechanism of formation is not still known today, it is assumed that CH_2Br_2 and CHBr_3 are produced in marine organisms via a successive enzymatic bromination of ketone metabolites [19, 20]. The same origin of CH_2Br_2 and CHBr_3 is reflected by the good correlation (correlation factor 0.92) between both compounds we found in different seawater samples of the Arctic (Fig. 3).

On the other hand, no correlation could be found between any of the iodinated compounds and the brominated compounds, which is represented by Fig. 4 for methyl iodide and bromoform with a correlation factor of 0.04. These results, which means good correlation between the brominated methanes and no correlation between CH_3I and the brominated methanes, is in accordance with findings in Antarctica [4, 11]. This indicates that the biological production mechanism must be different for both types of halogenated organic substances. The reaction of dimethylsulfonium ions with iodide, which both exist in marine organisms [21], is assumed to be one possible way for the formation of methyl iodide.

The mixed bromochloromethanes also correlate well with CH_2Br_2 and CHBr_3 , respectively. These compounds can be formed in the seawater by nucleophilic substitution of bromide by chloride



The concentrations found for these mixed bromochloromethanes (Table 2) are in accordance with equations (1)–(3) because CHBr_2Cl is the most abundant of these compounds formed from bromoform with the highest content in seawater. A second nucleophilic substitution step by reaction (2) is less probable, which explains the much lower concentrations found for CHBrCl_2 .

Table 3. Concentration of methyl iodide in seawater of different regions

Region	Concentration [ng/l] ^a	Reference
Antarctic Peninsula	2.6 ± 2.1	[4]
Atlantic Ocean	0.6 ± 0.3	[7]
Oregon	0.5 ± 0.1	[18]
Spitzbergen	0.5 ± 0.4	This work

^a The given standard deviations are not related to the analytical method but to the variation of the concentration of the analysed substance from different samples in the indicated region

Table 4. Concentration of brominated methanes in seawater of different regions

Region	Concentration [ng/l] ^a				Reference
	CH_2Br_2	CHBr_3	CHBrCl_2	CHBr_2Cl	
South Atlantic	1.3	4.5	0.3	0.2	[17]
	0.3	0.8	0.1	0.1	[9]
Antarctic Peninsula	0.9 ± 0.3	6.2 ± 4.1	0.3 ± 0.2	0.6 ± 0.4	[11]
Spitzbergen	2.7 ± 1.4	17.9 ± 12.3	0.2 ± 0.1	1.1 ± 0.6	This work

^a See Table 3

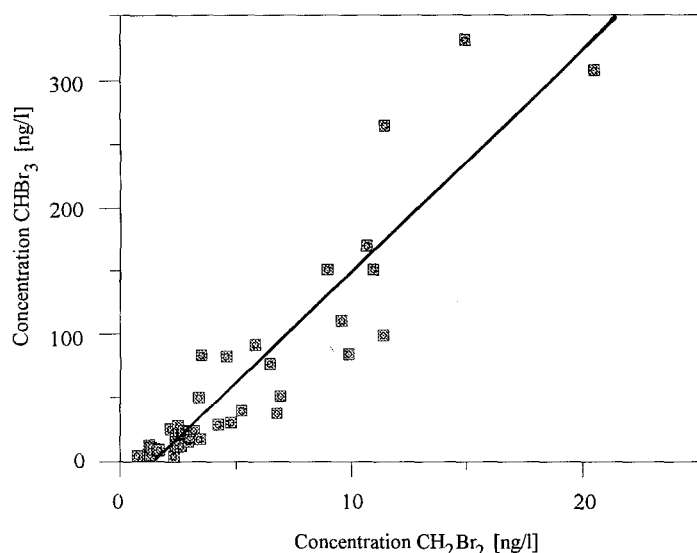


Fig. 3. Correlation between bromoform and dibromomethane in Arctic seawater samples

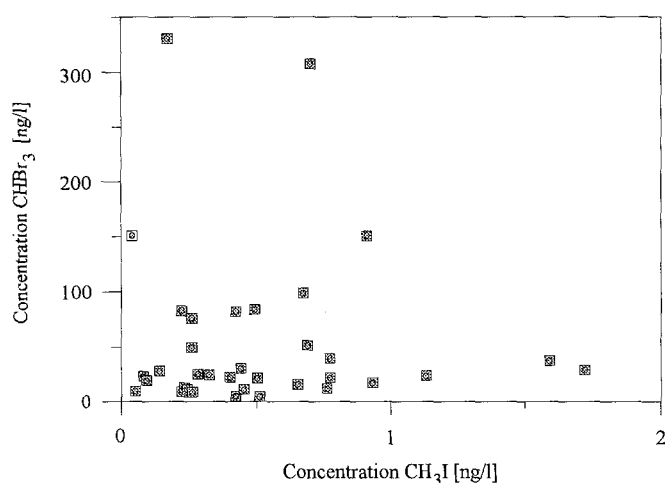


Fig. 4. Correlation between bromoform and methyl iodide in Arctic seawater samples

Air analyses

In Tables 5 and 6 the results of our investigations of Arctic air samples are listed for the iodinated compounds and the brominated methanes, respectively. 1- and 2-propyl iodide have been detected and quantified for the first time in about 30% of all air samples. It is therefore especially surprising that such a relatively high 2-propyl iodide concentration was found in these samples compared with CH_3I . Methyl iodide was the only iodinated compound constantly found in the past in the marine atmosphere, whereas CH_2ClI and CH_2I_2 could only be detected in a few samples [4, 9]. Our result demonstrates that other iodinated hydrocarbons than CH_3I must also be taken into consideration for the global iodine budget in the atmosphere and that methyl iodide is not necessarily always the most dominant iodine species in the marine atmosphere as assumed in the past [22].

The atmospheric concentrations determined in this work are compared with those of other regions in Tables 7 and 8 for methyl iodide and the bromomethanes, respectively. It

Table 5. Concentration of iodinated organic compounds in the Arctic atmosphere

Compound	Concentration [pptv]	
	Mean ^b	Range (17) ^a
CH_3I	1.04 (14)	<0.004 - 2.12
CH_2I_2	0.46 (8)	<0.08 - 1.02
CH_2ClI	0.07 (9)	<0.004 - 0.18
$\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$	0.20 (4)	<0.02 - 0.28
$\text{CH}_3\text{CHICH}_3$	2.00 (6)	<0.02 - 5.98

^a And ^b see Table 1

Table 6. Concentration of brominated methanes in the Arctic atmosphere

Compound	Concentration [pptv]	
	Mean ^b	Range (17) ^a
CH_2Br_2	0.45 (16)	<0.008 - 1.82
CHBr_3	0.45 (16)	<0.02 - 1.19
CHBrCl_2	0.12 (12)	<0.007 - 0.29
CHBr_2Cl	0.33 (12)	<0.01 - 1.00

^a And ^b see Table 1

Table 7. Concentration of methyl iodide in the atmosphere of different regions

Region	Concentration [pptv] ^a	Reference
Atlantic Ocean	1.2 ± 10.0	[6]
Antarctic Peninsula	2.4 ± 1.5	[4]
South Pole	1.8 ± 0.4	[18]
Oregon	1.5 ± 0.2	[18]
Alaska	1.3 ± 0.2	[18]
Iceland	22 ± 5	[18]
Spitzbergen	1.0 ± 0.5	This work

^a See Table 3

Table 8. Concentration of brominated methanes in the atmosphere of different regions

Region	Concentration [pptv] ^a				Reference
	CH_2Br_2	CHBr_3	CHBrCl_2	CHBr_2Cl	
South Atlantic	2	2	0.3	0.3	[9]
Antarctic Peninsula	3.7 ± 1.8	6.3 ± 6.2	3.8 ± 2.6		[11]
Spitzbergen (spring)	19	26			[20]
Spitzbergen (late summer)	0.4 ± 0.4	0.4 ± 0.4	0.1 ± 0.1	0.3 ± 0.3	This work

^a See Table 3

can be seen that our CH₃I data for Spitzbergen agree well with other regions. From this it follows that the atmospheric methyl iodide concentration does not vary very much and can normally be found in the range of (1–2.5) pptv. This is in accordance with the estimation of an average global concentration in the atmosphere of about 2 pptv by Cicerone [23], although spot concentrations have been found at some single places, e.g. in Iceland [18] (see Table 7).

The concentrations of brominated methanes determined in the atmosphere of Spitzbergen during September 1992 are best comparable with those from the South Atlantic (Table 8), although the seawater concentrations were much higher for the Arctic (see Table 4). A different transfer rate of these substances from the seawater to the atmosphere and different meteorological conditions may be responsible for these differences. High spots of CH₂Br₂ and CHBr₃ have been analysed in the atmosphere of Spitzbergen during spring time [20] (Table 8).

Atmospheric input by the Arctic Ocean

On the basis of our results we could calculate the annual flux of CH₃I and CHBr₃ under certain assumptions using a simple two-phase model described by Liss and Slater [24]. By this model the substance flux *F* from seawater into the atmosphere is given by

$$F = K \times (c_1 - c_g/H) \quad (4)$$

where *K* is the substance specific exchange constant, *c*₁ and *c*_g are the concentrations in seawater and the atmosphere, respectively, and *H* is Henry's constant with respect to seawater under the Arctic temperature conditions. For CH₃I, *K* and *H* are calculated to be 10.2 cm/h and 0.117 [4], for CHBr₃ to be 3.8 cm/h [25] and 0.009 [10]. Using our mean values for CH₃I (Table 3 and 5) and for CHBr₃ (Tables 4 and 6) and assuming a constant annual flow rate from the ocean into the atmosphere, the annual flux for the Arctic area (9.5 × 10⁶ km²) can be calculated to be 4 × 10⁹ g for methyl iodide and 5.4 × 10¹⁰ g for bromoform. This calculation is extremely uncertain, because it does not consider possible annual and local variations in the concentration of these biogenic substances. However, it shows that essential amounts of biogenic halogenated hydrocarbons are emitted into the atmosphere where they can affect atmospheric reactions.

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