Bromoform concentrations

of the Arctic Ocean

in the Svalbard area

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ABSTRACT

Analysis of bromoform in the 1-100 ng/l range shows that bromoform is present at all depths in the Eastern Arctic Ocean The bromoform depth profiles indicate that in shore algae belts produce bromoform. High bromoform concentrations at 20 and 30 m depth in Isfjorden indicate an additional source, possibly from sea water chlorination at Barentsburg. It might be possible to use bromoform as a tracer for the deep water formation in the Svalbard area.

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RÉSUMÉ

Concentration du tribromométhane de l'océan Arctique
dans la région de Svalbard

L'analyse du tribromométhane dans la gamme de concentration 1-100 ng/l montre que ce composé existe à toutes les profondeurs dans l'est de l'océan Arctique. Les profils verticaux de ce composé indiquent qu'il est produit par la bordure côtière d'algues. Les concentrations très élevées mesurées à 20 et 30 m dans la région de Isfjorden montrent qu'il existe une autre source pour ce composé, qui est probablement la chloruration, à Barentsburg et Longyearbyen, de l'eau de mer. Le tribromométhane pourrait être utilisé comme traceur pour suivre la formation de l'eau profonde dans la région de Svalbard.

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INTRODUCTION

Previous work on the Baltic Sea, Kattegatt and Skagerrak (Eklund et al., 1980) has shown that it is possible to measure several halocarbons in the ng/l range. A special investigation outside the Ringhals Nuclear Power Plant showed that considerable amounts of bromoform ($CHBr_3$) are formed when Kattegatt water is chlorinated for its use as cooling water (Eklund et al., 1979). Formation of bromoform in chlorinated or ozonized sea water has been confirmed and discussed by several authors (see Helz, Hsü, 1978, and references therein). It has also been reported that bromoform is toxic to marine molluscs (Gibson et al., 1979). The data for Kattegatt showed, however, that there must be an additional source of bromoform. Several investigations (McConnell, Fenical, 1977; Theiler et al., 1978) point at red benthic algae as this source.

The Swedish Arctic Ocean Expedition Ymer 80 provided us with the opportunity to carry out an oceanographic survey of volatile halocarbons in August and September 1980. Bromoform, e. g., might be used as a tracer for water that has passed through an algae belt. Volatile halocarbons, e. g. chloroform, carbon tetrachloride, trichloroethylene and tetrachloroethylene, that are produced in large quantities (McConnell et al., 1975) contaminate the ocean surface water (Correia et al., 1977; Helz, Hsü, 1978; Singh et al., 1979) and can then be used as tracers for sinking waters.

In practice our gas chromatographic technique with direct injection on glass capillary columns and electron capture detection (Eklund et al., 1980) showed that we are able to measure chloroform ($CHCl_3$), 1,1,1-trichloroethane (CH_3CCl_3), carbon tetrachloride (CCl_4), trichloroethylene ($CHCl=CCl_2$), tetrachloroethylene

(CCl$_2$=CCl$_2$), dibromochloromethane (CHBr$_2$Cl) besides bromoform. This work will deal with bromoform, while the results on other halocarbons will be treated separately.

EXPERIMENTAL

Sampling

The water samples were collected in three different ways. The major part was taken with 2.5 l Niskin bottles (General Oceanics, USA) mounted as a Rosette on a CTD probe (Conductivity, Temperature, Depth). When lowered into the water the probe recorded a salinity-temperature trace. The samplers were then closed at selected depths when bringing up the probe. A drawback with these Niskin bottles was that they made measurements on trichloroethylene impossible due to contamination. Some samples were therefore taken with "TPN" water samplers (Hydrobios, Kiel, FRG), which were tested to give no contamination. Through an intake in the ship's hull water could be drawn from a depth of 7 m. In this way a few investigations were made while cruising out from a coastal area. The samples were stored in 100 ml glass volumetric flasks, which were sealed with glass stoppers so that no air remained in the flask. Analyses were performed within 24 hours in a container laboratory on board the Swedish ice-breaker Ymer.

Extraction procedure

Hundred ml of the sea water sample was extracted in the storage flask by 5 minutes shaking with 1 ml of pentane (Merck, p. a.) containing 5 µg/l bromotrichloromethane (CBrCl$_3$) as internal standard. In order to preconcentrate the halocarbons as much as possible, this small volume of pentane was chosen, despite the extraction yield was somewhat diminished (see Table 1, cf. Eklund et al., 1978). The yields in Table 1 were used to calculate the sea water concentrations.

Table 1
Pentane extraction yields for some halocarbons in sea water.

Compound	Extraction yield (%)	s. dev. (%)	n
CCl$_4$	92	2	8
CHCl=CCl$_2$	67	16	8
CCl$_2$=CCl$_2$	91	6	8
CHBr$_2$Cl	67, 71	–	2
CHBr$_3$	64	7	8

Gas chromatography

Gas chromatographic analyses were performed on a Fractovap 4160 gas chromatograph (Carlo Erba, Italy) equipped with an on column injector and a Nickel-63 electron capture detector. The column used was a glass capillary, length 30 m, i. d. 0.3 mm, with SE-52 as stationary phase. The chromatographic parameters were chosen to give both a high resolution in the beginning of

the chromatogram and a reasonable retention time for bromoform. Thus it was possible to measure all of the halocarbons in sufficiently low concentrations in the same run. The gas chromatographic conditions were: injector air cooled, detector temperature 275°, column temperature 40° isothermal, carrier gas (hydrogen) rate 30 cm/sec., purge (argon with 5% methane) flow 30 ml/min. 10 µl of the pentane extract was injected directly into the column at a rate of 2 µl/s.

Standardization and detection limits

Bromotrichloromethane was chosen as an internal standard since it does not seem to be present in natural waters and since it appears as a well separated peak in the chromatogram (see Fig. 1, and cf. Eklund et al., 1978). The concentrations of the different halocarbons were determined from standard pentane solutions using the peak ratio to the internal standard. Since the peak base width is practically constant for each halocarbon, the peak heights were used to calculate the concentrations. The pentane is to a small extent contaminated, and the peak heights were corrected by subtracting the background from the pentane.

A number of double samples, some of them taken with different types of samplers, were analyzed in order to estimate the precision of the bromoform determination.
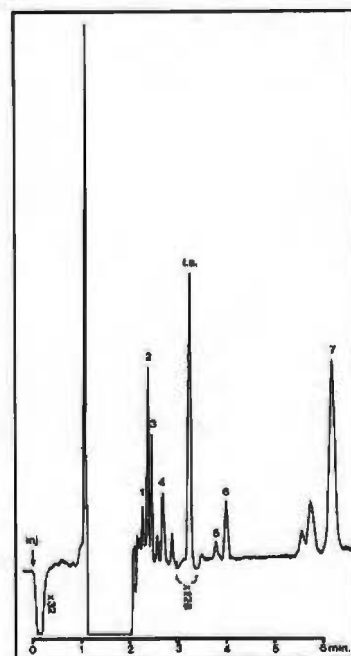

Figure 1
Chromatogram of a sea water sample outside Tromsö. Peaks: 1 = CHCl$_3$, 2 = CH$_3$CCl$_3$, 3 = CCl$_4$, 4 = CHClCCl$_2$, 5 = CHBr$_2$Cl, 6 = CCl$_2$CCl$_2$, 7 = CHBr$_3$, i.s. = CBrCl$_3$.

Table 2
Detection limits for some halocarbons in sea water. The standard deviations vary between 15 and 30%.

Compound	Det. lim. (ng/l)
CCl$_4$	0.03
CHCl=CCl$_2$	0.3
CCl$_2$=CCl$_2$	0.09
CHBr$_2$Cl	0.4
CHBr$_3$	1.6
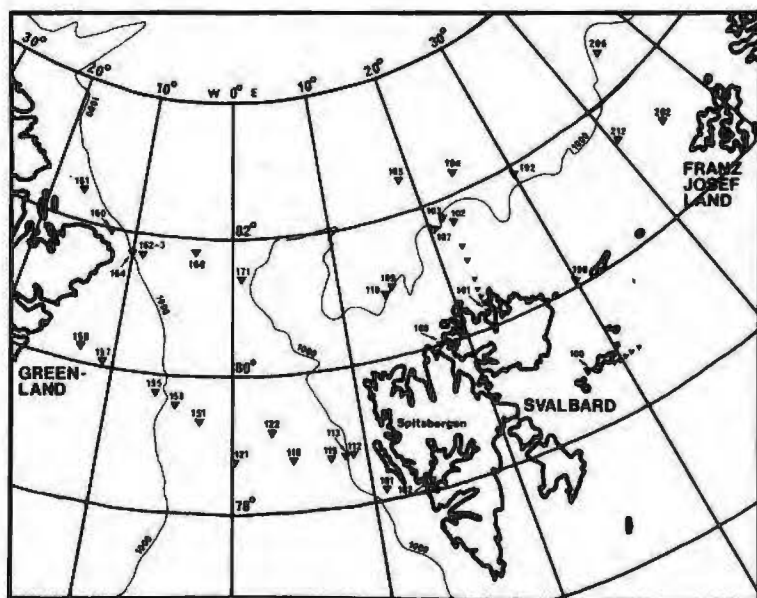
The data (Eklund *et al.*, 1980) indicate that the two determinations differ from 2 to 20% of the mean concentration when this drops from 150 to 2 ng/l. This corresponds to 150 ± 3 and 2 ± 0.3 ng/l.

The detection limits for sea water samples are given in Table 2. These limits are given as peak heights twice the noice width of the base line. They should be regarded as the limits for proper concentration evaluations. Even smaller peaks can confirm the existence of a compound. In practical work the detection limits can be lowered for each compound by altering the chromatographic parameters.

Figure 4
Bromoform depth profiles close to land in unpopulated areas of Svalbard, station 100 ($\bigcirc$) at Kongsöya, station 101 ($\triangle$) in Rijpfjorden and station 108 ($\square$) in Hinlopen Renna.

RESULTS AND CONCLUSIONS

All concentration data are given in a special report (Eklund *et al.*, 1980) together with station numbers, positions, sampling dates, depths, temperatures, salinities and nitrate concentrations. Additional data are reported by Anderson and Dyrssen (1980). Figure 2 shows the station locations.

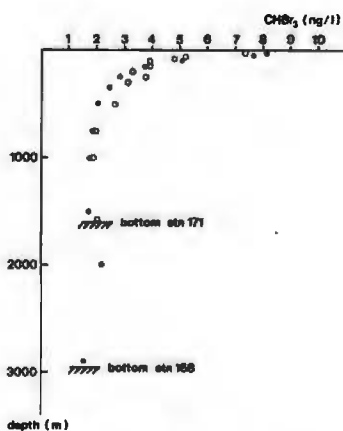Figure 3 shows the depth profiles for two stations between Greenland and Spitsbergen, one (168) in the

East Greenland Current and one (171) in the Atlantic water flowing into the Arctic Ocean from the Norwegian Sea according to CTD data. We conclude from this figure that the East Greenland and Spitsbergen waters have practically the same bromoform concentrations.

Figure 4 shows the depth profiles from stations 100 (Kongsöya), 101 (Rijpfjorden) and 108 (Hinlopen Renna). These areas are unpopulated. Our conclusion from Figures 3 and 4 is that high bromoform concentrations close to land are due to a natural source, which most likely is production from algae belts. These belts seem to effect the water close to the surface, i. e. above 40 m. There is also an indication of a second introduction level of bromoform at 40 to 80 m.

In a geographically similar area, but populated, the picture is somewhat different. Figure 5 shows the results

Figure 3
Bromoform concentrations versus depth at two stations, 168 ($\bullet$) in the East Greenland Current and 171 ($\bigcirc$) in the Atlantic water flowing into the Arctic Ocean.
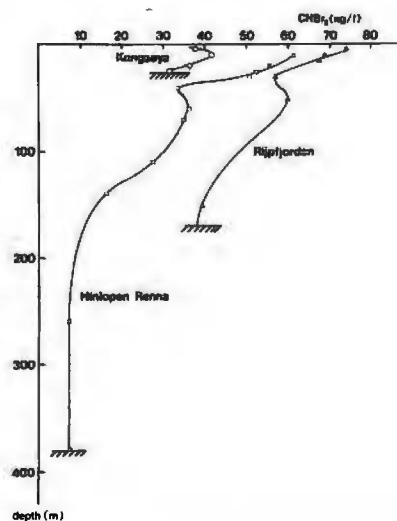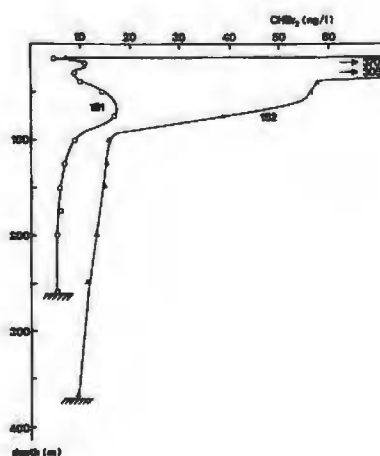

Figure 5
Bromoform depth profiles outside Isfjorden, station 181 ($\bigcirc$), and just inside the entrance to the fjord, station 182 ($\triangle$). The two communities Barentsburg and Longyearbyen are located at Isfjorden.
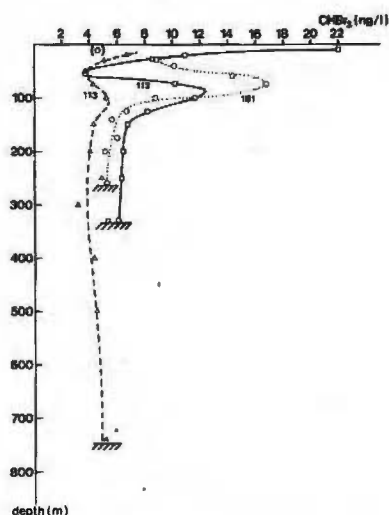
Figure 6

Bromoform depth profiles at three stations west of Isfjorden, station 181 (○) outside the entrance to the fjord, station 112 (□) located on the shelf about 40 nautical miles to the north-west and station 113 (△) still further to the west.

for stations 181 outside Isfjorden and 182 just inside the entrance to Isfjorden close to Svensksunddjupet. There is a very high bromoform concentration at 20 and 30 m. Such high bromoform concentrations have been observed in Kattegatt outside Ringhals Nuclear Power Plant (Eklund *et al.*, 1979). It appears as if sea water from Isfjorden is being chlorinated at Barentsburg which is located at Isfjorden. The surface waters at 15 m depth have high nitrate and low oxygen concentrations at these two stations. Similar values are found in the bottom water west of Spitsbergen. The surface values at these two stations are most likely a consequence of bottom water upwelling. Figure 6 shows the data for stations 112 and 113 in addition to station 181 plotted also in Figure 5. The surface water at 20-30 m from Isfjorden can not be traced at these stations north of the fjord. The surface concentrations at station 112 are quite normal for coastal water (cf. Fig. 7). A second maximum is also observed at 50 to 90 m depth, which coincides with the results from the unpopulated areas shown in Figure 4. At the shallow water stations (≤ 200 m) that were located near the North-Eastern Greenland coast, i. e. stations 157, 158, 160 and 161, we did not find the high
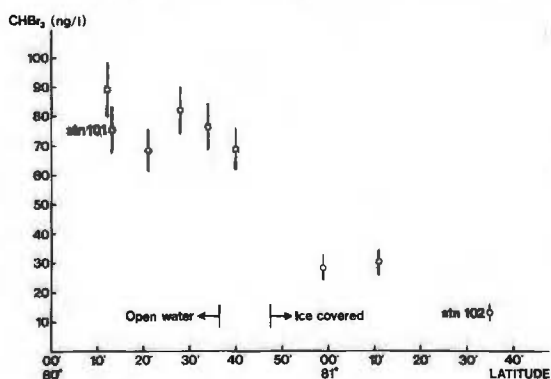

Figure 7

Bromoform concentrations in surface water samples (7 m depth) collected while cruising from Rijpfjorden (station 101) to the north (station 102). In comparison, the surface concentrations for station 101 (7 m depth) and 102 (10 m depth) are also plotted in the same figure. The lines indicate the estimated experimental errors.

bromoform concentrations (10-20 ng/l, cf. Fig. 8) in the surface layer that were common in the area of Svalbard. The maximum values were about 9 ng/l and the variations with depth were small. This is possibly due to lack in algae production at this coast, which is ice-covered most of the year.

In Figure 6 is demonstrated how the bromoform concentration diminishes as we move away from Spitsbergen (see Fig. 2). This decrease is also demonstrated in Figure 7 which shows the bromoform data from a depth of 7 m when cruising from station 101 in Rijpfjorden to the north into the drift ice at station 102. Figure 8 gives the bromoform versus depth data at stations 102, 103 and 107 together with the CTD trace for station 103. The bromoform depth profile is very similar for stations that are closeby. The temperature and salinity profiles in Figure 8 demonstrate three types of water: cold surface water that has a low salinity due to melting of ice, warm Atlantic water which has sunken under the surface layer and finally cold bottom water which is supposed to be formed in the Greenland or Norwegian Sea (Aagaard, 1980).
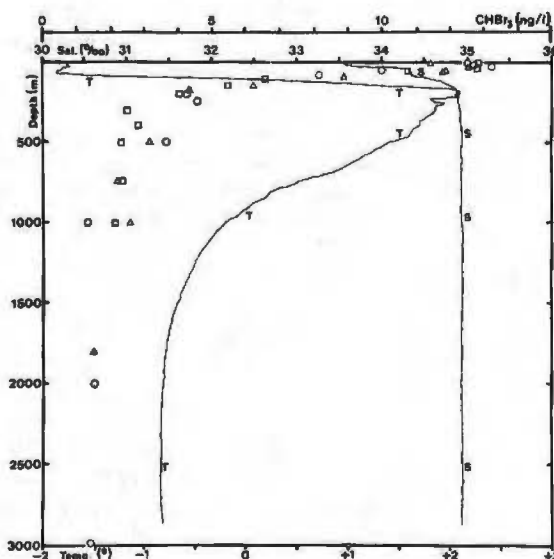

Figure 8

The concentrations of bromoform at three stations that are closeby, 102 (□), 103 (○) and 107 (△), plotted together with the CTD trace for station 103.

The bromoform depth profile is not changed very much as we move up to the most northerly station (105) at 82°30'N which is shown in Figure 9 together with the temperature, salinity and nitrate profiles for that station. The bromoform concentration (ng/l) is negatively correlated (corr. coeff. -0.98) with the nitrate concentration (μmol/l). A correlation with nitrate with a coefficient below -0.96 was also obtained at stations 109, 153, 168, 171 and 206. The equations and correlation coefficients are presented in Table 3. The general picture is that the bromoform concentration decreases with depth while the nitrate concentration increases. In most cases, however, the straight line relationship is not significant. Also the intercepts and slopes vary from station to station.

Figure 9

The concentrations of bromoform (ng/l) (○) and nitrate (μmol/l) (▽) are given together with the CTD trace for the most northerly station (105). The bromoform concentrations are correlated to the nitrate concentrations according to the equation $[CHBr_3] = 10.1 - 0.67 \times [NO_3^-]$. The correlation coefficient is -0.98.

The question remains whether plankton produce bromoform in open sea water, and to what extent this would effect the use of bromoform as a tracer for the deep water formation.

Attention should be paid to the oxidation of sea water (e. g. by ozone or chlorine), which increases the bromoform concentration in coastal areas where bromoform in some way might be involved in the ecological system.

FUTURE WORK

This work calls for several additional investigations. For the use of bromoform as a tracer (see Östlund, 1980) it is necessary to know the decay rate of bromoform in sea water at different temperatures, oxygen concentrations and pH (or alkalinities and total carbonates; see Anderson, Dyrssen, 1981). One also needs to study the formation rates in algae belts at different seasons. This could be carried out by a cooperation with marine biologists and skin divers. Laboratory experiments with algae should also be performed. Thereby one should analyze both the tank water and seaweed extracts. Furthermore one should find out if phytoplankton can produce appreciable amounts of bromoform. The source of bromoform in Isfjorden remains to be substantiated.

Table 3

Correlation between the concentrations of bromoform (ng/l) and nitrate (μmol/l) according to the equation $[CHBr_3] = A + B \times [NO_3^-]$.

Station	Intercept (A)	Slope (B)	Corr. coeff.
105	10.14	−0.669	−0.98
109	17.16	−1.184	−0.99
153	10.84	−0.783	−0.97
168	10.73	−0.728	−0.98
171	10.47	−0.659	−0.98
206	16.80	−1.163	−0.99

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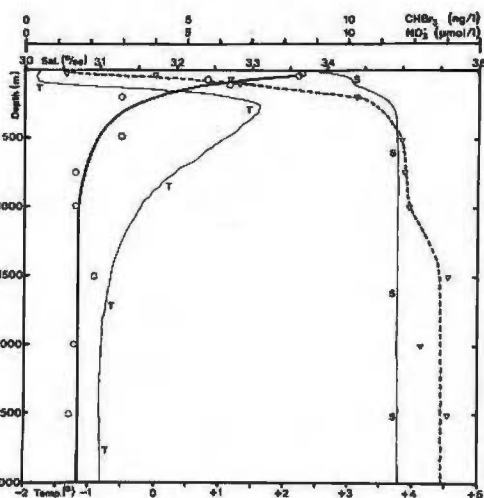Theiler R., Cook J. C., Hager L. P., Siuda J. F., 1978. Halohydrocarbon synthesis by bromoperoxidase, *Science*, 202, 1094-1096.