

Distribution, transport, and production of volatile halocarbons in the upper waters of the ice-covered high Arctic Ocean

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[1] Volatile halogenated compounds (CHBr_3 , CH_2Br_2 , CHBr_2Cl , and CH_2ClI) were measured in the water column and in sea ice brine across the Arctic Ocean, from Barrow, Alaska, to Svalbard, during the Beringia 2005 expedition (August–September) with RV/IB *Oden*. High concentrations of brominated compounds (up to 42 pmol kg^{-1} of bromoform) were found under multiyear ice in the surface waters over the Makarov Basin and the Lomonosov Ridge, near the North Pole. Even higher concentrations (bromoform up to 160 pmol kg^{-1}) were found in sea ice brine. We propose that the high load of riverine dissolved organic matter that is transported in the Transpolar Drift is a main factor responsible for the high concentration of brominated volatile compounds found in sea ice brine and upper waters and that cycles of freezing and thawing during the transport enhance the transfer of halocarbons to the seawater. The iodinated compound (CH_2ClI) showed a completely different distribution with highest concentrations in water of Pacific origin in the mixed layer and upper halocline of the northern Canada Basin and over the Alpha Ridge. In the southern Canada Basin, low concentrations of halocarbons were found in upper waters. Higher concentrations in water of Pacific origin, especially on the continental shelf, indicate production in the shelf regions, likely in the Chukchi Sea and the East Siberian Sea.

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1. Introduction

[2] Halogenated compounds in the Arctic have been in focus mainly due to involvement, primarily of BrO , in the dramatically decreased concentration of boundary layer ozone during polar sunrise, which was first noted in the 1980s [Barrie *et al.*, 1988; Bottenheim *et al.*, 1986]. Ozone is involved in atmospheric oxidation reactions and is also a greenhouse gas in the troposphere. These ozone depletion events (ODEs) therefore have strong influence on the chemistry and physics of the Arctic atmosphere.

[3] Many processes may form reactive atmospheric halogen species such as BrO [Le Bras and Platt, 1995]. Inorganic photochemical/radical reactions involving bromide and occurring on aerosols, ice surfaces, frost flowers, in surface water, or in the atmosphere are generally considered. Barrie *et al.* [1988] also suggested that bromoform, biologically formed in the ocean, may be an important source of atmospheric BrO .

Several studies seemed to confirm this since anticorrelations between bromoform (as well as other organic brominated compounds) and ozone were found [Carpenter *et al.*, 2005; Li *et al.*, 1994; Sturges *et al.*, 1993]. The conclusion was that bromoform indeed could be important for Arctic ODEs [Sheridan *et al.*, 1993]. Additionally, even though bromoform has a short lifetime in the troposphere, it has been found in the Arctic stratosphere [Berg *et al.*, 1984; Sturges *et al.*, 2000] and can therefore also be a carrier of bromine involved in the degradation of stratospheric ozone. The most efficient transport from the troposphere to the stratosphere, however, occurs in the tropics [Law *et al.*, 2007].

[4] With further research, and with the possibility of estimating BrO with satellite data [Chance, 1998], the current view is that the major source of reactive atmospheric halogen compounds is sea salt and not volatile halogenated organic compounds (halocarbons) [Simpson *et al.*, 2007]. The understanding of the production, transport, and fluxes of halocarbons in and from the Arctic Ocean, the sea ice and snow, is, however, still poor, and the contribution to the ODEs still to be quantified. Mahajan *et al.* [2010] found elevated concentrations of iodocarbons in air passing over polynyas in the Hudson Bay. Model calculations indicated that these compounds were a major source of the observed levels of IO, which, locally, could accelerate the bromine-catalyzed depletion of ozone.

[5] Few water column studies on halocarbons have been performed in the Arctic Ocean. Krysell [1991] found a subsurface maximum of bromoform (ranging from $\sim 12 \text{ pmol L}^{-1}$ to $\sim 28 \text{ pmol L}^{-1}$) in a section in the Nansen Basin in 1987

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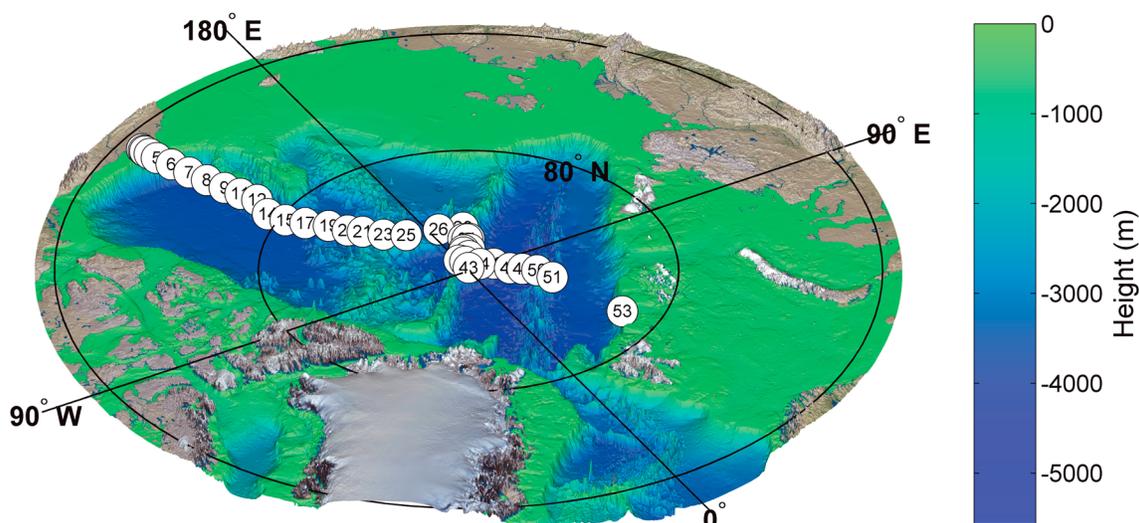


Figure 1. Location of depth profiling stations, with station labeling, during the Beringia 2005 expedition with RV/IB *Oden* in August–September 2005.

(82–86°N at 30°E) that was attributed to production from pelagic algae. During a cruise in the Svalbard area in 1980, *Fogelqvist* [1985] found high surface concentrations of bromoform, at average 27 pmol L⁻¹ in open ocean, 38 pmol L⁻¹ in ice-covered areas, and 230 pmol L⁻¹ at stations closest to the Svalbard coast. The high concentrations near coast have been attributed to benthic macroalgae, which also is supported by other studies. Local concentrations of up to 1.2–1.5 nmol L⁻¹ have been found in Isfjorden, Svalbard [*Dyrssen and Fogelqvist*, 1981], and in a field of algae in Kongsfjord, Svalbard, a bromoform concentration of 650 pmol L⁻¹ have been measured [*Schall and Heumann*, 1993]. Additionally, incubation studies have been performed, e.g., on 22 different species of macroalgae collected in Kongsfjord, where some species were found to release as much as 0.3 μg [g FW]⁻¹ d⁻¹ of bromoform [*Laternus*, 1996].

[6] There have also been reports of high concentrations of bromoform in sea ice and snow [*Sturges*, 1997]. The high concentrations in sea ice were thought to originate from biogenic production by ice algae, which have been shown to produce halocarbons [*Cota and Sturges*, 1997; *Manley and De La Cuesta*, 1997; *Sturges et al.*, 1992; *Tokarczyk and Moore*, 1994]. The high concentration in snow was suggested by *Sturges* [1997] to originate from emission from the sea ice. However, since then production of halocarbons in snow has been shown [*Swanson et al.*, 2002]. *Carpenter et al.* [2005] also found elevated concentrations of several brominated and iodinated compounds in air passing over the ice-covered Hudson Bay. It was suggested that these compounds were formed abiotically from reactions of reactive halogen species and organic matter in sea ice/snow.

[7] Marine production of halocarbons, primarily by macroalgae and microalgae, is still a process that is not fully understood. Several enzymatic pathways have been identified [*Manley*, 2002; *Van Pée and Unversucht*, 2003], and for halogenated methanes (with two or three bromine, chlorine, and/or iodine atoms), reactions involving haloperoxidases are thought to be most important [*Lin and Manley*, 2012; *Moore et al.*, 1996; *Wever et al.*, 1991; *Wever et al.*, 1993]. It has also been found that dissolved organic matter (DOM) is a key factor for speciation and magnitude of production [*Lin*, 2011].

[8] During the Beringia 2005 expedition (August–September) with RV/IB *Oden*, we measured the concentrations of a suite of halocarbons in the water column from Barrow, Alaska, over the North Pole to Svalbard. Here we present new insight in the distribution, transport, and production in the ice-covered Arctic Ocean. The main focus is on CHBr₃, which is generally considered as the main product of halocarbon formation in algae [*Quack and Wallace*, 2003]. Also, CHBr₂Cl which is the product of halide substitution of CHBr₃ is discussed, as well as CH₂Br₂ and CH₂ClI. Measurements in sea ice and snow were also performed during the expedition and will be discussed in depth in a separate publication (A. Karlsson et al., manuscript in preparation, 2013).

2. Methods

2.1. Location

[9] During the Beringia 2005 Expedition, from Barrow, Alaska, across the North Pole to Svalbard, 39 stations for depth profiling (in total 1085 samples for halocarbons) were occupied between 21 August and 23 September 2005 (Figure 1). The cruise path was approximately straight through the Canada Basin to the Makarov Basin, then followed the Lomonosov Ridge from the Siberian side to the Greenland side for ~400 km, before proceeding through the Amundsen and Nansen Basin to the destination at Svalbard. Stations were closely spaced over the Lomonosov Ridge as substantial focus of the cruise was to map the Lomonosov Ridge to investigate a gap in the ridge, where water flows from the Makarov Basin to the Amundsen Basin [*Björk et al.*, 2007].

2.2. Materials and Methods

[10] Water was collected with Niskin flasks from a 36-bottle rosette sampler, equipped with a conductivity-temperature-depth (CTD) instrument (Sea Bird 911+) and two fluorometers, Seapoint for chlorophyll *a*, and Haardt for colored dissolved organic matter (CDOM) (data courtesy of R. M. W. Amon et al., 2013). The role of sea ice processes on the distribution of dissolved organic matter in the Arctic Ocean, manuscript in preparation, 2013). Alkalinity, nutrients, and salinity were analyzed as

described by Jones *et al.* [2008]. The hydrochemistry data is available online [Anderson *et al.*, 2011].

[11] Samples for halocarbon analysis were drawn directly from the Niskin flasks, without headspace, in 40 mL glass vials, sealed with screw caps with Teflon®-septa, or with 100 mL gastight glass syringes. Prior to onboard analysis, which was performed within 20 h, the samples were stored in darkness and cooled (~0°C) under flowing seawater from the ship surface water pump system. At each station, the samples were run in random order to minimize possible errors from system drift, carryover, or related to storage time. If the samples had been run in order by depth, such errors might otherwise not have been revealed from the depth profiles. To minimize contamination, and on the basis of low cell density, the samples were not filtered. This may have had a minor effect on the halocarbon composition in samples late in the sample sequence as biological production or degradation could have occurred. However, no such artifacts were evident from the depth profiles.

[12] Three systems were used to determine the halocarbon contents of the samples: a custom-made purge-and-trap system [Ekdahl and Abrahamsson, 1997] coupled to a Varian 3800 gas chromatograph/electron capture detector (GC/ECD) and two Velocity XPT purge-and-trap systems with AQUATEk 70 autosamplers (Teledyne Tekmar). These systems were coupled to either a Varian 3800 GC/ECD or an Agilent Technologies 6890 GC/micro-ECD. The samples (27 mL) were purged for 10 min at 60 °C with Nitrogen (BIP® (built-in purifier) grade, ScanGas) at 100 mL min⁻¹, and the volatiles were trapped with either Porapak N (80–100, Alltech) at -10 °C (custom-made system), or Vocarb® 3000 at ambient temperature (commercial systems). The compounds were then desorbed at 140 °C (custom-made system) or 250°C (commercial systems), and separation was performed with DB-624 capillary columns (length = 60 m, ID = 0.32 mm, film thickness = 1.8 µm, J&W) at 3.0 mL min⁻¹ (N₂) with a temperature program from 35°C to 260°C. The systems were calibrated with seawater standard solutions prepared from Arctic Ocean bottom water with added halocarbons. The halocarbons were stepwise diluted in methanol from high concentration (submolar) stock solutions of different mixes of halocarbons in methanol (purge and trap grade, ≥99.8% (GC), Sigma-Aldrich®), gravimetrically prepared from the pure compounds just prior to the cruise and then stored at -20°C. Each calibration (performed once a week) was based on mixed standards of four different concentrations of each compound in the range of the concentrations encountered in the samples and each final standard solution had the same concentration of methanol (100 ppmv). The detector response was linear in the calibration range and the calibration curves yielded R² > 0.98. The highest detection limits for the three systems of CH₂Br₂, CHBr₂Cl, CHBr₃, and CH₂ClI were 2.4 fM, 2.3 fM, 7.9 fM, and 1.3 fM, respectively. This was significantly lower than the lowest concentrations found during the expedition, i.e., all analyzed halocarbons could be quantified in all samples. The precision, determined by standards and replicate seawater samples, was 99% for CH₂Br₂, CHBr₂Cl and CHBr₃, and 98% for CH₂ClI. It was confirmed, from replicate samples of surface seawater, that the three instruments were equivalent after calibration and that all instruments could be used interchangeably to analyze the water column samples. For several stations, samples were analyzed with all three systems, which made it possible to detect an error in one system.

2.3. Other Data Sources and Tools

[13] All figures and calculations were done in Matlab® R2011b. For bathymetric data, ETOPO1 (1 min), was used (<http://www.ngdc.noaa.gov/mgg/global/global.html>) [Amante and Eakins, 2009]. Seawater properties was calculated with the Thermodynamic Equation of Seawater-2010 (<http://www.teos-10.org/>) using the GSW Oceanographic Toolbox [McDougall and Barker, 2011]. Ice thickness, constructed from Ice, Cloud, and land Elevation Satellite (ICESat) data [Kwok and Cunningham, 2008], was retrieved from <http://rkwok.jpl.nasa.gov/icesat/download.html>. Sea Ice extent for September 2005 was provided by NSIDC (National Snow and Ice Data Center, University of Colorado, USA., <ftp://sidacs.colorado.edu/DATASETS/NOAA/G02135/shapefiles/>).

3. General Description of the Arctic Ocean

3.1. Water Masses

[14] The Arctic Ocean is divided in two main oceanic basins: the Eurasian Basin and the Amerasian Basin, separated by the Lomonosov Ridge. These basins are surrounded by shelf regions. Surface water flows mainly from the Atlantic side and to a lesser degree from the Pacific Ocean through the Bering Strait. The water is freshened by precipitation and by river water, mainly from the large Russian rivers (e.g., Lena, Yenisey, and Ob) and the Mackenzie River on the American side (Figure 2).

[15] The Arctic Ocean can be divided in three main layers; upper water, intermediate water, and deep water, separated by the $\sigma_0 = 27.70$ and $\sigma_{0.5} = 30.444$ isopycnals, respectively [Rudels, 2001]. The upper waters consist of the polar mixed layer (PML) and a halocline that prevents mixing and heat flux from below to the cooler surface water. Essentially, the halocline is formed when the surface water is freshened by sea ice melt, river water, and precipitation and when high-salinity sea ice brine rejected from freezing ice sinks down the water column. The halocline can further be divided into two regimes, an upper and a lower part. The lower halocline has been proposed to be formed as Atlantic waters entering the Arctic Ocean encounter the ice edge north of Fram Strait [Rudels *et al.*, 1996]. The upper halocline is formed as water of Pacific origin, less saline than Atlantic water, entering through the Bering Strait, is subjected to sea ice freezing and thawing on the continental shelves and as the brine-enriched water on the shelf bottom enters the Canada Basin. High concentrations of nutrients in this water have been suggested to originate from remineralization on the Chukchi shelf [Jones and Anderson, 1986]. The upper halocline is mainly found in the Amerasian Basin [Rudels, 2001].

[16] The intermediate waters consist of a warm (0–3°C) layer of Atlantic water at between 200m and 700m in the Eurasian Basin and between 300m and 800m in the Amerasian Basin and below this layer upper Polar Deep Water (uPDW). In the deep waters below, the difference between the basins increase below the $\sigma_{1.5} = 35.142$ isopycnal, which marks the sill depth of the Lomonosov Ridge [Rudels, 2001].

3.2. Determination of Water Fractions

[17] The fraction of Pacific water (f_{PW}), Atlantic water (f_{AW}), river water (f_{riv}), and ice meltwater ($f_{ice\ melt}$) can be estimated from the difference in conservative parameters of these different waters. Several approaches have been used,

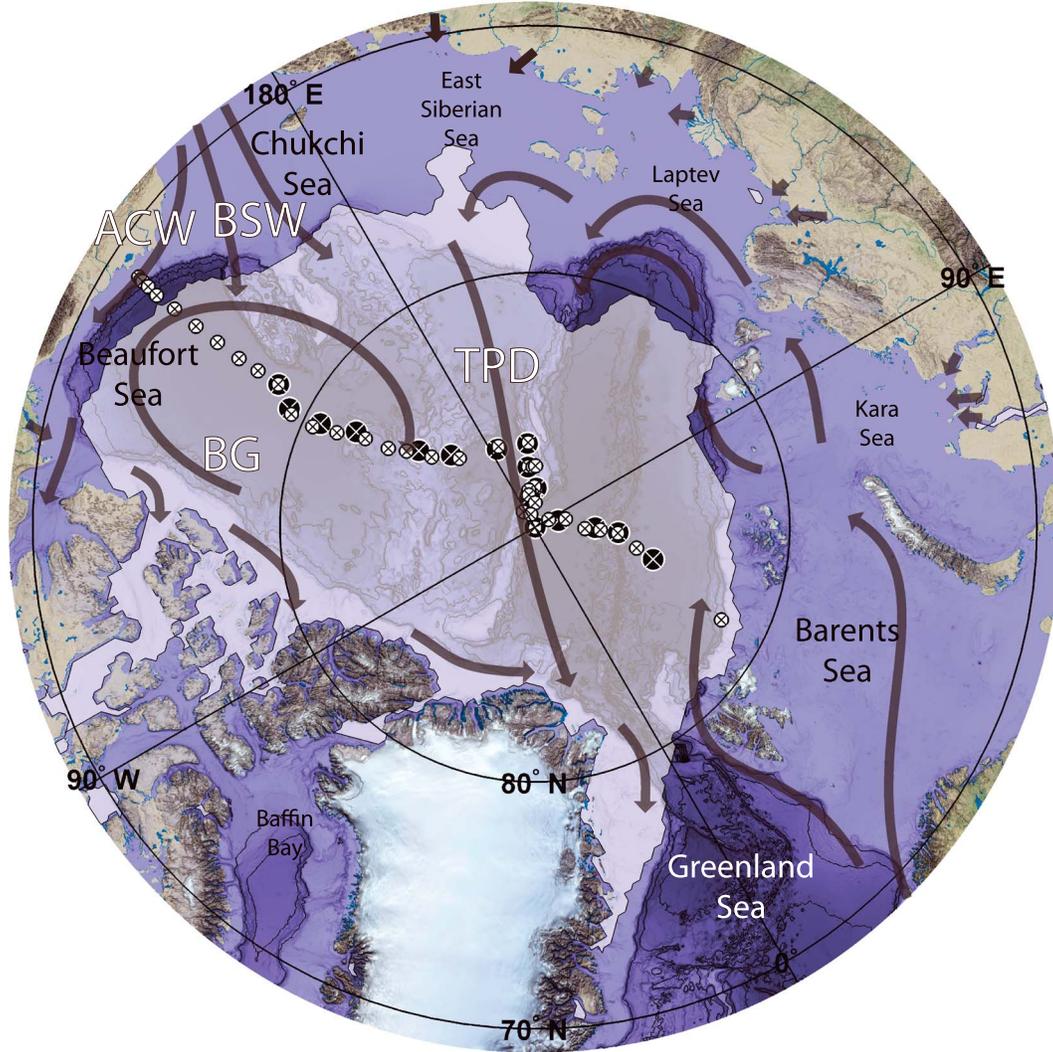


Figure 2. General circulation patterns of surface water and sea ice in the Arctic Ocean are shown. Depth stations are shown with white markers. Stations for ice sampling are shown with black markers. Also denoted are the approximate paths of the Transpolar Drift Stream (TPD), the Bering Strait Water inflow (BSW), the Alaskan Coastal Water (ACW), and the Beaufort Gyre (BG). The median ice extent for September 2005 (National Snow and Ice Data Center (NSIDC), University of Colorado, USA) is shown as a transparent layer. Depth contours are shown for intervals of 1000m.

with different sets of compounds [Carmack *et al.*, 2008]. For this cruise, Beringia 2005, Jones *et al.* [2008] estimated these fractions from salinity (S), alkalinity (A_T), and phosphate/nitrate relationships. The following equations were solved:

$$1 = f_{PW} + f_{AW} + f_{riv} + f_{ice\ melt} \quad (1)$$

$$A_T = f_{PW}A_{T,PW} + f_{AW}A_{T,AW} + f_{riv}A_{T,riv} + f_{ice\ melt}A_{T,ice\ melt} \quad (2)$$

$$S = f_{PW}S_{PW} + f_{AW}S_{AW} + f_{riv}S_{riv} + f_{ice\ melt}S_{ice\ melt} \quad (3)$$

$$[PO_4] = (f_{AW} + f_{riv} + f_{ice\ melt}) [PO_4]_{AW,riv,ice\ melt} + f_{PW}[PO_4]_{PW} \quad (4)$$

$$[NO_3] = (f_{AW} + f_{riv} + f_{ice\ melt}) [NO_3]_{AW,riv,ice\ melt} + f_{PW}[NO_3]_{PW} \quad (5)$$

$$[PO_4]_{PW} = k_{PW}[NO_3]_{PW} + m_{PW} \quad (6)$$

$$[PO_4]_{AW,riv,ice\ melt} = k_{AW,riv,ice\ melt}[NO_3]_{AW,riv,ice\ melt} + m_{AW,riv,ice\ melt} \quad (7)$$

[18] It was assumed that the same nitrate to phosphate relationship found in Atlantic water could be used for river

water and sea ice meltwater. The validity of this assumption was discussed by Jones *et al.* [2008], who also did a sensitivity analysis. For these equations to yield only one solution, the slopes, $k_{AW,riv,ice\ melt} = k_{PW}$, must be equal. To circumvent this problem, in the present study, the equations were solved with the condition that the nitrate concentrations in each fraction had to be in the range of measured data, 0–16 $\mu\text{mol kg}^{-1}$. The mean values of the resulting concentration ranges that met this condition were then chosen. The salinity, alkalinity, and phosphate/nitrate end-members used for the calculations are shown in Table 1. They were basically the same as those used by Jones *et al.* [2008], except for Pacific water alkalinity, which we found to better fit to $A_T = 2207 \mu\text{mol kg}^{-1}$ (compared to 2250 $\mu\text{mol kg}^{-1}$) for the PW selection criterion defined by Jones *et al.* [2008]. Negative $f_{ice\ melt}$ were interpreted as net ice formation, i.e., brine, but with no quantitative explanatory power.

Table 1. End-members used for the Calculation of Source Fractions^a

	Pacific Water	Atlantic Water	River Water	Ice Meltwater
A_T [$\mu\text{mol kg}^{-1}$]	2207	2292	1000	175
S	32	34.85	0	2.5
k	0.0653	0.0545	0.0545	0.0545
m [$\mu\text{mol kg}^{-1}$]	0.94	0.1915	0.1915	0.1915

^a k and m defined as: $[\text{PO}_4] = k*[\text{NO}_3] + m$.

4. Results and Discussion

4.1. Bromoform in Intermediate and Deep Waters

[19] As expected for a short-lived and volatile biogenic compound, bromoform was highly concentrated in the upper waters. The same general picture was true for all measured iodinated and brominated compounds. A detailed discussion of the distribution in the intermediate and deep waters is out of the scope of this article, which focuses on the upper waters. Briefly, bromoform, generally considered as the most important marine biogenic halocarbon, decreased with depth and was lower in the Canada Basin than in the Eurasian Basin (Amundsen and Nansen Basins), with intermediate concentration in the Makarov Basin (Table 2 and Figure 3). The concentration difference reflected the difference in age between the basins. The mean age of the bottom water of the Canada Basin has been estimated to be ~ 200 years older than in the Eurasian Basin, ~ 450 years compared to ~ 250 years [Schlosser *et al.*, 1997]. The average concentration below the sill depth of the Lomonosov Ridge was 3.3 times higher in the Eurasian Basin (3.9 pmol kg^{-1}) than in the Canada Basin (1.2 pmol kg^{-1}). This is in line with a bromoform halide substitution half life of 74 years, as given by Geen [1992] for cold waters (2°C), and indicates that this reaction is the primary degradation pathway in these waters. Basically, the distribution of bromoform in deep and intermediate waters followed the mean age distribution [Tanhua *et al.*, 2009], which suggests that the bromoform load to these waters during

the last ~ 400 years has been relatively constant. Also, the measurements of Krysell [1991] in the Nansen Basin ($82\text{--}86^\circ\text{N}$ at 30°E) in July 1987 show almost identical concentration profiles as our measurements in the Eurasian Basin. At the bottom, below 3000 m, Krysell measured $\sim 3\text{--}4 \text{ pmol L}^{-1}$, and surface maxima ranged from $\sim 12 \text{ pmol L}^{-1}$ to $\sim 28 \text{ pmol L}^{-1}$. In the present study, for stations in the Eurasian Basin (#39–#53, 11 stations), concentrations below 3000 m were $2.4\text{--}4.1 \text{ pmol kg}^{-1}$ (mean 3.5 pmol kg^{-1} , $n=41$) while surface maxima ranged between 14 and 24 pmol kg^{-1} (mean 18 pmol kg^{-1}). We conclude that there is no dramatic change in the concentration of bromoform in surface waters of the Eurasian Basin in 2005 compared to 1987.

4.2. Halocarbons in Upper Waters

4.2.1. Lower Halocline—Transport and Degradation of Halocarbons

[20] The lower halocline, predominately of Atlantic origin, is closest to the surface in the Eurasian Basin where it may extend to the polar mixed layer (PML). On the Amerasian side of the Lomonosov ridge, this water is displaced below the upper halocline (mainly of Pacific origin). The lower halocline water is either formed from Atlantic water entering through the Fram Strait (the Fram Strait branch) or through the Barents Sea (the Barent Sea branch) (Figure 2). The Fram Strait branch halocline water primarily enters the Eurasian Basin or is transported north of the Siberian shelf over the Lomonosov Ridge to the Makarov and northern Canada Basin. The Barents Sea branch basically follows the Siberian continental slope and eventually enters the Canada Basin south of the Chukchi Cap [Rudels *et al.*, 2004]. In the basins, the circulation of lower halocline water has been proposed to resemble the circulation of intermediate waters, i.e., counterclockwise gyres in the large basins (the Eurasian Basin, the Makarov Basin, and the Canada Basin where two circulation patterns are separated by the Chukchi Cap) [Jones, 2001; Rudels *et al.*, 1994]. The dominant

Table 2. Average Bromoform Concentrations (Weighted Against Sample Depth Interval), Standard Deviations, and Ranges in Main Layers in the Canada Basin, the Makarov Basin, and the Eurasian Basin (Amundsen and Nansen Basin)^a

	Canada Basin CHBr ₃ pmol kg ⁻¹	Makarov Basin CHBr ₃ pmol kg ⁻¹	Eurasian Basin CHBr ₃ pmol kg ⁻¹	Water classification
<i>Upper Waters</i>				
$\sigma_0 < 27.20$	10 ± 6.1 (2.1–41), $n=160$	18 ± 8.4 (7.2–42), $n=48$	15 ± 3.7 (7.4–24), $n=51$	PML, Pacific inflow, shelf waters, upper halocline
$27.20 < \sigma_0 < 27.70$	4.9 ± 1.3 (2.7–8), $n=43$	6.3 ± 0.85 (4.7–8.1), $n=38$	7.9 ± 3.2 (5.1–21), $n=42$	Lower halocline
<i>Intermediate Waters</i>				
$27.70 < \sigma_0 < 27.97$	3.9 ± 0.91 (1.9–6.3), $n=72$	5.4 ± 0.52 (3.9–6.4), $n=60$	6.7 ± 1.2 (4.8–13), $n=84$	warm Atlantic Layer
$27.97 < \sigma_0, \sigma_{0.5} < 30.444$	3 ± 0.8 (1.5–4.5), $n=66$	4.1 ± 0.5 (3.3–5.5), $n=40$	5 ± 0.74 (3.6–7.2), $n=62$	DAAW, DAW, AIW, uPDW
<i>Deep Waters</i>				
$30.444 < \sigma_{0.5}, \sigma_{1.5} < 35.142$	2.4 ± 0.69 (1.2–3.6), $n=22$	3.3 ± 0.44 (2.3–4), $n=18$	4.2 ± 0.72 (2.1–5.5), $n=23$	Above sill depth of Lomonosov Ridge
$35.142 < \sigma_{1.5}$	1.2 ± 0.5 (0.4–2.9), $n=66$	1.8 ± 0.35 (1.1–2.7), $n=30$	3.9 ± 0.45 (2.4–4.8), $n=78$	Below sill depth of Lomonosov Ridge

^aFor the upper waters of the Canada Basin, data from the continental shelf slope offshore Barrow, Alaska, are also included. The water mass classifications are simplified from Rudels *et al.* [2012]. For all basins, the average concentration in each water mass is significantly higher ($\alpha=0.05$, Welch t test) than the average concentration in the water mass below. n =number of samples. PML, Polar Mixed Layer; DAW, Dense Atlantic Water; DAAW, Dense Arctic Atlantic Water; AIW, Arctic Intermediate Water; and uPDW, Upper Polar Deep Water.

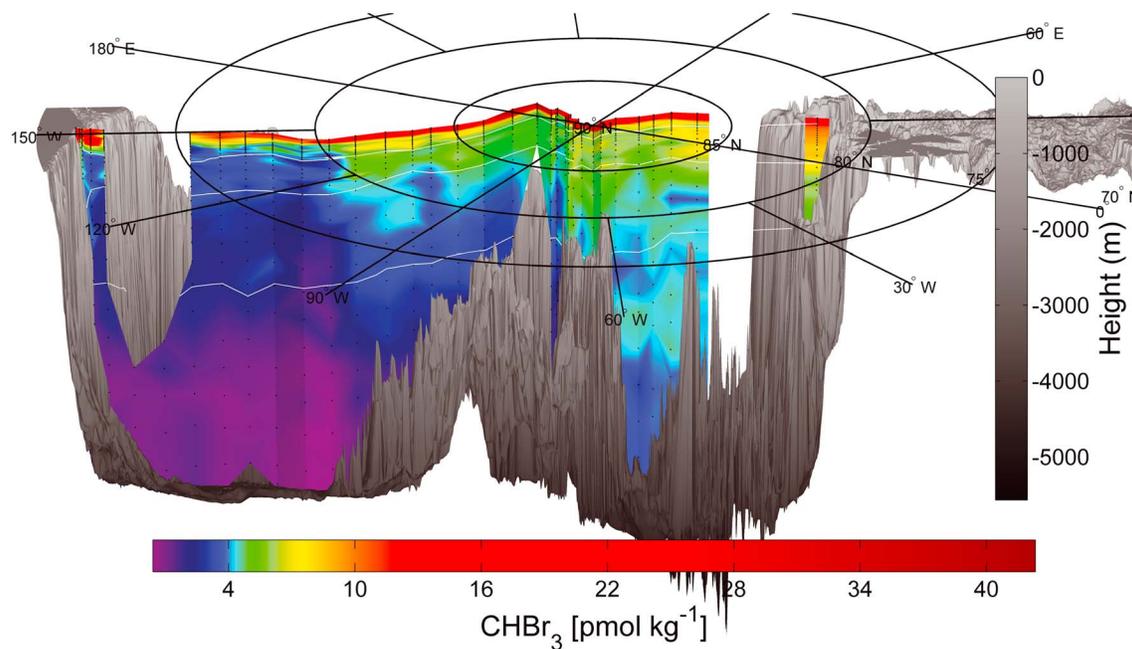


Figure 3. Depth distribution of bromoform from (left) Barrow, Alaska, to (right) Svalbard during the Beringia 2005 expedition is shown. Isopycnals (white) for $\sigma_0 = 27.70$, $\sigma_0 = 27.97$, and $\sigma_{0.5} = 30.444$ are shown, marking the transitions between upper waters, intermediate waters, and deep waters as defined in Table 2. There is no smoothing of data; the color at each data point (black dots) corresponds to the measured value. Interpolation is then performed between data points.

outflow of lower halocline water, not being mixed downward or upward, is through the Fram Strait [Rudels *et al.*, 2004].

[21] The concentrations of the measured halocarbons were, with the exception of CHBr_2Cl , significantly lower in the lower halocline ($27.20 < \sigma_0 < 27.70$) than in the upper halocline (Figure 4). For bromoform, there was also a trend of decreasing concentration with distance, from Svalbard to Barrow, in the lower halocline (Figure 5). This trend was not explained just by the increasing depth of this layer. The same trend was seen in the underlying Atlantic Layer, which seems to confirm the similarity in circulation of these waters. For CH_2Br_2 and CH_2ClI , no clear trend with distance was shown. Local minima of bromoform occurred in the middle of the basins (Amundsen, Makarov, and Canada Basin). This may be due to the circulation pathways, which would cause more stagnant and older water in the center of the basins. The lower halocline is mainly below the photic zone, and bromoform production is thought to be low, with decreasing concentrations due to abiotic and biotic degradation. CHBr_2Cl , which is a product of chloride substitution of bromoform, increased in this layer from Svalbard to the Alpha Ridge. Also, CHBr_2Cl sharply decreased in the Canada Basin (Figure 5). In the Canada Basin the main origin of the lower halocline water is the Barents Sea branch of the Atlantic inflow. It could be expected that this water, compared to the Fram Strait branch, should contain more halocarbons as it had been transported over, or closer, to the shelf during its formation. However, this was not the case as the concentration of both CHBr_3 and CHBr_2Cl was lowest in the Canada Basin lower halocline. Instead, it seems that the longer distance traveled did cause higher degree of degradation or that the Fram Strait branch was enriched in bromoform as it passed over the Eurasian Basin. Alternatively, the Barents

Sea branch had been more exposed to the atmosphere which, depending on air mixing ratios, could cause degassing of supersaturated bromoform.

[22] Formation of lower halocline water could be considered a sink for surface water bromoform, available for air-sea exchange, as the strong density gradient formed prevents mixing with the polar mixed layer.

4.2.2. Upper Halocline—Bering Strait Water and Alaskan Coastal Water—A Possible Sink for Halocarbons Produced on the Shelf

[23] In the upper halocline, waters of different origins can be identified [Steele *et al.*, 2004]. Alaskan Coastal Water (ACW) enters the Arctic Ocean through Barrow Canyon, i.e., close to the Alaskan coast, and is transported along the coast, and then mixes in the Beaufort Gyre in the Canada Basin (Figure 2). ACW is strongly influenced by river runoff, especially the Yukon River south of the Bering Strait. Summer Bering Strait Water (sBSW) enters the Arctic Ocean closer to the Siberian side, through Central canyon or Herald canyon, and is transported near the Chukchi Cap before entering the Beaufort Gyre or the Transpolar Drift stream. Part of the sBSW may take a similar route along the Alaskan coast as the ACW. The ACW is warmer and less saline than sBSW and is identified by a maximum in the temperature depth profile at $31 < S < 32$, while sBSW is identified by a temperature maximum at $32 < S < 33$ [Steele *et al.*, 2004]. Below the sBSW, another type of halocline water, winter Bering Strait Water (wBSW), with origin on the Chukchi shelf and with a temperature minimum at $S = 33.1$, may be found [Jones and Anderson, 1986].

[24] The signals of these types of water were strongest in the southern Canada Basin. Here the concentrations of the brominated compounds (CHBr_3 , CH_2Br_2 , and CHBr_2Cl)

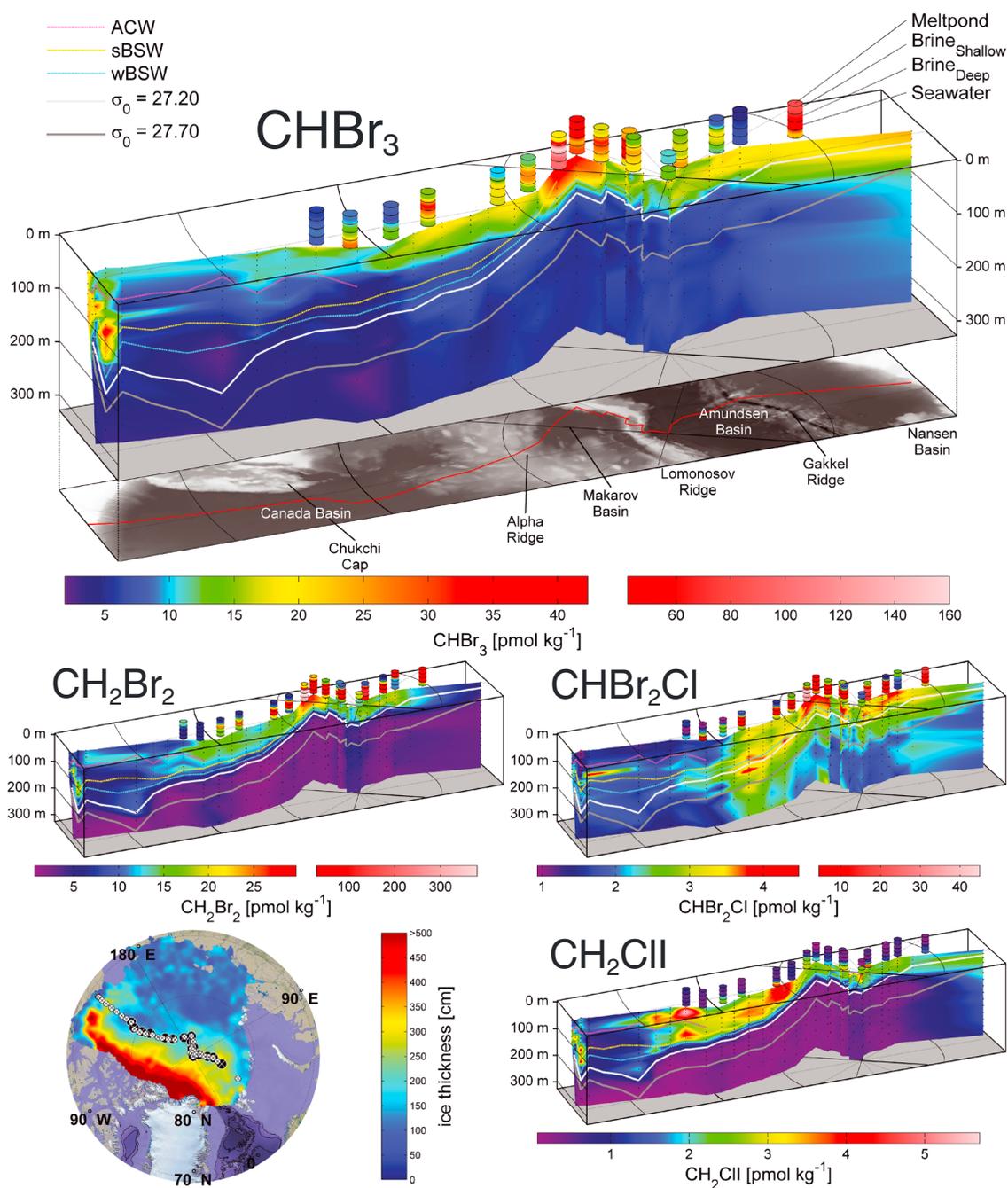


Figure 4. Depth distribution of CHBr_3 , CH_2Br_2 , CHBr_2Cl , and CH_2ClI in the upper 320 m is shown. Also shown, on top, are the concentrations in melt ponds, sea ice brine (two ice depths), and seawater just below the sea ice. Where identified, Alaskan Coastal Water (ACW), summer Bering Strait Water (sBSW), and winter Bering Strait Water (wBSW) are noted. On the bottom left, the ice thickness produced from ICESat data, for 21 October 2005 to 24 November 2005 [Kwok and Cunningham, 2008], is also shown.

were similar in water samples with influence of wBSW and sBSW and higher in ACW (Figure 4). Average values, including the Alaskan continental shelf slope (Table 3) of CHBr_3 and CH_2Br_2 in sBSW were, however, elevated due to high concentrations found in this water type at these more coastal stations. In the Canada Basin, concentrations of nutrients in wBSW and sBSW were high and oxygen levels low (Figure 6). The concentrations of all brominated compounds were lower in the Canada Basin upper halocline, especially

south of the Chukchi Cap, than in water of the same potential density in the Makarov and Eurasian Basin. On the other hand, for CH_2ClI , the highest concentrations during the whole cruise were found in the upper halocline, above the wBSW, of the northern Canada Basin and in the PML near the Chukchi Cap and over the Alpha Ridge.

[25] At the Alaskan continental shelf slope, offshore Barrow, high concentrations of halocarbons, especially CHBr_3 and CH_2Br_2 , were found relatively deep, with maximum

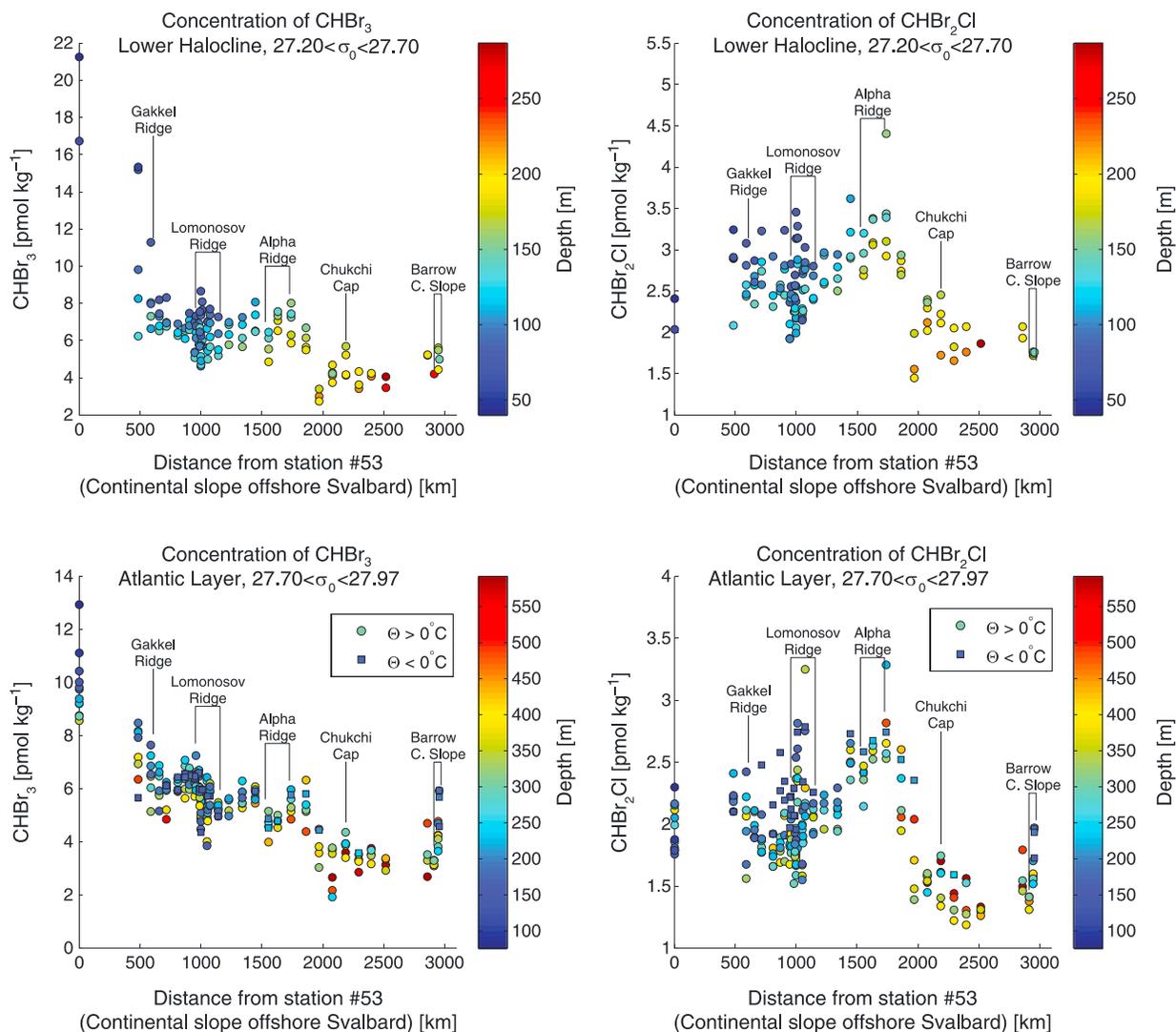


Figure 5. Concentration trend of bromoform and dibromochloromethane in the lower halocline ($27.2 < \sigma_0 < 27.70$) and in the Atlantic layer ($27.70 < \sigma_0 < 27.97$) with distance from the station (#53) at the Continental slope offshore Svalbard, 81.85°N , 33.55°E , into the Eurasian Basin, over the Lomonosov Ridge, into the Makarov Basin, over the Alpha Ridge, into the Canada Basin and up over the Continental slope offshore Barrow, Alaska.

concentration below chlorophyll *a* maximum (Figure 7), down to ~ 150 m (station 4). These maximum values coincided with the highest fraction, 100%, of Pacific water. Temperature maxima at $32 < S < 33$ (although not as clear for station 4

where the temperature rise was obscured by high surface temperatures) indicated that this water could be classified as sBSW. Also, local oxygen maxima were found to coincide with these bromocarbons.

Table 3. Mean Concentration and Standard Deviation of Halocarbons in the Polar Mixed Layer in Different Regions of the Arctic Ocean and Concentrations in the Different Water Types Found in the Upper Halocline in the Amerasian Basin^a

	CHBr_3 pmol kg^{-1}	CH_2Br_2 pmol kg^{-1}	CHBr_2Cl pmol kg^{-1}	CH_2ClI pmol kg^{-1}	<i>n</i>	Station #
<i>Polar Mixed Layer</i>						
Alaskan shelf/slope	13 ± 3	7 ± 3	1.4 ± 0.4	1 ± 0.6	4	1–4
Canada Basin	14 ± 3	12 ± 3	2.2 ± 0.8	2.2 ± 0.9	22	5–21
Makarov Basin	29 ± 11	22 ± 7	3.7 ± 0.7	3.3 ± 0.8	6	23–26
Eurasian Basin	18 ± 3	15 ± 4	3.3 ± 0.5	2.6 ± 0.6	24	42–53
<i>Upper Halocline in the Amerasian Basin and Over the Alaskan Continental Shelf/Slope</i>						
ACW	11 ± 4	11 ± 3	1.7 ± 0.3	1.9 ± 0.5	9	1–24
sBSW	10 ± 9	12 ± 4	2.5 ± 0.6	2.8 ± 0.7	14	– –
wBSW	6 ± 2	6 ± 3	2.5 ± 0.8	1.1 ± 0.7	19	– –

^aACW, Alaskan Coastal Water (temperature maximum at $31 < S < 32$); sBSW, summer Bering Strait Water (temperature maximum at $32 < S < 33$); wBSW, winter Bering Strait Water (temperature minimum at $S = 33.1$).

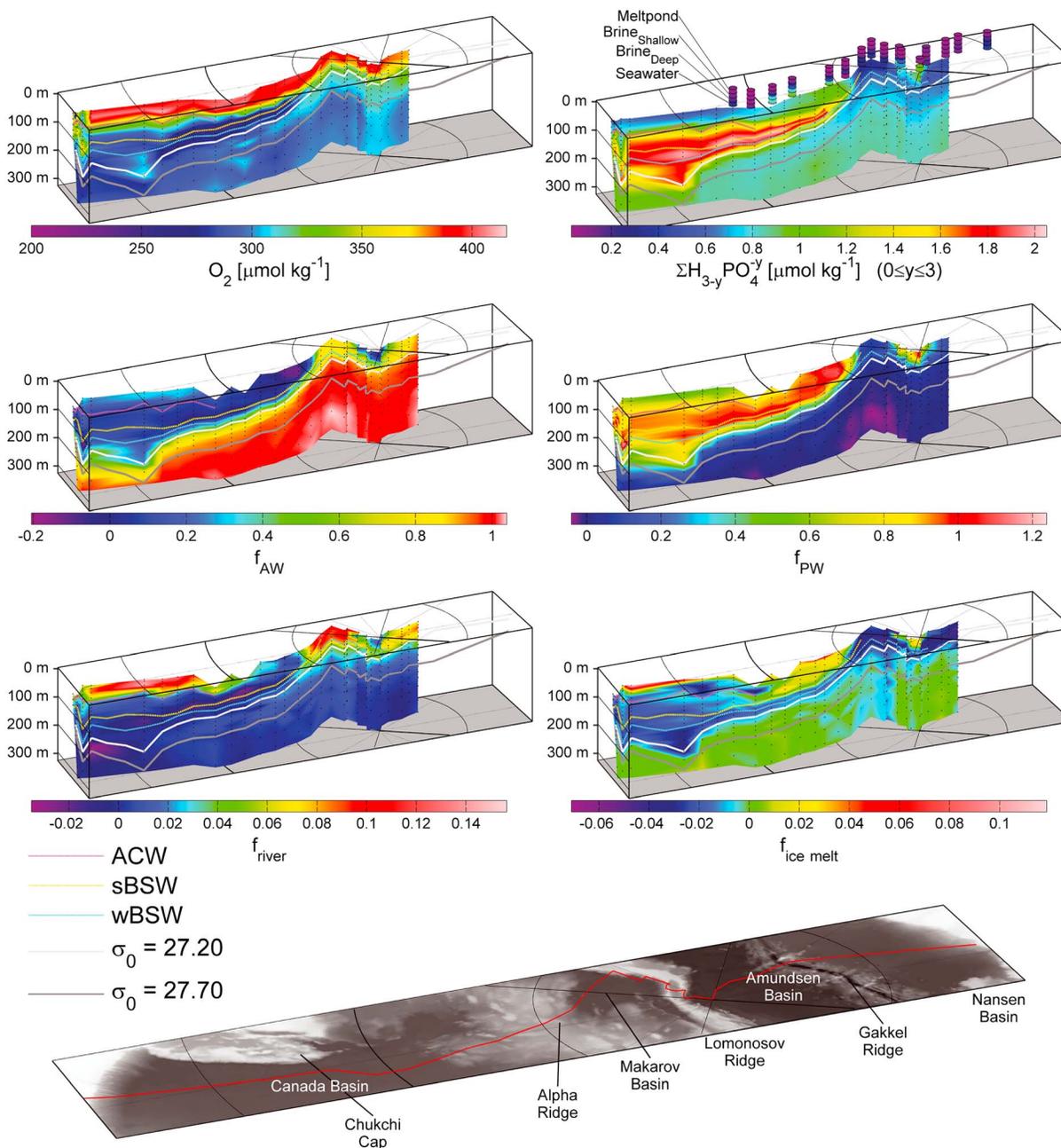


Figure 6. Depth distribution of oxygen and phosphate and fractions of Pacific Water (f_{PW}), Atlantic Water (f_{AW}), river water (f_{river}), and sea ice meltwater ($f_{ice\ melt}$), as calculated from salinity and alkalinity end-members and phosphate/nitrate relationships.

[26] On the next station, 55 km to the north of the preceding station, over the southern Canada Basin (~3550m depth) the bromoform maximum was almost gone (Figure 7), while CH_2Br_2 and CHBr_2Cl still showed a slight maximum in the Pacific-derived water in the upper halocline, and remained so continuing north until the Makarov Basin (where the upper halocline decreased to a maximum depth of 100m, compared to 250 m as deepest in the Canada Basin). From here, over the Lomonosov Ridge to the Eurasian Basin, the concentrations of all measured brominated and iodinated compounds were highest in the PML (Table 3).

[27] In spring and summer the productivity on the Chukchi shelf is high, due to the nutrient-rich Pacific Water [Mathis

et al., 2007]. High primary production has also been reported over the Barrow Canyon [Hill and Cota, 2005]. Primary production has also been shown to be high in the sea ice in this region [Gradinger, 2009]. It is plausible that the high subsurface concentrations of CHBr_3 and CH_2Br_2 in Pacific-derived water over the shelf break and continental slope offshore Barrow (Figure 7) originates from these regions. Another indication of this was the correlation with oxygen, since halocarbon production is linked to photosynthesis.

[28] It could be argued that the high halocarbon concentrations were carried from the Pacific Ocean. However, high ratio of CHBr_3 to, the degradation product, CHBr_2Cl (above 10 times) at the shelf stations, and much less pronounced

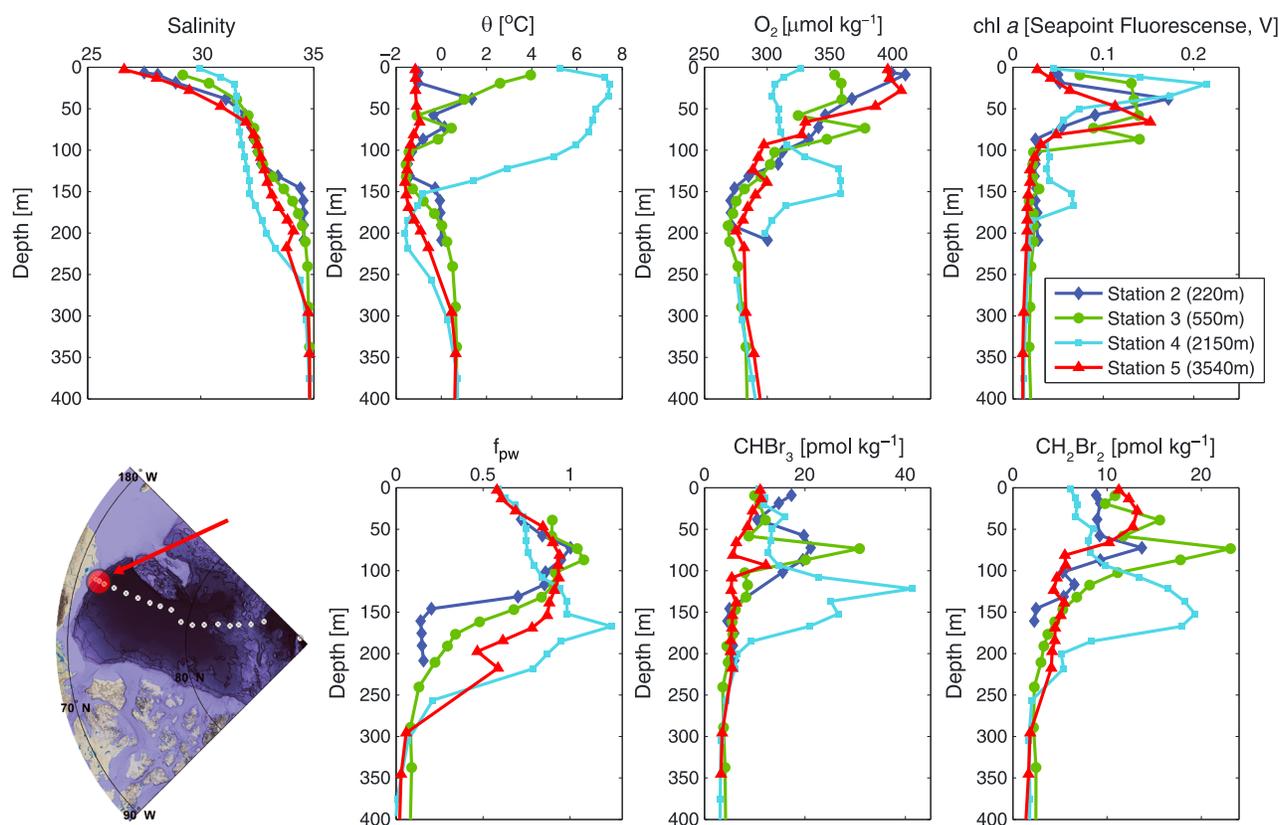


Figure 7. Depth profiles (400m) for stations on the shelf and over the continental slope offshore Barrow, Alaska (indicated on map). Profiles for salinity, potential temperature, oxygen, chl *a*, Pacific water fraction, bromoform, and dibromomethane are shown.

depth profile maximum for CHBr_2Cl than for CHBr_3 , indicated that the source was not too far away in time and space. Additionally, increasing maximum concentrations away from land over the continental shelf suggested that there might not have been a nearshore dependence, at least not to the coastal zone outside Barrow.

[29] We therefore suggest that there is a biogenic source of halocarbons in the Chukchi Sea or in the East Siberian Sea. The significance of this source is however uncertain without measurements in these regions.

[30] As the Pacific Water-derived upper halocline water is followed from the Alaskan continental slope into the Canada Basin, a trend of decreasing bromoform concentration with decreasing oxygen concentration, and increasing nutrient concentration could be seen (Figure 8). Also, the CHBr_2Cl maximum coincided with the oxygen minimum, and there was a weak trend of increasing CHBr_2Cl with decreasing oxygen concentration. It is plausible that microbial processes that regenerated the nutrients and consumed the oxygen [Cota *et al.*, 1996] also degraded bromoform. It has been suggested from a mesocosm study in Kongsfjord, Svalbard, that bacterial degradation of bromoform may be an important removal pathway in Arctic waters [Hopkins *et al.*, 2012].

[31] CH_2Br_2 , on the other hand, showed a concentration maximum varying between 50 m and 100 m in the Canada Basin upper halocline, with concentrations slightly lower than the highest concentrations at the Alaskan continental slope, i.e., it did not seem to be degraded as fast as bromoform. At some stations (most clear at station #12,

closest to the Chukchi Cap), two concentration maxima of CH_2Br_2 in the upper halocline could be seen, approximately located at the signal of ACW and sBSW (Figure 4).

4.2.3. Polar Mixed Layer in the Canada Basin, the Beaufort Gyre—Low Concentrations, a Possible Sink for Halocarbons

[32] The polar mixed layer, composed of Atlantic water, Pacific water, river water, and sea ice meltwater (Figure 6), was low in brominated compounds over the Canada Basin (Table 3) compared to the Makarov and Eurasian Basins. The lowest concentrations were found in the southern part (the Beaufort Sea) up to the Chukchi Cap (Figure 4). The low surface concentrations was also accompanied by low concentrations of nutrients (Figure 6) and chl *a* (from Seapoint fluorometer; R. M. W. Amon *et al.*, The role of sea ice processes on the distribution of dissolved organic matter in the Arctic Ocean, in preparation) and coincided with the accumulation of freshwater in the Beaufort Gyre [Jones *et al.*, 2008]. The freshwater came from river water, ice melt, and precipitation and had mixed with the Pacific water and the high-salinity Atlantic water (Figure 6). The largest freshwater component was identified as river water, probably to a large degree from the nearby Mackenzie delta.

[33] For bromoform, this layer in the southern Canada Basin in the Beaufort gyre with high freshwater content could be suspected to be a sink for atmospheric bromoform. The surface concentrations of $\sim 10 \text{ pmol kg}^{-1}$ found here (14 pmol kg^{-1} in average for the whole Canada Basin, Table 3) would correspond to an air mixing ratio of $\sim 1.3 \text{ pptv}$

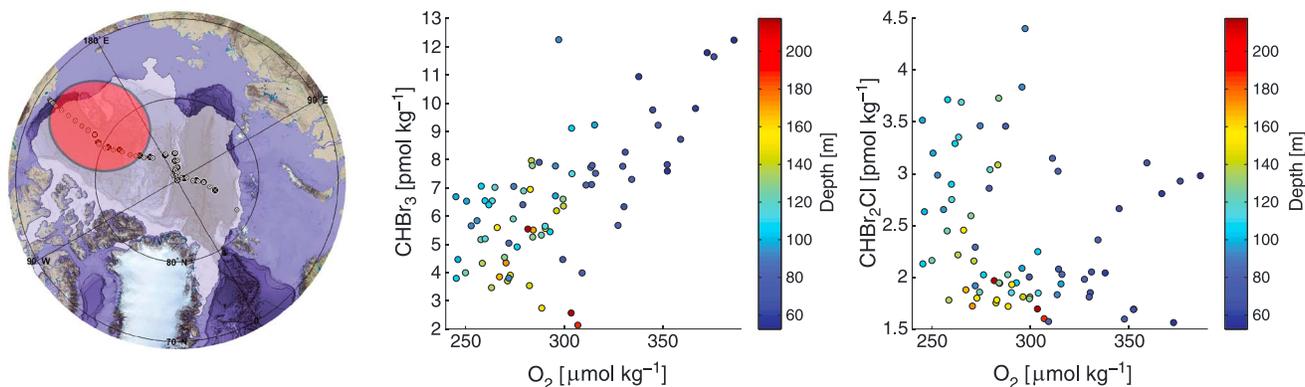


Figure 8. Concentration of bromoform and dibromochloromethane, versus oxygen concentration, in the upper halocline ($\sigma_0 < 27.2$, depth > 50 m) in the Canada Basin (stations #5–#23, shown in red circle on map) is shown.

at equilibrium at sea surface temperature (SST) (with Henry's Law constant from Moore *et al.* [1995]), which is in the lower range of measured values over the Arctic [Quack and Wallace, 2003]. Air mixing ratios of bromoform measured during the expedition, at the ice stations (Figure 2), were 2.9 pptv at average (range 2.3–4.6 pptv, $n=7$), which translates to a concentration in water at equilibrium at SST of approximately 22 pmol kg^{-1} (range 18–33 pmol kg^{-1}).

[34] The low concentrations of chl *a* indicated that this was a region with low primary production. Halocarbon production in these waters could therefore also be suspected to be low. Continuous freezing and melting cycles could have removed halocarbons, which further would have decreased their concentrations. During freezing, these volatile compounds have been shown not to behave conservatively. A. Granfors *et al.* (personal communication, 2012) showed that halocarbons decreased faster than bulk salinity in sea ice during freezing and proposed a mechanism of partitioning of halocarbons in gas bubbles formed from dissolved gases during freezing and subsequent upward transport through the ice and to the atmosphere. A similar explanation, of increased diffusion through the ice due to gas-filled pore spaces, was given by Loose *et al.* [2011] for their observations of the behavior of O_2 and SF_6 in artificial sea ice. If halocarbons are transported with gas bubbles formed during freezing, this could lead to undersaturated underlying water compared to the atmosphere. Sea ice would then act as a barrier maintaining this undersaturation as liquid diffusion through brine channels, in ice in static condition, is slow.

4.2.4. Polar Mixed Layer in the Makarov Basin, Over the Lomonov Ridge and in the Eurasian Basin—Transport of Riverine Water in Transpolar Drift and Connection to Multiyear Sea Ice and CDOM

[35] North of the Chukchi Cap, over the Alpha Ridge and into the Makarov Basin, the concentration of halocarbons

in the PML increased. Bromoform reached maximum values of 42 pmol kg^{-1} near the Lomonosov Ridge, with highest concentration close to the sea ice interface (Figure 4). The other brominated compounds (CH_2Br_2 and CHBr_2Cl) showed the same trend, but CH_2ClI was completely different with low concentrations at the maximum concentrations of the brominated compounds.

[36] In this region the ice was increasingly thicker, i.e., older, (Figure 4, bottom left). This was also in the path of the Transpolar Drift, the wind-driven system that transports water and ice from the Siberian shelf (Figure 2) mainly to the Fram Strait [Mysak, 2001]. A large fraction of riverine water was found here (Figure 6), most likely from the large Russian rivers, and this fraction coincided with the high concentrations of brominated compounds (Figure 4). Also, a large amount of CDOM was carried with this river water [Stedmon *et al.*, 2011].

[37] Strongest correlations between water fractions and brominated compounds were found for the river fraction (Table 4). In the ice melt fraction, weaker anticorrelations were seen. However, $f_{\text{ice melt}}$ was negative in this region, indicating contribution of brine rejected from ice, i.e., the anticorrelation could be interpreted as a weak positive correlation of brominated compounds with brine. This possibly arises from the fact that halocarbons are concentrated in brine as seawater freezes. For CH_2ClI , no correlation with river water was seen. Instead, this compound followed the Pacific fraction which was in line with the findings in the Canada Basin (except in the southernmost part), where CH_2ClI also followed the Pacific Water (Figures 4 and 6).

[38] Even higher concentrations of halocarbons than in the surface water were found in the overlying ice (Karlsson *et al.*, in preparation) (Figure 4). Brominated compounds were consistently higher in sea ice brine than in the surface water in this region. Up to 160 pmol L^{-1} of CHBr_3 and 380 pmol L^{-1} of

Table 4. Spearman Rank Correlation Coefficients, ρ , for Concentrations of Halocarbons and Water Fractions, for Stations in Approximate Region of the Transpolar Drift (stn #24–#50, Figure 9) in the Polar Mixed Layer and Upper Halocline ($\sigma_0 < 27.2$, depth ~ 90 m)

	CHBr_3	CH_2Br_2	CHBr_2Cl	CH_2ClI
f_{river}	0.49 ($p < < 0.001$)	0.49 ($p < < 0.001$)	0.27 ($p = 0.01$)	0.10 ($p = 0.37$)
$f_{\text{ice melt}}$	−0.29 ($p = 0.005$)	−0.35 ($p = 0.001$)	−0.22 ($p = 0.034$)	0.15 ($p = 0.17$)
f_{AW}	−0.05 ($p = 0.63$)	0.03 ($p = 0.77$)	0.12 ($p = 0.25$)	−0.49 ($p < < 0.001$)
f_{PW}	−0.05 ($p = 0.66$)	−0.13 ($p = 0.22$)	−0.18 ($p = 0.09$)	0.42 ($p < < 0.001$)

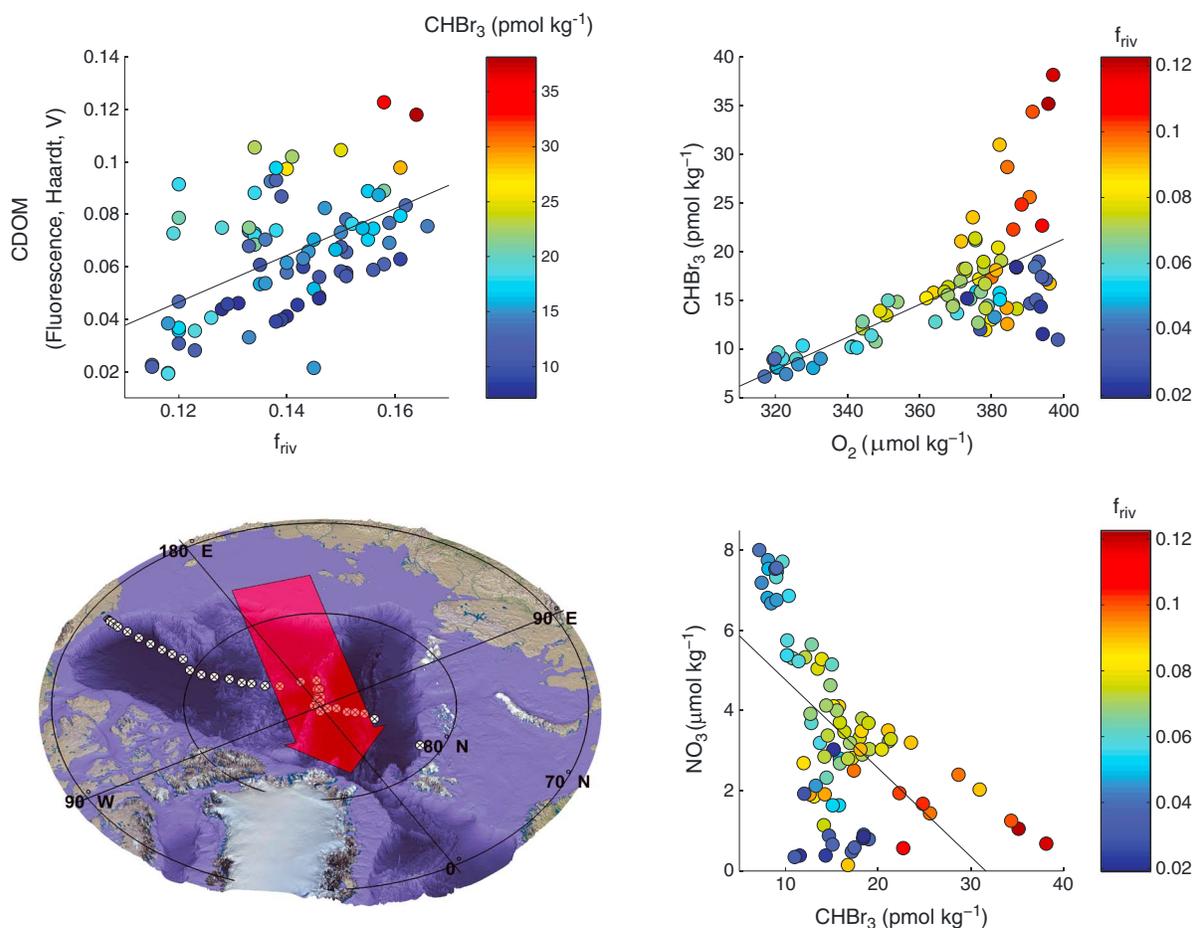


Figure 9. (bottom left) Relationships in the polar mixed layer (PML) and upper halocline ($\sigma_0 < 27.2$) in the approximate region of the Transpolar Drift Stream are shown. (top left) CDOM (from Haardt fluorometer) is plotted against calculated river fraction with data points colored by bromoform concentration. Bromoform is also shown versus (top right) oxygen and (bottom right) nitrate concentrations, with colors corresponding to the river fraction. The trends (linear regression) shown are all significant positive or negative with confidence interval $> 95\%$.

CH_2Br_2 were found in sea ice brine. These maximum values coincided, for the water depth profile closest to this site, with the highest concentrations in surface waters found for the entire cruise, 42 pmol kg^{-1} of CHBr_3 and 30 pmol kg^{-1} of CH_2Br_2 . In the ice samples, the sea ice brine salinity was lower than the salinity in the PML, i.e., the ice was in a melting phase and with possible intrusion of seawater. Corrected for this dilution, the concentration difference between the sea ice and the surface water would be even more dramatic.

[39] Our hypothesis is that the cycles of freezing and thawing of sea ice with large fractions of riverine water had led to an accumulation of halocarbons in the underlying seawater due to biological processes mainly in the sea ice, and we suggest the following mechanism. As ice is formed, the seawater components (nutrients, DOM, etc.) are concentrated in the brine, providing favorable conditions for ice algae. During the spring bloom, the primary production is likely to indirectly cause production of halocarbons from the activation of haloperoxidases due to the formation of reactive oxygen species during photosynthesis. As sea ice-air flux is limited in the static ice layer, a large part of the formed halocarbons are concentrated in the brine channels. Partial

melting, from the bottom, possibly also with intrusion of seawater from below, then causes release of these compounds to the surface water. Probably, there is also halocarbon production in this upper seawater layer even if the strongest source seems to be the sea ice brine.

[40] This mechanism of concentration of halocarbons would be most effective in regions of multiyear ice which is always ice covered and prevents large fluxes to the atmosphere. The halocarbon production seemed to be enhanced by high concentrations of DOM. As for the brominated compounds, CDOM correlated with the river fraction in this region (Figure 9, top left). A positive trend of bromoform with oxygen and a negative trend with nitrate suggested that bromoform production was related to primary production (Figure 9).

[41] The depth profiles of brominated compounds at stations crossing over the Lomonosov Ridge showed maximum concentrations near the sea ice and sharpest increase at stations with highest fraction of river water (Figure 10). Such sharp concentration maxima would not be likely if the high concentrations were just caused by transport of river water/ice enriched in brominated compounds from the Russian

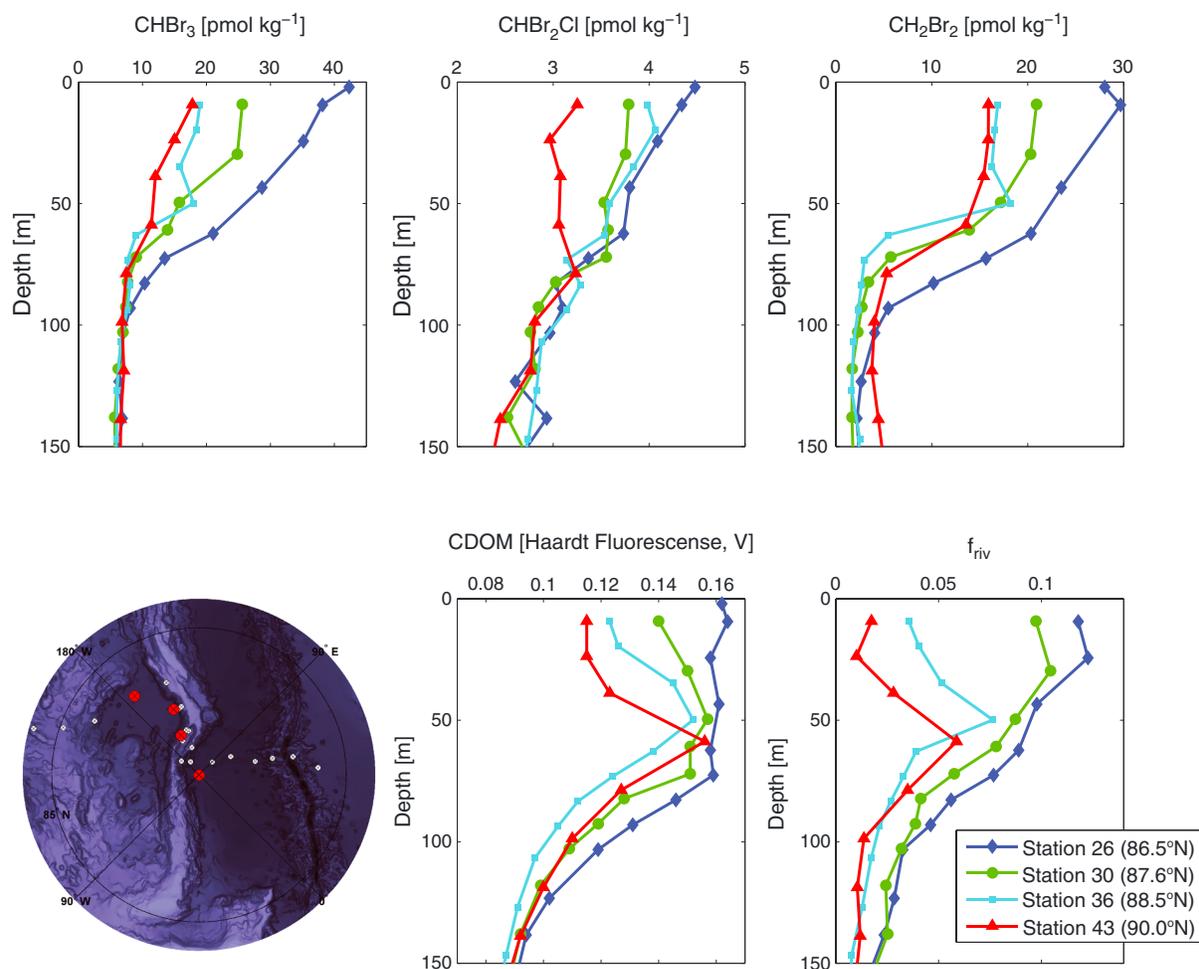


Figure 10. Depth profiles for the top 150 m at four stations along the Lomonosov Ridge, from the Siberian side to the North Pole (map). Three brominated compounds, the CDOM signal (Haardt fluorometer), and the calculated river water fraction (f_{riv}) are shown.

ivers, as substantial mixing in that case would have occurred. Together with the relationship with oxygen and nutrients, this strongly suggests that these compounds were produced in the sea ice during the transport with the Transpolar Drift. It also suggests that the components from the riverine water were key factors for the production of brominated compounds. CDOM, on the other hand, did not show the same sharp increase toward the sea ice. Instead, uniform distributions in the top 50 m, or maximum concentrations at ~50 m signals, were found. In other words, CDOM followed the river fraction but seemed to have been depleted in water near the sea ice.

[42] As CDOM is incorporated in brine channels during formation of sea ice, a likely explanation is that it was utilized or transformed in the sea ice. When the brine then was released with melting ice, not all CDOM was retrieved. DOM, as indicated by CDOM, could be used directly as a substrate source for biogenic formation of halocarbons, intracellular or extracellular by both bacteria and phytoplankton. It is primarily utilized by heterotrophic bacteria [Horner and Alexander, 1972], but it has also been shown that microalgae in sea ice can incorporate small organic compounds [Smith and Clement, 1990]. It was first proposed by Wever *et al.* that HOBr, produced by bromoperoxidases from

Br^- and H_2O_2 , could be released from macroalgae and, which by reaction with DOM, could produce halogenated compounds such as CHBr_3 [Wever *et al.*, 1991]. It has then been shown that production of halocarbons by the macroalgae *Ulva Lactuca* in light decreased with >80% when DOM was removed from the incubation seawater [Manley and Barbero, 2001], which supports such a mechanism. More recently, it has also been shown that species of diatoms release HOBr and IOBr, which may react with extracellular DOM [Hill and Manley, 2009]. Although most widespread in eukaryotic organisms, bromoperoxidases, although generally with lower halogenating activity, have also been identified in bacteria, e.g., in *Pseudomonas aureofaciens* [Van Pée and Lingens, 1985], and it has been shown that cyanobacteria may produce halocarbons [Johnson *et al.*, 2011; Karlsson *et al.*, 2008; Schall *et al.*, 1996]. So even if algae were the most likely producers of the halocarbons measured, it cannot be excluded that bacteria were partly responsible for the halocarbon production. However, again, the positive correlation of bromoform with oxygen and negative correlation with nutrients (Figure 9, only nitrate shown but a similar trend was also seen for phosphate), especially strong in samples of high river fraction, suggest that the production was linked to photosynthesis.

[43] The completely different behavior of the iodocarbon, CH₂I₂, is an interesting feature. It should be noted that the chemical speciation of inorganic iodine in seawater is much more complicated than for chlorine or bromine. The thermodynamically favored form in oxygenated water at normal seawater pH is iodate, IO₃⁻, but still iodine is found to a large degree as iodide, especially in surface waters. It is not clear what causes this reduction to the metastable form. Several authors, e.g., Wong *et al.* [2002], have attributed the transformation to phytoplankton activity, but this has also disputed, e.g., by Truesdale *et al.* [2003]. Spokes and Liss [1996] instead suggested a photochemical transformation dependent on DOM. Since iodide is the substrate for haloperoxidases, the iodate/iodide ratio is highly important for the formation of iodocarbons. If a high iodate to iodide ratio in the sea ice is the reason for the comparably low concentrations of CH₂I₂ can only be speculated. The terrestrial characteristics of the CDOM over the Lomonosov Ridge, as compared to the CDOM in the Canada Basin [Stedmon *et al.*, 2011], with much higher lignin concentrations in the former [Amon *et al.*, 2012], is another factor which may be important. Another explanation could be a high selectivity for bromide for haloperoxidases in the ice algae in this region.

5. Conclusions

[44] This investigation has given new insights in factors controlling the distribution of halocarbons in the Arctic Ocean. In the upper halocline in the Canada Basin and on the continental slope near Barrow, elevated concentrations of halocarbons could be found in waters identified as summer Bering Strait Water (sBSW) and Alaskan Coastal Water (ACW). This suggested that halocarbons were produced on the shelf, in the Chukchi Sea and the East Siberian Sea. Sea ice, especially in areas with multiyear ice, influenced the halocarbon surface water concentrations to a large extent. Most striking was the high concentrations of brominated compounds in the mixed layer and upper halocline over the Makarov Basin and the Lomonosov Ridge. The correlation with river fraction and DOM and the even higher concentrations in the sea ice brine as well as maximum seawater concentrations closest to the ice indicate that DOM is a key factor for production of bromocarbons in the sea ice. The polar mixed layer (PML) in the southern Canadian basin was identified as a possible sink for atmospheric bromoform. The distributions of CHBr₃ and CHBr₂Cl were in line with the large-scale circulation patterns of waters below the upper halocline. The half life of bromoform in cold waters of ~74 years (at 2°C) [Geen, 1992] could be confirmed by relating the bromoform concentrations to the mean age of the bottom waters of the Amerasian Basin compared to the Eurasian Basin. Potentially, with better estimates of chemical degradation kinetics, these compounds could be used to give additional insight in circulation pathways not possible with traditional tracers, and they may also carry information of historical variations in biological activity.

[45] So far, the concentration of brominated compounds in surface waters of the Arctic Ocean seems not to have changed dramatically over the last two decades. However, recent observations in the Arctic with the retreat of sea ice, and changes in precipitation and river runoff, might change the distribution of halocarbons significantly, due to changes

in primary productivity, species composition, circulation patterns, formation of halocline water, load of terrestrial DOM, and air-sea exchange.

[46] **Acknowledgments.** This study was funded by the Swedish Research Council, the Swedish Research Council Formas, and the Knut and Alice Wallenberg Foundation. We also thank the Swedish Polar Research Secretariat for outstanding logistical support. The excellent technical assistance by Erika Trost was very valuable. We are also indebted to Rainer M. W. Amon at the Texas A&M University and his team for sharing his CDOM data with us. Finally, we acknowledge our fellow colleagues on board and the skilful and professional crew of RV/IB *Oden* who helped out far above their responsibilities.

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