Methyl halides in surface seawater and marine boundary layer of the northwest Pacific

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Received 7 August 2009; revised 6 April 2010; accepted 10 June 2010; published 8 October 2010.

[1] The partial pressures of methyl halides (CH3X; X = Cl, Br, or I) and of CHClF2 (HCFC-22), which are all volatile organic compounds (VOCs), were measured in the air of the marine boundary layer (pVOCair) and in surface seawater (pVOCwater) during a cruise from the subarctic to subtropical regions of the northwest Pacific in summer of 2008. In the northern transition water (TWN) with high biological activity, high levels of the three CH3Xs in surface seawater were frequently observed, probably owing to their enhanced production by phytoplankton. Supersaturation of CH3Br was only present in TWN water, with a saturation anomaly (SCH3Br) of 0.95 [SCH3X = (pCH3Xwater − pCH3Xair)/pCH3Xair]. The highest saturation anomalies for CH3Cl (SCH3Cl = 1.6) and CH3I (SCH3I = 91) were found in the southern subtropical water (STS) with low biological production south of the subtropical front. We found that the molar concentrations of CH3Cl (CH3Cl) and CH3I (CH3I) sharply increased with increasing sea surface temperature (SST) in the subtropical waters. The maximum CH3Cl (144 pmol l−1) was present in STS water at SST = 30°C and is 1.5 times the value extrapolated from the previously reported relationship between CH3Cl and SST. Photochemical production might have contributed to the production of CH3Cl and CH3I in STS water.


1. Introduction

[2] Methyl chloride (CH3Cl) and methyl bromide (CH3Br) have been regarded as the largest contributors of naturally produced halogens to the stratosphere, where they are responsible for ozone destruction [World Meteorological Organization (WMO), 2007], while methyl iodide (CH3I) primarily affects ozone destruction in the troposphere [Chameides and Davis, 1980] and in the lower stratosphere [Solomon et al., 1994].

[3] A number of studies have investigated the oceanic sources and sinks of methyl halides (CH3X). Biological sources include macroalgae [Manley and Dastoor, 1987; Manley, 1992; Giese et al., 1999], phytoplankton [Scarratt and Moore, 1996; Manley and dela Cuesta, 1997; Scarratt and Moore, 1998], and bacteria for CH3I [Amachi et al., 2001; Smythe-Wright et al., 2006]. Bacterial degradation of CH3Cl and CH3Br is reportedly an important oceanic sink for these molecules [Tokarczyk et al., 2003a, 2003b]. Abiotic processes involving methyl halides include nucleophilic substitution of CH3Br and CH3I by Cl− (chloride substitution), resulting in CH3Cl [Elliott and Rowland, 1993; Jones and Carpenter, 2007], as well as photochemical production of CH3I from I− and methyl radicals [Moore and Zafiriou, 1994; Happell and Wallace, 1996; Yokouchi et al., 2001, 2008; Richter and Wallace, 2004; Chuck et al., 2005] and CH3Cl from colored dissolved organic compounds (CDOM) [Moore, 2008].

[4] To estimate the global oceanic distributions of methyl halides and their oceanic fluxes, several studies examined correlations between CH3X concentrations and key oceanic parameters such as sea surface temperature (SST). The relationships between SST and concentrations of CH3Cl and CH3Br were used to estimate global oceanic fluxes, by extrapolation from the global SST distribution, for CH3Cl
subarctic to subtropical regions by means of a liquid gas equilibrator and gas chromatograph (GC).

Butler et al. [2007] reported the average CH$_3$I flux in major oceanic waters, tropical, subtropical, temperate, polar, subpolar, and coastal, and extrapolated the results to obtain the global oceanic flux of 0.6 Tg y$^{-1}$. Details of CH$_3$X measurements are described elsewhere [Ooki and Yokouchi, 2008]. Briefly, the equilibrator consists of six silicone tubes (length, 10 m; o.d., 2.0 mm; i.d., 1.5 mm) housed in a polyvinyl chloride (PVC) pipe. Pure air was continuously supplied to the silicone tubes at a flow rate of 25 mL min$^{-1}$, regulating the inner pressure to +0.14 MPa. The gas-phase sample of VOCs at equilibrium with the seawater could be obtained from the outlet of the silicone tube. The equilibrator was cleaned by compressed air to remove deposits after Leg 1.

Outside air was drawn from the upper deck (17 m above the sea level) of the ship through a PTFE tube (length, 60 m; i.d., 11 mm) at a flow rate of 50 L min$^{-1}$. We obtained a portion of the air from the PTFE tube at a flow rate of 25 mL min$^{-1}$ using a metal bellows pump. The gas phase sample (equilibrated air or outside air) was dehumidified by means of Nafion® dryer and then transferred to a pre-concentration/GC-MS system [Yokouchi et al., 2006]. Partial pressures of CH$_3$Cl, CH$_3$Br, CH$_3$I, and HCFC-22 in the sample of equilibrated air or outside air were measured at 70 min intervals. A gravimetrically prepared standard gas (Taiyo Nissan, Inc., Tokyo) containing these chemical species was used for the calibration. The detection limits (S/N = 3) were 2.1 pptv for CH$_3$I, 2.9 pptv for CH$_3$Br, and 1.3 pptv for CH$_3$Cl. This means that there were no blank values or loss of CH$_3$X in seawater.

For understanding the CH$_3$X variability in surface seawater associated with mesoscale water mass structure, CH$_3$X concentrations need to be determined with high frequency at a measurement cycle of several hours intervals on a ship which corresponds to several tens kilometers intervals. Recently, high-frequency measurements of CH$_3$I and brominated halocarbons have been carried out in surface seawater associated with mesoscale water mass structure, [Anbar et al., 1996; Smythe-Wright et al., 2006; Butler et al., 2007]. However, there have been no high-frequency measurement studies of the 3 CH$_3$X species in the NW Pacific, including the subarctic and mixed water (subarctic-subtropical transition zone) with well-known high primary production, and the oligotrophic subtropical region, which has the warmest SST, of up to 30°C in summer. To characterize the oceanic distributions of CH$_3$X in the NW Pacific, we measured 3 CH$_3$X (CH$_3$Cl, CH$_3$Br and CH$_3$I) and HCFC-22 in surface seawater and in the marine boundary layer (MBL) of the NW Pacific from subarctic to subtropical regions by means of a liquid-gas equilibrator and GC-MS system as a part of the Japanese Surface Ocean Lower Atmosphere Study (J-SOLAS). HCFC-22 is long-lived in air with lifetime of 12.0 years [WMO, 2007] and is derived from terrestrial anthropogenic sources. Because it is mainly affected by physical processes such as air-sea exchange, temperature-dependent solubility and mixing, it was investigated as an indicator of the behavior of a dissolved gas that is not affected by chemical or biological processes.

2. Methods

2.1. VOC Measurements

VOC measurements were conducted aboard the R/V Hakuho-maru (cruise KH08-2) in 2008 from 29 July to 19 August (Leg 1) and from 23 August to 15 September (Leg 2) in the NW Pacific (Figure 1). Surface seawater was pumped from a seawater intake on the bottom of the ship (5 m depth), and supplied to the laboratory, passing through a seawater pipe with the inner wall coated with nylon for most of its length. The surface seawater was continuously supplied to a silicone membrane tube equilibrator at a flow rate of 15 L min$^{-1}$. Details of CH$_3$X measurements are described elsewhere [Ooki and Yokouchi, 2008]. For quantitative predictions of changes in CH$_3$X flux, it is essential to understand the mechanisms of production and loss of CH$_3$X in seawater.

For understanding the CH$_3$X variability in surface seawater associated with mesoscale water mass structure, CH$_3$X concentrations need to be determined with high frequency at a measurement cycle of several hours intervals on a ship which corresponds to several tens kilometers intervals. Recently, high-frequency measurements of CH$_3$I and brominated halocarbons have been carried out in surface seawater associated with mesoscale water mass structure, [Anbar et al., 1996; Smythe-Wright et al., 2006; Butler et al., 2007]. However, there have been no high-frequency measurement studies of the 3 CH$_3$X species in the NW Pacific, including the subarctic and mixed water (subarctic-subtropical transition zone) with well-known high primary production, and the oligotrophic subtropical region, which has the warmest SST, of up to 30°C in summer. To characterize the oceanic distributions of CH$_3$X in the NW Pacific, we measured 3 CH$_3$X (CH$_3$Cl, CH$_3$Br and CH$_3$I) and HCFC-22 in surface seawater and in the marine boundary layer (MBL) of the NW Pacific from subarctic to subtropical regions by means of a liquid-gas equilibrator and GC-MS system as a part of the Japanese Surface Ocean Lower Atmosphere Study (J-SOLAS). HCFC-22 is long-lived in air with lifetime of 12.0 years [WMO, 2007] and is derived from terrestrial anthropogenic sources. Because it is mainly affected by physical processes such as air-sea exchange, temperature-dependent solubility and mixing, it was investigated as an indicator of the behavior of a dissolved gas that is not affected by chemical or biological processes.
with the ship's regular sampling system. The surface seawater was drawn in by a stainless-steel screw pump through a fluororesin tube (length, 10 m; i.d., 12 mm), and transferred to the brand-new equilibrator through a Tygon® tube (length, 20 m; i.d., 13 mm). VOCs would permeate through the Tygon tube to some extent. To minimize the influence of VOCs permeation, surface seawater flowed over 3 h before the sampling line artifact test. The residence time of seawater in the Tygon tube was about 15 s. We considered that contaminations and losses of CH$_3$X in the brand-new sampling line are negligible. Comparisons were done at 4 different times, 3 times during leg 1 and once during leg 2.

2.3. Chlorophyll-a Measurement

Some of the environmental parameters (salinity, temperature, and chlorophyll-a) were continuously monitored with an AMEMBO II, which was a modified version of the AMEMBO system [Tsuda et al., 1993]. The system consisted of a bubble trap, thermosalinograph (SeaBird SBE21) and in vivo chlorophyll fluorometer (Wetlab). Seawater was pumped up to the system from the bottom of the ship. The chlorophyll-a concentrations determined by the AMEMBO II were calibrated against those of 107 extracted chlorophyll-a from filter samples, which were measured on board using a Turner Designs fluorometer [Welschmeyer, 1994].

3. Results

3.1. Sampling Line Artifact

We found that for CH$_3$Cl and CH$_3$Br, there were no significant differences in their partial pressures when the sampling lines were switched (Figure 2). This result suggests that contamination and loss of these compounds in the sampling lines were negligible. As for CH$_3$I, the partial pressure was consistently lower by about 12% when the sampling line was switched from the "brand new" line to the "regular" line during the second leg. This indicates that about 12% of CH$_3$I in seawater was lost in the regular line during the second leg. This methyl iodide might have been lost through interaction with the iron mold-like deposits that were found on the inner surface of the equilibrator. We applied a 12% correction to the measured $p$CH$_3$I in the surface seawater during the second leg under the assumption that the constant rate (12%) of the CH$_3$I had been lost.

3.2. Water Type and Chlorophyll-a Concentration

The frontal structure in the subarctic-subtropical transition area in NW Pacific is characterized by the cold Oyashio current and the warm Kuroshio current [Yasuda, 2003]. From the conductivity-temperature-depth (CTD) profiles obtained at intervals of 1° along 155°E from 44°N to 12°N, we identified the subarctic front, the subarctic boundary, the Kuroshio extension front, and the subtropical front at around 44°N, 40°N, 32°N, and 25°N, respectively (Figure 3). Latitudinal distributions of SST and chlorophyll-a concentration in surface seawater are shown in Figure 3. We classified the surface seawater into five water types: (1) subarctic water (SA) to the north of the subarctic front in 44–49°N (approximately SST = 11–16°C); (2) northern transition water (TWN) between the subarctic front and the subarctic boundary in 44–49°N;
16–20°C); (3) southern transition water (TWN) in 32–40°N (approximately SST = 20–27°C); (4) northern subtropical water (STS) in 32–25°N (approximately SST = 27–28°C); and (5) southern subtropical water (STN) to the south of the subtropical front in 25–12°N (approximately SST = 28–30°C). Warm water with SST = 28–29°C was found around 35°N 155°E within the TWS water that came from the Kuroshio current.

[12] We found high concentrations of chlorophyll-a in SA surface seawater (average, 0.68 µg l⁻¹) and in TWN water (average 0.56 µg l⁻¹). The average chlorophyll-a concentrations of TWS, STN, and STS were 0.15 µg l⁻¹, 0.07 µg l⁻¹, and 0.05 µg l⁻¹, respectively. The biological production in the oligotrophic STN and STS waters was low compared to the waters of the other regions.

3.3. Latitudinal Distributions of pCH₃X and pHCFC-22 in Surface Seawater and the Marine Boundary Layer

[13] Latitudinal distributions of pVOCwater and pVOCair are shown in Figure 4. The variation of pCH₃Xwater during the cruise was much less than that of pCH₃Xwater. The saturation anomaly of a VOC (S)VOC is defined as:

\[ S_{VOC} = (p_{VOC_{water}} - p_{VOC_{air}})/p_{VOC_{air}}. \]  

where \( p_{VOC_{water}} \) is the partial pressure in water and \( p_{VOC_{air}} \) in air. Values for \( p_{VOC} \) and \( S_{VOC} \) are summarized in Tables 1 and 2, respectively.

3.3.1. HCFC-22

[14] The average \( p_{HCFC-22_{air}} \) of 203 pptv (1 σ = 9.0, n = 99) during the cruise was consistent with the summertime average (204 pptv) in 2008 at Cape Ochiishi (43°N, 145°E) in the northern part of Japan [Yokouchi et al., 2009]. The \( p_{HCFC-22_{water}} \) in SA, TWS, TSW, and STN waters were slightly higher than the average \( p_{HCFC-22_{air}} \) of all the samples, whereas \( p_{HCFC-22_{water}} \) in STS water was slightly below the average of \( p_{HCFC-22_{air}} \). We found higher SHCFC-22 in the colder waters, ranging from −0.02 to 0.10 (Table 2). SST increased in SA water (+4°C month⁻¹) at 45°N, 155°E from July to August 2008 and at a faster rate than in STS water (+0.5°C month⁻¹) at 25°N, 155°E according to Japan Meteorological Agency (http://www.jma.go.jp/jma/index.html). The relatively high SHCFC-22 in SA water could be explained by the rapid decrease of solubility as a result of the rise in SST.

3.3.2. CH₃Cl

[15] The average \( p_{CH₃Cl_{air}} \) of 583 pptv (1 σ = 47, n = 110) during the cruise was higher than the annual global average of 550 pptv [WMO, 2007]. On the whole, \( p_{CH₃Cl_{water}} \) increased toward the south. For most of the SA water, \( p_{CH₃Cl_{water}} \) was less than \( p_{CH₃Cl_{air}} \), with an average SCH₃Cl of −0.07. In TWS, TWN, high levels of \( p_{CH₃Cl_{water}} \) (up to 1313 pptv) were frequently observed. In TSW water, there were high levels of \( p_{CH₃Cl_{water}} \) (up to 1645 pptv) around 35°N 155°E in the warm Kuroshio water. In STS water, the \( p_{CH₃Cl_{water}} \) maximum was present between 15°N and 20°N, where a SST maximum of up to 30°C could be seen (Figure 3b). The highest \( p_{CH₃Cl_{water}} \) in STS (1893 pptv) was 1.6 times the previously reported highest value (1200 pptv) in the subtropical East Pacific [Moore et al., 1996]. A higher (or lower) SCH₃Cl compared to SHCFC-22 suggests chemical or biological production (or loss) of CH₃X in surface seawater, because the saturation anomaly of long-lived HCFC-22 is mainly controlled by changes of temperature-dependent solubility in seawater and air-sea exchange. The supersaturation levels of CH₃Cl (SCH₃Cl = 0.48–1.6), which were higher than those of HCFC-22 (SHCFC-22 = −0.02 to 0.08) in TWS, TWS, STN, and STS waters, indicates net production of CH₃Cl in these waters. Similar levels of supersaturation (SCH₃Cl = 0.38) in surface seawater warmer than 12°C around 40°N in the northwest Atlantic in summer were attributed to net production of CH₃Cl [MacDonald and Moore, 2007]. In contrast, the slight undersaturation (SCH₃Cl = −0.07) in SA water suggests net loss of CH₃Cl in the surface seawater. Similar levels of undersaturation (SCH₃Cl = −0.03 to −0.15) have been found in the North Atlantic around 45–50°N in summer [MacDonald and Moore, 2007] and were attributed to bacterial degradation [Tokarczyk et al., 2003a, 2003b].

3.3.3. CH₃Br

[16] The average \( p_{CH₃Br_{air}} \) of 8.2 pptv (1 σ = 1.1, n = 110) during the cruise was consistent with the northern hemispheric average of 7.7 pptv in summer of 2008 [Yvon-Lewis et al., 2009]. As with CH₃Cl, in SA water most \( p_{CH₃Br_{water}} \) values were less than \( p_{CH₃Br_{air}} \), with SCH₃Br = −0.12, and in TWS water, high levels of \( p_{CH₃Br_{water}} \) (up to 35 pptv) were frequently present, with
SCH$_3$Br = 0.95. In TW$_S$ water, $p_{CH_3Br_{water}}$ gradually declined southward, from 10 pptv to 8 pptv, and dropped below $p_{CH_3Br_{air}}$ at 32°N near the Kuroshio extension front. In ST$_N$ and ST$_S$ waters, $p_{CH_3Br_{water}}$ remained below $p_{CH_3Br_{air}}$ with average SCH$_3$Br values of −0.27 and −0.33, respectively. The values of SCH$_3$Br in SA, ST$_N$ and ST$_S$ (−0.12, −0.27 and −0.33) were similar to those in polar and tropical waters of the Atlantic and Pacific Oceans (SCH$_3$Br = −0.15 to −0.36) from the cruises in spring/summer of 1998−1999 [King et al., 2002]. SCH$_3$Br of 0.95 in TW$_N$ was higher than the supersaturation (SCH$_3$Br = 0.5−0.6) observed in Atlantic Ocean water (41−42°N) in summer of 1998 [King et al., 2000]. Yvon-Lewis et al. [2009] estimated the change of annual saturation state of CH$_3$Br in the global ocean, shifting from −0.12 in 1996 to −0.06 in 2007, owing to the decline of atmospheric CH$_3$Br level during the phaseout period since 1998. The saturation state of CH$_3$Br in our study area would have been affected by the decline of atmospheric CH$_3$Br level. However, we cannot analyze the interannual change of the saturation state in detail, because our measurements are limited to the NW Pacific from subarctic to subtropical in summer of 2008. More measurements covering the oceans where the saturation states of CH$_3$Br have been measured before the phaseout should be required to evaluate the interannual change of the saturation state.

![Figure 4](image-url) Latitudinal distributions of partial pressures (pptv) of CH$_3$X and HCFC-22 in surface seawater (squares) and the MBL (circles). SA, subarctic water; ST$_N$, northern subtropical water; and ST$_S$, southern subtropical water; TW$_N$, northern transition water; and TW$_S$, southern transition water. See section 3.2 for water mass details. The plots of $p_{CH_3I_{air}}$ were decoupled in the figure.

<table>
<thead>
<tr>
<th>Water Mass</th>
<th>CH$_3$Cl Water (pptv)</th>
<th>CH$_3$Br Water (pptv)</th>
<th>CH$_3$I Water (pptv)</th>
<th>HCFC-22 Water (pptv)</th>
<th>Air (pptv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA (44–49°N)</td>
<td>446–742 (537)</td>
<td>5.4–12 (7.1)</td>
<td>11–40 (17)</td>
<td>214–229 (220)</td>
<td>0.56–2.5 (1.5)</td>
</tr>
<tr>
<td>TW$_N$ (40–44°N)</td>
<td>462–1313 (841)</td>
<td>7.0–35 (16)</td>
<td>7.6–9.9 (8.1)</td>
<td>209–263 (220)</td>
<td>0.56–1.9 (0.91)</td>
</tr>
<tr>
<td>TW$_S$ (32–40°N)</td>
<td>801–1645 (1007)</td>
<td>6.4–13 (8.4)</td>
<td>7.4–14 (8.7)</td>
<td>200–246 (212)</td>
<td>0.35–1.9 (0.84)</td>
</tr>
<tr>
<td>ST$_N$ (25–32°N)</td>
<td>798–1095 (871)</td>
<td>4.9–7.9 (5.5)</td>
<td>7.3–7.9 (7.6)</td>
<td>199–208 (204)</td>
<td>0.36–0.48 (0.41)</td>
</tr>
<tr>
<td>ST$_S$ (12–25°N)</td>
<td>1072–1893 (1530)</td>
<td>4.3–6.2 (5.2)</td>
<td>7.5–8.1 (7.8)</td>
<td>194–221 (204)</td>
<td>0.30–0.98 (0.63)</td>
</tr>
<tr>
<td>All (12–49°N)</td>
<td>446–1894 (959)</td>
<td>4.3–35 (9.8)</td>
<td>7.3–14 (8.2)</td>
<td>190–234 (203)</td>
<td>0.30–2.5 (0.99)</td>
</tr>
</tbody>
</table>

$^a$pVOC$_{water}$ is the partial pressure in water and pVOC$_{air}$ in air. Abbreviations are as follows: SA, subarctic water; ST$_N$, northern subtropical water; ST$_S$, southern subtropical water; TW$_N$, northern transition water; and TW$_S$, southern transition water. See section 3.2 for water mass details. Here pptv = $1 \times 10^{-12}$. Values in parentheses represent averages.

Table 1. Ranges (Averages) of pVOC$_{air}$ and pVOC$_{water}$ in Different Water Masses$^a$

5 of 11
3.3.4. CH$_3$I

[17] The range of $p$CH$_3$I$_{\text{air}}$ was 0.30–2.5 pptv (average 0.99 pptv, $\sigma$ = 0.57, n = 95) during the cruise and was consistent with the previously reported values of 0.5–2 pptv in the MBL over the NW Pacific in August–October when an annual maximum was found [Yokouchi et al., 2001]. On the whole, $p$CH$_3$I$_{\text{water}}$ increased toward the south. During the cruise, $p$CH$_3$I$_{\text{water}}$ was much higher than $p$CH$_3$I$_{\text{air}}$ with an average $\text{SCH}_3$I of 31, indicating net production of CH$_3$I in the surface seawater. As with CH$_3$Cl, high levels of $p$CH$_3$I$_{\text{water}}$ were frequently observed in TWN water and in the warm Kuroshio water at 35°N, 155°E. The $p$CH$_3$I$_{\text{water}}$ maximum was between 15°N and 20°N. Previous studies have also reported higher values for $p$CH$_3$I$_{\text{water}}$ in the mixed water and the subtropical water [Schall et al., 1997; Smythe-Wright et al., 2006]. The average $p$CH$_3$I$_{\text{water}}$ (32 pptv) during the cruise was somewhat higher than the previously reported values for tropical water (average 25 pptv, range 11–44 pptv), central gyre water (average 21 pptv, range 6.2–49 pptv), and coastal water (average 15 pptv, range 2.9–32 pptv) of the Atlantic and Pacific Oceans observed during various seasons [Butler et al., 2007].

3.4. Air-Sea Flux and Chloride Substitution

[18] In order to discuss production and loss of CH$_2$Xs in seawater, we estimated air-sea flux and chloride substitution of CH$_2$Xs in the mixed layer of the ocean along the ship’s track along 155°E from 13°N to 44°N and 160°E from 40°N to 47°N at 1° intervals, where the CTD depth profiles were obtained. Air-sea flux of CH$_3$X (FCH$_3$X; nmol m$^{-2}$ h$^{-1}$) were calculated by:

\[
FCH_3X = -K \cdot \left( pCH_3X_{\text{water}} - pCH_3X_{\text{air}} \right) \cdot HCH_3X,
\]

where K is the gas transfer velocity (cm s$^{-1}$), which depends on wind speed [Wanninkhof, 1992]. The average wind speed over the 2 weeks prior to sampling at each location was obtained from the meteorological analysis data of HYSPLIT (NOAA; http://www.ready.noaa.gov/ready/open/hysplit4.html) and used for the air-sea flux calculation. HCH$_3$X is the temperature-dependent Henry’s law constant (mol l$^{-1}$ atm$^{-1}$) obtained from Moore [2000] for CH$_3$Cl, Wilhelm et al. [1977] for CH$_3$Br, and Hunter-Smith et al. [1983] for CH$_3$I. Positive and negative values of air-sea flux mean air-to-sea influx and sea-to-air efflux, respectively.

[19] Molar concentrations (pmol l$^{-1}$) of CH$_3$X (CCH$_3$X) in seawater were calculated by:

\[
CCH_3X = HCH_3X \cdot pCH_3X_{\text{water}}.
\]

The loss rates of CH$_3$Br and CH$_3$I per unit volume (VCH$_3$Br and VCH$_3$I; pmol l$^{-1}$ h$^{-1}$) via chloride substitution can be calculated by the following equations:

\[
VCH_3Br = -kCH_3Br \cdot CCH_3Br \cdot [Cl^-]
\]

\[
VCH_3I = -kCH_3I \cdot CCH_3I \cdot [Cl^-],
\]

where [Cl$^-$] is the molar concentration of Cl$^-$ (pmol l$^{-1}$) in seawater. The chloride substitution rate constants kCH$_3$Br and kCH$_3$I depend on wind speed [Wanninkhof, 1992].

Table 2. Averages of the Saturation Anomaly$^a$

<table>
<thead>
<tr>
<th>Water Type</th>
<th>SA (44–49°N)</th>
<th>TW$_N$ (40–44°N)</th>
<th>TW$_S$ (32–40°N)</th>
<th>ST$_N$ (25–32°N)</th>
<th>ST$_S$ (12–25°N)</th>
<th>All (12–49°N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$Cl</td>
<td>-0.07</td>
<td>0.50</td>
<td>0.67</td>
<td>0.48</td>
<td>1.6</td>
<td>0.64</td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>-0.12</td>
<td>0.95</td>
<td>-0.03</td>
<td>-0.27</td>
<td>-0.33</td>
<td>0.20</td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>10</td>
<td>29</td>
<td>35</td>
<td>72</td>
<td>91</td>
<td>31</td>
</tr>
<tr>
<td>HCFC-22</td>
<td>0.10</td>
<td>0.08</td>
<td>0.04</td>
<td>0.04</td>
<td>-0.02</td>
<td>0.05</td>
</tr>
</tbody>
</table>

$^a$Abbreviations are as follows: SA, subarctic water; ST$_N$, northern subtropical water; ST$_S$, southern subtropical water; TW$_N$, northern transition water; and TW$_S$, southern transition water. See section 3.2 for water mass details.

Table 3. Air-Sea Flux and Chloride Substitution Rate per Unit Area in the Mixed Layer of the Ocean Surface$^b$

<table>
<thead>
<tr>
<th>Water Type</th>
<th>SA</th>
<th>TW$_N$</th>
<th>TW$_S$</th>
<th>ST$_N$</th>
<th>ST$_S$</th>
<th>Average</th>
<th>Global Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed layer depth (m)</td>
<td>15</td>
<td>18</td>
<td>17</td>
<td>21</td>
<td>38</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Wind speed (m s$^{-1}$)</td>
<td>4.1</td>
<td>5.2</td>
<td>5.7</td>
<td>6.1</td>
<td>4.4</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>SST (°C)</td>
<td>13.9</td>
<td>17.8</td>
<td>25.3</td>
<td>27.4</td>
<td>29.3</td>
<td>24.6</td>
<td></td>
</tr>
<tr>
<td>Air-sea flux</td>
<td>CH$_3$Cl</td>
<td>+0.71</td>
<td>-4.1</td>
<td>-4.1</td>
<td>-5.5</td>
<td>-4.2</td>
<td>-2.0 to -4.1$^b$</td>
</tr>
<tr>
<td>Air-sea flux</td>
<td>CH$_3$Br</td>
<td>+0.05</td>
<td>+0.21</td>
<td>+0.32</td>
<td>+0.47</td>
<td>+1.7</td>
<td>0.75</td>
</tr>
<tr>
<td>Air-sea flux</td>
<td>CH$_3$I</td>
<td>-0.03</td>
<td>-0.15</td>
<td>-0.16</td>
<td>-0.16</td>
<td>-0.37</td>
<td>-0.22</td>
</tr>
<tr>
<td>Air-sea flux</td>
<td>CH$_3$I</td>
<td>-0.15</td>
<td>-0.37</td>
<td>-0.39</td>
<td>-0.51</td>
<td>-0.41</td>
<td>-0.39</td>
</tr>
<tr>
<td>Air-sea flux</td>
<td>CH$_3$I</td>
<td>-0.02</td>
<td>-0.07</td>
<td>-0.16</td>
<td>-0.31</td>
<td>-1.3</td>
<td>-0.53</td>
</tr>
</tbody>
</table>

$^b$Positive values indicate addition to the mixed layer (air-to-sea influx and chloride substitution production); negative values indicate removal from the mixed layer (sea-to-air efflux and chloride substitution loss). Abbreviations are as follows: SA, subarctic water; ST$_N$, northern subtropical water; ST$_S$, southern subtropical water; TW$_N$, northern transition water; and TW$_S$, southern transition water. See section 3.2 for water mass details.

$^c$See Khalil et al. [1999], Moore [2000], and Yoshida et al. [2004].

$^d$See Lobert et al. [1995], Groszko and Moore [1998], and King et al. [2002].

$^e$See Bell et al. [2002] and Butter et al. [2007].
and kCH₃I (1 mol⁻¹ s⁻¹) were obtained from Elliott and Rowland [1993] and Jones and Carpenter [2007], respectively, as:

\[ k_{CH₃Br} = (9.53 \times 10^{12}) \cdot \exp(-12679/T) \]

\[ k_{CH₃I} = (3.66 \times 10^{13}) \cdot \exp(-13317/T), \]

where T is seawater temperature (°C). Production rate of CH₃I per unit area (ACH₃I; nmol m⁻² h⁻¹) in the mixed layer was defined by:

\[ ACH₃I = VCH₃I \cdot z, \]

where z is the mixed layer depth (MLD; m), defined as the depth where the potential density has increased by 0.125 kg m⁻³ compared to that at the reference depth of 10 m. Positive and negative values of ACH₃X mean production and loss of CH₃X via chloride substitution in the mixed layer, respectively.

[20] The averages of air-sea flux and chloride substitution rate per unit area from this study are summarized in Table 3. In TW₅, TW₆, ST₅, and ST₆ waters, the average sea-to-air efflux of CH₃Cl (4.1–5.5 nmol m⁻² h⁻¹) was higher than the annual global oceanic mean efflux of 2.0–4.1 nmol m⁻² h⁻¹ [Khalil et al., 1999; Moore, 2000; Yoshida et al., 2004]. In these same waters of our study, the production of CH₃Cl via chloride substitution (0.21–1.7 nmol m⁻² h⁻¹) compensated for 5–32% of the sea-to-air efflux.

[21] On average, the ocean surface in our study area was a weak source of CH₃Br, with an average sea-to-air efflux of 0.02 nmol m⁻² h⁻¹, most of which was attributable to the strong efflux of 0.20 nmol m⁻² h⁻¹ in TW₅ water. On annual global average, the ocean surface is estimated to be a net sink for CH₃Br, with a mean influx of 0.03–0.07 nmol m⁻² h⁻¹ [Lobert et al., 1995; Groszko and Moore, 1998; King et al., 2002]. The chloride substitution loss of CH₃Br (0.03 nmol m⁻² h⁻¹) in SA water was comparable to the air-to-sea influx (0.03 nmol m⁻² h⁻¹). In contrast, the chloride substitution loss in ST₅ and ST₆ waters (0.16–0.37 nmol m⁻² h⁻¹) was 3–12 times the air-to-sea influx (0.03–0.05 nmol m⁻² h⁻¹). This suggests that chloride substitution loss has largely contributed to the decline of CH₃Br levels to undersaturation in ST₅ and ST₆ waters.

[22] The average sea-to-air efflux of CH₃I (0.39 nmol m⁻² h⁻¹) in our study area was a little smaller than the averaged global oceanic efflux of 0.50 nmol m⁻² h⁻¹ [Bell et al., 2002]. The total of sea-to-air efflux and chloride substitution loss of CH₃I increased going southward from SA water (0.17 nmol m⁻² h⁻¹) to ST₅ water (1.7 nmol m⁻² h⁻¹). This indicates that the net production of CH₃I in the subtropical water is much greater than in the subarctic water.

### 3.5. Relationships Between Seawater VOC Concentrations and SST

[23] Previous studies have given relationships between saturation anomalies for CH₃Cl and CH₃Br and SST. As for CH₃I, saturation anomaly is significantly affected by the change of pCH₃I_air (0.30–2.5 pptv). Production and loss of CH₃I in seawater are reflected in the change of CH₃I rather than CH₃Cl. To examine production and loss of CH₃X, we use the relationships between CVOC and SST. The averages and ranges of the CVOCs are listed in Table 4. The relationships between CVOC and SST are shown in Figure 5.
The concentrations of individual VOCs in seawater at equilibrium with the respective average pVOC\textsubscript{air} were calculated by equation (3) and shown as thin solid lines in Figure 5. Bold gray lines in the CH\textsubscript{3}Cl and CH\textsubscript{3}Br panels present empirical relationships on the basis of: SCH\textsubscript{3}Cl (\%) = -24.1 + 0.159T\textsuperscript{2} [Khalil et al., 1999] and SCH\textsubscript{3}Br (\%) = 0.17065T\textsuperscript{2} + 1.91413T - 33.85496 for T < 16°C; SCH\textsubscript{3}Br (\%) = 0.48994T\textsuperscript{2} - 26.70125T + 349.14043 for T > 16°C [King et al., 2002]. SCH\textsubscript{3}Cl and SCH\textsubscript{3}Br are the saturation anomalies for CH\textsubscript{3}Cl and CH\textsubscript{3}Br, respectively, and T = SST (°C). Saturation anomalies of the empirical equations were converted to CVOCs (pmol l\textsuperscript{-1}) by equations (1) and (3) using a respective constant pVOC\textsubscript{air} value. The average pCH\textsubscript{3}Cl\textsubscript{air} (583 pptv) during this cruise was used to convert the empirical equation of SCH\textsubscript{3}Cl by Khalil et al. [1999].

The atmospheric CH\textsubscript{3}Br level has been declined during the phaseout period owing to the Montreal Protocol [Yokouchi et al., 2002]. The average pCH\textsubscript{3}Br\textsubscript{air} of 11 pptv measured during the phaseout period was used to convert the empirical equation of SCH\textsubscript{3}Br by King et al. [2002].

3.5.1. CH\textsubscript{3}Cl Versus SST

[24] The scatterplot of CCH\textsubscript{3}Cl versus SST has high values and much scatter both in the SST range from 16 to 20°C (TW\textsubscript{SN} water) and from 27 to 30°C (ST\textsubscript{SN} and ST\textsubscript{TS} waters) (Figure 5). Between SSTs of 16 and 20°C, where high concentrations of chlorophyll-a were observed, the average CCH\textsubscript{3}Cl (97 pmol l\textsuperscript{-1}) and the maximum CCH\textsubscript{3}Cl (156 pmol l\textsuperscript{-1}) are 1.1 and 1.8 times that of the average value (84 pmol l\textsuperscript{-1}) calculated from the empirical equation in the same SST range. As direct evidence for the production of CH\textsubscript{3}Cl from phytoplankton has been reported [e.g., Scarratt and Moore, 1996, 1998], we considered that the high CCH\textsubscript{3}Cl in TW\textsubscript{SN} was due to enhanced production by phytoplankton.

[25] In the SST range 27–30°C, where the chlorophyll-a concentrations were low, CCH\textsubscript{3}Cl sharply increased from 66 pmol l\textsuperscript{-1} to 144 pmol l\textsuperscript{-1} with the SST rise. The maximum CCH\textsubscript{3}Cl (144 pmol l\textsuperscript{-1}) observed at SST = 30°C is 1.5 times the value of 95 pmol l\textsuperscript{-1} calculated with the empirical equation at the same SST [Khalil et al., 1999]. Chloride substitutions of CH\textsubscript{3}Br and CH\textsubscript{3}I has been regarded as an important abiotic process of CH\textsubscript{3}Cl production in seawater [Elliott and Rowland, 1993; Jones and Carpenter, 2007], and was estimated to account for ~40–75% of the global oceanic source of CH\textsubscript{3}Cl [Moore et al., 1996]. The chloride substitution production of CH\textsubscript{3}Cl (1.7 nmol m\textsuperscript{-2} h\textsuperscript{-1}) in ST\textsubscript{S} water is estimated to compensate for 31% of the sea-to-air efflux (5.5 nmol m\textsuperscript{-2} h\textsuperscript{-1}), even though the determination of MLD could directly influence the flux calculation as expressed in equation (9).

[26] This result implies that there is still a large source of CH\textsubscript{3}Cl in the surface ST\textsubscript{S} water other than chloride substitution production; for example, photochemical reactions involving colored dissolved organic matter (CDOM) in seawater [Moore, 2008]. Moore [2008] reported that terrestrially derived humic-like CDOM in a chloride solution yielded CH\textsubscript{3}Cl through a photochemical process. He also found that high-molecular-weight (HMW) DOM of 1 kDa to 0.2 μm in size, which had been extracted from subsurface water (at 600 m depth) in the subtropical North Pacific, showed some ability to enhance photochemical production of CH\textsubscript{3}Cl, while HMW-DOM from surface seawater did not.

[27] It should be mentioned that Moore [2008] found that surface seawater with no HMW-DOM supplement produced CH\textsubscript{3}Cl at a rate of ~5 pmol l\textsuperscript{-1} h\textsuperscript{-1} after irradiation by a solar simulator with wavelengths between 300 and 800 nm. This result implies the existence of certain kind of DOM, other than HMW-DOM, involving the photochemical production of CH\textsubscript{3}Cl in seawater, that is, low-molecular-weight DOM (LMW-DOM) < 1 kDa in size which accounts for a large fraction (65–80%) of the bulk DOM from surface to deep waters [Ogawa and Tanoue, 2003]. Humic-like DOM would be necessary for the photochemical production of CH\textsubscript{3}Cl as referred above. In the surface layer of the open ocean, in situ production of humic-like fluorescent DOM (FDOM; excitation maximum at λ = 320 nm), which occurs simultaneously with photochemical degradation, was ascertained by field observation [Yamashita and Tanoue, 2008]. We suggest that it is possible that humic-like LMW-FDOM, which can be produced in the surface of the open ocean, is capable of producing CH\textsubscript{3}Cl through photochemical reactions, and that the photochemical production rate of CH\textsubscript{3}Cl by LMW-FDOM at the surface (probably 5 pmol l\textsuperscript{-1} h\textsuperscript{-1} in maximum) is considerably higher than the chloride substitution production rate of 0.04 pmol l\textsuperscript{-1} h\textsuperscript{-1} observed in ST\textsubscript{S} water of the NW Pacific. If LMW-FDOM is biologically produced by temperature-dependent enzymatic reactions in seawater, the higher SST could lead the higher photochemical production rate of CH\textsubscript{3}Cl. Photochemical production as well as chloride substitution would contribute to production of CH\textsubscript{3}Cl in the surface of subtropical waters.

3.5.2. CH\textsubscript{3}Br Versus SST

[28] In the SST range 16–20°C (TW\textsubscript{SN} water), we found a significant peak of CCH\textsubscript{3}Br (up to 7.5 pmol l\textsuperscript{-1}), and the average CCH\textsubscript{3}Br of 3.3 pmol l\textsuperscript{-1} is close to the value calculated from the empirical equation (2.9 pmol l\textsuperscript{-1}) for the same SST range during the prephaseout period. The average CCH\textsubscript{3}Br of 1.8 pmol l\textsuperscript{-1} within SST range 11–16°C and 0.72 pmol l\textsuperscript{-1} within 28–30°C are lower than the values of 3.3 pmol l\textsuperscript{-1} and 1.3 pmol l\textsuperscript{-1} calculated from the empirical equation for the same SST ranges, respectively.

[29] We compared CCH\textsubscript{3}Cl and CCH\textsubscript{3}Br in SA and TW\textsubscript{SN} waters (Figure 6a). We found strong correlations between CCH\textsubscript{3}Br and CCH\textsubscript{3}Cl in SA water (r\textsuperscript{2} = 0.78) and in TW\textsubscript{SN} water (r\textsuperscript{2} = 0.85). A strong correlation (r\textsuperscript{2} = 0.89) between concentrations of these two compounds has been also found in subarctic northwest Atlantic waters cooler than 23°C, and attributed to similarities in biological production and/or loss of these gases [MacDonald and Moore, 2007]. There is no correlation between CCH\textsubscript{3}Cl and CCH\textsubscript{3}Br (r\textsuperscript{2} = 0.15) in ST\textsubscript{SN} and ST\textsubscript{TS} waters where the biological production was low based on chlorophyll-a concentration data. It is clear that production and loss processes of CH\textsubscript{3}Br in ST waters are different from those of CH\textsubscript{3}Cl.

3.5.3. CH\textsubscript{3}I Versus SST

[30] As with CH\textsubscript{3}Cl, the plot of CCH\textsubscript{3}I versus SST had concentration peaks both for SST = 16–20°C (up to 15 pmol l\textsuperscript{-1}) and for SST = 27–30°C (up to 12 pmol l\textsuperscript{-1}). Similar substantial increases of CH\textsubscript{3}I (up to 9.7 pmol l\textsuperscript{-1}) have been measured in the mixed water region of the Atlantic (40°S), where substantially higher chlorophyll-a concentrations have been also detected [Schall et al., 1997]. There is direct evidence for the production of CH\textsubscript{3}I from phyto-
plankton [e.g., Manley and dela Cuesta, 1997; Scarratt and Moore, 1998]. We considered that high CCH$_3$I in SST range 16–20°C (TWN water) was due to enhanced production by phytoplankton. For SST = 27–30°C (STN and STS waters), we found that CCH$_3$I sharply increased from 4.4 pmol l$^{-1}$ to 12 pmol l$^{-1}$ with the increase in SST. Similar significant increases ranging from 6.0 to 12 pmol l$^{-1}$ have been found in summer in the subtropical South Atlantic (19°S) [Happell and Wallace, 1996].

[31] The significant increase of CCH$_3$I with SST rise in STN and STS waters could be due to photochemical production of CH$_3$I for the following reasons. Moore and Zafiriou [1994] proposed for CH$_3$I production a radical recombination mechanism of methyl radicals formed from the photolysis of humic materials with I radical formed from the photochemical oxidation of I$^-$. Dissolved I$^-$ concentrations in oligotrophic subtropical waters are much higher than those in nutrient rich, subpolar and polar waters, because IO$_3$ can be reduced to I$^-$ in the absence of NO$_3$ by enzymatic reaction [Campos et al., 1999]. Chuck et al. [2005] also suggested that photochemical production of CH$_3$I is associated with nitrate reductase activity which could reduce IO$_3$. In general, enzymatic reactions are highly dependent on temperature. Therefore, the higher SST in subtropical water would lead to a higher photochemical production rate of CH$_3$I. The averaged photochemical production rate of CH$_3$I within the mixed layer of tropical seawater (MLD = 30 m) is estimated to be 1 nmol m$^{-2}$ h$^{-1}$ [Richter and Wallace, 2004], which is close to the total of sea-to-air efflux and chloride substitution loss (1.7 nmol m$^{-2}$ h$^{-1}$) from our results in STS water.

[32] Other than photochemical production, the importance of biological production of CH$_3$I by Prochlorococcus, a genus of cyanobacteria that predominates in subtropical waters, was suggested by Smythe-Wright et al. [2006]. Although Prochlorococcus would directly produce CH$_3$I, it may also contribute to the biological reduction of IO$_3$ to I$^-$ similar to Synechococcus (a genus of cyanobacteria) [Wong et al., 2002].

[33] Wang et al. [2009] pointed out two reasons why photochemical reactions can account for the positive correlation ($r^2 = 0.37$) that they observed in the North Atlantic (37–59°N) between CH$_3$I concentration and water temperature. First, higher temperature could promote biological CDOM formation, and second, photochemical reaction rate could be positively influenced by temperature. We supposed that higher SST and stronger light intensity in subtropical waters have promoted CH$_3$I production through photochemical pathway and biological pathways by direct emission of CH$_3$I from Prochlorococcus and/or by formations of...
intermediates of photochemical reactions such as $\Gamma$ and LMW-FDOM as a source of methyl radical. Furthermore, high correlation between CCH$_3$I and CCH$_3$Cl ($r^2 = 0.67$) in ST$_N$ and ST$_S$ waters (Figure 6b) implies a similarity in the production pathways of the 2 methyl halides.

3.6. Regression Analysis of Methyl Halide Concentrations

[34] Empirical regression curves of CH$_3$X concentrations are expressed as exponential functions of SST (Figure 7) and their formulas are listed in Table 5. As with the CH$_3$Cl and CH$_3$I concentration data presented above, the regression formulas are divided into 3 SST ranges of 11–20°C (SA and TW$_N$ waters), 20–27°C (TW$_S$ water), and 27–30°C (ST$_N$ and ST$_S$ waters). The CH$_3$Br regression formula is split at SST = 17°C, where the peak CCH$_3$I was found in TW$_N$ water. Tokarczyk and Moore [2006] point out that the saturation anomaly of CH$_3$Br in surface seawater cannot be predicted from the temperature data only in temperate areas with high biological activity where production and degradation processes of CH$_3$Br are likely to be more dynamic than SST change. Further research on the CH$_3$X distributions in various ocean waters for all seasons is needed for the precise estimation of global distributions of CH$_3$X and their oceanic air-sea flux.

4. Summary

[35] The partial pressures of CH$_3$X ($X = \text{Cl, Br, and I}$) in the surface seawater of the NW Pacific from subarctic to subtropical regions were found to vary spatially. In the northern transition water (mixed water region), which had high biological activity, high levels for the 3 CH$_3$X were frequently observed because phytoplankton could have contributed to their production. In the subtropical water, which had very low biological production, the latitudinal distributions of pCH$_3$Cl$_{\text{water}}$ and pCH$_3$I$_{\text{water}}$ had a peak between 15°N and 20°N where high SST values (up to 30°C) were observed. We found that CCH$_3$Cl and CCH$_3$I sharply increased with an SST rise in the subtropical water. We propose that photochemical production of CH$_3$I and CH$_3$Cl largely contributed to their enrichment in the surface of subtropical water. This may be the result of temperature-dependent enzymatic reactions producing intermediates of photochemical reactions such as LMW-FDOM and $\Gamma$.

[36] We calculated empirical regression formulas for CH$_3$X concentrations in surface seawater as exponential functions of SST. Regression formulas of CH$_3$I and CH$_3$I were divided into 3 SST ranges corresponding to the oceanic frontal boundaries. The regression formula for CH$_3$I was split at SST = 17°C. Further research on CH$_3$X measurements in all seasons for various water types is needed for precise estimations of the global distributions of CH$_3$X and their air-sea flux.

[37] Acknowledgments. We would like to thank the chief scientists, captain, and crews of Hakuto-maru (cruse KH-08-2). We would also like to thank J. Nishioka and T. Yoshimura for the chlorophyll-a data. This research has been supported by the Grant-in-Aid for Scientific Research in priority areas Western Pacific Air-Sea Interaction Study under grant 18067012. This research is a contribution to the Surface Ocean Lower Atmosphere Study Core Project of the International Geosphere-Biosphere Programme.

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