Correlations and emission ratios among bromoform, dibromochloromethane, and dibromomethane in the atmosphere

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[1] Bromoform (CHBr 3), dibromochloromethane (CHBr 2 Cl), and dibromomethane (CH 2 Br 2) in the atmosphere were measured at various sites, including tropical islands, the Arctic, and the open Pacific Ocean. Up to 40 ppt of bromoform was observed along the coasts of tropical islands under a sea breeze. Polybromomethane concentrations were highly correlated among the coastal samples, and the ratios CH 2 Br 2/CHBr 3 and CHBr 2 Cl/ CHBr 3 showed a clear tendency to decrease with increasing CHBr 3 concentration. These findings are consistent with the observations that polybromomethanes are emitted mostly from macroalgae whose growth is highly localized to coastal areas and that CHBr 3 has the shortest lifetime among these three compounds. The relationship between the concentration ratios CHBr 3/CH 2 Br 2 and CHBr 2 Cl/CH 2 Br 2 suggested a large mixing/dilution effect on bromomethane ratios in coastal regions and yielded a rough estimate of 9 for the molar emission ratio of CHBr 3/CH 2 Br 2 and of 0.7 for that of CHBr 2 Cl/CH 2 Br 2. Using these ratios and an global emission estimate for CH 2 Br 2 (61 Gg/yr (Br)) calculated from its background concentration, the global emission rates of CHBr 3 and CHBr 2 Cl were calculated to be approximately 820(±310) Gg/yr (Br) and 43(±16) Gg/yr (Br), respectively, assuming that the bromomethanes ratios measured in this study are global representative. The estimated CHBr 3 emission is consistent with that estimated in a very recent study by integrating the sea-to-air flux database. Thus the contribution of CHBr 3 and CHBr 2 Cl to inorganic Br in the atmosphere is likely to be more important than previously thought.


1. Introduction

[2] Polybromomethanes such as bromoform (CHBr 3) are produced mostly by marine macroalgae [Manley et al., 1992; Sturges et al., 1992; Itoh, 1997; Carpenter and Liss, 2000], and some of what is produced is emitted into the atmosphere. There, polybromomethanes undergo photolytic degradation and react with hydroxyl radical (OH) to produce inorganic bromine, which affects stratospheric/tropospheric ozone chemistry. Polybromomethanes produced by marine macroalgae are estimated to account for 15% of stratospheric bromine, but with great uncertainty [World Meteorological Organization (WMO), 2003], owing primarily to poor characterization of their emission strength and difficulties in modeling the complexities of the transport processes.

[3] Measured concentrations of polybromomethanes in the marine boundary air vary greatly because of their localized source distribution and short atmospheric lifetimes. Typical values over the open ocean are 0.2–3 ppt for CHBr 3, 0.1–0.5 ppt for dibromochloromethane (CHBr 2 Cl), and 0.5–2 ppt for dibromomethane (CH 2 Br 2), and concentrations are significantly higher in coastal regions, especially that of CHBr 3, which occasionally exceeds 10 ppt [Penkett et al., 1985; Class and Ballschmiter, 1988; Blake et al., 1999, 2001, 2003; Atlas et al., 1992, 1993; Schall and Heumann, 1993; Yokouchi et al., 1997, 1999; Schauffler et al., 1999; Carpenter et al., 2003; Quack and Wallace, 2003].

[4] Global emission rates of polybromomethanes have been estimated on the basis of background concentrations and atmospheric lifetimes, or by integrating the sea-to-air flux. Concentrations in the tropical boundary layer (1.1–1.83 ppt for CHBr 3, 0.07–0.20 ppt for CHBr 2 Cl, and 1.07–1.33 ppt for CH 2 Br 2) from Table 2–8 of WMO [2003] based
on the studies by Blake et al. [1999, 2001, 2003] have yielded
global emissions estimates of 150–250 Gg/yr (Br) for
CHBr2, 4.2–12 Gg/yr (Br) for CHBr2Cl, and 55–67 Gg/yr
(Br) for CH3Br [WMO, 2003, Table 2–9; WMO, 1999,
chap. 2]. However, as we show below, the rather short
timelines of CHBr3 (26 days [WMO, 2003]) and CHBr2Cl
(69 days [WMO, 2003]) would lead to their global emission
rates being underestimated by this method, owing to their
high concentrations in source regions being neglected;
whereas the lifetime of CH3Br2, 120 days, would seem to
be long enough for it to become uniformly distributed
throughout the troposphere. Emission estimates based on
oceanic flux studies are available for CHBr3. Carpenter
and Liss [2000] estimated global CHBr3 emission to be
220 Gg/yr by summing the amounts of CHBr3 released
from macroalgae, and their result is consistent with sink-
based estimates. Recently, a much higher estimate for
CHBr3 emission, 800 Gg/yr (Br) (240–1760 Gg/yr), has
been reported by Quack and Wallace [2003], who reas-
versed oceanic emissions on the basis of published aqueous
and airborne concentration data.

In this study, we measured concentrations of these
three bromomethanes in various areas and used their ratios
to deduce their emission rates.

2. Experiment

Air samples were collected at two sites on San
Cristobal Island (1.0°S, 89.4°W, 9 samples in February–
March 2002 and 8 samples in March 2003), at three sites on
Christmas Island (2.0°N, 157.7°W, January 2003, 11
samples), on Java Island (7.5°S, 112.6°E, January 2003, 12
data sets). Air samples were collected in evacuated stainless
steel canisters, which were a component of the working standard
(100 ppt

\[
\text{CH}_2\text{Br}_2 (m/z 174) \quad \text{for CH}_3\text{Br}_2, \quad \text{m/z 173 for CH}_2\text{Br}_2 \quad \text{and m/z 129 for CHBr}_2\text{Cl}. \quad \text{The three polybromomethanes were quantified on the basis of their sensitivity relative to tetrachloroethylene (C}_2\text{Cl}_4 \quad \text{}(m/z 166), \quad \text{which was a component of the working standard (100 ppt in a polished aluminum cylinder). The sensitivities relative to C}_2\text{Cl}_4 \quad \text{were determined on the basis of the analysis of a vaporized liquid standard, and the results were consistent with those obtained from a primary standard gas containing 1 ppm each of CH}_2\text{Br}_2, \quad \text{CHBr}_2\text{Cl, and C}_2\text{Cl}_4 (CHBr}_2\text{Cl was not included in the standard). The primary standard gas was analyzed at least once a month, and the relative sensitivity of CH}_2\text{Br}_2/C}_2\text{Cl}_4 showed a standard deviation of 13%, and that of CHBr}_2/C}_2\text{Cl}_4 5%, for the whole observational period. Assuming a similar deviation for the ratio CHBr}_2Cl/C}_2\text{Cl}_4 \quad \text{and taking into account the 3–5% measurement error for these compounds, based on dual samples collected at Cape Grim and Alert, we can expect an analytical precision of around 20% for the measurements of polybromomethanes in this study. A stability test for these compounds in the canisters had shown no significant change for 6 months after sampling [Yokouchi et al., 1999].

3. Results and Discussion

Average, maximum, and minimum values of the polybromomethane concentrations at each site are listed
in Table 1. The highest concentrations were observed at
tropical coastal sites on San Cristobal Island (S-1), and
Christmas Island (C-1, C-2). The mean concentrations of
CHBr3 at these three sites, which ranged from about 14 to
24 ppt, are within the top 5% of 100 separate mean values
for CHBr3 in marine air measured worldwide (reviewed by
Quack and Wallace [2003]). Because most air arriving in
the lower stratosphere passes through the tropical tropo-
pause [Holton et al., 1995; WMO, 2003], high emissions of
polybromomethanes from sites near tropical islands may
contribute greatly to stratospheric ozone depletion
[Salawitch et al., 2005]. At other sites on these same islands
(S-2 on San Cristobal Island and C-3 on Christmas Island),
polybromomethane concentrations were substantially lower.
Sites S-1, C-1, and C-2 are directly exposed to onshore
winds, whereas the winds affecting sites S-2 and C-3 have
first rounded or crossed over the islands. After those
measured on the equatorial islands, the next highest con-
centrations of polybromomethanes were detected at Cape
Ochiishi, Rishiri Island, and Cape Grim, which are coastal
temperate zone sites. The lowest concentrations were found
over the open western Pacific Ocean and inland on Java
Island; their mean values (0.9–1.1 ppt for CHBr2Cl, 0.2 ppt
for CHBr2Cl, and 0.9–1.0 ppt for CHBr3) were similar to
background concentrations that have been measured during
airborne expeditions over the Pacific Ocean: TRACE-P,
Pem-Tropics B, and PEM-Tropics A (median values:
1.1–1.83 ppt for CHBr3, 0.07–0.20 ppt for CHBr2Cl, and
1.07–1.33 ppt for CHBr3 [WMO, 2003; after Blake et al.,
1999, 2001, 2003]). These findings are consistent with the
observation that polybromomethanes are mostly emitted
from localized macroalgal sources in coastal regions
and become diffused over the open ocean or in inland
areas, where they undergo chemical reaction. Recently,
Quack et al. [2004] reported an evidence of a source of
CHBr3 throughout the tropical Atlantic. So, there is a
possibility that the data from equatorial Pacific might
also be affected somewhat by an open oceanic source of
polybromomethanes.

In Figure 2, we present the relationships between
CH2Br2 and CHBr3 and between CHBr2Cl and CHBr3 for
each of the data sets. Correlations were high for the coastal
Figure 1. Sampling locations. A, Alert; R, Rishiri Island; O, Cape Ochiishi; S, San Cristobal Island; C, Christmas Island; J, Java Island; CG, Cape Grim; crosses, sampling points over the western Pacific (C/V Fuji Transworld); circles, sampling points over the equatorial Pacific (R/V Mirai). Locations of the various sites on San Cristobal Island and on Christmas Island are shown on the bottom.

Table 1. Measured Concentrations of Bromoform, Dibromomethane, and Dibromochloromethane in the Atmosphere

<table>
<thead>
<tr>
<th>Location</th>
<th>Period</th>
<th>Number of Samples</th>
<th>CHBr₃</th>
<th>CHBr₂Cl</th>
<th>CH₂Br₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>San Cristobal Island</td>
<td></td>
<td></td>
<td>Mean</td>
<td>SD</td>
<td>Max</td>
</tr>
<tr>
<td>S-1 (Lobelia)</td>
<td>Feb.–Mar. 2002, Mar. 2003</td>
<td>14</td>
<td>14.2</td>
<td>10.1</td>
<td>43.6</td>
</tr>
<tr>
<td>S-2 (INAMHI)</td>
<td>Feb.–Mar. 2002</td>
<td>3</td>
<td>2.6</td>
<td>1.3</td>
<td>4.0</td>
</tr>
<tr>
<td>Christmas Island</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-1 (Topono)</td>
<td>Jan. 2003</td>
<td>2</td>
<td>23.8</td>
<td>10.7</td>
<td>31.4</td>
</tr>
<tr>
<td>C-2 (Captain Hook Hotel)</td>
<td>Jan. 2003</td>
<td>3</td>
<td>22.8</td>
<td>2.5</td>
<td>25.5</td>
</tr>
<tr>
<td>C-3 (London C)</td>
<td>Jan. 2003</td>
<td>6</td>
<td>5.6</td>
<td>3.5</td>
<td>10.2</td>
</tr>
<tr>
<td>Cape Ochiishi</td>
<td>Jan.–Dec. 2003</td>
<td>22</td>
<td>3.6</td>
<td>2.3</td>
<td>10.3</td>
</tr>
<tr>
<td>Rishiri Island</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-1 (near the shore)</td>
<td>Sept.–Oct. 2003</td>
<td>9</td>
<td>6.9</td>
<td>3.9</td>
<td>13.3</td>
</tr>
<tr>
<td>R-2 (1 km from the shore)</td>
<td>Sept.–Oct. 2003</td>
<td>21</td>
<td>1.6</td>
<td>0.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Cape Grim</td>
<td>Jan.–Dec. 2003</td>
<td>26</td>
<td>2.9</td>
<td>1.2</td>
<td>6.4</td>
</tr>
<tr>
<td>Alert</td>
<td>Jan.–Dec. 2003</td>
<td>24</td>
<td>2.0</td>
<td>1.3</td>
<td>6.2</td>
</tr>
<tr>
<td>Pacific equator</td>
<td>Jan.–Feb. 2002, Jan. 2003</td>
<td>19</td>
<td>1.9</td>
<td>0.9</td>
<td>3.5</td>
</tr>
<tr>
<td>Western Pacific</td>
<td>Jan.–Dec. 2003</td>
<td>61</td>
<td>1.1</td>
<td>0.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Java Island</td>
<td>Jan. 2003</td>
<td>12</td>
<td>0.9</td>
<td>0.4</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Figure 2. Correlations of polybromomethane concentrations. [CH$_2$Br$_2$] versus [CHBr$_3$] is denoted by solid symbols, and [CHBr$_2$Cl] versus [CHBr$_3$] is denoted by open symbols. (a) San Cristobal Island (site S-1 in black, site S-2 in gray, circles for March 2002, and triangles for March 2003); (b) Christmas Island (circles for site C-1 (in black) and site C-3 (in gray) and triangles for site C-2); (c) Cape Ochiishi; (d) Cape Grim; (e) Rishiri Island (site R-1 in black and site R-2 in gray); (f) Alert; (g) western and equatorial Pacific (western Pacific in gray and equatorial Pacific in black); and (h) Java Island.
samples: the correlation coefficients ($R^2$) between CH$_2$Br$_2$ and CHBr$_3$ and between CHBr$_2$Cl and CHBr$_3$ were 0.92 and 0.98 at San Cristobal, 0.88 and 0.97 at Christmas Island, 0.71 and 0.79 at Cape Ochiishi, and 0.86 and 0.83 at Rishiri, respectively. For the open ocean samples over the equatorial or western Pacific and for inland Java Island, correlations were weak or absent and the CHBr$_3$ concentration was consistently low (<3.5 ppt).

[10] In Figure 3, the concentration ratios of CH$_2$Br$_2$/CHBr$_3$ and CHBr$_2$Cl/CHBr$_3$ are plotted against CHBr$_3$ concentrations on a log–log scale. Both these ratios decreased with increasing CHBr$_3$ concentration. CHBr$_3$ concentration-dependent changes of polybromomethane concentration ratios have also been reported in previous studies for the Arctic [Li et al., 1994] and for Mace Head, Ireland [Carpenter et al., 2003], and these changes have been discussed mostly in terms of differences in the chemical reactivities of these compounds in the atmosphere. That is, changes in the concentration of CHBr$_3$, which has a relatively short atmospheric lifetime, are expected to be more pronounced than changes in the concentrations of the longer-lived CH$_2$Br$_2$ and CHBr$_2$Cl. However, dilution of samples with background air in which the longer-lived polybromomethanes are present at higher percentages than in emission gases would result in a similar relationship; that is, the ratios CH$_2$Br$_2$/CHBr$_3$ and CHBr$_2$Cl/CHBr$_3$ would be higher at lower concentrations of CHBr$_3$. Near an emission source, such as at San Cristobal Island, such mixing and dilution might be expected to contribute more to reductions in polybromomethane concentrations than chemical decay. [11] The effects of chemical decay and dilution on the concentration ratios of atmospheric gases have been studied quantitatively by McKeen and Liu [1993]. For three species, $X$, $Y$, and $Z$ (where $\tau_X > \tau_Y > \tau_Z$, $\tau$ = atmospheric lifetime), they defined a “dilution line” and a “chemical decay line” on a log–log plot of the concentration ratios $Z/X$ versus $Y/X$ by assuming that the species have common sources and that their emission ratios are constant on a regional scale. The dilution line, which represents the relationship for the case where all three species are inert and the background concentrations of species $Y$ and $Z$ are zero, is a straight line with slope 1 on a log-log plot, on which the data points for more diluted air tend to lie along the lower end. The chemical decay line, which indicates the relationship for the case where removal of a species is governed by a pseudo-first-order chemical reaction, is a straight line whose slope is predicted by the ratio ($k_2 - k_3$)($k_X - k_Z$), where $k_X$, $k_Y$, and $k_Z$ are the rate constants for $X$, $Y$, and $Z$, respectively, in the pseudo-first-order chemical reaction [Roberts et al., 1984; Parrish et al., 1992; McKeen and Liu, 1993]. These two lines cross at the point equivalent to the emission ratios $Z/X$ and $Y/X$.

[12] For a mesoscale model, McKeen and Liu [1993] have shown that all calculated hydrocarbon ratios lie between the photochemical decay (lower limit) and dilution (upper limit) lines, with the emission ratio at the top of the envelope. Thus they showed that the concentration ratio is a function of both chemistry and atmospheric transport, and such ratios are meaningful as a gauge of net atmospheric processing of an emission plume.

[13] Here, we wished to use the above-described relationship to deduce the emission ratios of polybromomethanes. Therefore we plotted [CHBr$_3$]/[CH$_2$Br$_2$] versus [CHBr$_2$Cl]/[CH$_2$Br$_2$] on a log–log scale for all data sets (Figure 4). Here the data sets from the same island (S-1 and S-2, C-1 and C-2 and C-3, R-1 and R-2) were combined. The result for the data set from San Cristobal (Figure 4a) approximated a dilution line with a slope of 1 (dotted lines in Figure 4), suggesting that the change of polybromomethane ratios at that site was caused by dilution with background air having extremely low levels of CHBr$_3$ and CHBr$_2$Cl. This interpretation is reasonable because the island is surrounded by open ocean and the sampling sites were very close to the coastal sources, thus allowing no reactive loss during transport. When we plotted the same ratios for other data sets from coastal sites (Christmas Island, Cape Ochiishi, Rishiri Island, Cape Grim), the points generally close to the dilution line (Figures 4b–4e). Data sets from the other sites, however, showed more scattered plots, and most data points plotted below the dilution line, suggesting that the ratios were affected by chemical decay during a long period of transport.

[14] All the data sets shown as separate plots in Figures 4a–4g (excluding the inland data) are shown together in one graph in Figure 5. As mentioned above, data points in plots of ln([CHBr$_3$]/[CH$_2$Br$_2$]) versus ln([CHBr$_2$Cl]/[CH$_2$Br$_2$]) are expected to lie in the envelope defined by the dilution and decay lines, with the emission ratio at the top where the lines intersect. The slope of the decay line, $k_{CHBr3}/k_{CH2Br2}(k_{CH2Br2Cl} - k_{CH2Br2})$, was calculated from the lifetime of each species (CHBr$_3$, 26 days; CHBr$_2$Cl, 69 days; CH$_2$Br$_2$, 120 days) to be 4.89.

[15] The global emission rates, estimated on the basis of atmospheric sink values, of CHBr$_3$ (200 Gg/yr (Br)), CHBr$_2$Cl (12 Gg/yr (Br)), and CH$_2$Br$_2$ (58 Gg/yr (Br)) [WMO, 1999, 2003] give a molar emission ratio for [CHBr$_3$]/[CH$_2$Br$_2$] of 2.3, and for [CHBr$_2$Cl]/[CH$_2$Br$_2$] of 0.2 (point “A” in Figure 5). Most of the observed data points are outside of the envelope defined by these emission ratios. Apparently, the emission ratios of both [CHBr$_3$]/[CH$_2$Br$_2$] and [CHBr$_2$Cl]/[CH$_2$Br$_2$] must be higher to explain the observed results. The emission rates of the short-lived compounds CHBr$_3$ and CHBr$_2$Cl estimated from atmospheric sink values might be underestimates, because these compounds tend to be more depleted in background air than CH$_2$Br$_2$. Carpenter et al. [2003] obtained different global emission ratio estimates, using the slopes of the concentration correlations (CH$_2$Br$_2$ vs. CHBr$_3$ and CHBr$_2$Cl vs. CHBr$_3$) measured at Cape Grim and Mace Head, of [CHBr$_3$]/[CH$_2$Br$_2$] = 4–6.8 (average, 5.4) and [CHBr$_2$Cl]/[CH$_2$Br$_2$] = 0.22, which corresponds to point “B” in Figure 5. Again, most of the data points fall outside of the envelope defined by that emission ratio. A possible explanation for this inconsistency is that the slope of the concentration correlations does not represent the emission ratios correctly when the chemical reactive loss is not negligible. Other reasons may be the different sampling sites or times from the present study, and different calibration scales used by Carpenter et al. [2003] compared to this study.

[16] If we assume that the ratios of polybromomethane emission rates are the same from various source regions of the oceans, then the emission ratios would be predicted by the top of the envelope that includes most of the data points.
Figure 3. Ratios of $[\text{CH}_2\text{Br}_2]/[\text{CHBr}_3]$ and $[\text{CHBr}_2\text{Cl}]/[\text{CHBr}_3]$ plotted versus $[\text{CHBr}_3]$ on a log-log scale. $[\text{CH}_2\text{Br}_2]/[\text{CHBr}_3]$ versus $[\text{CHBr}_3]$ is denoted by solid symbols, and $[\text{CHBr}_2\text{Cl}]/[\text{CHBr}_3]$ versus $[\text{CHBr}_3]$ is denoted by open symbols. (a) San Cristobal Island; (b) Christmas Island; (c) Cape Ochiishi; (d) Cape Grim; (e) Rishiri Island; (f) Alert; (g) western and equatorial Pacific (western Pacific in gray and equatorial Pacific in black); and (h) Java Island.
Figure 4. Ratios of \([\text{CHBr}_3]/[\text{CH}_2\text{Br}_2]\) plotted versus \([\text{CHBr}_2\text{Cl}]/[\text{CH}_2\text{Br}_2]\) on a log–log scale. (a) San Cristobal Island; (b) Christmas Island; (c) Cape Ochiishi; (d) Cape Grim; (e) Rishiri Island; (f) Alert; (g) western and equatorial Pacific (western Pacific in gray and equatorial Pacific in black); and (h) Java Island. Dotted line is “dilution line” approximated for the data set from San Cristobal in Figure 4a.
plotted in Figure 5. This assumption is reasonable, because a dilution line passing through the coordinate point (1.0 for \([\text{CHBr}_2\text{Cl}]/[\text{CH}_2\text{Br}_2]\), 13 for \([\text{CHBr}_3]/[\text{CH}_2\text{Br}_2]\)) with a slope of 1 can be derived from all of the data sets from near-source sites (Figure 4), suggesting a constant emission ratio of 13 for \([\text{CHBr}_3]/[\text{CHBr}_2\text{Cl}]\) on a regional scale. Thus we can roughly estimate \([\text{CHBr}_3]/[\text{CH}_2\text{Br}_2]\) to be around 9 and \([\text{CHBr}_2\text{Cl}]/[\text{CH}_2\text{Br}_2]\) to be around 0.7 (point C in Figure 5). The analytical precision of around 20% for the measurements of polybromomethanes in this study would give a combined error of 28% for their ratios (For multiplication and division, error is propagated as the squared relative standard deviation). Assuming a possible error of the line fitting around 20%, the estimated emission ratios come up with a total uncertainty of 35%. Considering that it is not possible to collect any emission gas before it has become mixed and diluted, the emission ratio might lie even higher along the dilution line. These high emission ratios of \([\text{CHBr}_3]/[\text{CH}_2\text{Br}_2]\) (9) and \([\text{CHBr}_2\text{Cl}]/[\text{CH}_2\text{Br}_2]\) (0.7) seem to be feasible, if we compare with the average molar emission ratios from brown algae, 13.5(±7.9) for \([\text{CHBr}_3]/[\text{CH}_2\text{Br}_2]\) and 0.9(±0.4) for \([\text{CHBr}_2\text{Cl}]/[\text{CH}_2\text{Br}_2]\), which were calculated from the previously reported emission rates summarized by Carpenter et al. [2000]. As for the polybromomethane ratios in the seawater, Carpenter and Liss [2000] showed that CHBr3 was more predominant near the coast, and reported the molar ratio of CHBr3:CH2Br2:CHBr2Cl of 21:2.7:1 for nearshore of Mace Head, which corresponded to 7.8 for \([\text{CHBr}_3]/[\text{CH}_2\text{Br}_2]\) and 0.4 for \([\text{CHBr}_2\text{Cl}]/[\text{CH}_2\text{Br}_2]\).

Using the above estimated ratios and the global emission rate of CH2Br2 estimated from the background concentration (61 ± 6 Gg/yr (Br), the range is 25th–75th quartile [WMO, 2003]) (which we consider to be a more reliable estimate than those for CHBr3 and CHBr2Cl because of the longer lifetime of CH2Br2), we calculated the global emission rates of CHBr3 and CHBr2Cl to be approximately 820 ± 310 Gg/yr (Br) and 43 ± 16 Gg/yr (Br), respectively. Here, the total error, 38% came from the combination of 15% error of CH2Br2 estimate (standard deviation equals to 1.5 × quartile deviation for normally distributed data) and 35% error of the molar ratios above discussed. The estimated CHBr3 emission rate is consistent with that reported recently by Quack and Wallace [2003], who integrated the sea-to-air flux by using atmospheric and oceanic database values (3–22 Gmol/yr (Br) or 240–1760 Gg/y(Br)), and it is much higher than the estimates based on background concentrations. The contribution of naturally derived polybromomethanes as a source of atmospheric inorganic Br is thus likely to be more important than previously thought. Particularly high emission of bromoform, as high as 820±310 Gg Br/yr, should be contributing to the tropospheric ozone destruction in the marine boundary layer very efficiently.

In this study, we estimated emission ratios of CHBr3 and CHBr2Cl versus CH2Br2 that are much higher than those previously reported, and from these ratios and the reported emission rate for CH2Br2, we calculated the global emission rates of CHBr3 and CHBr2Cl. Our estimates are based on the assumptions that (1) regional polybromomethane emission ratios are constant and (2) the atmospheric-sink-based estimate for the global emission rate of CH2Br2 is accurate. Further investigations taking into account more detailed sea-to-air flux measurements and using measurements of polybromomethanes from a variety of source

![Figure 5](image_url)

Figure 5. Ratios of \([\text{CHBr}_3]/[\text{CH}_2\text{Br}_2]\) plotted versus \([\text{CHBr}_2\text{Cl}]/[\text{CH}_2\text{Br}_2]\) on a log-log scale for all data sets. Points A, B, and C are explained in the text. Solid lines are “dilution lines,” and dashed lines are “chemical decay lines.”
regions might give more insight into polybromomethane emission rates.

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