GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 21, GB1023, doi:10.1029/2006GB002732, 2007

Oceanic distributions and emissions of short-lived halocarbons

James H. Butler,[1] Daniel B. King,[2,3] Jürgen M. Lobert,[3,4] Stephen A. Montzka,[1]
Shari A. Yvon-Lewis,[3,5] Bradley D. Hall,[1] Nicola J. Warwick,[6] Debra J. Mondeel,[3]
Murat Aydin,[7] and James W. Elkins[1]

Received 2 April 2006; revised 11 August 2006; accepted 7 September 2006; published 23 March 2007.

[1] Using data from seven cruises over a 10-year span, we report marine boundary layer mixing ratios (i.e., dry mole fractions as pmol mol^{-1} or ppt), degrees of surface seawater saturation, and air-sea fluxes of three short-lived halocarbons that are significant in tropospheric and potentially stratospheric chemistry. $CHBr_3$, CH_2Br_2, and CH_3I were all highly supersaturated almost everywhere, all the time. Highest saturations of the two polybrominated gases were observed in coastal waters and areas of upwelling, such as those near the equator and along ocean fronts. CH_3I distributions reflected the different chemistry and cycling of this gas in both the water and the atmosphere. Seasonal variations in fluxes were apparent where cruises overlapped and were consistent among oceans. Undersaturations of these gases were noted at some locations in the Southern Ocean, owing to mixing of surface and subsurface waters, not necessarily biological or chemical sinks. The Pacific Ocean appears to be a much stronger source of $CHBr_3$ to the marine boundary layer than the Atlantic. The high supersaturations, fluxes, and marine boundary layer mixing ratios in the tropics are consistent with the suggestion that tropical convection could deliver some portion of these gases and their breakdown products to the upper troposphere and lower stratosphere.

Citation: Butler, J. H., D. B. King, J. M. Lobert, S. A. Montzka, S. A. Yvon-Lewis, B. D. Hall, N. J. Warwick, D. J. Mondeel, M. Aydin, and J. W. Elkins (2007), Oceanic distributions and emissions of short-lived halocarbons, *Global Biogeochem. Cycles*, *21*, GB1023, doi:10.1029/2006GB002732.

1. Introduction

[2] The roles of short-lived halogenated gases in atmospheric chemistry have become increasingly apparent over the past two decades. Although it is now clear that halogens are significant oxidizers and must be taken into account in understanding the budgets of ozone and other reactive gases in the marine boundary layer, the relative contributions of the organic source gases to tropospheric chemistry, though in some cases small, are not well understood. In addition, recent attention has focused on these gases as potentially significant contributors to stratospheric ozone depletion [e.g., *Salawitch*, 2006; *Yang et al.*, 2005]. Traditionally thought of as weak or nonexistent participants in stratospheric ozone chemistry, short-lived halogenated gases, or their breakdown products, could be delivered from the marine boundary layer to the lower stratosphere via rapid, deep convection [*Kritz et al.*, 1993; *Solomon et al.*, 1994, 2005]. Their potential contribution is underscored by a substantial excess (~20–35%) of bromine in the stratosphere that cannot be accounted for by the longer-lived brominated gases, i.e., CH_3Br and halons [*Pfeilsticker et al.*, 2000]. Unfortunately, the determination of ozone depletion potentials [*Solomon et al.*, 1992] for these gases is not straightforward because their short atmospheric lifetimes leave them poorly mixed in the troposphere [*Junge*, 1963]. Thus the ozone depletion potential of a short-lived species ($\tau < 0.5$y) depends upon its distribution in the atmosphere and the location of its source [*Ko and Poulet*, 2003]. For example, a short-lived gas that is emitted at a time and place of potential deep convection, for example, late summer in the tropics, has a higher probability of reaching the stratosphere than it does at high latitudes in the winter.

[3] Thus, because the ocean as a whole is by far the largest source of short-lived, organic brominated and iodinated gases to the atmosphere [e.g., *Quack and Wallace*, 2003], it is critical to know their oceanic distributions and sea-air fluxes on a global basis if we are to account for the presence of excess bromine in the stratosphere. Several recent, comprehensive investigations [e.g., *Carpenter et*

---

[1] Global Monitoring Division, NOAA Earth System Research Laboratory, Boulder, Colorado, USA.
[2] Now at Chemistry Department, Drexel University, Philadelphia, Pennsylvania, USA.
[3] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, USA.
[4] Now at Analytical Services, Entegris Inc., Franklin, Massachusetts, USA.
[5] Now at Department of Oceanography, Texas A&M University, College Station, Texas, USA.
[6] Centre for Atmospheric Science, Chemistry Department, University of Cambridge, Cambridge, UK.
[7] Department of Earth System Science, University of California, Irvine, California, USA.

Copyright 2007 by the American Geophysical Union.
0886-6236/07/2006GB002732$12.00

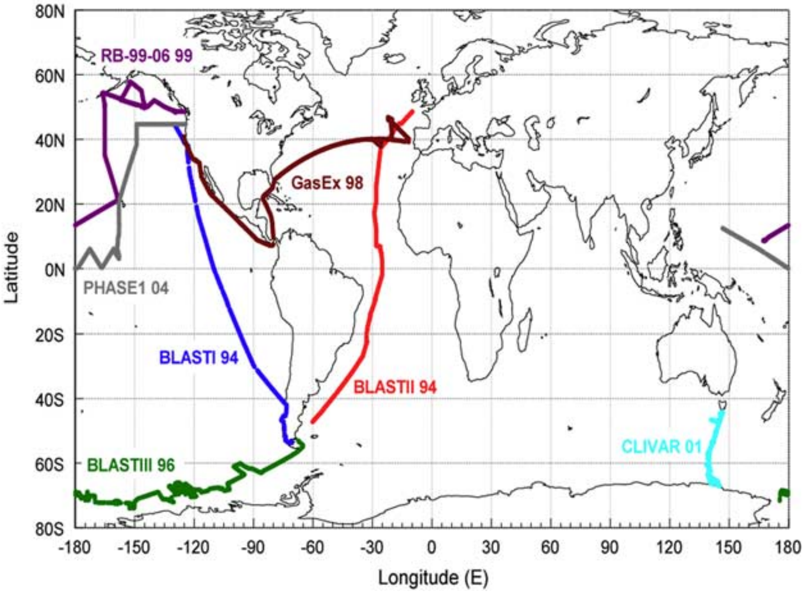

Figure 1. Cruise map 1994–2004. Cruise details provided in Table 1.

al., 2003; *Chuck et al.*, 2005; *Quack and Wallace*, 2003; *Yokouchi et al.*, 2005] have provided high-quality measurements of these gases in the ocean, the atmosphere, or both. Some have focused on midlatitude or tropical coastal areas, whereas others have crossed broader swaths of the ocean. In those cases where both air and water have been analyzed, however, the sampling and analytical techniques have differed and the calculation of saturations has usually depended upon extraction efficiencies and Henry's law constants. Further, most investigations, though involving careful calibration, have not left a legacy of standards traceable to a long-term scale. Nevertheless, findings of these investigations are consistent and tell a story of high and variable saturations of most of the short-lived, organic halocarbons.

[4] This study is an attempt to provide a consistent, traceable record of the three predominant short-lived halocarbons – $CHBr_3$, CH_2Br_2, and CH_3I – across several of the world's oceans in different seasons. The data were collected as part of a long-term effort to understand the oceanic distribution and air-sea fluxes of CH_3Br [e.g., *King et al.*, 2000, 2002; *Lobert et al.*, 1995, 1996, 1997; *Tokarczyk et al.*, 2001, 2003; *Tokarczyk and Saltzman*, 2001; *Yvon and Butler*, 1996; *Yvon-Lewis and Butler*, 1997; *Yvon-Lewis et al.*, 2004]. At the time the measurements were made, we had only preliminary calibration scales for $CHBr_3$, CH_2Br_2, and CH_3I. We are now able to report data for each of these gases on a common calibration scale that minimizes uncertainty associated with cruise location and timing and provides a reasonable degree of comparability among data sets.

2. Methods

[5] These gases were studied as part of seven research cruises aimed at understanding the exchange of halogenated trace gases between the ocean and atmosphere (Figure 1). The cruises were conducted over 10 years and all involved

Table 1. Research Cruises and Method Descriptions

Cruise Name	Dates	Ship	References[a]
BLAST I	Jan–Feb 1994	NOAA Ship *Discoverer* (US)	*Lobert et al.* [1995, 1996]
BLAST II	Oct–Nov 1994	FS Polarstern (DE)	*Lobert et al.* [1996]
BLAST III	Feb–April 1996	RV *Nathaniel Palmer* (US)	*Lobert et al.* [1997]
GasEx-98	May–July 1998	NOAA Ship *Ron Brown* (US)	*King et al.* [2000]
RB-99-06	Sep–Oct 1999	NOAA Ship *Ron Brown* (US)	*King et al.* [2002]
CLIVAR-01	Nov–Dec 2001	RSV *Aurora Australis* (AU)	*Yvon-Lewis et al.* [2004][b]
PHASE I-04	June–July 2004	RV *Wecoma* (US)	*Dahl et al.* [2005][c]

[a] For the most part, analytical methods were similar, although there were some differences in choice of trapping adsorbents and chromatographic techniques among cruises. These differences, when they existed, are noted in the individual descriptions.

[b] Surface water measurements on CLIVAR were compromised owing to a crack in the equilibrator, but periodic water measurements were available from hydrocast surface bottles.

[c] *Dahl et al.* [2005] do not detail the analytical system used for these measurements during PHASE I-04, but do provide cruise details. The analytical system was identical to those for GasEx-98, RB-99-06, and CLIVAR-01.

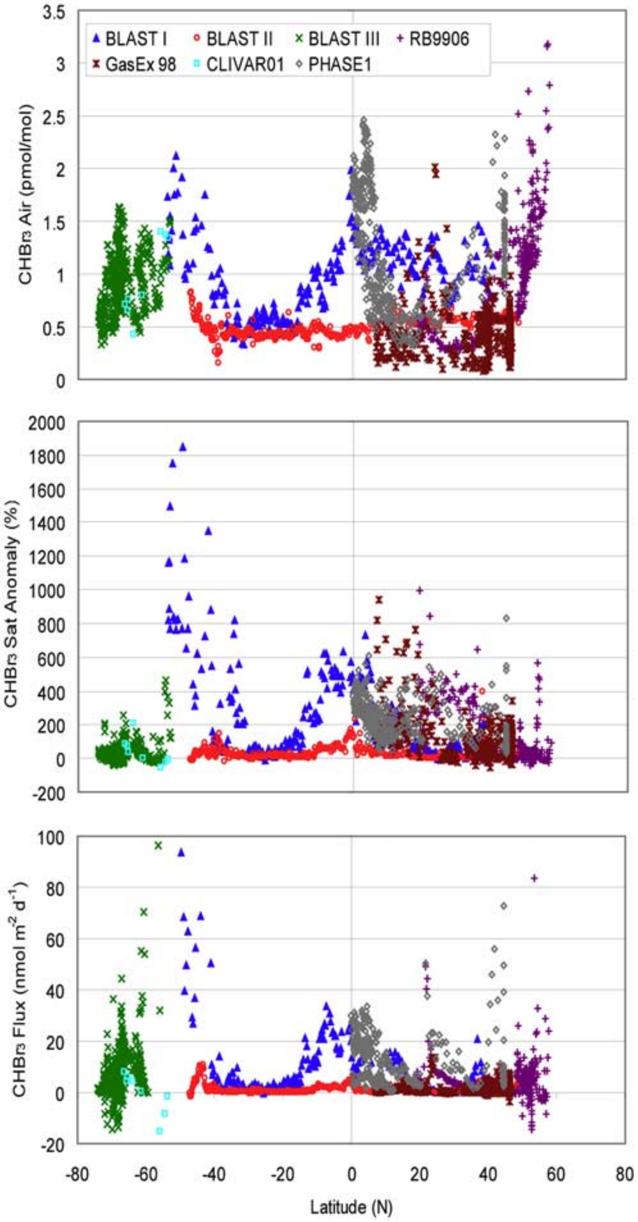

Figure 2. $CHBr_3$ air mixing ratio, saturation anomaly, and sea-air flux from seven research cruises plotted as a function of latitude.

continuous, high-frequency measurement of ~25 gases in the air and equilibrated surface water by gas chromatography–mass spectrometry (GCMS). The cruises, analytical procedures, and calculations (e.g., saturation anomaly, air-sea fluxes) are described in several earlier publications (Table 1). Some changes in technique were made over time and are described below with other sampling and analytical details specific to these gases.

2.1. Sampling and Analysis

[6] The overall sampling approach and chromatography for the three BLAST cruises (1994–1996) are described in detail by *Lobert et al.* [1996]. For subsequent cruises (1998–2004), the trapping system, instrument, and procedure were modified as described by *King et al.* [2000]. Essentially, the alterations allowed for acquisition of larger samples and more rapid sampling by employing separate collection and focusing traps, lowering the trapping temperature, and allowing for back-flushing of the chromatography column. The instrument used at sea was linear within 5% to over 100 ppt for these gases, which encompasses the range of all air and water measurements made on these cruises. The desiccant used for the BLAST cruises was Sicapent (P_2O_5), but thereafter was replaced with $Mg(ClO_4)_2$ salt because of ease of use. Although we have occasionally had

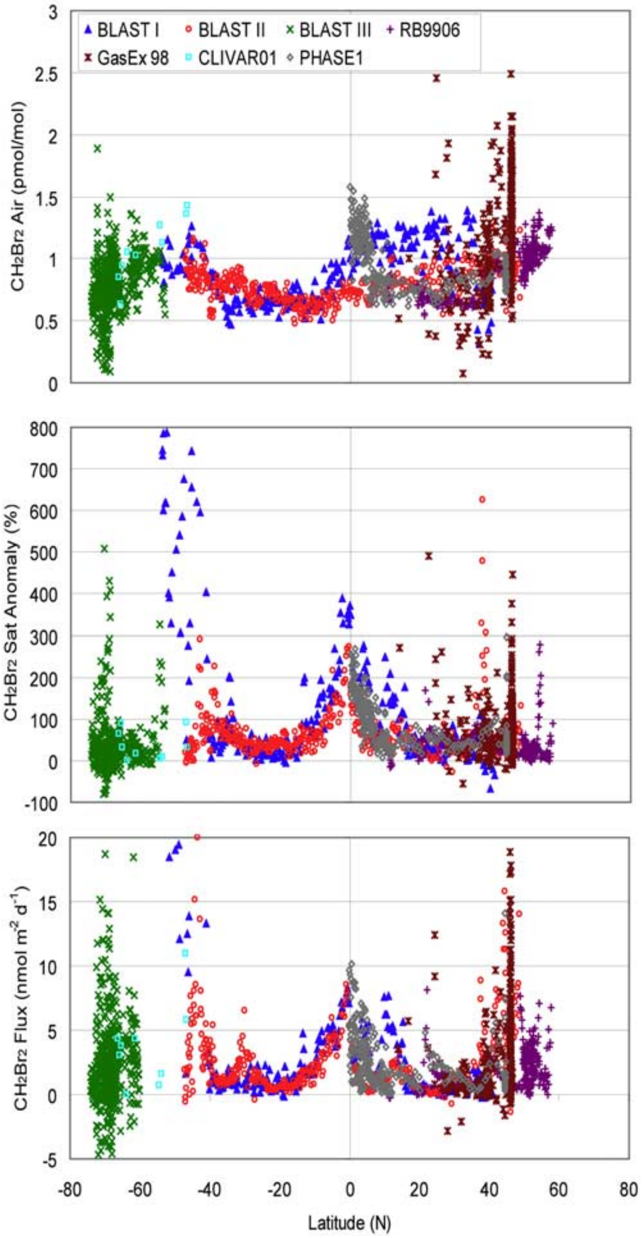

Figure 3. CH_2Br_2 air mixing ratio, saturation anomaly, and sea-air flux from seven research cruises plotted as a function of latitude.

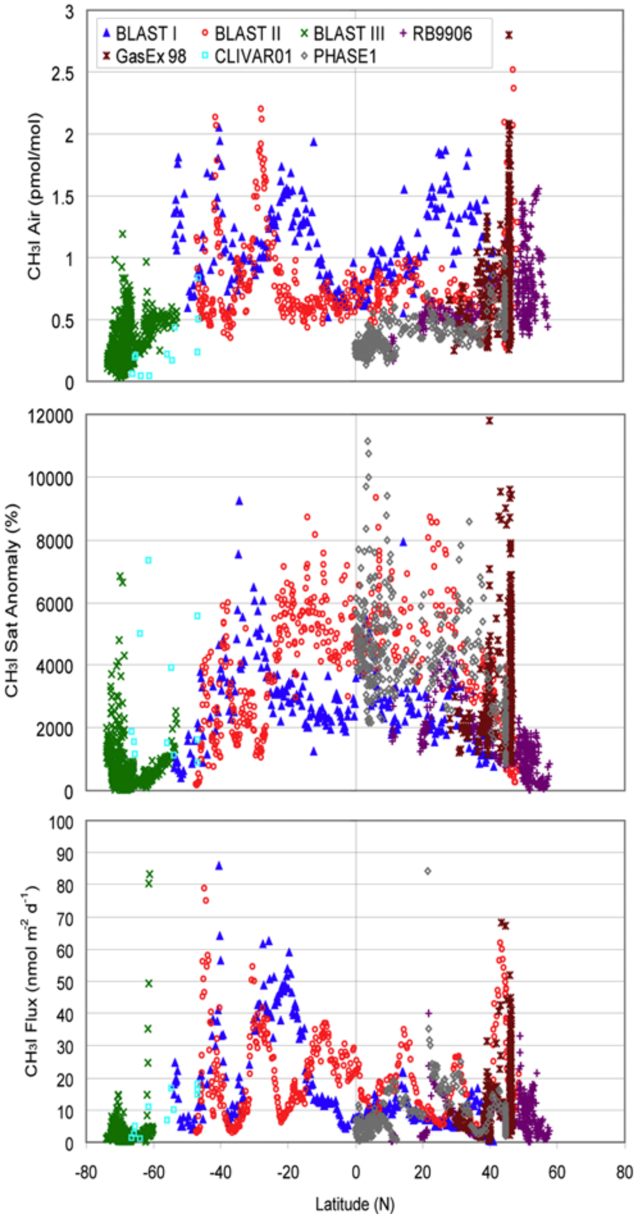

Figure 4. CH_3I air mixing ratio, saturation anomaly, and sea-air flux from seven research cruises plotted as a function of latitude.

some trouble with degradation of gases in dry air using $Mg(ClO_4)_2$, these three gases were unaffected by either desiccant in moist samples or premoistened adsorbent. Laboratory comparisons of measurements made through $Mg(ClO_4)_2$, Nafion, and no adsorbent showed no significant difference among samples for these gases.

[7] Surface water measurements on all cruises were made by pumping seawater continuously into a Weiss-type, gas-liquid equilibrator [*Butler et al.*, 1988; *Johnson*, 1999] in which the recirculated gas phase is vented to barometric pressure. The amount of analyte is measured in this gas phase after drying, which is the same way the atmospheric measurements are made. The success of this system depends upon the solubility of each gas and upon its rate of production or consumption in a system containing marine detritus and organisms. These gases are all highly soluble in seawater, with Bunsen solubilities of ~5 to 75, so re-equilibration to recover from withdrawing a sample is of the order of seconds [*Butler et al.*, 1988]. However, enhanced production or degradation in the equilibrator could be a problem if it is faster than the re-equilibration rate. The best way to test this is by comparing discrete surface samples periodically with measurements from the equilibrator. We were able to make this comparison on PHASE I (2004) and found no significant difference for $CHBr_3$ and CH_2Br_2 between the discrete samples collected and the equilibrated water over a 14-day period during which the comparison was made. Unfortunately, data for CH_3I in the discrete samples were too noisy to make a reliable comparison. Although we cannot rule out some possible effect of production or degradation in the equilibrator affecting CH_3I measurements, such rates would have to be extremely high given the short turnover time for this gas in the headspace (10–60 sec).

2.2. Calibration

[8] A key feature of these data is that all measurements are traceable to common, established calibration scales maintained at NOAA's Earth System Research Laboratory (http://www.cmdl.noaa.gov/hats/standard/standard.html). A common scale is critical in comparing data from different cruises and often troublesome when attempting to compare data from research efforts by different investigators (e.g., discussions in work by *Quack and Wallace* [2003]). Although most of the very short-lived (VSL) halocarbons were measured on all cruises, we maintained only relative scales in the early years. We recently developed calibration scales, identified as NOAA-2003 for $CHBr_3$, and NOAA-2004 for CH_2Br_2, and CH_3I, and have applied them to measurements from all cruises. We traced the scales back in time to 1994 by comparing numerous secondary standards (whole air in Aculife-treated aluminum and stainless steel cylinders) to each other and to gravimetrically prepared primary standards. Because the atmospheric mixing ratios of $CHBr_3$, CH_2Br_2, and CH_3I are very low (0.2–0.8 ppt in the secondary standards), maintaining a consistent calibration scale over time is difficult and subject to greater relative uncertainty compared to gases such as CH_3CCl_3 and CCl_4. Although we can assure consistency among cruises to within ~5%, the absolute certainty of these scales is 10–20% (see auxiliary material[1]).

[9] Results for those gases for which we have long-term calibration scales are posted on a NOAA ftp site (ftp://140.172.192.211/hats/ocean/Ocean%20GCMS%20Data%201994-2004/), archived at the Carbon Dioxide Information Analysis Center (CDIAC) at Oak Ridge National Laboratory in Oak Ridge, Tennessee, and at the World Meteorological Organization World Data Centre for Greenhouse Gases (WDCGG) at the Japan Meteorological Agency in

---

[1] Auxiliary material data sets are available at ftp://ftp.agu.org/apend/gb/2006gb002732. Other auxiliary material files are in the HTML.

Table 2. Regional $CHBr_3$ Averages and Ranges

	$CHBr_{3air}$, ppt	$CHBr_{3water}$, ppt	Δ,[a] %	Flux, nmol/m^2/d
		Tropics		
Mean	1.0	3.5	210	9.1
Median	0.8	2.3	210	5.7
Range,[b] 90%	0.4 to 2.1	0.5 to 8.1	13 to 480	0.2 to 27
		Southern Ocean		
Mean	0.9	1.2	48	5.4
Median	0.9	1.1	27	4.4
Range,[b] 90%	0.5 to 1.4	0.7 to 1.7	12 to 140	−7.6 to 32
		"Gyres"		
Mean	0.7	1.1	81	2.7
Median	0.5	0.8	43	1.4
Range,[b] 90%	0.2 to 1.5	0.4 to 2.5	−4 to 330	−0.2 to 9.3
		Coastal Waters		
Mean	0.8	3.0	230	220
Median	0.6	1.2	110	2.1
Range,[b] 90%	0.2 to 1.9	0.6 to 14	−11 to 820	−1.8 to 520

[a] Saturation anomaly (Δ) is calculated as the difference between water and air mixing ratios divided by the air mixing ratio.

[b] This corresponds to the central range of values that constitute 90% of the data.

Tokyo, Japan, and appended as auxiliary material to this manuscript. Although other VSL halocarbons, such as CH_2BrCl, $CHBr_2Cl$, CH_2ClI and CH_2I_2, were detected in surface waters on some of the cruises and scales have recently been developed for all but CH_2ClI, atmospheric mixing ratios were below our detection limits on all cruises.

3. Global Distributions

[10] Key features in the distributions of all three gases are clearly evident when cruise data are plotted together vs. latitude (Figures 2–4). Common features in the surface water data are (1) supersaturated surface water, virtually everywhere, all the time, except in regions of substantial mixing with subsurface waters, (2) periodic, extremely high supersaturations near coasts, often in association with beds of attached macroalgae, (3) high supersaturations in equatorial regions and near apparent divergences, and (4) moderate supersaturations in the central gyres. Patterns in the atmospheric (marine boundary layer) data are similar to those for the surface waters, but less prominent. For the most part, the atmospheric mixing ratios of all three gases ranged from <0.5 ppt to a little over 2 ppt (Tables 2–4 and Figures 2–4). Higher values in the air are commonly seen in the same locations that ocean fluxes are highest, although care is needed in interpreting these correlations.

[11] There are also identifying features and anomalies in these general patterns peculiar to each gas. For example, distribution patterns among the three gases are most consistent for CH_2Br_2 (Figure 3). The atmospheric lifetime of CH_2Br_2, at about 4 months, may contribute to the more consistent, repeatable atmospheric mixing ratios, but its saturation anomaly and its flux also are reasonably consistent among the cruises. The tropical peaks in saturation anomaly and flux are quantitatively consistent for both the Atlantic and Pacific Oceans. Fluxes are lowest in the subtropical and lower temperate waters, elevated in coastal waters, and occasionally undersaturated in the Southern Ocean and near coasts. We do not take these undersaturations, however, to represent in situ consumption. Unlike methyl bromide, which is consumed by chemical and biological processes and undersaturated in large areas of the ocean, the only aquatic consumption mechanisms for CH_2Br_2 are very slow, as they are for $CHBr_3$ [*Goodwin et al.*, 1997; *Yvon-Lewis and Butler*, 2002]. Most likely the undersaturations in the Southern Ocean resulted from mixing of CH_2Br_2-depleted subsurface waters. This is evidenced in the data for inert tracers of atmospheric origin, such as chlorofluorocarbon-11 (CFC-11, or CCl_3F), which were largely undersaturated (10–30%) where deep water was brought to the surface [*Yvon-Lewis et al.*, 2004]. Negative saturations elsewhere, particularly in the coastal regions, could have resulted from mixing or from transport of air masses with elevated concentrations, owing to terrestrial or coastal emissions, and similarly would not necessarily represent in situ loss.

[12] The latitudinal distributions of $CHBr_3$ in the air and water are similar to those for CH_2Br_2, with one major exception (Figure 2). Both air and surface water mixing ratios of $CHBr_3$ on average are substantially lower in the Atlantic than in the Pacific. We make this statement with some caution because it relies in good part upon the results of one cruise, BLAST II (1994). However, air mixing ratios and water saturations were also lower in the Atlantic during GasEx-98 than on the Pacific cruises (Table 5), and results reported by *Quack et al.* [2004] and *Chuck et al.* [2005] for the tropical and subtropical Atlantic, although generally

Table 3. Regional CH_2Br_2 Averages and Ranges

	CH_2Br_{2air}, ppt	CH_2Br_{2water}, ppt	Δ,[a] %	Flux, nmol/m^2/d
		Tropics		
Mean	0.9	1.9	100	2.6
Median	0.8	1.5	80	1.9
Range,[b] 90%	0.6 to 1.3	0.8 to 3.8	20 to 240	0.4 to 6.9
		Southern Ocean		
Mean	0.8	1.0	42	7.5
Median	0.8	1.0	19	1.6
Range,[b] 90%	0.4 to 1.1	0.6 to 1.4	−17 to 190	−3.4 to 24
		"Gyres"		
Mean	1.0	1.5	58	2.0
Median	1.0	1.3	42	1.3
Range,[b] 90%	0.4 to 1.7	0.9 to 2.8	−10 to 200	−.9 to 7.6
		Coastal Waters		
Mean	1.0	2.8	180	110
Median	0.9	1.5	75	4.8
Range,[b] 90%	0.6 to 1.9	0.8 to 8.1	−14 to 740	−3.4 to 660

[a] Saturation anomaly (Δ) is calculated as the difference between water and air mixing ratios divided by the air mixing ratio.

[b] This corresponds to the central range of values that constitute 90% of the data.

Table 4. Regional CH_3I Averages and Ranges

	CH_3I_{air}, ppt	CH_3I_{water}, ppt	Δ,[a] %	Flux, $nmol/m^2/d$
		Tropics		
Mean	0.6	25	4,600	13
Median	0.6	24	4,500	10
Range,[b] 90%	0.2 to 1.1	11 to 44	2,300 to 7,400	1.6 to 33
		Southern Ocean		
Mean	0.3	1.6	620	17
Median	0.3	1.3	370	2.0
Range,[b] 90%	0.1 to 0.7	0.8 to 3.2	51 to 2,001	0.4 to 9.8
		"Gyres"		
Mean	0.8	21	2,800	14
Median	0.7	18	2,500	9.8
Range,[b] 90%	0.4 to 1.6	6.2 to 49	410 to 6,100	2.2 to 40
		Coastal Waters		
Mean	0.8	15	1,800	164.2
Median	0.7	14	1,500	15.0
Range,[b] 90%	0.4 to 1.6	2.9 to 31.7	370 to 4,400	2.0 to 900.0

[a] Saturation anomaly (Δ) is calculated as the difference between water and air mixing ratios divided by the air mixing ratio.

[b] This corresponds to the central range of values that constitute 90% of the data.

higher than the BLAST II Atlantic values, are substantially lower than the corresponding Pacific values reported here. Tropical fluxes of $CHBr_3$ in the BLAST II data set are elevated relative to temperate waters, but not nearly as much as in the Pacific.

[13] Unlike CH_2Br_2 and $CHBr_3$, CH_3I mixing ratios in the marine boundary layer, though still elevated in the tropics, do not peak at the equator, but rather at high tropical and subtropical latitudes. This likely reflects the complex atmospheric chemistry and photochemistry of the gas [e.g., *Carpenter*, 2003; *Smythe-Wright et al.*, 2005]. Methyl iodide's chemistry in water as well is more complex than that of $CHBr_3$ and CH_2Br_2, as it is actively involved in photochemical reactions. Supersaturations of CH_3I are extremely high everywhere, running in the thousands of percent and reflecting its high photochemical and biological production rates in the water. Because these saturation anomalies also result in part from rapid or variable degradation of CH_3I in the air, calculated fluxes need to be interpreted with the caveat that the measured air values may not necessarily represent the air from which the water has equilibrated. This would be of concern, except that CH_3I is so highly supersaturated that the error in having determined the "appropriate" air value is small relative to the difference in partial pressure between water and air. Fluxes for this gas calculated simply by assuming that the atmospheric partial pressure was zero would lead to a $\sim$5% error. Also, the spatial and temporal patchiness of a gas that is produced and degraded as rapidly as CH_3I in seawater can be problematic in determining representative fluxes. Although the flux calculated from any individual pair of measurements can always be questioned, taking the average of a group of these measurements over space and time incorporates the variability resulting from these effects. These caveats are less of a concern for $CHBr_3$, which, though less supersaturated than CH_3I, is still highly supersaturated and is degraded more slowly in air and hardly at all in the water. This is not a concern for CH_2Br_2, for which the chemical lifetime in the atmosphere is of the order of months and degradation lifetimes in seawater are months to years.

[14] Further variability in all three gases may be attributed to seasonal effects. For example, RB-99-06 and Phase I crossed similar regions in the North Pacific during different seasons, during which the saturation anomalies of all three gases in the subtropical gyre were reduced by a factor of as much as two in the fall relative to the spring or summer [*King et al.*, 2004]. We previously reported similar variability for CH_3Br [*King et al.*, 2002]. Although this latter effect was driven in good part by the influence of sea surface

Table 5. Comparison of Atlantic and Pacific Ocean Results[a]

	Atlantic (All Cruises)	Pacific (All Cruises)	N. Atlantic (GasEx 98)	N. Atlantic (BLASTII)
		$CHBr_3$		
Air, pmol/mol	0.4 ± 0.1	1.1 ± 0.5	0.4 ± 0.2	0.5 ± 0.1
Water, pmol/mol	0.6 ± 0.2	3.1 ± 2.4	0.7 ± 0.2	0.7 ± 0.1
Sat anom, %	55 ± 56	186 ± 160	78 ± 61	25 ± 29
Flux, $nmol/m^2/d^1$	1.1 ± 1.4	8.1 ± 8.5	1.5 ± 1.9	0.8 ± 1.0
Number of measurements	793	903	433	168
		CH_2Br_2		
Air, pmol/mol	1.0 ± 0.4	0.9 ± 0.2	1.2 ± 0.4	0.8 ± 0.1
Water, pmol/mol	1.6 ± 0.7	1.6 ± 0.8	2.0 ± 0.7	1.3 ± 0.3
Sat anom, %	68 ± 61	67 ± 65	76 ± 72	56 ± 42
Flux, $nmol/m^2/d^1$	2.6 ± 3.0	2.2 ± 1.8	3.1 ± 3.4	2.5 ± 3.0
Number of measurements	763	812	398	171
		CH_3I		
Air, pmol/mol	0.8 ± 0.4	0.7 ± 0.4	0.8 ± 0.4	0.8 ± 0.3
Water, pmol/mol	28 ± 12	17 ± 12	26 ± 14	30 ± 12
Sat anom, %	3820 ± 1860	2900 ± 1900	3420 ± 1740	4260 ± 2050
Flux, $nmol/m^2/d^1$	17 ± 12	11 ± 11	15 ± 11	18 ± 13
Number of measurements	776	892	408	173

[a] Uncertainties are expressed as ±1 s.d.

Table 6. Global Oceanic Fluxes of Major Short-Lived Halocarbons

Gas	Global Oceanic Flux, Gmol Br or I yr^{-1}	Open Ocean Flux, Gmol Br or I yr^{-1}
$CHBr_3$	10	1.9
CH_2Br_2	3.5	0.6
CH_3I	4.3	2.1

temperature (SST) on the degradation rate of CH_3Br, it was clear that productivity played a part as well [e.g., *Yvon-Lewis et al.*, 2002]. That would be the likely case for these short-lived species, for which significant, in situ, aquatic degradation mechanisms are lacking.

4. Global and Regional Fluxes

[15] Although they do not offer full global coverage, these seven cruises crossed areas representative of all major oceanic regimes – tropics and subtropics, temperate waters, polar and subpolar waters, and coastal waters – and represent each of these areas, with the exception of polar and subpolar waters, in several seasons. Thus it is instructive to use these data to estimate global and regional fluxes (Table 6 and Figure 5). We subdivided the ocean in part based upon geography and in part based upon shifts in the data. For example, coastally influenced waters could extend beyond what is traditionally thought of as coastal (i.e., 200 m depth), and definition of the boundary of the Southern Ocean is not always straightforward. A detailed explanation of these subdivisions is included in the auxiliary material. Our one caveat is the estimate of coastal fluxes, which we have some concern about because of the high variability of measurements in those waters (Tables 2–4) and the difficulty in estimating exactly which coastal waters are represented by a given concentration. Extrapolating coastal measurements in this data set to an area representative of coastal and coastally influenced waters (~10% of the ocean's coverage [e.g., *Ryther*, 1969]) yields fluxes equal to as much as five times the contribution from the rest of the ocean. This clearly underscores the potential importance of coastal waters in contributing to the total global flux. We must restate, however, that these cruises were aimed at evaluating open-ocean characteristics, and it would be a disservice to hint that they could adequately represent coastal influences, which have been studied in detail by numerous investigators [e.g., *Carpenter et al.*, 1999, 2003; *Laturnus*, 1996; *Laturnus et al.*, 1998; *Schall and Heumann*, 1993]. Because of the high variability of halocarbon fluxes in coastal waters, global estimates need to be interpreted with some caution.

[16] Our open ocean flux of $CHBr_3$ is five times less than our global estimate, which indicates that contributions from coastal waters play a potentially significant role in delivering this gas to the atmosphere. This is consistent with earlier findings, as is our quantitative estimate of 1.9 Gmol yr^{-1} (Table 6). The most recent previous estimate of the global oceanic flux of $CHBr_3$ comes from *Quack and Wallace*

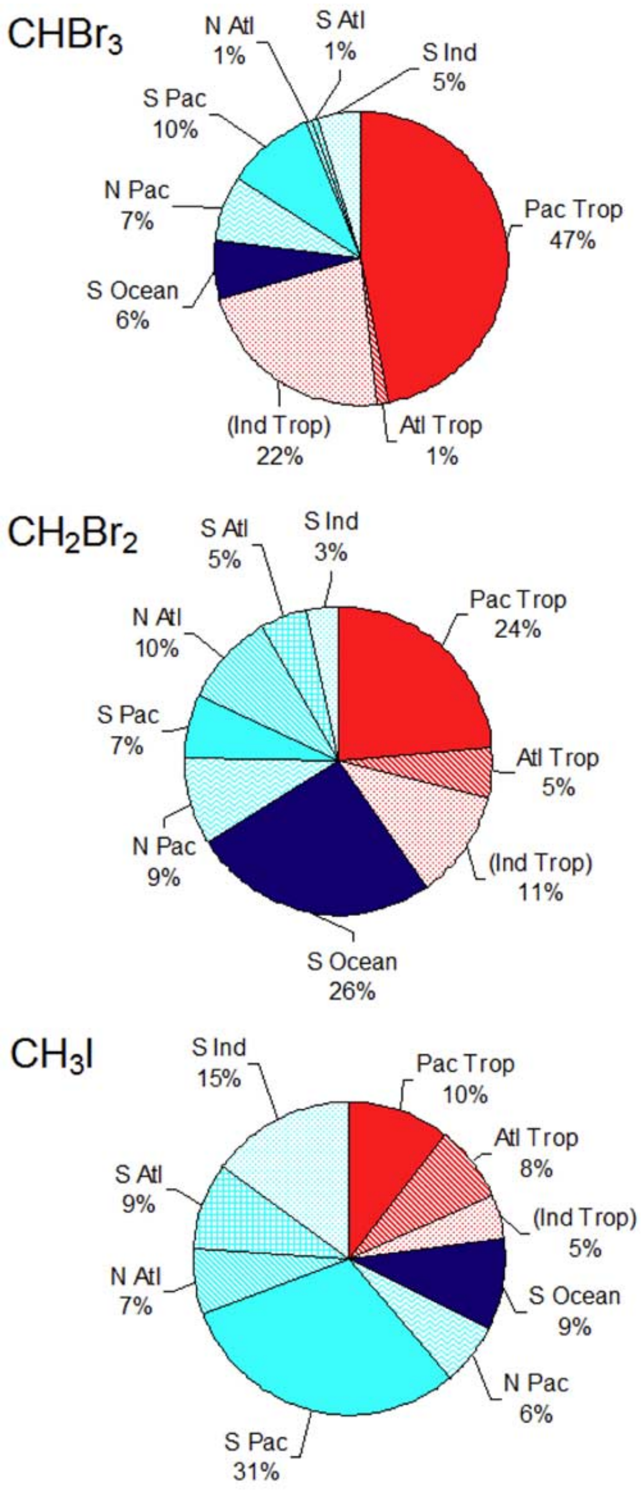

Figure 5. Open ocean sea-air fluxes of $CHBr_3$, CH_2Br_2, and CH_3I by oceanic region. The tropics are identified by the warmer colors, while the temperate and polar waters are designated with cooler colors. Indian Ocean fluxes are assumed to parallel those at comparable latitudes in the Pacific. Percentages represent the contribution of each region to the global open-ocean flux; coastal fluxes have not been included in this calculation.

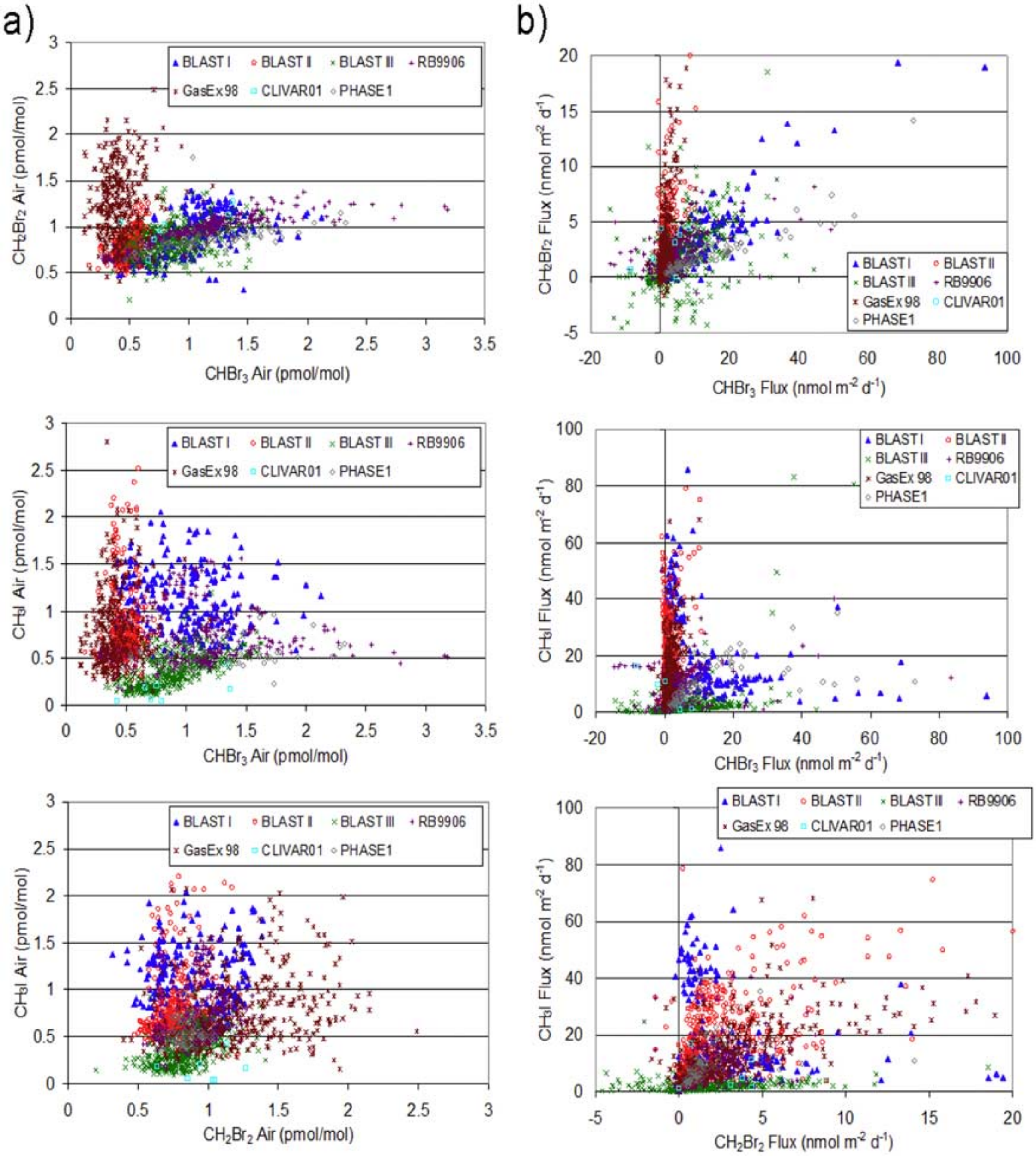

Figure 6. Cross correlations between air mixing ratios and sea-air fluxes of $CHBr_3$, CH_2Br_2, and CH_3I.

[2003], who surveyed and summarized the findings of dozens of earlier studies. Our value of 10 Gmol Br yr^{-1} for the global flux of $CHBr_3$ is identical to their global estimate of 10 (3–22) Gmol Br yr^{-1}, and our value of 1.9 Gmol Br yr^{-1} for the open ocean is similar to the 3 Gmol Br yr^{-1} in their estimate. Although somewhat lower, our result for the open ocean is also generally consistent with the global, sink-based estimate of 3.5 Gmol Br yr^{-1} of *Dvortsov et al.* [1999], which, as noted by *Quack and Wallace* [2003], is largely based upon measurements over the open ocean. This agreement among the open ocean flux estimates of our study and that of *Quack and Wallace* [2003] and the top-down estimate of *Dvortsov et al.* [1999] is remarkable, since different data and dramatically different approaches were used in all three studies. Globally, tropical fluxes of bromoform account for almost 2/3 of emissions from the open ocean, with the Pacific alone accounting for ½ of the open ocean flux (Figure 5).

[17] Fewer attempts have been made to estimate global oceanic fluxes of CH_2Br_2. The most recent, comprehensive update is the ∼0.7 Gmol Br yr^{-1} given by *Ko and Poulet* [2003], which is calculated from rate constants in work by *Sander et al.* [2002] and measurements from *Blake et al.* [1997, 2001]. Again, our value of 0.6 Gmol Br yr^{-1} for CH_2Br_2 from the open ocean is virtually identical to the earlier top-down estimate, which, as for $CHBr_3$, was based upon concentrations from over the open ocean. Our total global flux is almost six times larger, owing to the contribu-

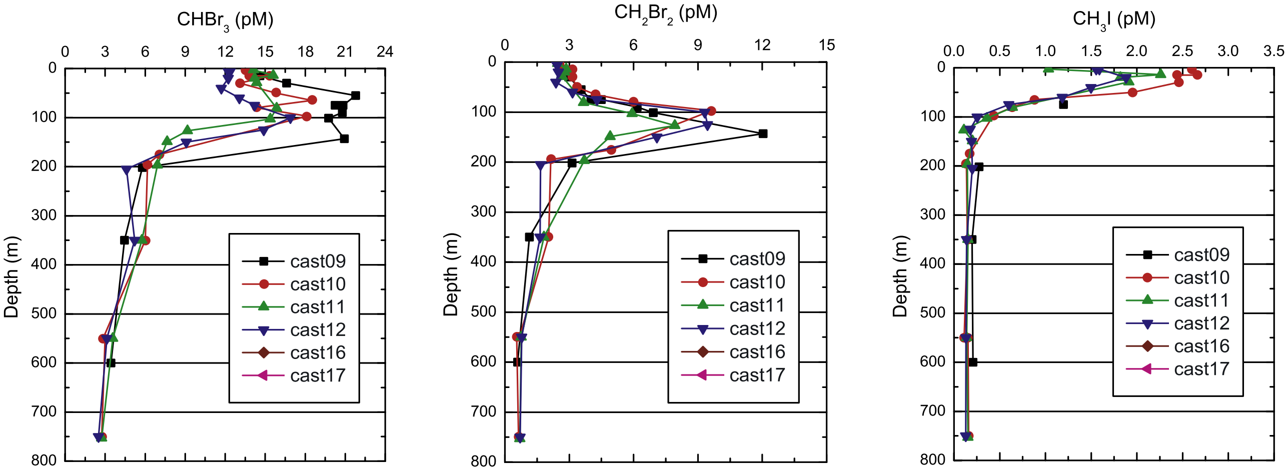

Figure 7. Bromoform, dibromomethane and methyl iodide depth profiles from the equatorial region (0°–2.5°N), collected during the PHASE 1 cruise.

tion from coastal waters. Open ocean fluxes of CH_2Br_2 appear to be evenly divided among the tropics, polar waters, and the temperate and subtropical latitudes (Figure 5).

[18] Methyl iodide fluxes are more widely reported than the other two gases. Evaluating data from *D. R. Blake et al.* [1996] and *N. J. Blake et al.* [1996] and using some of the data presented in this paper, *Bell et al.* [2002] suggested a global oceanic source of 1.5 Gmol I yr^{-1}, which amounts to about one third of our global estimate, but is very near our estimate for the open ocean. Again, the top-down estimate of *Bell et al.* [2002] was based largely upon oceanic sources. Our measurements agree very well with those of *Moore and Groszko* [1999], who reported air partial pressures (0.2–1.6 patm) and water partial pressures (10–50 patm) almost identical to ours (Table 4) and whose transect across the Pacific Ocean yielded a similar pattern of increased fluxes in the subtropical and lower temperate latitudes. The tropics account for only about ¼ of emissions from the open ocean for this gas.

[19] The tropical fluxes of all three gases in the open ocean correlate well ($p < 0.01$) with air mixing ratios in the marine boundary layer. (Correlation coefficients for $CHBr_3$, CH_2Br_2, and CH_3I are 0.73, 0.37, and 0.61). However, fluxes in the remainder of the ocean did not correlate at all with air mixing ratios. Cross correlations between gases in the atmosphere show different relationships between CH_2Br_2 and $CHBr_3$ in the Pacific than in the Atlantic (Figure 6a). This is further supported by the cross correlations of fluxes between these two gases (Figure 6b). CH_3I did not correlate well with CH_2Br_2 or $CHBr_3$, however. This is not unexpected, since the distribution patterns of CH_3I, with the higher fluxes in the subtropical waters, are somewhat different than those for the other gases. The low fluxes of CH_3I in polar waters are also reflected in the cross-correlation plots (Figures 6a and 6b).

5. Implications of Flux Distributions

[20] Several studies have suggested that short-lived, halogenated gases and their breakdown products are successfully transported to the upper troposphere and lower stratosphere, where they are involved in the depletion of stratospheric ozone [e.g., *Ko and Poulet*, 2003; *Pfeilsticker et al.*, 2000; *Solomon et al.*, 1994]. It is also clear from this and other studies that the mixing ratios and fluxes of the short-lived gases are often high in the tropics, where deep convection is most prevalent. Values reported here show that up to 9 ppt of Br is available from $CHBr_3$ and CH_2Br_2 alone in the tropical marine boundary layer air and that these mixing ratios are supported by high ocean-air fluxes.

[21] Our data suggest that there is a positive correlation between the fluxes of these gases and sea-surface temperature (SST). If polar and coastal waters are excluded, both $CHBr_3$ and CH_3I sea-air fluxes correlate well ($p < 0.01$) with SST. This suggests that increases in the temperature of the open ocean might yield an increased sea-air flux of these gases. However, other, possibly more influential processes come into play in this relationship. Instantaneous sea-air flux of a gas is fundamentally a factor of SST and windspeed, where SST determines the solubility and diffusivity of the gas (salinity differences making minor contributions) and windspeed is the kinetic driver of transfer. Further, the ultimate limit on sea-air exchange is the net production rate of the gas in the water. For $CHBr_3$ and CH_2Br_2, which have very limited in situ loss processes [*Goodwin et al.*, 1997, 1998], this can be attributed almost exclusively to gross production, which in turn is biologically driven and therefore ultimately limited by the supply rate of nutrients. In some locations, nutrient supply could be enhanced by higher windspeeds; in others it could be suppressed by increased stratification owing to surface warming. CH_3I concentrations in the surface water are determined by both production and degradation, making its response to SST changes even more difficult to decipher. Finally, it is not clear here whether the observed temperature relationships are simply proxies for other covarying phenomena, such as incident radiation or even latitude. Consequently, we do not want to read too much into the correlations, but note simply that they may at least be indicators of potential direct or indirect climate change effects.

[22] Depth profiles obtained on some of our latter cruises suggest that these two bromomethanes are produced near the bottom of the mixed layer of the ocean (Figure 7), whereas CH_3I appears to be produced at the top of the mixed layer. This phenomenon is common throughout the ocean in data from these latter cruises (in the tropics, subtropics, and midlatitudes) although there are occasional exceptions (S. A. Yvon-Lewis et al., manuscript in preparation, 2007). *Moore and Groszko* [1999] also reported some methyl iodide profiles with higher values in the mixed layer, but this is not necessarily inconsistent with our findings. Subsurface maxima of $CHBr_3$ in or near the photic zone also were reported recently by *Quack et al.* [2004] and earlier by *Moore and Tokarczyk* [1993]. Assuming that there are no significant degradation mechanisms for these two brominated gases in the surface water (none have been identified), this combination of subsurface maxima and surface supersaturations suggests that the gases are produced at depth, where light is low in intensity, nutrients are available, and temperature is modified in good part by the cooler waters below the thermocline. Available mechanisms for transporting these gases to the surface are dispersal (diffusion) or upwelling (advection). Upwelling is a faster but more sporadic and spatially constrained transport mechanism than dispersal. All three of these gases are destroyed slowly through chemical reaction in seawater, which explains their values of zero or near-zero in deep water [*Goodwin et al.*, 1997, 1998; *Mabey and Mill*, 1978]. Nevertheless, a quasi-steady state appears to be in place, given the consistency in distribution patterns in the water.

[23] We suggest here that the high surface water concentrations and fluxes of methyl iodide result mainly from processes in the mixed layer and hence would tend to correlate better with temperature (which also is a proxy for integrated, incident radiation) than would the two bromocarbons, which appear to be produced at depth, in cooler, nutrient-rich waters. This difference has implications when one considers potential impacts of climate change on these fluxes and the fate of stratospheric ozone. Clearly, any climatic change that increases tropical convection or alters the locations of deep convection would affect the transport of all short-lived gases from the boundary layer. Changes in upwelling patterns or intensity would influence the production of these gases both in the surface water and at depth, but also would alter the rate of transport of the bromocarbons to the surface. An increase in sea-surface temperature, however, might affect more strongly the production of gases in the surface water, but also would have the potential to slow upwelling of the deeper waters. Thus evaluation of the potential effects of climate change on the sea-air fluxes of these gases depends upon an understanding of their mechanisms of production and transport within the surface ocean.

6. Conclusions

[24] The open ocean is a large, significant source of the three dominant, short-lived halocarbons presented here. Though it appears that CH_3I is produced at different depths, perhaps by different mechanisms, than are $CHBr_3$ and CH_2Br_2, all three gases are highly supersaturated in the surface waters in most of the open ocean. An excess of Br is available in the tropical marine boundary layer, more than sufficient to account for the Br deficit in the stratosphere, and this excess is supported by high sea-air fluxes. How much of this Br is actually delivered to the stratosphere, and how frequently, are questions that remain to be answered. It is clear from our data, as well as those of others, that coastal waters and coastal environments are very large contributors to the global budget of these short-lived gases. Whether or not coastal emissions provide Br to the lower stratosphere depends upon their location relative to deep convection. Tropical coastal regions could be very significant [e.g., *Yokouchi et al.*, 2005]. Nevertheless, the open ocean maintains a continuous supply of Br ubiquitously throughout the tropics, where deep convection takes place. The relative contributions of the open ocean, coastal waters, and coastal environments at this time are unresolved.

[25] **Acknowledgments.** The authors would like to thank the captains and crews of all of the ships that enabled the collection of these data: NOAA Ship *Discoverer*, FS *Polarstern*, RV *Nathaniel Palmer*, NOAA Ship *Ronald H. Brown*, RSV *Aurora Australis*, and RV *Wecoma*. The generous support of the following funding agencies made this work possible: Methyl Bromide Global Coalition, NOAA's Ocean Atmosphere Carbon Exchange Study and Atmospheric Composition and Climate Change Programs, NASA's Ocean Biology/Biogeochemistry and Upper Atmosphere Research Programs, and NSF grant OCE-0221472.

References

Bell, N., L. Hsu, D. J. Jacob, M. G. Schultz, D. R. Blake, J. H. Butler, D. B. King, J. M. Lobert, and E. Maier-Reimer (2002), Methyl iodide: Atmospheric budget and use as a tracer of marine convection in global models, *J. Geophys. Res.*, *107*(D17), 4340, doi:10.1029/2001JD001151.

Blake, D. R., T.-Y. Chen, T. W. Smith Jr., C. J.-L. Wang, O. W. Wingenter, N. J. Blake, F. S. Rowland, and E. W. Mayer (1996), Three-dimensional distribution of NMHCs and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A), *J. Geophys. Res.*, *101*, 1763–1778.

Blake, N. J., D. R. Blake, B. C. Sive, T.-Y. Chen, F. S. Rowland, J. E. Collins, G. W. Sachse, and B. E. Anderson (1996), Biomass burning emissions and vertical distribution of atmospheric methyl halides and other reduced carbon gases in the South Atlantic region, *J. Geophys. Res.*, *101*, 24,151–24,164.

Blake, N. J., D. R. Blake, T.-Y. Chen, J. E. Collins Jr., G. W. Sachse, B. E. Anderson, and F. S. Rowland (1997), Distribution and seasonality of selected hydrocarbons and halocarbons over the Western Pacific basin during PEM-West A and PEM-West B, *J. Geophys. Res.*, *102*, 28,315–28,331.

Blake, N. J., et al. (2001), Large-scale latitudinal and vertical distributions of NMHCs and selected halocarbons in the troposphere over the Pacific Ocean during the March-April 1999 Pacific Exploratory Mission (PEM-Tropics B), *J. Geophys. Res.*, *106*, 32,627–32,644.

Butler, J. H., J. W. Elkins, C. M. Brunson, K. B. Egan, T. M. Thompson, T. J. Conway, and B. D. Hall (1988), Trace gases in and over the West Pacific and East Indian Oceans during the El Niño-Southern Oscillation event of 1987, *Data Rep. ERL ARL-16*, 104 pp., Natl. Oceanic and Atmos. Admin., Silver Spring, Md.

Carpenter, L. J. (2003), Iodine in the marine boundary layer, *Chem. Rev.*, *103*, 4953–4962.

Carpenter, L. J., et al. (1999), Short-lived alkyl iodides and bromides at Mace Head, Ireland: Links to biogenic sources and halogen oxide production, *J. Geophys. Res.*, *104*, 1679–1689.

Carpenter, L. J., P. S. Liss, and S. A. Penkett (2003), Marine organohalogens in the atmosphere over the Atlantic and Southern Oceans, *J. Geophys. Res.*, *108*(D9), 4256, doi:10.1029/2002JD002769.

Chuck, A. L., S. M. Turner, and P. S. Liss (2005), Oceanic distributions and air-sea fluxes of biogenic halocarbons in the open ocean, *J. Geophys. Res.*, *110*, C10022, doi:10.1029/2004JC002741.

Dahl, E. E., S. A. Yvon-Lewis, and E. S. Saltzman (2005), Saturation anomalies of alkyl nitrates in the tropical Pacific Ocean, *Geophys. Res. Lett.*, *32*, L20817, doi:10.1029/2005GL023896.

Dvortsov, V. L., M. A. Geller, S. Solomon, S. M. Schauffler, E. L. Atlas, and D. R. Blake (1999), Rethinking reactive halogen budgets in the midlatitude lower stratosphere, *Geophys. Res. Lett.*, *26*, 1699–1702.

Goodwin, K. D., M. E. Lidstrom, and R. S. Oremland (1997), Marine bacterial degradation of brominated methanes, *Environ. Sci. Technol.*, *31*, 3188–3192.

Goodwin, K. D., J. K. Schaefer, and R. S. Oremland (1998), Bacterial oxidation of dibromomethane and methyl bromide in natural waters and enrichment cultures, *Appl. Environ. Microbiol.*, *64*(12), 4629–4636.

Johnson, J. E. (1999), Evaluation of a seawater equilibrator for shipboard analysis of dissolved oceanic trace gases, *Anal. Chim. Acta*, *395*, 119–132.

Junge, C. (1963), *Air Chemistry and Radioactivity*, Elsevier, New York.

King, D. B., J. H. Butler, S. A. Montzka, S. A. Yvon-Lewis, and J. W. Elkins (2000), Implications of methyl bromide supersaturations in the temperate North Atlantic Ocean, *J. Geophys. Res.*, *105*, 19,763–19,769.

King, D. B., J. H. Butler, S. A. Yvon-Lewis, and S. A. Cotton (2002), Predicting oceanic methyl bromide saturation from SST, *Geophys. Res. Lett.*, *29*(24), 2199, doi:10.1029/2002GL016091.

King, D. B., J. H. Butler, S. A. Yvon-Lewis, D. J. Mondeel, and B. D. Hall (2004), Fluxes of short-lived organic halogens into the marine boundary layer, *Eos Trans. AGU*, *85*(47), Fall Meet. Suppl., Abstract A43-0067.

Ko, M. K. W., and G. Poulet (2003), Very short-lived halogen and sulfur substances, in *Scientific Assessment of Ozone Depletion: 2002*, edited by C. A. Ennis, chap. 2, pp. 2.1–2.57, World Meteorol. Org., Geneva.

Kritz, M. A., S. W. Rosner, K. K. Kelly, M. Lowenstein, and K. R. Chan (1993), Radon measurements in the lower tropical stratosphere: Evidence for rapid vertical transport and dehydration of tropospheric air, *J. Geophys. Res.*, *98*, 8725–8736.

Laturnus, F. (1996), Volatile halocarbons released from arctic macroalgae, *Mar. Chem.*, *55*, 359–366.

Laturnus, F., F. C. Adams, and C. Wiencke (1998), Methyl halides from Antarctic macroalgae, *Geophys. Res. Lett.*, *25*, 773–776.

Lobert, J. M., J. H. Butler, S. A. Montzka, L. S. Geller, R. C. Myers, and J. W. Elkins (1995), A net sink for atmospheric CH_3Br in the East Pacific Ocean, *Science*, *267*, 1002–1005.

Lobert, J., J. Butler, S. Yvon, S. Montzka, R. Myers, A. Clarke, and J. Elkins (1996), Blast 94: Bromine Latitudinal Air/Sea Transect, 1994, Report on oceanic measurements of methyl bromide and other compounds, *Tech. Memo. ERL CMDL-10*, Environ. Res. Lab., Natl. Oceanic and Atmos. Admin., Boulder, Colo.

Lobert, J. M., S. A. Yvon, J. H. Butler, S. A. Montzka, and R. C. Myers (1997), Undersaturation of CH_3Br in the Southern Ocean, *Geophys. Res. Lett.*, *24*, 171–172.

Mabey, W., and T. Mill (1978), Critical review of hydrolysis of organic compounds in water under environmental conditions, *J. Phys. Chem. Ref. Data*, *7*, 383–415.

Moore, R. M., and W. Groszko (1999), Methyl iodide distribution in the ocean and fluxes to the atmosphere, *J. Geophys. Res.*, *104*, 11,163–11,171.

Moore, R. M., and R. Tokarczyk (1993), Volatile biogenic halocarbons in the northwest Atlantic, *Global Biogeochem. Cycles*, *7*, 195–210.

Pfeilsticker, K., et al. (2000), Lower stratospheric organic and inorganic bromine budget for the Arctic winter 1998/99, *Geophys. Res. Lett.*, *27*, 3305–3308.

Quack, B., and D. W. R. Wallace (2003), Air-sea flux of bromoform: Controls, rates, and implications, *Global Biogeochem. Cycles*, *17*(1), 1023, doi:10.1029/2002GB001890.

Quack, B., E. Atlas, G. Petrick, V. Stroud, S. Schauffler, and D. W. R. Wallace (2004), Oceanic bromoform sources for the tropical atmosphere, *Geophys. Res. Lett.*, *31*, L23S05, doi:10.1029/2004GL020597.

Ryther, J. H. (1969), Photosynthesis and fish production in the sea, *Science*, *166*, 72–76.

Salawitch, R. J. (2006), Biogenic bromine, *Nature*, *439*, 275–277.

Sander, S. P., et al. (2002), Chemical kinetics and photochemical data for use in atmospheric studies: Evaluation number 14, *JPL Publ.*, *02-25*.

Schall, C., and K. G. Heumann (1993), GC determination of volatile organoiodine and organobromine compounds in Arctic seawater and air samples, *J. Anal. Chem.*, *346*, 717–722.

Smythe-Wright, D., S. M. Boswell, C. H. Lucas, A. L. New, and M. S. Varney (2005), Halocarbon and dimethyl sulphide studies around the Mascarene Plateau, *Philos. Trans. R. Soc., Ser. A*, *363*, 169–185, doi:110.1098/rsta.2004.1485.

Solomon, S., A. F. Tuck, M. Mills, L. E. Heidt, and W. H. Pollock (1992), On the evaluation of ozone depletion potentials, *J. Geophys. Res.*, *97*, 825–842.

Solomon, S., R. R. Garcia, and A. R. Ravishankara (1994), On the role of iodine in ozone depletion, *J. Geophys. Res.*, *99*, 20,491–20,499.

Solomon, S., D. W. J. Thompson, R. W. Portmann, S. J. Oltmans, and A. M. Thompson (2005), On the distribution and variability of ozone in the tropical upper troposphere: Implications for tropical deep convection and chemical-dynamical coupling, *Geophys. Res. Lett.*, *32*, L23813, doi:10.1029/2005GL024323.

Tokarczyk, R., and E. S. Saltzman (2001), Methyl bromide loss rates in surface waters of the North Atlantic Ocean, Caribbean Sea, and eastern Pacific Ocean (8°–45°N), *J. Geophys. Res.*, *106*, 9843–9852.

Tokarczyk, R., K. D. Goodwin, and E. S. Saltzman (2001), Methyl bromide loss rate constants in the North Pacific Ocean, *Geophys. Res. Lett.*, *28*, 4429–4432.

Tokarczyk, R., K. D. Goodwin, and E. S. Saltzman (2003), Methyl chloride and methyl bromide degradation in the Southern Ocean, *Geophys. Res. Lett.*, *30*(15), 1808, doi:10.1029/2003GL017459.

Yang, X., R. A. Cox, N. J. Warwick, J. A. Pyle, G. D. Carver, F. M. O'Connor, and N. H. Savage (2005), Tropospheric bromine chemistry and its impacts on ozone: A model study, *J. Geophys. Res.*, *110*, D23311, doi:10.1029/2005JD006244.

Yokouchi, Y., T. Inagaki, K. Yazawa, T. Tamaru, T. Enomoto, and K. Izumi (2005), Estimates of ratios of anthropogenic halocarbon emissions from Japan based on aircraft monitoring over Sagami Bay, Japan, *J. Geophys. Res.*, *110*, D06301, doi:10.1029/2004JD005320.

Yvon, S. A., and J. H. Butler (1996), An improved estimate of the oceanic lifetime of atmospheric CH_3Br, *Geophys. Res. Lett.*, *23*, 53–56.

Yvon-Lewis, S. A., and J. H. Butler (1997), Potential effect of oceanic biological degradation on the lifetime of atmospheric CH_3Br, *Geophys. Res. Lett.*, *24*, 1227–1230.

Yvon-Lewis, S. A., and J. H. Butler (2002), Effect of oceanic uptake on atmospheric lifetimes of selected trace gases, *J. Geophys. Res.*, *107*(D20), 4414, doi:10.1029/2001JD001267.

Yvon-Lewis, S. A., J. H. Butler, E. S. Saltzman, P. A. Matrai, D. B. King, R. Tokarczyk, R. M. Moore, and J. Zhang (2002), Methyl bromide cycling in a warm-core eddy of the North Atlantic Ocean, *Global Biogeochem. Cycles*, *16*(4), 1141, doi:10.1029/2002GB001898.

Yvon-Lewis, S. A., D. B. King, R. Tokarczyk, K. D. Goodwin, E. S. Saltzman, and J. H. Butler (2004), Methyl bromide and methyl chloride in the Southern Ocean, *J. Geophys. Res.*, *109*, C02008, doi:10.1029/2003JC001809.

M. Aydin, Department of Earth System Science, University of California, Irvine, CA 92697, USA. (maydin@uci.edu)

J. H. Butler, J. W. Elkins, B. D. Hall, and S. A. Montzka, Global Monitoring Division, NOAA Earth System Research Laboratory, 325 Broadway, Boulder, CO 80305, USA. (james.h.butler@noaa.gov; james.w.elkins@noaa.gov; bradley.hall@noaa.gov; stephen.a.montzka@noaa.gov)

D. B. King, Chemistry Department, Drexel University, Philadelphia, PA 19104, USA. (daniel.king@drexel.edu)

J. M. Lobert, Analytical Services, Entegris Inc., Franklin, MA 02038, USA. (science@jurgenlobert.net)

D. J. Mondeel, Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309, USA. (debra.j.mondeel@noaa.gov)

N. J. Warwick, Centre for Atmospheric Science, Chemistry Department, University of Cambridge, Cambridge CB2 1TN, UK. (nicola.warwick@atm.ch.cam.ac.uk)

S. A. Yvon-Lewis, Department of Oceanography, Texas A&M University, College Station, TX 77843, USA. (syvon-lewis@ocean.tamu.edu)