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Bromoform and dibromomethane above the Mauritanian upwelling: Atmospheric distributions and oceanic emissions

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[1] Natural sources of bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2), including oceanic emissions, contribute to stratospheric and tropospheric O_3 depletion. Convective transport over tropical oceans could deliver large amounts of these short-lived organic bromine species to the upper atmosphere. High mixing ratios of atmospheric $CHBr_3$ in air masses from the northwest African coast have been hypothesized to originate from the biologically active Mauritanian upwelling. During a cruise into the upwelling source region in spring 2005 the atmospheric mixing ratios of the brominated compounds $CHBr_3$ and CH_2Br_2 were found to be elevated above the marine background and comparable to measurements in other coastal regions. The shelf waters were identified as a source of both compounds for the atmosphere. The calculated sea-to-air emissions support the hypothesis of a strong upwelling source for reactive organic bromine. However, calculated emissions were not sufficient to explain the elevated concentrations observed in the coastal atmosphere. Other strong sources that could contribute to the large atmospheric mixing ratios previously observed over the Atlantic Ocean must exist within or near West Africa.

1. Introduction

[2] Reactive organohalogens, with atmospheric lifetimes of weeks, are an important halogen source to the troposphere and to the lower stratosphere [*WMO*, 2003; *Salawitch*, 2006]. Short-lived bromine compounds may contribute 20–30% of stratospheric and tropospheric O_3 depletion [*Salawitch et al.*, 2005; *Yang et al.*, 2005] directly, or indirectly by delivering their bromine content as inorganic bromine BrO_x (Br + BrO) to higher altitudes.

[3] Oceanic bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2) with atmospheric lifetimes of 3 weeks and months, respectively, represent, together with the longer-lived methyl bromide (CH_3Br), the largest natural sources for atmospheric organic bromine. Estimates of global oceanic emissions are 1.5–10 Gmol Br ($CHBr_3$) yr^{-1} [*Carpenter and Liss*, 2000; *Quack and Wallace*, 2003; *WMO*, 2003; *Yokouchi et al.*, 2005; *Butler et al.*, 2006] and 0.67–3.5 Gmol Br (CH_2Br_2) yr^{-1} [*WMO*, 2003; *Yokouchi et al.*, 2005; *Butler et al.*, 2006] and 0.78 Gmol Br (CH_3Br) yr^{-1} [*WMO*, 2003]. The larger uncertainties in the $CHBr_3$ emission estimates are due to the short lifetime of this compound. Higher model resolutions and the consideration of elevated concentrations and fluxes in strong source regions [e.g., *Quack and Wallace*, 2003; *Yokouchi et*

al., 2005; *Butler et al.*, 2006] lead to higher estimates. Atmospheric sink calculations, which are based mainly on marine background atmospheric concentrations, lead to lower estimates [*Dvortsov et al.*, 1999; *WMO*, 2003]. Estimates for CH_2Br_2 appear not as variable, likely because of its longer lifetime and hence reduced variability.

[4] Emissions of $CHBr_3$, calculated with the actual wind speeds during the time of measurements, can vary by 4 orders of magnitude between coastal and open ocean waters [*Quack and Wallace*, 2003]: observed fluxes from the open tropical ocean ranged from −100 to 2500 pmol m^{-2} hr^{-1} [*Quack et al.*, 2004]. Emission ratios for CH_2Br_2/$CHBr_3$ have been measured between 0.11–0.25 in coastal regions [*Carpenter et al.*, 2003; *Yokouchi et al.*, 2005] and, on the basis of atmospheric sink estimates, a global emission ratio of 0.29–0.38 has been estimated [*WMO*, 2003].

[5] The observed ratios of the atmospheric mixing ratios of CH_2Br_2/$CHBr_3$ range from 0.15 at coastal sites to 0.5 to 1 over the open oceans, likely reflecting combined effects of strong $CHBr_3$ emissions from coastal macro algae and the longer atmospheric lifetime for CH_2Br_2 [*Carpenter et al.*, 2000; *Yokouchi et al.*, 2005]. Elevated mixing ratios of the compounds have been observed over the tropical Pacific and especially over the eastern Atlantic [*Atlas et al.*, 1993; *Schauffler et al.*, 1999; *Class and Ballschmiter*, 1988; *Quack et al.*, 2004]. A recent study identified oceanic super saturations of $CHBr_3$ in the equatorial Atlantic upwelling, likely linked to elevated $CHBr_3$ concentrations in the deep chlorophyll maximum of the tropical Atlantic. These seem to contribute to higher oceanic emissions and the locally elevated atmospheric concentrations [*Quack et al.*, 2004].

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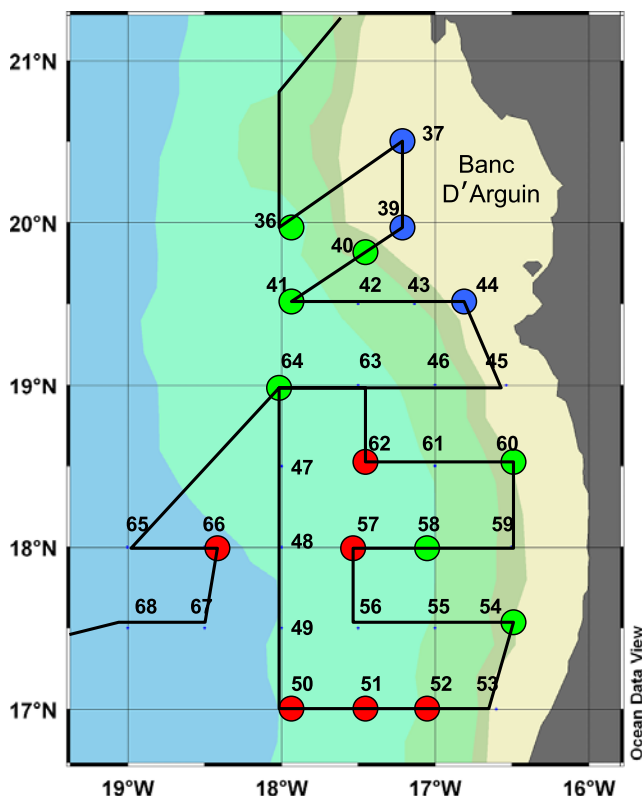
Figure 1. Cruise track and stations of Poseidon cruise 320/1 in the Mauritanian upwelling (March/April 2005). The color code of the stations shows clusters of sea surface temperatures (SST): blue (fresh upwelled, SST: 16.7–18°C), green (aged upwelled, SST: 18°C–21°C), and red (warm nutrient-depleted surface water, SST > 21°C).

[6] The distribution of $CHBr_3$ in the open ocean has generally been linked to the presence of phytoplankton [*Atlas et al.*, 1993; *Baker et al.*, 2000; *Quack et al.*, 2004], while in coastal regions macro algae are considered the most significant source [*Carpenter and Liss*, 2000]. Anthropogenic contamination by industrial or municipal effluents may mask the natural signals in coastal regions [*Quack and Wallace*, 2003]. The spatial and temporal distribution of $CHBr_3$ and its sources for atmosphere and ocean are still poorly understood, and this is even more true for CH_2Br_2. CH_2Br_2 was found to be a by-product during $CHBr_3$ formation in phytoplankton and macro algal cultures [*Tokarczyk and Moore*, 1994; *Manley et al.*, 1992], where it is formed according to the haloform reaction [*Wade*, 1999]. It is also a possible product from $CHBr_3$ during the process of reductive hydrogenolysis [*Vogel et al.*, 1987; *Tanhua et al.*, 1996] where, under anaerobic conditions, the halogen atoms are replaced sequentially by hydrogen atoms.

[7] It was hypothesized in an earlier study [*Quack et al.*, 2004] that regionally enhanced biogenic production in the water column of the northwest African (Mauritanian) upwelling and high sea-to-air fluxes might be responsible for very high atmospheric $CHBr_3$ mixing ratios of 14 to 27 pmol/mol, that were measured over the eastern tropical Atlantic [*Class and Ballschmiter*, 1988; *Quack et al.*, 2004]. In comparison, marine background values of 0.5 and 2 pmol/mol are typical [*Quack and Wallace*, 2003]. In order

to investigate the productive waters of the Mauritanian upwelling as a possible source region of radiatively and chemically active atmospheric trace gases, a cruise was conducted with RV *Poseidon* in March/April 2005.

[8] Here we present atmospheric and oceanic surface measurements of the trace gases bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2) from the Mauritanian shelf waters. In this paper, we describe the regional distributions of both compounds in the atmosphere of the Mauritanian upwelling, estimate their oceanic emissions, and discuss the oceanic contribution to the atmospheric mixing ratios. Data and observations from the water column and discussion of possible sources of the compounds are covered in a separate manuscript (B. Quack et al., Oceanic distribution and sources of bromoform and dibromomethane in the Mauritanian upwelling, submitted to *Journal of Geophysical Research*, 2006).

2. Environmental Conditions of the Study Area

[9] The Mauritanian upwelling is characterized by intense seasonal upwelling during late winter and spring, induced by the northeast trade winds [*Hagen*, 2001]. The upwelling waters of the Mauritanian coast are, in spring, mainly fed by the nutrient rich South Atlantic Central Water from 50 to 300 m depth [*Minas et al.*, 1982]. Low oxygen saturations and low temperatures at the surface reveal the influence of recent upwelling. During the cruise, temperatures (SST) of the sea surface (0 to 6 m) ranged from 16.7 to 22°C (Figure 1) and showed differences in physical, chemical, and biological parameters. Three oceanic surface clusters were distinguished, representing types of freshly upwelled (16.7–18°C), aged upwelled (18–21°C) and warmer nutrient-depleted surface waters (>21°C) (Table 1).

[10] The mean wind direction during the cruise was from the north (5°) and ranged from 320° to 30°, influenced by diurnal land-sea wind circulations of 40–50°. The winds during our investigation, with a mean high wind speed of 9.3 m/s, ranged from 3.4 to 14.4 m/s. Air temperatures ranged from 16.4 to 26.4°C (mean: 19.8°C). Air mass back trajectories (produced with HYSPLIT from the NOAA ARL Web site (http://www.arl.noaa.gov/ready/) revealed that the marine boundary layer air above the upwelling originated from different source regions. Four clusters of similar air mass source regions were identified (Figure 2). They include air masses from the open ocean in cluster A, air masses from the Canary Islands transported along the African Coast in cluster B, air masses from the West Saharan mainland, transported across the Banc D'Arguin in cluster C and from the Mauritanian coast and mainland in cluster D.

3. Method

3.1. Sampling and Analysis

[11] Bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2) were measured in the atmosphere and surface ocean during the cruise P320/1 of RV *Poseidon* from Las Palmas/Canary Islands, 21 March 2005 to Mindelo/Cape Verde Islands, 7 April 2005. Surface water samples along the cruise track were collected from 10 L Niskin bottles, mounted on a 12 bottle CTD rosette package (Figure 1). Nutrients (nitrate, phosphate, silicate) and nitrite were analyzed photometri-

Table 1. Oceanic and Atmospheric Mean Values and Ranges (Min−Max) of Physical and Chemical Variables, Chlorophyll a, of $CHBr_3$ and CH_2Br_2 Saturation Anomalies of the Top 6 m of the Entire Data Set and Three Oceanic Clusters[a]

Parameter	Unit	Entire Data, Mean	Oceanic Cluster		
			Fresh Upwelled 16.7−18°C	Aged Upwelled 18−21°C	Nutrient Depleted > 21°C
Temperature	°C	19.16	17.32 (16.77−17.9)	19.82 (18.23−20.88)	21.28 (20.93−21.77)
Salinity		35.92	36.03 (35.89−36.13)	35.99 (35.79−36.13)	35.99 (35.88−36.11)
Sum chlorophyll a	$\mu g\ L^{-1}$	1.29	3.2 (1.02−11.07)	3.3 (0.07−11.22)	0.8 (0.49−1.39)
Oxygen saturation	%	98.9	68.7 (56.7−84.7)	108.5 (92.2−114.8)	107.7 (105.0−112.5)
Nitrite	$\mu mol\ L^{-1}$	0.5	0.78 (0.49−1.28)	0.36 (0.10−0.80)	0.11 (0.01−0.23)
Nitrate	$\mu mol\ L^{-1}$	6.15	15.51 (14.40−17.16)	2.35 (0.02−7.91)	0.54 (0.04−1.14)
Phosphate	$\mu mol\ L^{-1}$	0.55	1.19 (1.10−1.27)	0.32 (0.14−0.66)	0.18 (0.11−0.26)
Silicate	$\mu mol\ L^{-1}$	3.32	9.60 (5.92−16.71)	0.91 (0.18−4.85)	0.59 (0.38−0.78)
Wind direction	°	6	14 (344−43)	5 (316−55)	5 (330−30)
Wind speed	m/s	9.3	9.2 (4.7−13.2)	9.8 (3.6−14.4)	7.8 (3.4−13.5)
Air temperature	°C	19.8	18.9 (16.4−21.1)	19.7 (16.7−24.4)	21.6 (18.7−26.4)
Humidity	%	84.5	88 (75−100)	85 (57−98)	80 (49−96)
CH_2Br_2 in water (Kiel/RSMAS)	$pmol\ L^{-1}$	4.9	5.1 (3.5−6.8)	4.1 (3.1−7.1)	5.2 (3.2−6.3)
$CHBr_3$ in water (Kiel)	$pmol\ L^{-1}$	12.5	9.5 (5.2−12.1)	11.6 (5.2−32.0)	13.3 (9.9−16.6)
CH_2Br_2 in air (Kiel/RSMAS)	$pmol\ mol^{-1}$	2.4	2.4 (1.75−3.44)	2.4 (1.75−3.44)	2.4 (1.75−3.44)
$CHBr_3$ in air (RSMAS)	$pmol\ mol^{-1}$	6.2	6.2 (3.11−11.84)	6.2 (3.11−11.84)	6.2 (3.11−11.84)
CH_2Br_2 saturation anomaly	%	68 (−30−340)			
$CHBr_3$ saturation anomaly[b]	%	165 (−60−1670)			

[a]Oceanic clusters are fresh upwelled (SST: 16.7−18°C), aged upwelled (SST: 18°C−21°C), and warm nutrient-depleted surface waters (SST > 21°C) during Poseidon 320/1. (Kiel; RSMAS) denotes the respective calibration scale.

[b]$CHBr_3$ saturation anomaly was calculated for the recalibrated values (water (Kiel calibration) plus air (RSMAS calibration × 0.4): water (Kiel calibration × 2.5) plus air (RSMAS calibration)).

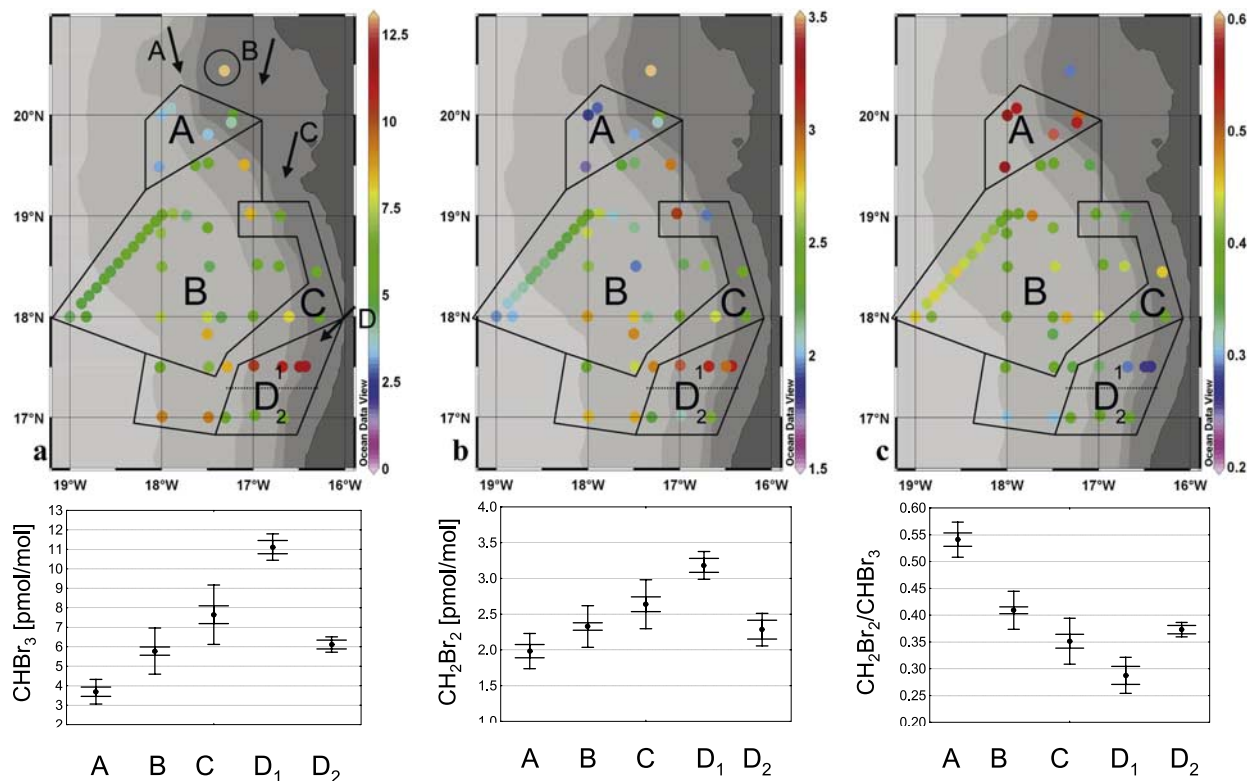**Figure 2.** Individual atmospheric mixing ratios of (a) $CHBr_3$, (b) CH_2Br_2, and (c) the ratio $CH_2Br_2/CHBr_3$ in the Mauritanian upwelling in March/April 2005. The samples were clustered (A−$D_{1,2}$) according to typical air mass back trajectories, of which one representative (arrows A−D) aims at the respective cluster. Circled point in Figure 2a marks an outlier with exceptional elevated mixing ratios (details are discussed in the text) of $CHBr_3$ and CH_2Br_2. Means and ranges of the clusters are shown with their standard deviation in the box whisker plots below the maps.

Table 2. Atmospheric Mixing Ratios of $CHBr_3$ and CH_2Br_2 in the Mauritanian Upwelling (Mean, Standard Deviation, and Ranges) and the Atmospheric Ratio of CH_2Br_2 and $CHBr_3$ of the Five Air Sample Clusters A−$D_{1,2}$[a]

Parameter	Unit	Atmospheric Cluster A	Atmospheric Cluster B	Atmospheric Cluster C	Atmospheric Cluster D_1	Atmospheric Cluster D_2
CH_2Br_2, mean	ppt	1.98	2.33	2.64	3.18	2.28
CH_2Br_2, (min−max)		(1.75−2.49)	(1.94−2.91)	(2.67−3.08)	(2.97−3.44)	(2.07−2.53)
CH_2Br_2, stdv of mean	%	13	23	12	18	12
$CHBr_3$, mean	ppt	3.69	5.78	7.65	11.12	6.11
$CHBr_3$, (min−max)		(3.11−5.04)	(4.22−8.51)	(5.27−9.22)	(10.27−11.84)	(5.79−6.55)
$CHBr_3$, stdv of mean	%	25	38	21	16	6
$CH_2Br_2/CHBr_3$, mean		0.54	0.40	0.35	0.29	0.37

[a]See Figure 3 and text for details.

cally in an autoanalyzer [*Grasshoff et al.*, 1999, pp. 159–228] and oxygen was analyzed according to the method of Winkler [*Grasshoff et al.*, 1999, pp. 75–89].

[12] Halocarbons in the water samples were analyzed on board, using a purge and trap multidimensional GC/MS analytical system. Samples of air (4−7 l) were also analyzed on board with the same GC/MS system. Marine air was continuously pumped through a Teflon Line (50−70 L min^{-1}) from the bow, while a subsample of 30−40 ml min^{-1} was sucked with a micro pump onto the cooled (−50 to −70°C) absorbent. The bromocarbons were quantified with volumetrically prepared standards in methanol in single ion mode. More details of the analytical system are described by *Quack et al.* [2004].

[13] Additionally 56 air samples were pressurized to about 200 kPa in precleaned stainless steel canisters (2.6 L) and were analyzed for volatile organics at the Rosenstiel School for Marine and Atmospheric Sciences (RSMAS) in August 2005 by the method according to *Schauffler et al.* [1999].

3.2. Intercalibration and Flux Calculations

[14] Intercalibration of the on board analysis and the air canister analysis was performed with a natural air standard, obtained from the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL, Boulder, Colorado, United States). Analysis of this standard, on a limited number of samples, gave reasonably good agreements between the NOAA, RSMAS, and Kiel calibration methods for CH_2Br_2: 0.60, 0.84, 0.56 and $CHBr_3$: 0.35, 0.51, 0.55 pmol/mol, respectively.

[15] Additionally the atmospheric mixing ratios were intercompared by parallel sampling of canisters and the on board system (15 samples). In spite of an apparent difference in comparing the NOAA standard mixture, the atmospheric data were in better than 5% agreement between the RSMAS and Kiel calibrations for CH_2Br_2; however in spite of the apparent good agreement in the NOAA standard comparison, the onboard measurements of $CHBr_3$ showed good correlation, but systematically lower mixing ratios (Kiel air = RSMAS air × 0.4). The results suggest that each analytical system provides internally consistent measurements, but consistency between analytical results requires an adjustment to the respective calibration scales of the Kiel and RSMAS data. The interpretation of the individual observations in the atmosphere is unaffected by the differences in the calibration scale; however the cali-

bration offset is important for the flux calculations, which are dependent on the concentration differences between air and water.

[16] At this point, we cannot decide what causes the differences between the calibration methods for $CHBr_3$ between the laboratories. For consistency of the data, we decided to use the same calibration scale for air and water measurements for the flux calculation, and report the fluxes for both calibration scales. Thus we report the saturation anomalies and fluxes for $CHBr_3$; (1) with the Kiel calibration scale (Kiel water measurements and RSMAS air × 0.4) and (2) with the RSMAS calibration scale (Kiel water measurements × 2.5 and RSMAS air). Application of these two calibrations yields a range of fluxes, which is the best we can obtain from the data. This calibration-scale difference affects the absolute fluxes (∼ factor of 2.5). However, this level of uncertainty does not impact our major findings and conclusions. To reduce uncertainties in future studies, laboratories measuring $CHBr_3$ in ocean water and air should work on a common calibration scale for this compound [*Butler et al.*, 2006]. In the presentation to follow, we report air and water concentrations of $CHBr_3$ on their individual calibration scales (RSMAS and Kiel, respectively) but show the effect of calibration differences on the flux calculation.

[17] The fluxes of the brominated halocarbons $CHBr_3$ and CH_2Br_2 across the air−sea interface were calculated according to the parameterization of *Nightingale et al.* [2000]. The transfer velocity of the brominated compounds was adapted according to the Schmidt numbers for both compounds according to the method for $CHBr_3$ [*Quack and Wallace*, 2003]. Oceanic saturation anomalies were determined using the Henry's law constants of *Moore et al.* [1995].

4. Results and Discussion

4.1. $CHBr_3$ and CH_2Br_2 Distribution in the Atmosphere

[18] The mean atmospheric mixing ratio of $CHBr_3$ above the Mauritanian upwelling of 6.2 pmol/mol (range: 3.1–11.8 pmol/mol) was higher than the typical marine background levels (0.5 and 2 pmol/mol, *Quack and Wallace* [2003]). Four clusters of similar air mass source regions were identified, that brought different atmospheric mixing ratios to the ship (Figure 2 and Table 2). Air masses from the open ocean contained mixing ratios of 3.1−5.0 (mean: 3.7) pmol/mol (cluster A), a range of 4.2−8.5 (mean: 5.8) (cluster B) coincided with trajectories from the Canary
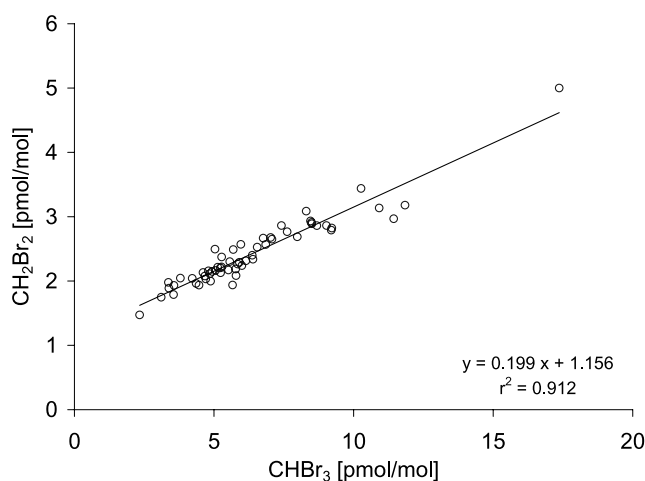
Figure 3. Atmospheric mixing ratio (pmol/mol) of CH_2Br_2 versus $CHBr_3$ during Poseidon cruise P320/1 above the Mauritanian upwelling in March/April 2005. Regression line indicates how the CH_2Br_2 mixing ratio (y) is related to the $CHBr_3$ mixing ratio (x).

Islands along the African coast and trajectories from the Banc D'Arguin area further increased the mixing ratios to 5.3–9.2 (mean: 7.6) pmol/mol (cluster C). The $CHBr_3$ mixing ratios therefore increased with increasing continental or coastal influence.

[19] The highest mixing ratios with a mean of 11.1 (10.3–11.8) pmol/mol were encountered in air masses, which had recently passed the coast close to the largest Mauritanian salt pan (Sebkha de Ndrhamcha) and the city of Nouakchott (cluster D_1). Further offshore the emissions from these source regions appeared to have been diluted to a mean mixing ratio of 6.1 (5.8–6.5) pmol/mol (cluster D_2). While other anthropogenic hydrocarbons or halocarbons were not elevated in these air masses (E. Atlas, unpublished data, 2005), an coincident increase of alkyl nitrates, having oceanic sources [*Atlas et al.*, 1993], suggests that $CHBr_3$ may indeed be produced in and emitted from coastal waters.

[20] One exceptional atmospheric sample, with back trajectories from the West Saharan coast (Figure 2, northernmost point, circled), had an elevated concentration of 17.3 pmol/mol $CHBr_3$. Only this one sample was in the range that we had expected to generally encounter in this region. On the basis of earlier observations of 14 and 27.2 pmol/mol further offshore [*Class and Ballschmiter*, 1988, *Quack et al.*, 2004], we generally expected mixing ratios > 20 pmol/mol over the upwelling, which could even after dilution contribute to the elevated atmospheric mixing ratios. Although interesting for speculating on possible sources, this mixing ratio was not considered further in the calculations, since it was north of the area of the oceanic investigations and was clearly an outlier from our data set.

[21] The CH_2Br_2 atmospheric distribution showed a tightly correlated pattern with $CHBr_3$ ($r^2 = 0.912$, Figures 3 and 2) and also a mean higher mixing ratio of 2.4 pmol/mol (1.8–3.4 pmol/mol), compared to typical marine background values of 0.3 to 1 pmol/mol [*Carpenter et al.*, 2003; *Yokouchi et al.*, 2005]. The smaller standard

deviation of CH_2Br_2 compared to $CHBr_3$ (Table 2) likely reflects the longer lifetime of CH_2Br_2 and possibly also a larger source variability of $CHBr_3$ in the region [*WMO*, 2003]. The elevated atmospheric mixing ratios for $CHBr_3$ and for CH_2Br_2 represented 23.4 (12.8–45.7) pmol/mol of reactive bromine from the two compounds.

[22] The observed ratio between the atmospheric mixing ratios of $CH_2Br_2/CHBr_3$ is between 0.29 and 0.59 (Figure 2 and Table 2) over the Mauritanian upwelling. These values fall between the range of 0.15 observed at coastal sites and 0.5 to 1 observed over the open oceans during earlier studies [*Carpenter et al.*, 2003; *Yokouchi et al.*, 2005]. The ratio $CH_2Br_2/CHBr_3$ is largest in air masses originating from the open ocean (mean: 0.59 in cluster A; Figure 2c and Table 2), reflecting the longer lifetime of CH_2Br_2 and/or larger emissions of this compound from the open ocean, while the lower $CH_2Br_2/CHBr_3$ ratio (mean: 0.29 in cluster D_1; Figure 2c and Table 2) close to the coast reveals an influence of increased local $CHBr_3$ emissions on the atmospheric composition.

[23] On one occasion a steady decline of $CHBr_3$ and CH_2Br_2 during day time was detected during a period with constant wind direction and strength (trajectories from the north) in the west of the upwelling (Figure 4). The data showed a decrease of both compounds from predawn to sunset, from 6.3 to 4.3 pmol/mol (30%) for $CHBr_3$ and from 2.3 to 2.0 pmol/mol (16%) for CH_2Br_2, which is in the range of the standard deviations of the overall air measurements. The ratio between both compounds also increased during the day from 0.36 in the early morning to 0.45 in the late afternoon. This complete changeover to marine background air (Cluster A in Table 1) can be caused by an uplift of the atmospheric boundary layer during day time or by the land-sea wind circulation, shifting the wind direction to the open ocean in the afternoon. Both processes would weaken the influence of local sources, and increase the proportion of aged air masses either from the higher troposphere or the open ocean. A general correlation between the time of day and the atmospheric distributions throughout the cruise could not be verified however, revealing the complex influence of mixing, advection, local air-sea exchange, and coastal sources on the atmospheric mixing ratios.

4.2. Oceanic Surface Distributions of $CHBr_3$ and CH_2Br_2 in the Mauritanian Upwelling

[24] Concentrations within the upper 6 m water column in the Mauritanian upwelling ranged from 5.2 to 32.0 pmol L^{-1} for $CHBr_3$ and from 3.1 to 7.1 pmol L^{-1} for CH_2Br_2 (Table 1). These represent open ocean concentrations, which have been observed to be around 1 to 30 pmol L^{-1} [*Quack and Wallace*, 2003; *Moore and Tokarczyk*, 1993]. The distributions of $CHBr_3$ and CH_2Br_2 in these near surface waters were very patchy (Figures 5a and 5b). Areas of enhanced concentrations of $CHBr_3$ were found close to the Banc D'Arguin, accompanied by low CH_2Br_2 concentrations, and also in the southwest of the investigated area. Generally $CHBr_3$ concentrations were lowest along the coast, coinciding with the most intense upwelling, and the concentrations increased toward the open ocean and warmer waters. The geographic $CHBr_3$ distribution in the surface ocean was, in a general sense, opposite to the atmospheric distribution (Figures 2a and 5a). The concentrations of
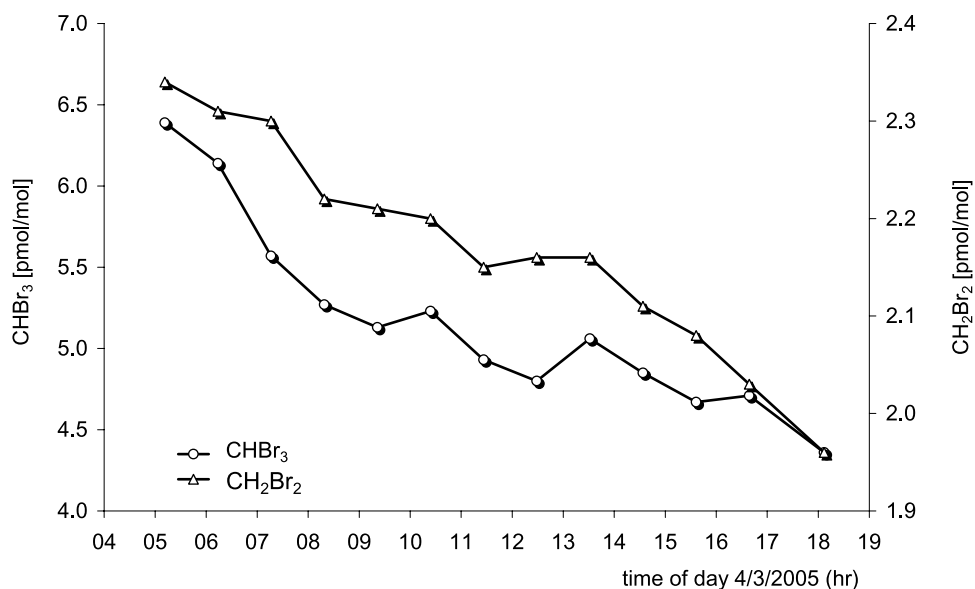
Figure 4. CHBr$_3$ and CH$_2$Br$_2$ atmospheric mixing ratio (pmol/mol) during Poseidon cruise P320/1 above the Mauritanian upwelling on the transect between 19°N 18°W to 18°N 19°W (see Figure 1) versus daytime of 3 April 2005 (transect day).

CH$_2$Br$_2$ were not significantly different among the surface water clusters (Table 1). The concentration ratio CH$_2$Br$_2$/CHBr$_3$ ranged from 0.2 to 0.9 and increased toward the east, and the coastal area of the most intense upwelling (Figure 5c). The mean CH$_2$Br$_2$/CHBr$_3$ ratio of 0.4 is higher than that of typical values between 0.1 to 0.2, which have often been encountered in other coastal and source areas [*Carpenter et al.*, 2003; *Moore and Tokarczyk*, 1993; *Reifenhäuser and Heumann*, 1992; *Schall and Heumann*, 1993].

4.3. Saturation Conditions and Air-Sea Fluxes of CHBr$_3$ and CH$_2$Br$_2$ in the Mauritanian Upwelling

[25] In order to account for the different timescales of atmospheric and oceanic variability and the resulting variability of the air-sea fluxes, a range of possible fluxes was calculated with the saturation anomalies, obtained from all combinations of the measured atmospheric mixing ratios and water concentrations, together with the range of calculated transfer coefficients from hourly mean wind speeds. The results are shown as frequency distributions of the possible air-sea fluxes above the Mauritanian upwelling (Figure 6).

[26] The large variability in the atmospheric and oceanic concentrations of CHBr$_3$ drives varying saturations of the gas in the Mauritanian upwelling (Table 1). The temperature effect on the saturation between the cold freshly upwelled water (SST: 17°C) and the warmer nutrient-depleted surface water (SST: 22°C) contributes about 30% for CH$_2$Br$_2$ and 40% for CHBr$_3$ to the overall variations of 400% for CH$_2$Br$_2$ and 1800% for CHBr$_3$ (Table 1). CHBr$_3$ was occasionally
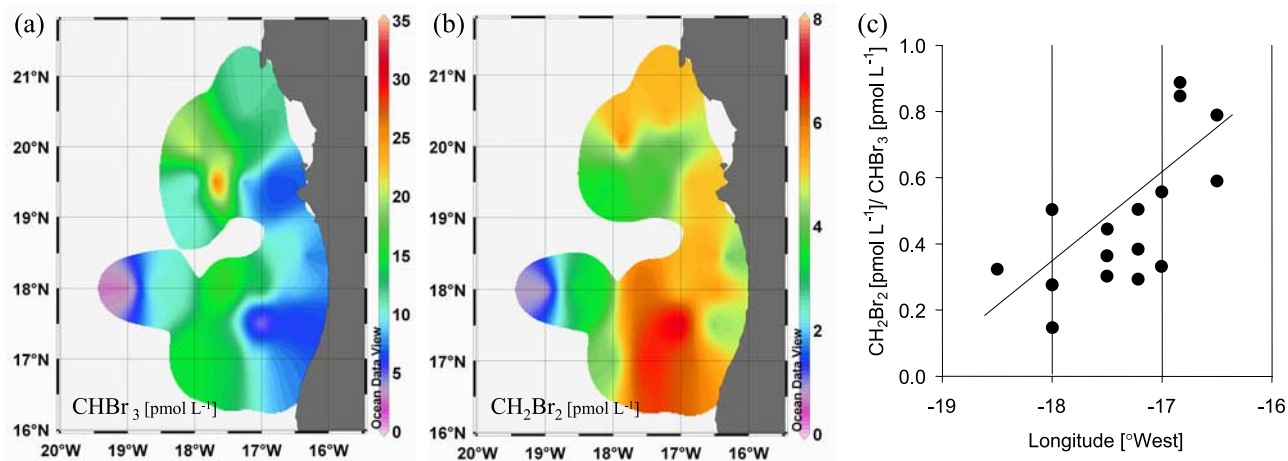

Figure 5. Distribution of (a) CHBr$_3$ and (b) CH$_2$Br$_2$ in the upper 6 m of the Mauritanian upwelling in March/April 2005. (c) The molar ratio CH$_2$Br$_2$/CHBr$_3$ of the top 6 m of the water column versus degrees longitude. The regression (r^2 = 0.47) is significant at the 95% level.

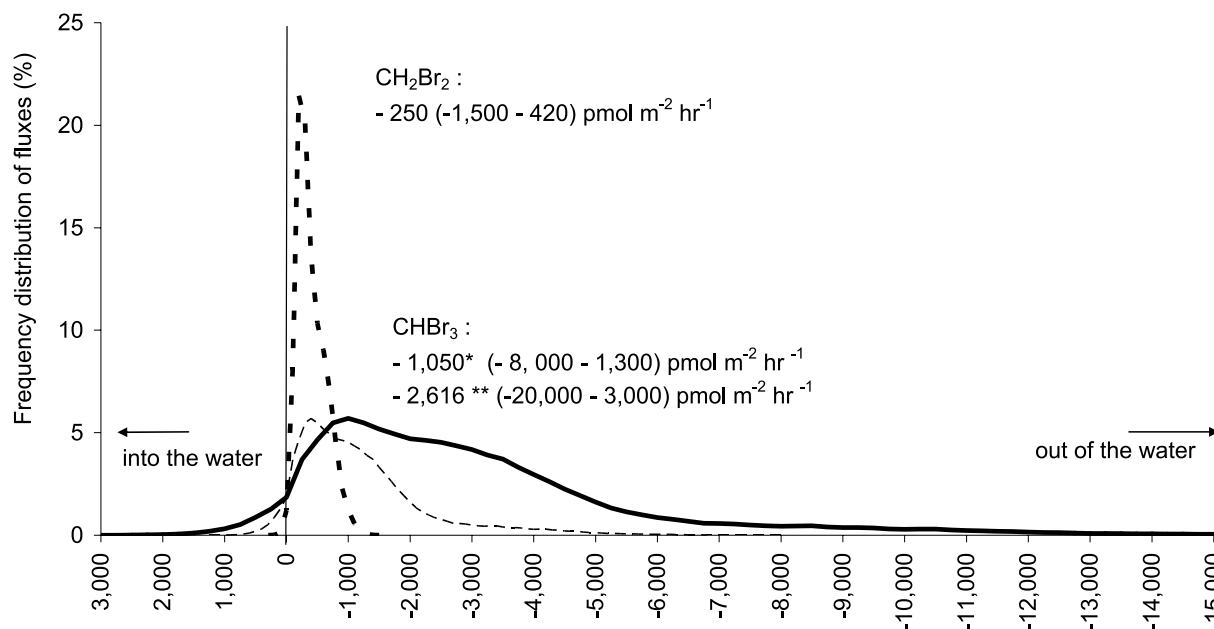**Figure 6.** Frequency distribution of possible air-sea fluxes of $CHBr_3$ (100 pmol m^{-2} hr^{-1} intervals (thin dashed line); 250 pmol m^{-2} hr^{-1} intervals (thick solid line)) and CH_2Br_2 (100 pmol m^{-2} hr^{-1} intervals) (thick dashed line). The fluxes were calculated with all combinations of observed water concentrations, atmospheric mixing ratios, and the hourly transfer coefficients. The fluxes for $CHBr_3$ were calculated with the calibration scale of Kiel (marked with one asterisk) and with the calibration scale of RSMAS (marked with two asterisks).

undersaturated in the upwelling region, especially in freshly upwelled waters close to the coast.

[27] The air-sea fluxes for $CHBr_3$ were calculated in two ways to account for the possible calibration differences between measurements in air and water as described earlier. The water measurements (Kiel scale) were multiplied by 2.5 and combined with the RSMAS air measurements to obtain one estimate of the air-sea flux. Alternately, the RSMAS air measurements were multiplied by 0.4 to compare to the water measurements based on the Kiel scale. The flux calculations from the latter method are shown in parentheses. The calculated fluxes show a large range from 3320 (1330) pmol m^{-2} hr^{-1} (into the ocean) to $-19,890$ (-7950) pmol m^{-2} hr^{-1} (out of the ocean) (Figure 6). For CH_2Br_2 the range extends from 420 pmol m^{-2} hr^{-1} (into the ocean) to -1500 pmol m^{-2} hr^{-1} (out of the ocean) (Figure 6). The frequency distributions of the possible fluxes show the larger variability of the air-sea exchange of $CHBr_3$ compared to CH_2Br_2. More than 90% of the $CHBr_3$ and CH_2Br_2 fluxes represent oceanic emissions (Figure 6).

[28] The overall net flux of 2620 (1050) pmol m^{-2} hr^{-1} for $CHBr_3$ is significant and is of the same magnitude as the flux from the equatorial tropical Atlantic in October/November 2002 [*Quack and Wallace*, 2003]. CH_2Br_2 shows a lower mean flux of 250 pmol m^{-2} hr^{-1} from the upwelling region. The emission ratio $CH_2Br_2/CHBr_3$ of the compounds therefore is 0.1 (0.25) for the entire data set. This is in the same range of previously reported emission rates of 0.11–0.25 from coastal regions [*Carpenter et al.*, 2003; *Yokouchi et al.*, 2005] and smaller than the estimate of 0.29–0.38 for the global ocean, derived from

atmospheric sink values [*WMO*, 2003]. The Mauritanian upwelling at this time of year is a strong source of both $CHBr_3$ and CH_2Br_2 for the atmosphere. However, despite the relatively large emissions from the ocean, the calculated rates are not sufficient to fully explain the observed atmospheric mixing ratios. This is discussed in the next section.

4.4. Possible Contribution of the Air-Sea Fluxes to the Atmospheric Mixing Ratios

[29] The maximum residence time of air was 10–12 hours over the Mauritanian upwelling (average wind speed: 9.2 m s^{-1}) and the marine boundary layer height was constant at about 250 m, according to the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model. We, however, believe that a mean boundary layer of 500–1000 m is more appropriate for this region and the HYSPLIT model output may be biased by the low resolution, relative to the ocean area investigated. A mean flux of 2600 (1000) pmol m^{-2} hr^{-1} of $CHBr_3$ (photochemical lifetime: 21 days) over a 12 hour period into the marine boundary layer of 500 m would increase the atmospheric mixing ratio by $\sim$1.5 (0.6) pmol/mol. A mean flux of 250 pmol m^{-2} hr^{-1} CH_2Br_2 (photochemical lifetime: 120 days) by $\sim$0.15 pmol/mol. Because of this short residence time of air over the upwelling region these mean fluxes appear not sufficient to explain the observed range between minimum and maximum mixing ratios for $CHBr_3$ and CH_2Br_2 (Table 2). Hence the hypothesis of *Quack et al.* [2004], that the upwelling waters are the principal source for the high levels of these compounds for the tropical atmosphere off West Africa is not supported by our measurements.

[30] The largest fluxes during the cruise of 15,000–20,000 (5000–8000) pmol m^{-2} hr^{-1} of CHBr$_3$ and 1500 pmol m^{-2} hr^{-1} of CH$_2$Br$_2$ could increase the atmospheric mixing ratio by roughly ~0.8 (0.3) pmol/mol, respectively, ~0.1 pmol/mol throughout the entire boundary layer of 500 m during 1 hour. Since the traveltime of air between, e.g., cluster A and cluster B was 1 to 6 hours, the observed elevations of CHBr$_3$ and CH$_2$Br$_2$ between these clusters (Table 2) could possibly be explained by such extreme oceanic emissions. However, although such very high fluxes could occur, they represent less than 0.5% of the possible air-sea fluxes, which makes this source unlikely.

[31] The elevated mixing ratios in cluster C would require even higher fluxes out of the Banc D'Arguin area because of the short fetch. The largest atmospheric mixing ratios in cluster D imply continuous fluxes of more than 15,000 (5000) pmol m^{-2} hr^{-1} CHBr$_3$ during 4 hours fetch between the Mauritanian coast and the sampling locations. Again, such high fluxes were scarcely observed during our cruise (Figure 6), but even higher fluxes cannot be ruled out for the nearshore area, since macroalgal sources at the coast can increase water concentrations of CHBr$_3$ by several orders of magnitude [*Carpenter and Liss*, 2000; *Quack and Wallace*, 2003]. We unfortunately have no data for the brominated compounds and their production by the macro algae: either from the Mauritanian coast or the Banc D'Arguin area. This makes further speculation impossible.

[32] The single high atmospheric value in the north of the area of investigation (Figure 2) would need continuous oceanic emissions of 30,000 to 50,000 pmol m^{-2} hr^{-1} during 1 day transit time from the source region at the West Saharan coast or higher localized fluxes. These fluxes are impossible to explain with the range of oceanic concentrations encountered.

[33] The observations imply that, although local enhancements of the atmospheric mixing ratios of both compounds (CHBr$_3$ and CH$_2$Br$_2$) may occasionally be explained by strong localized emission from the Mauritanian upwelling surface waters, additional (as yet unknown) coastal sources contribute. The mean oceanic emissions of CH$_2$Br$_2$ from the surface waters of the upwelling region can explain 10–15% of its atmospheric load, while the CHBr$_3$ emissions contribute 10–25%.

5. Summary and Conclusions

[34] Mean oceanic emissions of 1050–2620 pmol m^{-2} hr^{-1} for CHBr$_3$ and 250 pmol m^{-2} hr^{-1} for CH$_2$Br$_2$ support the hypothesis by *Class and Ballschmiter* [1988] and *Quack et al.* [2004] of a strong source for reactive organic bromine from the Mauritanian upwelling region. However, our work also shows that the elevated mixing ratios of CHBr$_3$ in air masses from northwest Africa during those earlier investigations are not dominated by emissions from these biologically active shelf waters. The mean oceanic emissions of CH$_2$Br$_2$ from the surface waters of the upwelling region can explain approximately 10 to 15% of its atmospheric load, while the CHBr$_3$ emissions contribute 10 to 25%. The atmospheric concentrations of CHBr$_3$ and CH$_2$Br$_2$ above the Mauritanian upwelling increase with continental influence. Thus additional strong sources that could contribute to the large atmospheric mixing ratios over the Atlantic Ocean must exist near, or in, West Africa.

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