Oceanic bromoform sources for the tropical atmosphere

B. Quack,[1] E. Atlas,[2,3] G. Petrick,[1] V. Stroud,[2] S. Schauffler,[2] and D. W. R. Wallace[1]

[1]   Oceanic bromoform ($CHBr_3$) is the major source of organic Br to the atmosphere and may be significant for ozone depletion through the contribution of reactive bromine to the upper troposphere and lower stratosphere of the midlatitudes and tropics. We report the first analyses of boundary layer air, surface and deep ocean waters from the tropical Atlantic. The data provide evidence of a source of $CHBr_3$ throughout the tropical open ocean associated with the deep chlorophyll maximum within the tropical thermocline. Equatorial upwelling carries the $CHBr_3$ to the surface, adding to increased concentrations in the equatorial mixed layer and driving oceanic emissions that support locally elevated atmospheric concentrations. In air masses that had crossed the coastal upwelling region off NW Africa even higher atmospheric mixing ratios were measured. The observations suggest a link between climate, wind-driven upwelling, and the supply of Br to the upper atmosphere of the tropics.   INDEX TERMS: 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 4820 Oceanography: Biological and Chemical: Gases; 1635 Global Change: Oceans (4203). **Citation:** 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.

1.   Introduction

[2]   Bromoform ($CHBr_3$) may be a major organic source for atmospheric reactive bromine BrO_x (Br+BrO) [*Quack and Wallace*, 2003]. It might supply the majority of BrO_x to the upper troposphere and lower stratosphere of the midlatitudes and tropics, contributing to ozone depletion events and trends in these regions [*Dvortsov et al.*, 1999; *Sturges et al.*, 2000; *World Meteorological Organization* (*WMO*), 2003]. A synergy between bromine and chlorine [*Lary*, 1996], coupled with increased levels of anthropogenic chlorine, implies that natural bromine sources exert a stronger influence on stratospheric ozone now than in the past. Macroalgae in coastal regions [*Carpenter and Liss*, 2000] and supersaturation of open ocean waters contribute to $CHBr_3$-emissions of order 10 Gmol Br yr^{-1}. Its short atmospheric lifetime of 2–4 weeks and spatial and temporal

variability in production and sea-to-air flux creates a strongly varying atmospheric $CHBr_3$ distribution [*Quack and Wallace*, 2003]. Atmospheric maxima of $CHBr_3$ are observed in the marine boundary layer (MBL) over both the equatorial Pacific and tropical Atlantic and have been assumed to reflect regionally enhanced biogenic production [*Atlas et al.*, 1993; *Class and Ballschmiter*, 1988; *Schauffler et al.*, 1999].

[3]   We present here the first combined data set for $CHBr_3$ from oceanic vertical profiles, surface water and boundary layer air from the tropical Atlantic. The atmospheric distributions are interpreted with air mass trajectories and air-sea flux calculations. Oceanic depth profiles and surface water data were correlated with oceanographic parameters, to investigate the sources and emissions of bromoform.

2.   Measurements and Flux Calculation Method

[4]   Atmospheric and oceanic $CHBr_3$-data were obtained during R/V *Meteor* cruise #55 (M55: Curacao/Netherland Antilles, 12 October to Douala/Cameroon, 17 November 2002). The cruise comprised a trans-Atlantic section from west to east along 10°N together with 2 mid-ocean north-south transects to the equatorial upwelling. The ship's track crossed the western oligotrophic Atlantic, touched the northern edge of the Amazon plume, approached the equatorial upwelling at 26°W, and crossed to mesotrophic coastal waters off Guinea. In the westernmost segments of the cruise track and during the meridional transects the ship encountered air masses from the open ocean, whereas in the eastern Atlantic air masses were encountered that had crossed the NW African upwelling and Canary Islands. We subdivided the 12,000 km cruise track into 9 segments (S1-9) on the basis of these varying regimes (Figure 1).

[5]   Air samples were collected in pressurized stainless steel canisters (34–36 psi) and were analysed for $CHBr_3$ at the National Center for Atmospheric Research (NCAR, Boulder, CO, USA) during February and March, 2003. Procedures involved cryogenic preconcentration and gas chromatography with selective ion mass spectrometric detection [*Schauffler et al.*, 1999]. Surface water samples were collected from a continuous sea water supply provided by a submersible pump at 5 m depth. Deep ocean samples were collected from 10 L Niskin bottles, mounted on a 24-bottle CTD-rosette package. All water samples were analysed on board using a purge-and-trap GC/MS analytical system constructed with all-glass transfer-lines and traps. Volatiles were pre-concentrated from 88 ml of a seawater sample using a purge flow of 40 ml He/min for 20 minutes, which was dried with 2 Nafion® dryers, with the temperature of the sample being ramped during purging from in situ temperature to 70–80°C. The volatiles were focused on Poraplot Q (80–100 mesh) at −70°C, and after thermodesorption separated by capillary gas chroma-

[1]Leibniz-Institut für Meereswissenschaften, Universität Kiel, Kiel, Germany.
[2]National Center for Atmospheric Research, Boulder, Colorado, USA.
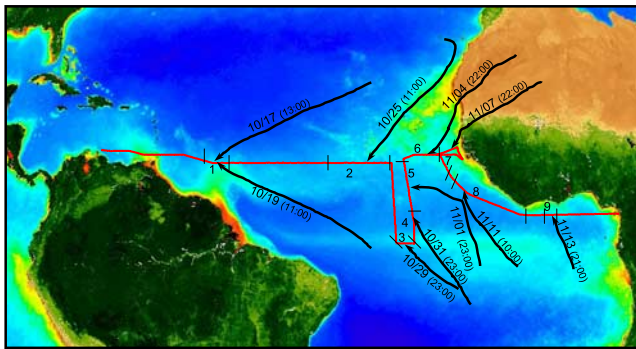[3]Now at Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida, USA.

Figure 1. Cruise track of R/V Meteor 55 (M55), with 9 subdivided segments (see text), including typical 120h back trajectories (HYSPLIT, http://www.arl.noaa.gov/ready/) with time and date, when the selected trajectory encountered the ship's track. The cruise track is superimposed on a map of SeaWiFS boreal autumn chlorophyll a (integrated data from 21 September–20 December of 1997 to 2001, http://seawifs.gsfc.nasa.gov).

tography (RTX®-VGC column, 0.25 mm, 0.15 μm, 60 m) with detection by mass spectrometry (Finnigan Trace MS) operated in selective ion mode. Quantification of $CHBr_3$ was performed with gravimetrically prepared external standards diluted in ultra pure water. Air and seawater measurements were intercalibrated. Uncertainties include an estimated deviation of the air and sea water standards of 10% and the analytical precisions of <15% for the air and the sea water measurements. Location of the chlorophyll maximum was determined from the fluorescence profile of a multi-channel fluorescence probe and by pigment-analysis of depth samples, using a modified method of Barlow [*Barlow et al.*, 1997].

[6] The available air-sea exchange parameterisations result in air-sea fluxes that can differ by a factor of two. We used Wanninkhof's parameterization of the wind speed related gas transfer coefficient, adapted to $CHBr_3$ [*Quack and Wallace*, 2003; *Wanninkhof*, 1992] and the Henry's Law constant of Moore and co-workers [*Moore et al.*, 1995a] for the flux-calculations. Fluxes were calculated from the measured sea surface concentration, local atmospheric mixing ratios and the instantaneous windspeed (1hour means), as well as from segment means. Flux-ranges, given in the text, are based on the above uncertainties.

3. Results and Discussion

[7] Atmospheric mixing ratios ranged from 0.5 to 27.2 pptv $CHBr_3$ (Figure 2a). Mixing ratios of $CHBr_3$ were strongly correlated with air mass back trajectories, with low levels measured during Northeastern Trades (S1: 0.5 to 1.0 pptv) and Southeastern Trades (S8, 9: 0.9 to 2.0 pptv) that had crossed over the open ocean. At the equator, atmospheric mixing ratios increased to 2.4–4.4 pptv (S3, 4), similar to the elevated levels (3 pptv) observed over the equatorial Pacific [*Atlas et al.*, 1993; *Schauffler et al.*, 1999]. Northeastern Trades that had passed over or close to West Africa also contained elevated mixing ratios over the open ocean (S2: >3 pptv) reaching >6 pptv at the eastern end of the section (S6, 7). An extremely high level of

25 pptv was analysed at 10°N 19.5°W, which is comparable to 15 pptv measured in 1984 at the same location [*Class and Ballschmiter*, 1988].

[8] Additional bromine contributions to the MBL include 2–6 ppt of inorganic Br on aerosol [personal communication A. Baker, 2003], 1–2 ppt Br in the form of inorganic gaseous bromine species [*Wamsley et al.*, 1998], 14–15 pptv Br from long-lived organic bromine compounds [*Montzka et al.*, 2003], and 1–4 pptv Br carried by other short-lived organics (eg. CH_2Br_2, $CHBr_2Cl$). $CHBr_3$, which shows the largest range in concentration, therefore contributes 7–80% (mean: 26%) of the total bromine in the MBL of the tropical Atlantic.

[9] Sea surface concentrations of $CHBr_3$ also varied strongly along the cruise track, ranging from 1.4 to 14 pmol L^{-1}. Elevated concentrations (8 to 14 pmol L^{-1}) were measured in equatorial surface waters (S3) where the temperature structure showed evidence of upwelling (Figure 2b). Elevated concentrations (>10 pmol L^{-1}) were also encountered in waters influenced by the Amazon plume (S1) and in shelf waters off Africa (S9). $CHBr_3$ concentrations showed a strong local inverse correlation with sea surface temperature (SST) close to the equator (Figure 3).

[10] Overall, the tropical Atlantic Ocean was a source of $CHBr_3$ for the atmosphere, with a mean flux of 400 (±130) pmol $CHBr_3$ m^{-2} hr^{-1}. The flux distribution was highly non-uniform however, ranging from 1,100 (±330) pmol
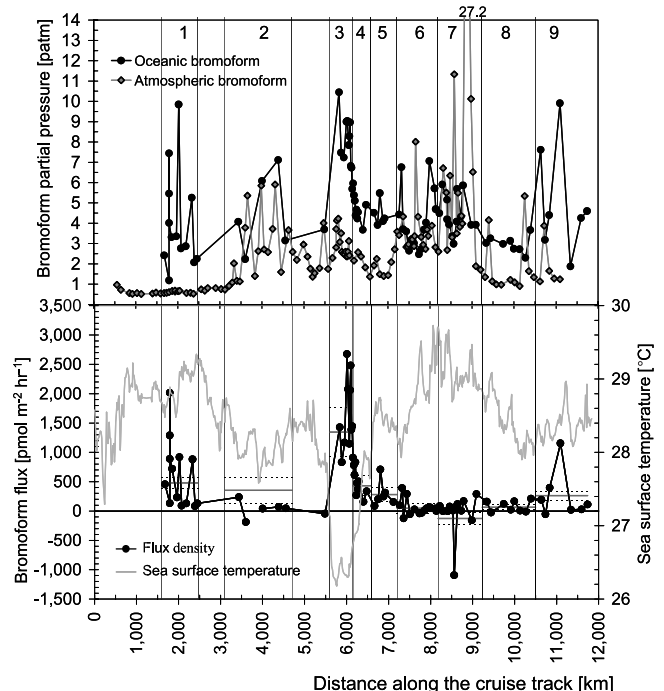

Figure 2. (a) Partial pressure of $CHBr_3$ in the atmosphere and surface ocean waters as a function of distance along the M55 cruise track, with the 9 cruise segments shown in Figure 1. (b) Instantaneous air-sea fluxes of $CHBr_3$ for individual atmospheric and oceanic sample pairs are shown superimposed on the sea surface temperature distribution. The grey horizontal lines show air-sea fluxes calculated from the mean atmospheric and oceanic $CHBr_3$ concentrations, wind speed and SST of each cruise track segment. The dashed lines indicate the errors of the mean flux.

$CHBr_3$ m^{-2} hr^{-1} into the ocean in the eastern Atlantic (S6, 7) to 2,700 ($\pm$800) pmol $CHBr_3$ m^{-2} hr^{-1} out of the ocean in the equatorial region (S3) (Figure 2b). A few 'hotspots' (<20% of the cruise track) contributed 70% of the total oceanic emissions.

[11] In order to gauge the contribution of local fluxes to the observed mixing ratios in the MBL, we calculated ratios of mean oceanic supply to atmospheric losses for the 9 segments of the cruise track (S1-9; Table 1). We assumed a lifetime of two weeks for $CHBr_3$ with respect to photo-oxidation [*Moortgat*, 1993], a background of 0.7 pptv $CHBr_3$, a mean MBL-height of 1000 m and a net flux of 350 mol air m^{-2} hr^{-1} out of the MBL. The latter is the annual mean vertical uplift of air between 15°N and 15°S [*WMO*, 2003]. The resulting balance between oceanic supply and atmospheric loss was highly variable. In the Amazon plume (S1), oceanic emissions were 5-fold higher than estimated losses. At the equator (S3, 4), oceanic emissions were sufficient to maintain the elevated atmospheric mixing ratios. In other segments of the cruise track (e.g., S2, S4-6, S8) the ocean could locally support only 3 to 55% of the atmospheric losses, and in the region with the highest air concentrations (S 7) the local ocean was a net sink for atmospheric $CHBr_3$ (Table 1). Hence, emissions from the open ocean are significant for the MBL in localized regions, but there are major non-local sources supplying $CHBr_3$, particularly to the air masses that cross the NW African upwelling and Canary Islands regions.

[12] $CHBr_3$ was found throughout the water column, from the surface to 5,000 m, at background concentrations ranging from 2 to 4 pmol L^{-1}. Much higher concentrations (14 to 60 pmol $CHBr_3$ L^{-1}) were encountered consistently between 30 and 80 m (Figure 4). This maximum lay beneath the mixed layer, within the top of the thermocline, and was closely associated with the subsurface chlorophyll maximum, indicating a local biological source. An exceptionally high concentration of approx. 4 nmol L^{-1} was measured at a depth of 40 m underneath the Amazon plume, at the interface of the low-salinity waters and more typical tropical ocean waters.

[13] Enhanced $CHBr_3$ concentrations in open ocean surface waters have generally been associated with the abundance of diatoms [*Baker et al.*, 1999; *Klick and Abrahamsson*, 1992], which have been shown to produce $CHBr_3$ in the laboratory [*Tokarczyk and Moore*, 1994]. A

Table 1. Rate of Oceanic Supply Versus Atmospheric Loss of $CHBr_3$ During M 55[a]

Segment	Position	Supply/Loss [%]
1	10°N, 53.7°W – 10°N, 49.1°W	633
2	10°N, 37.7°W – 10°N, 27.5°W	30
3	0.0°N, 25.4°W – 0.5°N, 23.5°W	116
4	0.7°N, 23.5°W – 3.7°N, 23.7°W	55
5	5.3°N, 24.0°W – 10°N, 24.7°W	45
6	10.5°N, 24.4°W – 11.7°N, 17.5°W	3
7	11°N, 17.1°W – 8.4°N, 18.5°W	−4
8	6.7°N, 17.0°W – 3.5°N, 8.1°W	10
9	3.5°N, 5.9°W – 3.7°N, 4.0°W	41

[a]Reported are rates of oceanic supply (mean flux, see Figure 2) versus atmospheric loss of $CHBr_3$ (combined loss due to both in-situ photo-oxidation and uplift out of the boundary layer, see text for details of the loss rate calculations) for the 9 cruise track segments discussed in the text and shown in Figures 1 and 2.

local production of $CHBr_3$ in the tropical thermocline may also correspond to the presence of specific organisms found within the chlorophyll maximum, or can be related to the increased abundance of photosynthetic active pigments, bromoperoxidase activity, the availability of organic substrates for $CHBr_3$ production, to grazing or enhanced microbial activity [*Moore et al.*, 1995b, 1996; *Quack and Wallace*, 2003; *Theiler et al.*, 1978]. The estimated air-sea
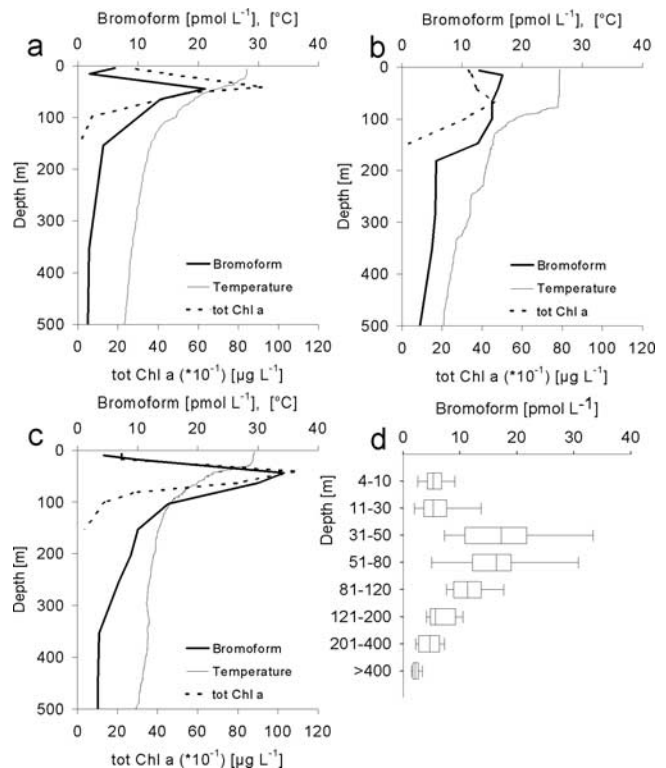
Figure 4. $CHBr_3$ [pmol L^{-1}], water temperature and total chlorophyll a from the upper 500 m water column at (a) 10,00°N, 41,77°W; (b) 0,00°N, 26,0°W; (c) 11,04°N, 17,69°W, showing the maximum of the measured $CHBr_3$ concentration in the thermocline, and the typical tropical deep maximum of chlorophyll a; (d) The box-plot shows the median (middle of box), the 25 and 75% (box-margins) and the 10 and 90% percentiles (outer marks) of $CHBr_3$-concentrations from 25 depth profiles of the tropical Atlantic.
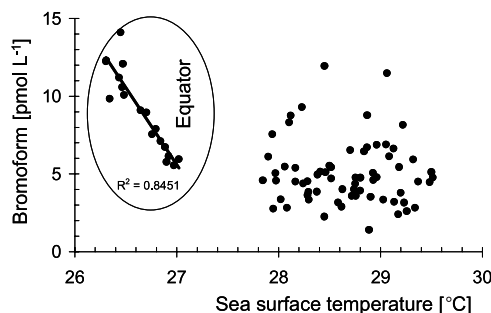

Figure 3. Correlation between sea surface temperature (SST) and $CHBr_3$ concentration [pmol L^{-1}] of surface samples during M55. The strong correlation between SST and $CHBr_3$ in the vicinity of the Equator is separately identified.

flux can be supplied by the flux along the concentration gradient between the subsurface $CHBr_3$ maximum (10 to 25 m below the mixed layer) and the mixed layer (21–50 m), using an eddy diffusion k_z order of $0.1–1$ cm^2 s^{-1} [*Pacanowski and Philander*, 1981], which yields 58–580 (11 to 1840) pmol m^{-2} hr^{-1}. Subsurface production thus seems adequate to supply the oceanic emission, which is supported by the distinct coexistence of the $CHBr_3$ and chlorophyll maxima. Clearly, within the uncertainties of the calculations, we can't rule out production of $CHBr_3$ in the entire euphotic zone, with trapping beneath the mixed layer.

[14] The inverse correlation of SST and surface $CHBr_3$ concentrations near the equator indicates that upwelling entrains elevated subsurface $CHBr_3$ locally into the mixed layer, and may additionally support $CHBr_3$ sources in the mixed layer. Hence, localised upwelling results in elevated atmospheric mixing ratios of $CHBr_3$ by linking subsurface processes directly with the atmosphere. We hypothesise that a similar link between high sea-to-air fluxes and upwelling of subsurface bromoform and surface production in the NW African upwelling is responsible for the very high levels of $CHBr_3$ measured in air masses that had crossed NW African coastal regions (S2, 6, 7).

4.　Conclusions

[15] The results from our expedition contradict certain key assumptions about the marine sources of $CHBr_3$. In the absence of sufficient measurements, modelling studies of the stratospheric supply of Br from $CHBr_3$ have assumed a spatially uniform oceanic source for $CHBr_3$ [*Dvortsov et al.*, 1999; *Nielsen and Douglass*, 2001]. Our data show that the sea-to-air flux is strongly localised, and includes intense emissions in tropical open ocean regions where Br can be transported rapidly to the troposphere-stratosphere boundary. Although coastal macroalgae are undoubtedly important global sources [*Carpenter and Liss*, 2000], our measurements show that there is also widespread production within the open ocean that can support elevated atmospheric $CHBr_3$ levels. Equatorial upwelling connects a subsurface biological production to the supply of Br to the tropical marine atmosphere, by vertical transport from the thermocline and possibly by supporting local production in the mixed layer. Similar pathways may underlie the very high $CHBr_3$ levels measured in air masses that had crossed over the NW African upwelling region. Our findings highlight the possibility that changes in climate and surface winds could contribute to the variability of the supply of Br to the tropical lower stratosphere [*WMO*, 2003] via changes in upwelling intensity [*Bakun*, 1990].

References

Atlas, E., W. Pollock, J. Greenberg, L. Heidt, and A. M. Thompson (1993), Alkyl nitrates, nonmethane hydrocarbons, and halocarbon gases over the equatorial Pacific Ocean during Saga-3, *J. Geophys. Res.*, 98, 16,933–16,947.

Baker, J. M., C. E. Reeves, P. D. Nightingale, S. A. Penkett, S. W. Gibb, and A. D. Hatton (1999), Biological production of methyl bromide in the coastal waters of the North Sea and open ocean of the northeast Atlantic, *Mar. Chem.*, 64, 267–285.

Bakun, A. (1990), Global climate change and intensification of coastal ocean upwelling, *Science*, 247, 198–201.

Barlow, R. G., D. G. Cummings, and S. W. Gibb (1997), Improved resolution of mono- and divinyl chlorophylls a and b and zeaxanthin and lutein in phytoplankton extracts using reverse phase C-8 HPLC, *Mar. Ecol. Prog. Ser.*, 161, 303–307.

Carpenter, L. J., and P. S. Liss (2000), On temperate sources of bromoform and other reactive organic bromine gases, *J. Geophys. Res.*, 105, 20,539–20,547.

Class, T. H., and K. Ballschmiter (1988), Chemistry of organic traces in air: Sources and distribution of bromo- and bromochloromethanes in marine air and surface water of the Atlantic Ocean, *J. Atmos. Chem.*, 6, 35–46.

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.

Klick, S., and K. Abrahamsson (1992), Biogenic volatile iodated hydrocarbons in the ocean, *J. Geophys. Res.*, 97, 12,683–12,687.

Lary, D. J. (1996), Gas phase atmospheric bromine photochemistry, *J. Geophys. Res.*, 101, 1505–1516.

Montzka, S. A., J. H. Butler, B. D. Hall, D. J. Mondeel, and J. W. Elkins (2003), A decline in tropospheric organic bromine, *Geophys. Res. Lett.*, 30(15), 1826, doi:10.1029/2003GL017745.

Moore, R. M., C. E. Geen, and V. K. Tait (1995a), Determination of Henry Law constants for a suite of naturally-occurring halogenated methanes in seawater, *Chemosphere*, 30(6), 1183–1191.

Moore, R. M., R. Tokarczyk, V. K. Tait, M. Poulin, and C. Geen (1995b), Marine phytoplankton as a natural source of volatile organohalogens, in *Naturally-Produced Organohalogens*, edited by A. Grimvall and E. W. B. de Leer, pp. 238–294, Kluwer Acad., Norwell, Mass.

Moore, R. M., M. Webb, R. Tokarczyk, and R. Wever (1996), Bromoperoxidase and iodoperoxidase enzymes and production of halogenated methanes in marine diatom cultures, *J. Geophys. Res.*, 101, 20,899–20,908.

Moortgat, G. K. (1993), Temperature dependence (256–296 K) of the absorption cross-sections of bromoform in the wavelength range 285–360 nm, in *The Tropospheric Chemistry of Ozone in the Polar Regions*, *NATO ASI Ser. I*, 7, 359–370.

Nielsen, J. E., and A. R. Douglass (2001), A simulation of bromoform's contribution to stratospheric bromine, *J. Geophys. Res.*, 106, 8089–8100.

Pacanowski, R. C., and S. G. H. Philander (1981), Parameterization of vertical mixing in numerical models of tropical oceans, *J. Phys. Oceanogr.*, 11, 1443–1451.

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.

Schauffler, S. M., E. L. Atlas, D. R. Blake, F. Flocke, R. A. Lueb, J. M. Lee-Taylor, V. Stroud, and W. Travnicek (1999), Distributions of brominated organic compounds in the troposphere and lower stratosphere, *J. Geophys. Res.*, 104, 21,513–21,535.

Sturges, W. T., D. E. Oram, L. J. Carpenter, and S. A. Penkett (2000), Bromoform as a source of stratospheric bromine, *Geophys. Res. Lett.*, 27, 2081–2084.

Theiler, R., J. C. Cook, and L. P. Hager (1978), Halohydrocarbon synthesis by bromoperoxidase, *Science*, 202, 1094–1096.

Tokarczyk, R., and R. M. Moore (1994), Production of volatile organohalogens by phytoplankton cultures, *Geophys. Res. Lett.*, 21, 285–288.

Wamsley, P. R., et al. (1998), Distribution of halon-1211 in the upper troposphere and lower stratosphere and the 1994 total bromine budget, *J. Geophys. Res.*, 103, 1513–1526.

Wanninkhof, R. (1992), Relationship between wind-speed and gas-exchange over the ocean, *J. Geophys. Res.*, 97, 7373–7382.

World Meteorological Organization (2003), Scientific assessment of ozone depletion: 2002, Global ozone research and monitoring project, *Rep. 47*, 498 pp., Geneva.

————————
　E. Atlas, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL, USA.

　G. Petrick, B. Quack, and D. W. R. Wallace, Leibniz-Institut für Meereswissenschaften, Universität Kiel, Düsternbrooker Weg 20, Kiel D-24145, Germany. (bquack@ifm-geomar.de)

　V. Stroud and S. Schauffler, National Center for Atmospheric Research, Boulder, CO, USA.