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**Air-sea fluxes of
biogenic bromine**

L. J. Carpenter et al.

Air-sea fluxes of biogenic bromine from the tropical and North Atlantic Ocean

L. J. Carpenter¹, C. E. Jones¹, R. M. Dunk^{1,*}, and K. E. Hornsby¹

¹Department of Chemistry, University of York, York, YO10 5DD, UK

*now at: Crichton Carbon Centre, Crichton University Campus, Dumfries, DG1 4ZL, UK

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Correspondence to: L. J. Carpenter (ljc4@york.ac.uk)

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Air-sea fluxes and bulk seawater and atmospheric concentrations of bromoform (CHBr_3) and dibromomethane (CH_2Br_2) were measured during two research cruises in the northeast Atlantic (53–59° N, June–July 2006) and tropical eastern Atlantic Ocean including over the African coastal upwelling system (16–35° N May–June 2007). Saturations and sea-air fluxes of these compounds generally decrease in the order coastal > upwelling > shelf > open ocean, and a broad trend of elevated surface seawater concentrations with high chlorophylla was observed. From limited data from eastern Atlantic coastlines, we tentatively suggest that globally, coastal and coastally-influenced waters together contribute $\sim 2.4 \text{ Gmol Br yr}^{-1}$ (24–56%) of CHBr_3 . We show that upwelling regions (coastal and equatorial) represent regional hot spots of bromocarbons, but are probably not of major significance globally, contributing only a few percent of the total global emissions of CHBr_3 and CH_2Br_2 . We also show that the concentration ratio of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ in seawater is a strong function of concentration (and location), with a lower $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ ratio found in coastal regions near to macroalgal sources.

1 Introduction

Oceanic production of short-lived organic bromine compounds such as CHBr_3 and CH_2Br_2 by phytoplankton and macroalgae has been proposed to represent an important link between ocean biology, atmospheric composition and climate (Carpenter and Liss, 2000; Quack et al., 2004; Yang et al., 2005; Salawitch, 2006). Bromine atoms, released both from photooxidation of organic bromine and, in the marine boundary layer (MBL), from heterogeneous cycling on sea-salt aerosol, enter catalytic ozone destruction cycles and also indirectly lead to a reduction in tropospheric ozone production by suppressing levels of nitrogen oxides (von Glasow and Crutzen, 2007 and references therein). Tropospheric ozone, a key greenhouse gas and air pollutant, may be reduced by 5–30% compared to simulations without bromine (e.g. von Glasow et

Air-sea fluxes of biogenic bromine

L. J. Carpenter et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



al., 2004; Yang et al., 2005). Short-lived halogenated compounds and their oxidation products may also be delivered to the stratosphere through rapid convection from the MBL (Solomon et al., 1994). CHBr_3 represents the single largest source of organic bromine from the ocean to the atmosphere and the contribution of short-lived bromine species, especially CHBr_3 , to total bromine in the lower stratosphere is believed to be around 20–60% (Sturges et al., 2000; Pfeilsticker et al., 2000; Nielson and Douglass, 2001).

Although there have been a number of extensive studies and reviews which have greatly increased our knowledge of biogenic short-lived bromine compounds (Quack and Wallace, 2003; Butler et al., 2007a), there are still uncertainties regarding their global distributions, exacerbated by the spatial variability in their sea-air fluxes. Models (e.g. von Glasow et al., 2004; Yang et al., 2005) assume a variety of parameterisations for oceanic bromine emissions, which require fuller validation by global oceanic measurements. Here we report air-sea fluxes and bulk, simultaneous, seawater and atmospheric concentrations of CHBr_3 and CH_2Br_2 measured during two research cruises in the northeast Atlantic (53–59° N, June–July 2006) and tropical eastern Atlantic including over the northwest African coastal upwelling system (16–40° N, May–June 2007).

2 Methods

Two Perkin Elmer Turbomass GC-MS systems with thermal desorption units (TD, Perkin Elmer) were deployed first onboard the Irish RV Celtic Explorer for the north Atlantic cruise as part of the European Union project MAP (Marine Aerosol Production) and the following year on the UK RV Discovery for the tropical Atlantic project RHaMBLe (Reactive Halogens in the Marine Boundary Layer experiment), funded by the UK SOLAS programme. One instrument was dedicated to online automated air measurements (air measurement every 2–3 h, 24 h/d) and one for purge-and-trap water measurements (water measurement every 2–3 h, ~16 h/d). Air measurements were made at a height of 25 m (MAP) and 8 m (RHaMBLe) above the ocean surface through

Air-sea fluxes of biogenic bromine

L. J. Carpenter et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



a 60 m Teflon PFA sampling manifold at a flow rate of several L min^{-1} . Air was sampled at 100 mL min^{-1} off this line and supplied to the online trapping system using a clean metal bellows pump (Aerospace Ltd.).

Gas-tight syringes (Samco) were used to draw discrete 40 mL seawater samples from a line connected to the ships onboard non-toxic seawater supply, which was allowed to flush for 2 min prior to the sample being drawn. The ships' intakes for the water supply were located at average depths of 2 m for the Celtic Explorer and 6 m for RV Discovery. Water samples were filtered using Minisart $0.45 \mu\text{m}$ cellulose filters, and, while the majority of water samples were analysed immediately, occasionally they were stored in gas-tight syringes (Samco) in the dark at $\sim 1^\circ\text{C}$ and sampled within 12 h. Dissolved trace gases were analysed by injecting into an opaque glass purge-and-trap vessel maintained at 50°C and sparged with $50 \text{ mL min}^{-1} \text{ N}_2$ (Grade 5.0, BOC) for 1 h. Sparging efficiencies were 91% for CH_2Br_2 and 94% for CHBr_3 . For further analytical details see Carpenter et al. (2007) and Wevill and Carpenter (2004).

Calibration of the GC-MS was achieved using a permeation system as described in Wevill and Carpenter (2004). Two glass gas-tight permeation tube holders containing disposable permeation tubes (Ecoscientific) filled with a single pure halocarbon ($>99.9\%$ Sigma Aldrich, verified in-house by mass spectrometry) are each placed in an aluminium block maintained at either 40°C (CH_2Br_2) or 70°C (CHBr_3). The permeation tubes are swept constantly with $50 \text{ mL min}^{-1} \text{ N}_2$ (Grade 5.0, BOC) and into a $10 \mu\text{l}$ sample loop, which is injected into a 100 mL min^{-1} flow of N_2 (Grade 5.0, BOC) to generate low part per trillion (ppt) mixing ratios of halocarbon mixtures. The accuracy of the calibration, which includes errors in the determination of permeation rates, sample loop volume and flow rates, is estimated as $\pm 12\%$. The total uncertainty of the measurements is $\sim \pm 13\%$ for air and $\sim \pm 16\%$ for seawater, with a precision of between 3–8% depending on compound and concentration. Limits of detection are ~ 0.01 – 0.05 ppt in air and 0.02 – $0.06 \text{ pmol dm}^{-3}$ in water. A comparison of our previous CHBr_3 atmospheric measurements at Mace Head and at Cape Grim (1998 and 1999 measurements) compare well to simultaneous observations by NOAA (2004 Scale) (Butler

**Air-sea fluxes of
biogenic bromine**

L. J. Carpenter et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



et al., 2007b). The analytical uncertainty for a sea-air flux calculation (Wanninkhof, 1992), is equivalent to the uncertainty for a water measurement for compounds which are supersaturated in seawater.

3 Results and discussion

3.1 Tropical Atlantic surface seawater and air distributions

The tropical north east Atlantic is characterised by a northeasterly trade wind system that converges into the Inter-Tropical Convergence Zone (ITCZ) from the north. In the ocean, the 1000 km wide and ~500 m deep Canary Current flows southward along the African coast between 30° N (north of Canary islands) and 10° N (south of Cape Verde islands) (Fedoseev, 1970). Within this current, the African coastal upwelling zone, located between approximately 25° N and 10° N and between ~30° W to the northwest African coast, is a year-round feature caused by coastal divergence resulting from the northeasterly wind field, showing a seasonal peak in winter/spring due to movement of the ITCZ (Hagen, 2001). Tomzcak (1980) identified that north of 21° N, the upwelling is fed mainly by the North Atlantic Central Water (NACW) mass, whereas south of 21° N it shows properties similar to the South Atlantic Central Water (SACW). In the region of 15° N, the Canary Current deviates westward under the influence of the Equatorial Countercurrent in document Peterson et al., 1996).

Samples from the RHaMBLe cruise were taken during 22 May – 6 June 2007 along a transect from the Canary Islands to the Cape Verde islands, then directly east towards the coastal upwelling, followed by a zig-zag transect through the upwelling heading north back to the Canaries. Figure 1 shows the CHBr_3 and CH_2Br_2 surface seawater concentrations along the RHaMBLe cruise track along with the distinctive Chl-*a* features (MODIS chlorophyll ocean colour satellite image) in the region, which were near stationary during the period 26 May – 6 June. Elevated bromocarbon concentrations are apparent in the high Chl-*a* containing waters of the upwelling, particularly in the re-

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



gion 16–20° N, 16–18° W. This is also apparent in Figs. 2 and 3 which shows time series of CHBr_3 and CH_2Br_2 concentrations in air and in water, calculated fluxes, ocean depth, Chl-*a* and the “temperature anomaly” – defined here as the instantaneous sea surface temperature (SST) subtracted from the average SST of the cruise. The upwelling centres near to the coast are clearly identifiable by the low SSTs (high temperature anomaly) and high Chl-*a* concentrations, attributed to cold, upwelled, nutrient-rich water. The cold signature of the upwelled water was confined mostly to the local inshore domain whereas the Chl-*a* distribution was very patchy, reflecting the nature of the upwelling process (Pradhan et al., 2006). The instantaneous bromocarbon seawater concentrations correlated weakly with Chl-*a* (+ve CHBr_3 – Chl-*a* correlation, $r^2=0.28$), with concentrations a factor of 2–4 higher within the upwelling region compared to outside the region (Table 1). Unlike previous cruises in the region where very high mixing ratios of CHBr_3 (~15 pptv) were observed in air transported from the African continent, attributed to an unknown coastal/continental source (Quack et al., 2004, 2007; Carpenter et al., 2007), here we observed much lower mixing ratios of 0.5–2 ppt over the upwelling region. We attribute this to the fact that easterly coastal/continental air masses were not experienced during the RHaMBLe cruise, rather the air masses were transported from the NE from over the upwelling. Seawater concentrations of CHBr_3 , CH_2Br_2 and Chl-*a* superimposed on a temperature/salinity plot (Fig. 4) all reveal rather higher concentrations in the more nutrient-rich SACW waters (Minas et al., 1982) of the upwelling compared to the NACW. A similar (although stronger) pattern was shown by Kock et al. (2008) in methane supersaturations.

3.2 North Atlantic surface seawater and air distributions

Halocarbons were sampled onboard the Celtic Explorer on the second leg of the MAP cruise between 25 June until 6 July with a transect from Killybegs in Donegal on the West Coast of Ireland out to the continental shelf off Ireland during a period of seasonally high plankton activity, into coastal waters of the Outer Hebrides, and finally into open waters of the Atlantic Ocean on the eastern edge of the North Atlantic Drift (NAD).

Air-sea fluxes of biogenic bromine

L. J. Carpenter et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-sea fluxes of biogenic bromine

L. J. Carpenter et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Figure 5 shows CHBr_3 and CH_2Br_2 surface seawater concentrations along the cruise track along with a 7 day composite MODIS chlorophyll ocean colour satellite image for the period 26 June–1 July 2006. Time series of bromocarbon concentrations and fluxes, along with Chl-*a* data and depth, are shown in Figs. 6 and 7. Extremely high concentrations of bromocarbons are clearly apparent in and over the shallow coastal waters. Concentrations of CHBr_3 and CH_2Br_2 and of Chl *a* were also elevated over the continental shelf (sampled during 29/30 June and 2/3 July) compared to the open waters (Table 2). Similarly to the RHaMBLe data, seawater CHBr_3 concentrations correlated weakly with Chl-*a* (+ve correlation, $r^2=0.39$, excluding coastal data).

3.3 Summary of Atlantic bromocarbon concentrations and fluxes and comparison with literature

Table 2 summarises the mean, median and ranges of concentrations and fluxes of the bromocarbons in the different regions of the Atlantic. CH_2Br_2 shows similar patterns to CHBr_3 ; both gases show saturations and sea-air fluxes decreasing in the order coastal>upwelling>shelf>open ocean. Coastal CHBr_3 concentrations (mean of 68 pmol dm^{-3} at depths between 20–40 m) were similar to measurements in waters of between 20–45 m depth off Mace Head, Ireland with a mean of $104 \pm 12 \text{ pmol dm}^{-3}$ (Carpenter et al., 2000). Chuck et al. (2005) measured coastal CHBr_3 fluxes of $\sim 200 \text{ nmol m}^{-2} \text{ d}^{-1}$ for waters around Gran Canaria, and Butler et al. (2007a) give global average “coastal water” fluxes of 220 and $110 \text{ nmol m}^{-2} \text{ d}^{-1}$ for CHBr_3 and CH_2Br_2 , respectively, compared to our mean Outer Hebrides coastal fluxes of 236 and $72 \text{ nmol m}^{-2} \text{ d}^{-1}$. Seawater concentrations in the African upwelling (mean of $11.5 \text{ pmol dm}^{-3}$ CHBr_3 and 3.1 pmol dm^{-3} CH_2Br_2) were similar to the mean concentrations measured by Quack et al. (2007) of $10.6 \text{ pmol dm}^{-3}$ CHBr_3 (both fresh and aged upwelled waters) and 4.6 pmol dm^{-3} CH_2Br_2 .

For the Atlantic open ocean, bromocarbon concentrations in tropical air and water were very similar to those measured further north. The higher tropical fluxes reflected

**Air-sea fluxes of
biogenic bromine**

L. J. Carpenter et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



both the warmer waters (mean of 20.4°C for RHaMBLe cf. 13.7°C for MAP) and higher wind speeds (mean of 9.1 ms⁻¹ for RHaMBLe cf. 6.9 ms⁻¹ for MAP) experienced during the RHaMBLe cruise. CH₂Br₂ was near to equilibrium with the atmosphere in some areas, whereas we found that the Atlantic Ocean was always saturated in CHBr₃, in contrast to Chuck et al. (2005) who found that large areas of the temperate Atlantic were a sink for CHBr₃. Our mean open ocean CHBr₃ seawater concentration (3.5 pmol dm⁻³ between 25–60° N) falls between the mean Atlantic concentration of 3.1 pmol dm⁻³ measured by Class and Ballschmiter (1988) and the mean North/South Atlantic (50° N–65° S) value of 5.1 pmol dm⁻³ reported by Chuck et al. (2005). For the North Atlantic open ocean, our atmospheric CHBr₃ data, with a mean mixing ratio of 0.3 ppt, agrees well with that of Butler et al. (2007a) who report an average N. Atlantic mean mixing ratio of 0.4 ppt, but is much lower than the Atlantic CHBr₃ observed by Chuck et al. (2005) of 2.2 ppt between 28° N and 20° S (hence the lower fluxes in this study). However, our CH₂Br₂ atmospheric mixing ratios are rather lower than the data presented by Butler et al. (2007a). The high temporal and spatial variability in both gases may explain some of these differences.

3.4 CH₂Br₂ and CHBr₃ correlations and their implications

Covariance between polybromomethanes in air and in seawater (e.g. CHBr₃, CH₂Br₂, CH₂BrCl) has been widely reported and used to infer common marine sources of these compounds and to calculate bromocarbon emission ratios (Li et al., 1994; Carpenter and Liss, 2000; Carpenter et al., 2003; Yokouchi et al., 2005; Zhou et al., 2008). Figure 8 presents an x-y plot of the seawater concentrations of CH₂Br₂ and CHBr₃ measured in this study, superimposed on previous measurements. The new data is consistent with previous ratios, which show a logarithmic dependence on concentration (Carpenter and Liss, 2000). As discussed in Carpenter and Liss (2000), the nature of this slope implies first order decay of the bromoalkanes in seawater, with lifetimes in the order CHBr₃ < CH₂Br₂. An alternative explanation is that the ratio of CH₂Br₂/CHBr₃ production (e.g. by phytoplankton) in the open ocean is higher than

**Air-sea fluxes of
biogenic bromine**

L. J. Carpenter et al.

that in coastal regions. Atmospheric ratios of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ are often interpreted in the light of their different atmospheric lifetimes (Li et al., 1994; Yokouchi et al., 2005; Zhou et al., 2008). The atmospheric lifetime of CH_2Br_2 is ~ 0.29 years (Zhang et al., 1997) compared to about 20 days for CHBr_3 (Bilde et al., 1998). Atmospheric bromo-carbon ratios have been used to deduce global estimates of their fluxes (Carpenter et al., 2003; Yokouchi et al., 2005) with an implicit assumption that the oceanic emission ratio is near constant. However, Fig. 8 shows that the surface seawater concentration ratio of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ is a function of concentration (and location), with a lower $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ slope found in coastal regions near to strong macroalgal sources, and dilution of the samples with background water resulting in higher percentages of the longer-lived halocarbon. This demonstrates that emission ratios deduced from coastal measurements should be treated with caution when inferring “global” average emission ratios.

The implication that CH_2Br_2 has a longer lifetime than CHBr_3 in seawater is somewhat contrary to current theory. The half life of CHBr_3 due to halide exchange is 1.3–18.5 yr at 25°C in seawater (Geen, 1992), and the half life due to hydrolysis is hundreds to thousands of years for both CH_2Br_2 and CHBr_3 (Mabey and Mill, 1978). The volatilisation lifetime of both gases is similar at a few weeks, depending on wind-speed and mixed-layer depth. The most rapid aqueous destruction pathway so far reported is bacterial oxidation of CH_2Br_2 (which apparently has no effect on CHBr_3), with a half life of only 2 days (Goodwin et al., 1998). This suggests that CH_2Br_2 should be lost more rapidly in seawater than CHBr_3 . The apparently shorter lifetime of CHBr_3 in surface seawater could be due to its faster photolysis compared to CH_2Br_2 (Carpenter and Liss, 2000). Ultraviolet photolysis of CHBr_3 in water is followed by water-catalysed dehalogenation to yield 3HBr , CO and HCOOH as ultimate products, with a relatively high photon quantum yield (for a solution-phase reaction) of ~ 0.46 (Kwok et al., 2004).

From Fig. 8, and correcting $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ concentration ratios to emission ratios by taking into account estimated differences in gas transfer velocities (Wanninkhof, 1992), leads to a “coastal” $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ molar emission ratio of ~ 0.12 (from a molar con-

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Air-sea fluxes of
biogenic bromine**

L. J. Carpenter et al.

centration ratio of 0.09–0.10) and an “open ocean” molar emission ratio of ~ 0.25 (from a molar concentration ratio of 0.20–0.21). Assuming that coastal sources contribute 23–75% of the world’s CHBr_3 (Quack et al., 2003; Butler et al., 2007a), the global oceanic emission ratio is therefore 0.15–0.22. Previously, we deduced a “coastal” $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ emission ratio of ~ 0.15 from atmospheric data at Mace Head, Ireland (Carpenter et al., 2003), although this might have been effected slightly by dilution, which would act to increase the value. Similarly, Zhou et al. (2008) recently reported $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ atmospheric ratios of 0.13 from the coast of Appledore Island, US, and 0.15 at a site ~ 25 km inland. From mostly coastal atmospheric measurements, Yokouchi et al. (2005) estimated a $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ ratio of 0.11, and used this to infer a global emission rate of CHBr_3 from CH_2Br_2 data.

3.5 Global and regional flux extrapolations

Recent work has stressed the potential importance of upwelling systems in providing bromocarbons to the atmosphere and their link to climate change via bromine-initiated reduction of ozone in the upper troposphere, where it is most effective as a greenhouse gas (Quack et al., 2004; Salawitch, 2006). Because most of the major upwelling regions (African, Peruvian, equatorial) occur in tropical regions, there is greater potential for supply to the upper atmosphere through deep convection. However, in agreement with Quack et al. (2007), we find that the areal flux of CHBr_3 and of CH_2Br_2 from the African upwelling is significantly less than from coastal regions. Coastal upwelling regions represent only about 0.1% of the ocean surface (Ryther, 1969), and offshore areas of high productivity, including equatorial upwelling regions, are believed to represent $\sim 2.5\%$ of the ocean surface (Ryther, 1969). Taking our data as representative of other coastal upwelling systems (mean fluxes of 41.2 and 13.3 $\text{nmol m}^{-2} \text{d}^{-1}$ for CHBr_3 and CH_2Br_2 , respectively) and that of Butler et al. (2007a) as representative of equatorial upwelling regions (mean fluxes of 9.1 and 2.6 $\text{nmol m}^{-2} \text{d}^{-1}$ for CHBr_3 and CH_2Br_2 , respectively), we estimate that upwelling regions contribute a total of 0.1 Gmol (Br) yr^{-1}

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

from CHBr_3 and $0.03 \text{ Gmol}(\text{Br}) \text{ yr}^{-1}$ from CH_2Br_2 , comprising around 1% of the total global emissions of these compounds (Quack et al., 2003; Butler et al., 2007a).

Although recent studies are in agreement on the total global emissions of CHBr_3 as ~ 10 (3–22) $\text{Gmol}(\text{Br}) \text{ yr}^{-1}$ (Quack et al., 2003; Butler et al., 2007a), there is a discrepancy regarding the contribution of different regions/processes to this budget. The study of Butler et al. (2007a) was designed to reduce uncertainties on open ocean emissions, and suggested that open seawater contributes around $1.9 \text{ Gmol}(\text{Br}) \text{ yr}^{-1}$ CHBr_3 , compared to Quack's estimate of $3 \text{ Gmol}(\text{Br}) \text{ yr}^{-1}$ CHBr_3 . Based on limited data from coastal regions, Butler et al. (2007a) tentatively concluded that coastal sources contribute up to $8 \text{ Gmol}(\text{Br}) \text{ yr}^{-1}$ of the world's CHBr_3 , whereas Quack et al. (2003), from a compilation of data sets, suggested a figure of $2.3 \text{ Gmol}(\text{Br}) \text{ yr}^{-1}$, with $4.7 \text{ Gmol}(\text{Br}) \text{ yr}^{-1}$ from "shelf" seas. The authors defined "coastal" regions in different ways, which partly explains why rather different fluxes were calculated. Clearly, the total global emission estimate for CHBr_3 is very sensitive to the assumptions made on such coastal emissions.

Global information on the geographical area of coastal regions is calculated using bathymetry/hypsometry, therefore in order to use such data to estimate coastal trace gas fluxes requires knowledge of how surface bromocarbon concentrations vary with ocean depth. Figure 9, using data from this study and previous data offshore of Mace Head (Carpenter and Liss, 2000), shows clearly that higher bromocarbon concentrations are observed in shallower seas. We use this limited information to provide a slightly more detailed analysis of potential coastal emissions. Coastal waters with a depth up to 180 m represent 7.5% of the world ocean area (Menard and Smith, 1966). The global area of shallow seas below 50 m is around $5 \times 10^{12} \text{ m}^2$ (Wyatt, 1987), i.e. 1.4% of the total ocean area (Riley and Chester, 1971). Our data indicate an average concentration of $\sim 200 \text{ pmol dm}^{-3}$ CHBr_3 for waters below 50 m and $\sim 10 \text{ pmol dm}^{-3}$ CHBr_3 for waters between 50–180 m depth, assuming an equal distribution of depths. Assuming a mean SST of 15°C and a wind speed of 7 ms^{-1} , we estimate tentatively that coastal and coastally-influenced waters together contribute

Air-sea fluxes of biogenic bromine

L. J. Carpenter et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Air-sea fluxes of
bromogenic bromine**

L. J. Carpenter et al.

around 2.4 Gmol Br yr⁻¹ (Table 3), much less than the 8 Gmol Br yr⁻¹ estimate of Butler et al. (2007a) but close to the near-shore estimate of Quack et al. (2003) of 2.3 (0.9–3.4) Gmol Br yr⁻¹ and to the bottom-up estimate of Carpenter and Liss (2000) from macroalgae of 1.6 (0.4–2.7) Gmol Br yr⁻¹. If the “coastal” emission of Butler et al. (2007a) is reduced to 2.4 Gmol Br yr⁻¹, the global emission flux from that study becomes 4.3 Gmol Br yr⁻¹, i.e. the coastal contribution to the global budget is 56%. However, we emphasise the requirement for further coastal seawater data, particularly in tropical regions which appear to produce large quantities of bromocarbons (Yokouchi, 2005). Future coastal bromocarbon data should be provided with bathymetry data to allow a more accurate assessment and definition of coastal emissions.

4 Conclusions

Simultaneous seawater and air measurements of CHBr₃ and CH₂Br₂ over a large part of the eastern Atlantic Ocean show that both gases are supersaturated throughout this region, with the exception of a few measurements of CH₂Br₂ in the open ocean. There is evidence that, outside of coastal regions, phytoplankton abundance partly controls surface bromocarbon concentrations, since elevated concentrations are observed where Chl-*a* levels are high, for example along the continental shelf and in upwelling regions. We suggest that upwelling systems are regional hot spots of bromocarbons, but are not of major significance globally. However, our data, along with others, show that coastal regions are a highly significant and possibly dominant source of bromocarbons, although the exact contribution to the global budget remains unresolved.

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[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

References

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Air-sea fluxes of biogenic bromine

L. J. Carpenter et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Air-sea fluxes of
biogenic bromine**

L. J. Carpenter et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Air-sea fluxes of
biogenic bromine**

L. J. Carpenter et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Air-sea fluxes of biogenic bromine

L. J. Carpenter et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 1. CHBr₃ and CH₂Br₂ concentration and flux averages and ranges in the Atlantic Ocean

| | °N | CHBr ₃ | | | | CH ₂ Br ₂ | | |
|------------------------------|-------|-------------------------------------|-------------------------------|---|--|---|---|--|
| | | Chl- <i>a</i> μg/dm ³ | CHBr ₃ air pptv | CHBr ₃ water pmol/dm ³ | CHBr ₃ flux nmol/m ² /d | CH ₂ Br ₂ air pptv | CH ₂ Br ₂ water pmol/dm ³ | CH ₂ Br ₂ flux nmol/m ² /d |
| <i>Upwelling^a</i> | | | | | | | | |
| mean | 16–23 | 4.1 | 1.1 | 11.5 | 41.2 | 0.3 | 3.1 | 13.3 |
| median | | 2.5 | 0.9 | 9.5 | 35.5 | 0.3 | 3.0 | 12.7 |
| range (10th – 90th%) | | 2.3–6.6 | 0.5–2.0 | 4.7–19.5 | 11.1–92.5 | 0.2–0.4 | 1.5–4.6 | 4.9–22.0 |
| N | | 32 | 32 | 31 | 31 | 26 | 32 | 32 |
| <i>Canaries</i> | | | | | | | | |
| mean | 27–28 | 0.1 | 0.7 | 14.4 | 47.5 | 0.1 | 2.6 | 9.1 |
| median | | 0.1 | / | / | / | / | / | / |
| range (10th – 90th%) | | 0.–0.1 | 0.6–0.7 | 13.1–15.6 | 11.2–83.9 | 0.1–0.1 | 2.6–2.7 | 2.2–16.1 |
| N | | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| <i>Open ocean</i> | | | | | | | | |
| mean | 25–35 | 0.1 | 0.3 | 3.5 | 10.0 | 0.2 | 0.9 | 2.8 |
| median | | 0.1 | 0.3 | 3.7 | 11.3 | 0.2 | 0.9 | 2.8 |
| range (10th – 90th%) | | 0.1–0.1 | 0.2–0.5 | 1.6–5.0 | 1.2–17.3 | 0.1–0.2 | 0.6–1.3 | 0.5–4.8 |
| N | | 10 | 10 | 10 | 10 | 9 | 10 | 10 |
| <i>Open ocean</i> | | | | | | | | |
| mean | 50–60 | 0.4 | 0.3 | 3.4 | 5.5 | 0.4 | 1.1 | 2.3 |
| median | | 0.3 | 0.2 | 2.9 | 2.1 | 0.4 | 1.2 | 1.1 |
| range (10th – 90th %) | | 0.2–1.5 | 0.1–0.6 | 2.1–4.9 | 0.2–18.5 | 0.3–0.5 | 0.5–2.1 | 0.0–7.7 |
| N | | 9 | 23 | 23 | 23 | 23 | 14 | 14 |
| <i>Shelf^b</i> | | | | | | | | |
| mean | 50–60 | 1.7 | 0.5 | 6.7 | 13.3 | 0.5 | 1.9 | 3.0 |
| median | | 1.8 | 0.4 | 5.1 | 5.6 | 0.5 | 1.5 | 1.0 |
| range (10th – 90th%) | | 1.5–2.1 | 0.3–0.8 | 3.9–12.3 | 1.9–4.2 | 0.4–0.6 | 0.5–3.3 | 0.0–9.6 |
| N | | 10 | 32 | 32 | 32 | 32 | 23 | 23 |
| <i>Coastal^c</i> | | | | | | | | |
| mean | 50–60 | 3.7 | 3.3 | 68.3 | 236 | 1.1 | 15.6 | 72.2 |
| median | | 3.7 | 2.9 | 65.5 | 266 | 1.0 | 14.7 | 65.4 |
| range (10th – 90th%) | | 3.6–3.7 | 1.9–4.9 | 36.6–102 | 127–322 | 0.9–1.4 | 13.5–18.0 | 62.7–84.5 |
| N | | 2 | 4 | 4 | 4 | 4 | 3 | 3 |

^aSelected from data with Chl-*a* values above 2 μg dm⁻³ in the region 16–25° N, 16–25° W

^bOcean depth 100–200 m

^cOcean depth <100 m

Air-sea fluxes of biogenic bromine

L. J. Carpenter et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-sea fluxes of biogenic bromine

L. J. Carpenter et al.

Table 2. Estimates of global coastal CHBr_3 and CH_2Br_2 fluxes.

| | % of ocean area | Mean CHBr_3 concentration (pmol dm^{-3}) | Mean CHBr_3 flux ($\text{nmol m}^{-2} \text{d}^{-1}$) | Global flux Gmol (Br) yr^{-1} |
|---------------------------------|-----------------|--|--|--|
| Coastal (0–50 m) | 1.4% | 200 | 349 | 1.9 |
| Coastally-influenced (50–200 m) | 6.1% | 10 | 21.5 | 0.5 |

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Air-sea fluxes of
biogenic bromine

L. J. Carpenter et al.

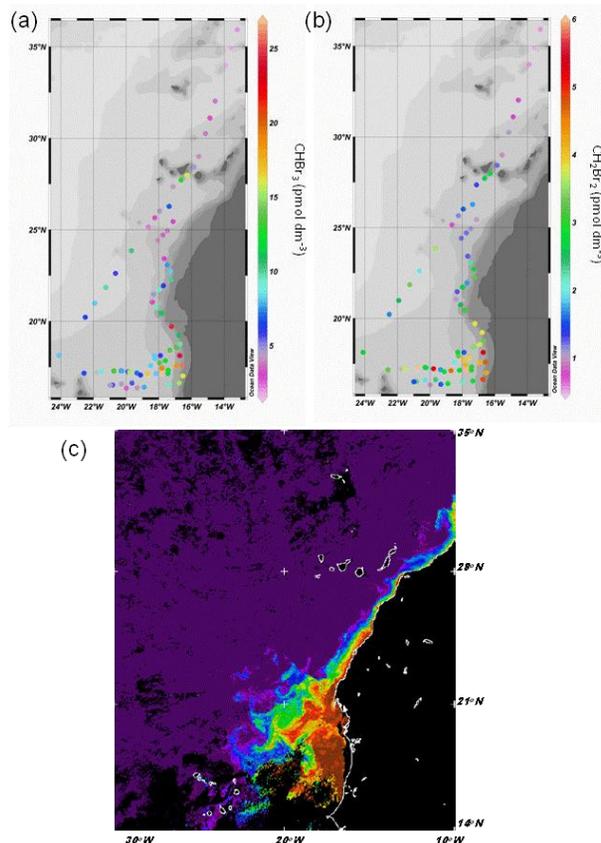


Fig. 1. Surface seawater data for the RHaMBLE cruise: **(a)** CHBr₃ concentrations, **(b)** CH₂Br₂ concentrations **(c)** Chl-*a* image from MODIS/Aqua ocean colour satellite, weekly composite from 20–26 May 2007. Chl-*a* is purple when concentrations are low, increasing through blue, green and yellow to high concentrations at orange and red. Black is cloud cover. Images processed by the NEODAAS Remote Sensing Group, Plymouth Marine Laboratory.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Air-sea fluxes of
biogenic bromine

L. J. Carpenter et al.

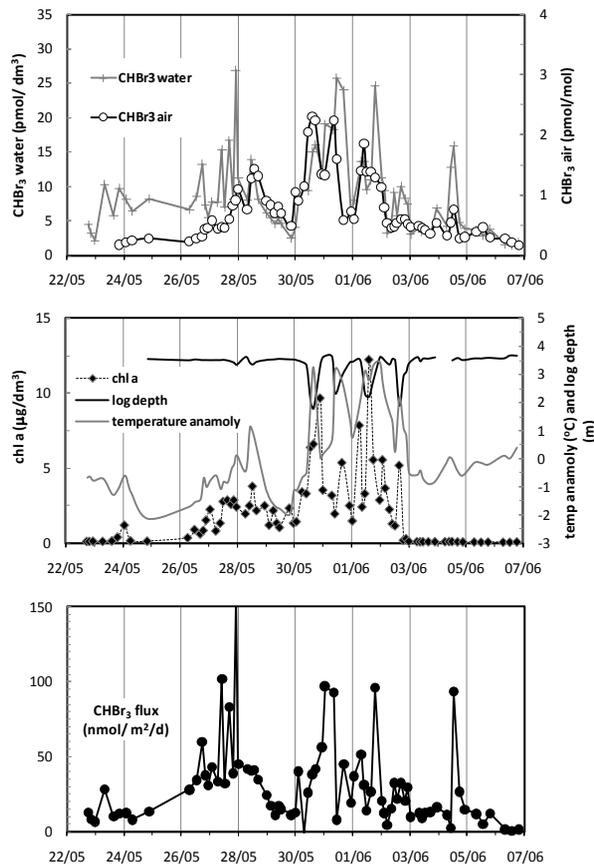


Fig. 2. Time series of CHBr₃ concentrations (air and water), fluxes, ocean depth and Chl-a for the RHaMBLe cruise.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Air-sea fluxes of
biogenic bromine

L. J. Carpenter et al.

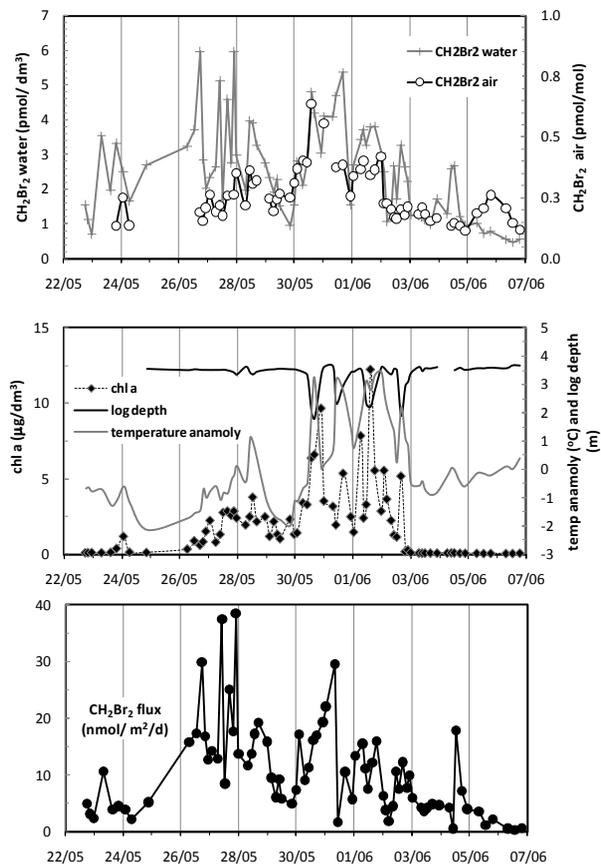


Fig. 3. Time series of CH_2Br_2 concentrations (air and water), fluxes, ocean depth and Chl-a for the RHaMBLe cruise.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Air-sea fluxes of
biogenic bromine

L. J. Carpenter et al.

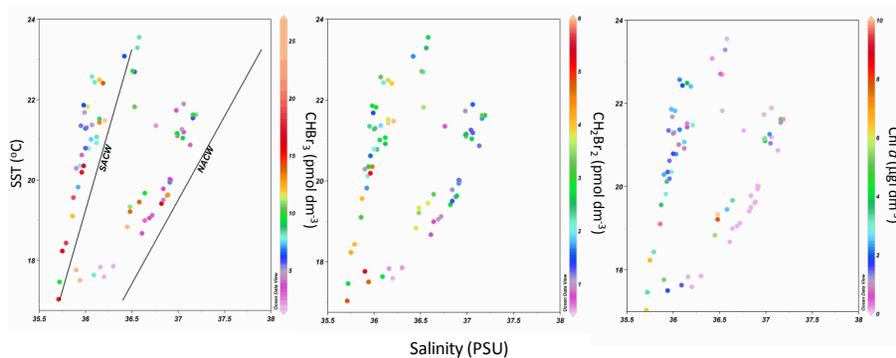


Fig. 4. T/S curves plotted with CH_2Br_2 , CHBr_3 and Chl-*a* concentrations for the RHaMBLE cruise.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Air-sea fluxes of
biogenic bromine

L. J. Carpenter et al.

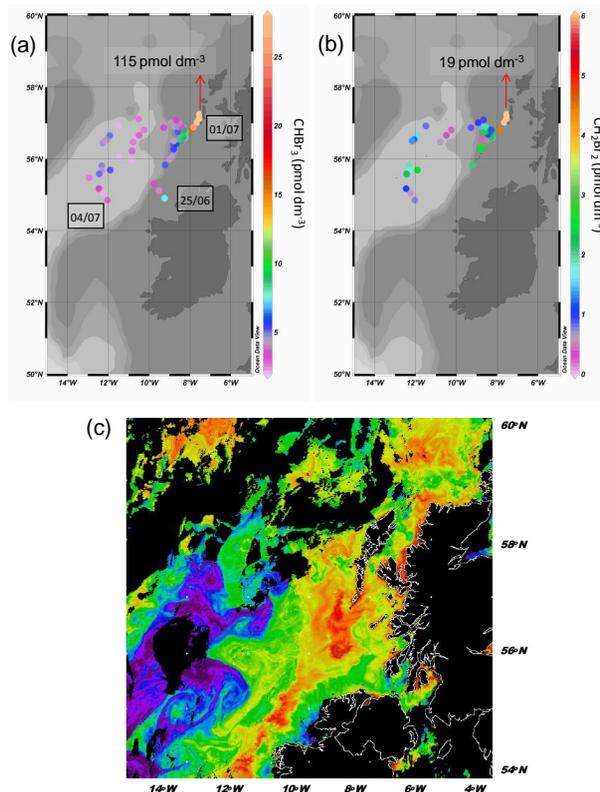


Fig. 5. Surface seawater data for the MAP cruise: **(a)** CHBr_3 concentrations, **(b)** CH_2Br_2 concentrations. Concentration scales for CHBr_3 and CH_2Br_2 are the same as for Fig. 1, note that concentrations are off scale near the coast of the Outer Hebrides, **(c)** Chl-*a* image from MODIS/Aqua ocean colour satellite, weekly composite from 26 June–1 July 2006. See Fig. 1 for more details.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Air-sea fluxes of
biogenic bromine

L. J. Carpenter et al.

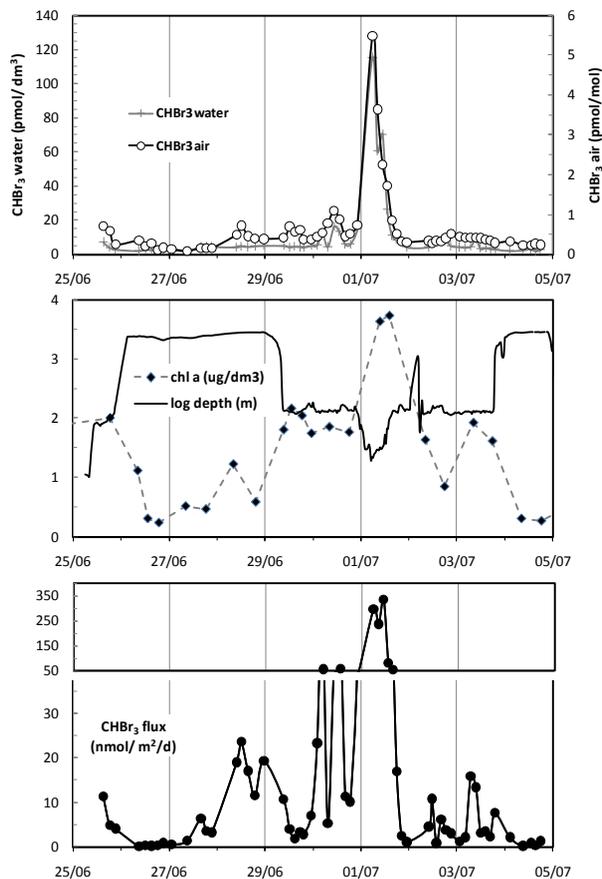


Fig. 6. Time series of CHBr₃ concentrations (air and water), fluxes, ocean depth and Chl-a for the MAP cruise.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Air-sea fluxes of biogenic bromine

L. J. Carpenter et al.

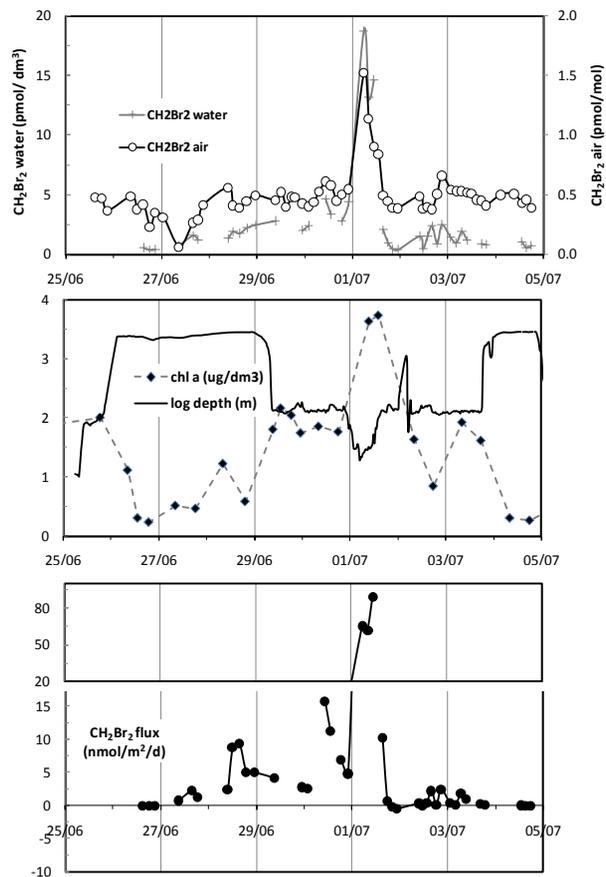


Fig. 7. Time series of CH_2Br_2 concentrations (air and water), fluxes, ocean depth and Chl-a for the MAP cruise.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Air-sea fluxes of biogenic bromine

L. J. Carpenter et al.

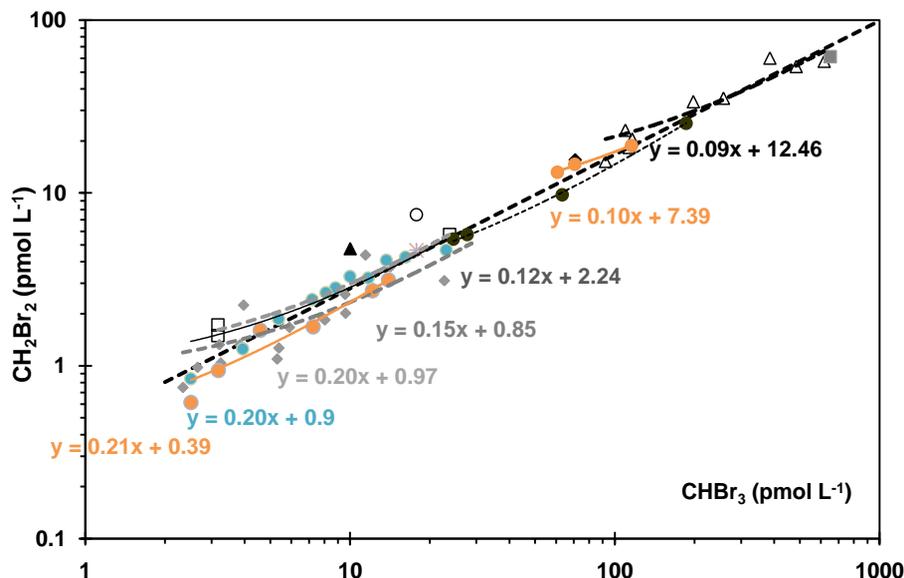


Fig. 8. Correlations of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ measured in surface seawater at different locations. Symbols represent the following: Orange circles, MAP data, separated and binned into coastal (high concentration data) and open ocean (low concentration data); Blue circles, RHaMBLe data, sub tropical N Atlantic; Open circles, Abrahamsson and Klick (1990), S. Atlantic open ocean; Open squares, Class et al. (1986), Atlantic open ocean; Filled triangles, Moore and Tokarczyk (1993), NW Atlantic open ocean; Filled gray diamonds, Schall et al. (1997), N. Atlantic open ocean; Filled circles, Reifenhauser and Heumann (1992), South Polar Sea; Filled black diamonds, Schall and Heumann (1993), Arctic coast; Filled squares, Schall and Heumann (1993), Arctic macroalgal field; Open triangles, Carpenter et al. (2000), NE Atlantic coast.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Air-sea fluxes of
biogenic bromine

L. J. Carpenter et al.

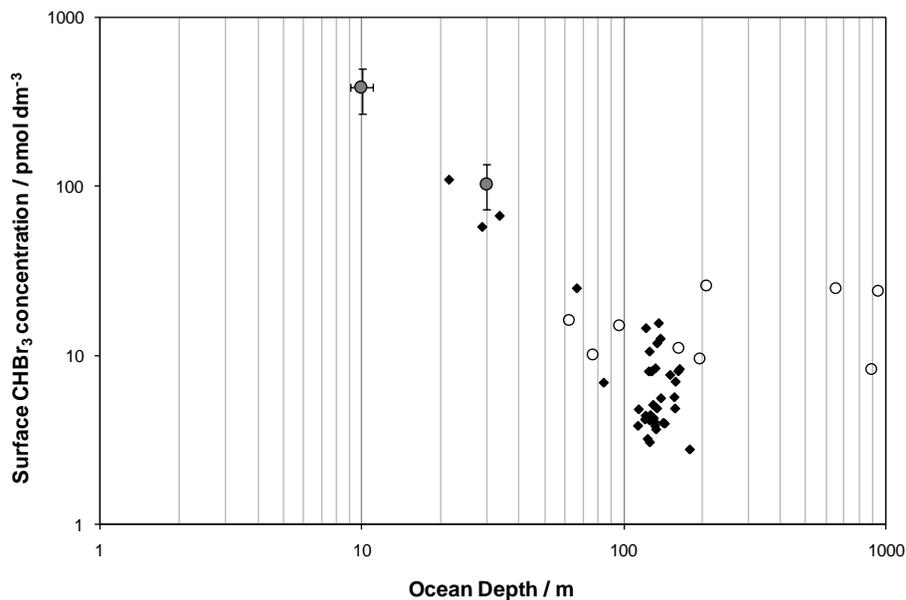


Fig. 9. Surface CHBr₃ concentrations in Atlantic waters of different depths. Filled diamonds – MAP data; open circles – RHaMBLe data; filled circles – average data from Mace Head measured in September 1998 – error bars represent 1σ of the data (Carpenter and Liss, 2000).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)