

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

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Abstract. Air-sea fluxes and bulk seawater and atmospheric concentrations of bromoform (CHBr₃) and dibromomethane (CH₂Br₂) 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 decreased in the order coastal > upwelling > shelf > open ocean, and outside of coastal regions, a broad trend of elevated surface seawater concentrations with high chlorophyll-*a* was observed. We show that upwelling regions (coastal and equatorial) represent regional hot spots of bromocarbons, but are probably not of major significance globally, contributing at most a few percent of the total global emissions of CHBr₃ and CH₂Br₂. From limited data from eastern Atlantic coastlines, we tentatively suggest that globally, coastal oceans (depth <180 m) together contribute ~2.5 (1.4–3.5) Gmol Br yr⁻¹ of CHBr₃, excluding influences from anthropogenic sources such as coastal power stations. This flux estimate is close to current estimates of the total open ocean source. We also show that the concentration ratio of CH₂Br₂/CHBr₃ in seawater is a strong function of concentration (and location), with a lower CH₂Br₂/CHBr₃ ratio found in coastal regions near to macroalgal sources.

1 Introduction

Oceanic production of short-lived organic bromine compounds such as CHBr₃ and CH₂Br₂ 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 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). CHBr₃ represents the single largest source of organic bromine from the ocean to the atmosphere and the contribution of short-lived bromine species to total bromine in the lower stratosphere is believed to be around 20–60% (Sturges et al., 2000; Pfeilsticker et al., 2000; Nielsen 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 better validation by global oceanic measurements. Here we report air-sea fluxes and bulk, simultaneous, seawater and atmospheric concentrations of CHBr₃ and CH₂Br₂ 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 (16–35° N, May–June 2007).



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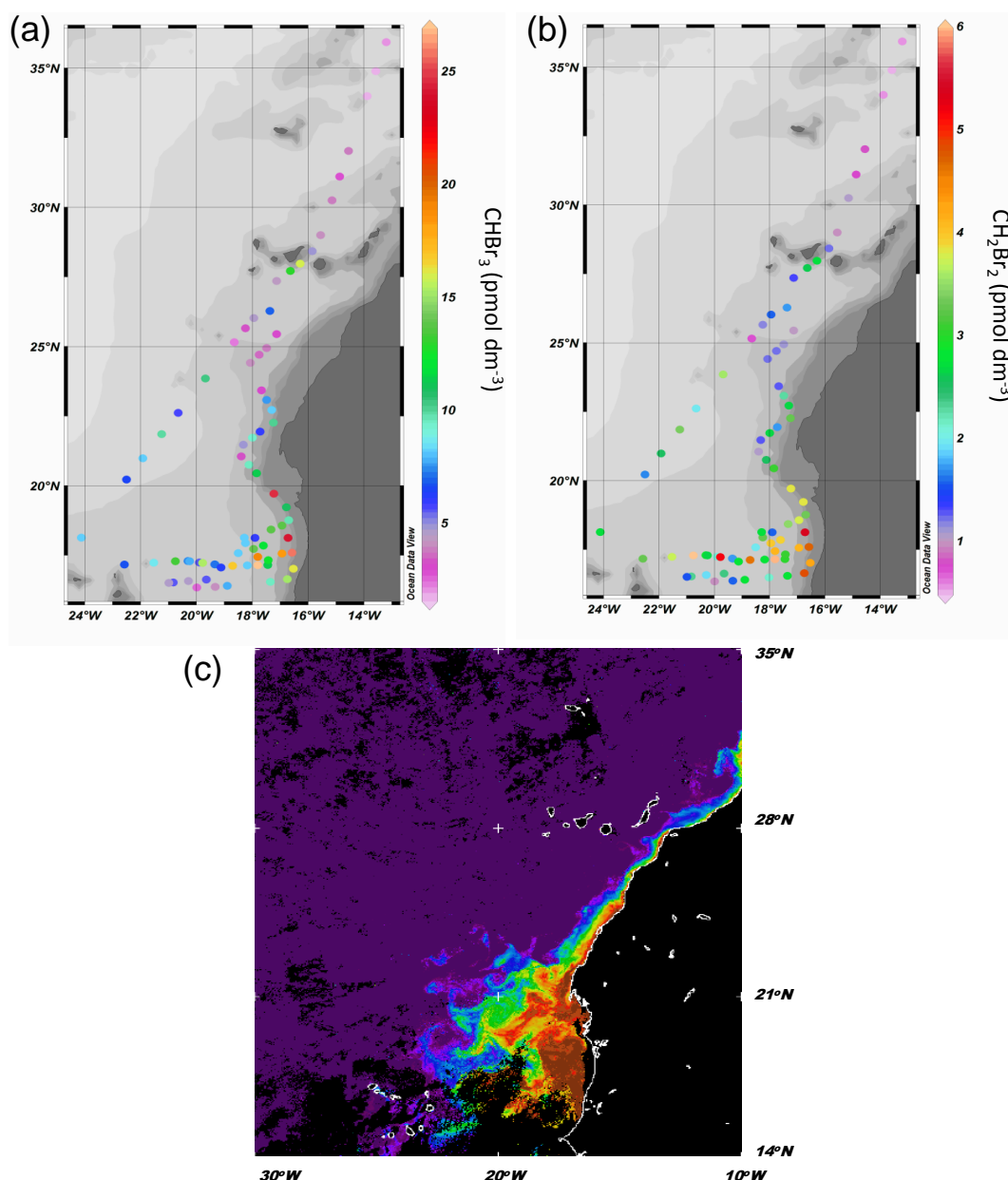


Fig. 1. Surface seawater data for the RHaMBLe cruise: (a) CHBr_3 concentrations, (b) CH_2Br_2 concentrations (c) $\text{Chl-}a$ image from MODIS/Aqua ocean colour satellite, weekly composite from 20–26 May 2007. $\text{Chl-}a$ is purple when concentrations are low, increasing through blue, green and yellow to high concentrations at orange and red. Black is cloud cover. Images processed by the NEODAAS Remote Sensing Group, Plymouth Marine Laboratory.

2 Methods

Two Perkin Elmer Turbomass GC-MS systems with thermal desorption units (TD, Perkin Elmer, UK) 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 NERC RRS *Discovery* for the tropical Atlantic project RHaMBLe (Reactive Halogens in the Marine Boundary Layer experi-

ment), funded by the UK SOLAS programme. One instrument was dedicated to online automated air measurements (air measurement every 2–3 h, 24 h d^{-1}) and one for purge-and-trap water measurements (water measurement every 2–3 h, $\sim 16 \text{ h d}^{-1}$). Air measurements were made at a height of 25 m (MAP) and 8 m (RHaMBLe) above the ocean surface through 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

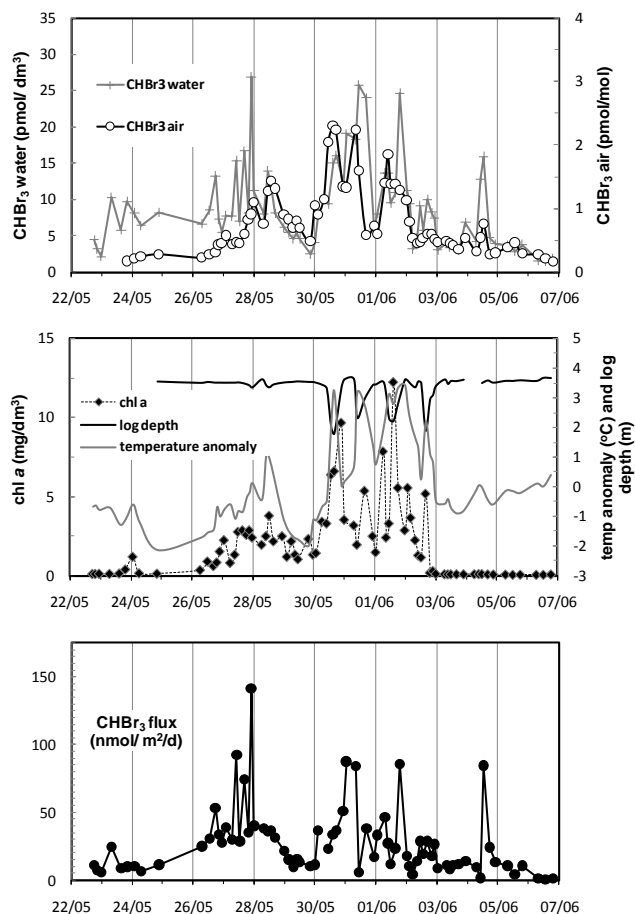


Fig. 2. Time series of CHBr_3 concentrations (air and water), fluxes, ocean depth and Chl-*a* for the RHaMBLe cruise.

using a clean metal bellows pump (Model MB118E, Senior Aerospace, USA).

Gas-tight syringes (40 mL, Samco, USA) 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 *RRS Discovery*. Water samples were filtered using Minisart 0.45 μm cellulose filters, and, while the majority of water samples were analysed immediately, occasionally they were stored in gas-tight syringes 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 mL min^{-1} N_2 (Grade 5.0, BOC) for 50 min. 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 dis-

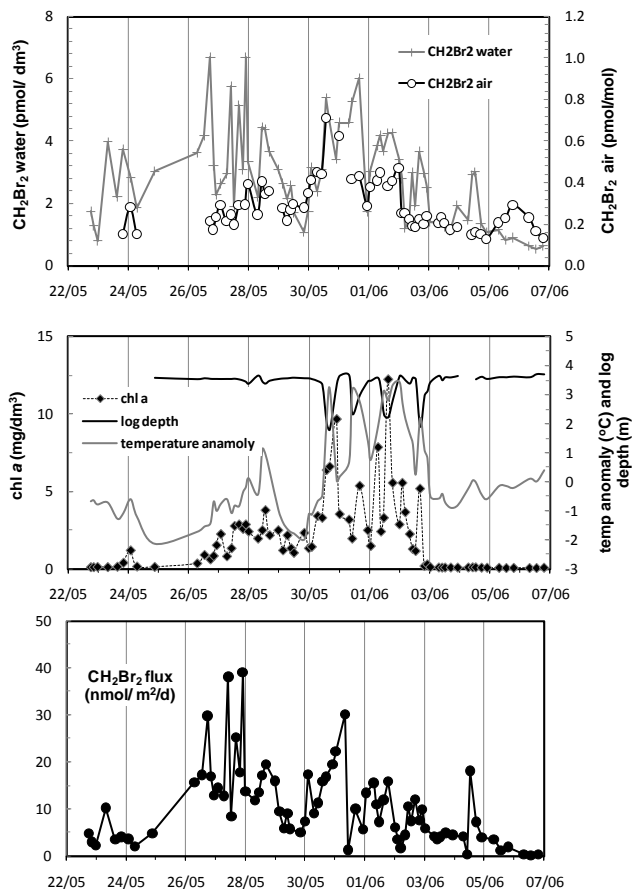


Fig. 3. Time series of CH_2Br_2 concentrations (air and water), fluxes, ocean depth and Chl-*a* for the RHaMBLe cruise.

posable permeation tubes (Trace SourceTM, 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 100 mL min^{-1} N_2 (Grade 5.0, BOC) and into a $10\ \mu\text{L}$ sample loop, which is injected into a 50 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 $\sim 0.01\text{--}0.05$ ppt in air and $0.02\text{--}0.06\text{ pmol dm}^{-3}$ 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 et al., 2007b). The analytical uncertainty for a sea-air flux calculation is dominated by the uncertainty in the water measurement for compounds which are supersaturated in seawater.

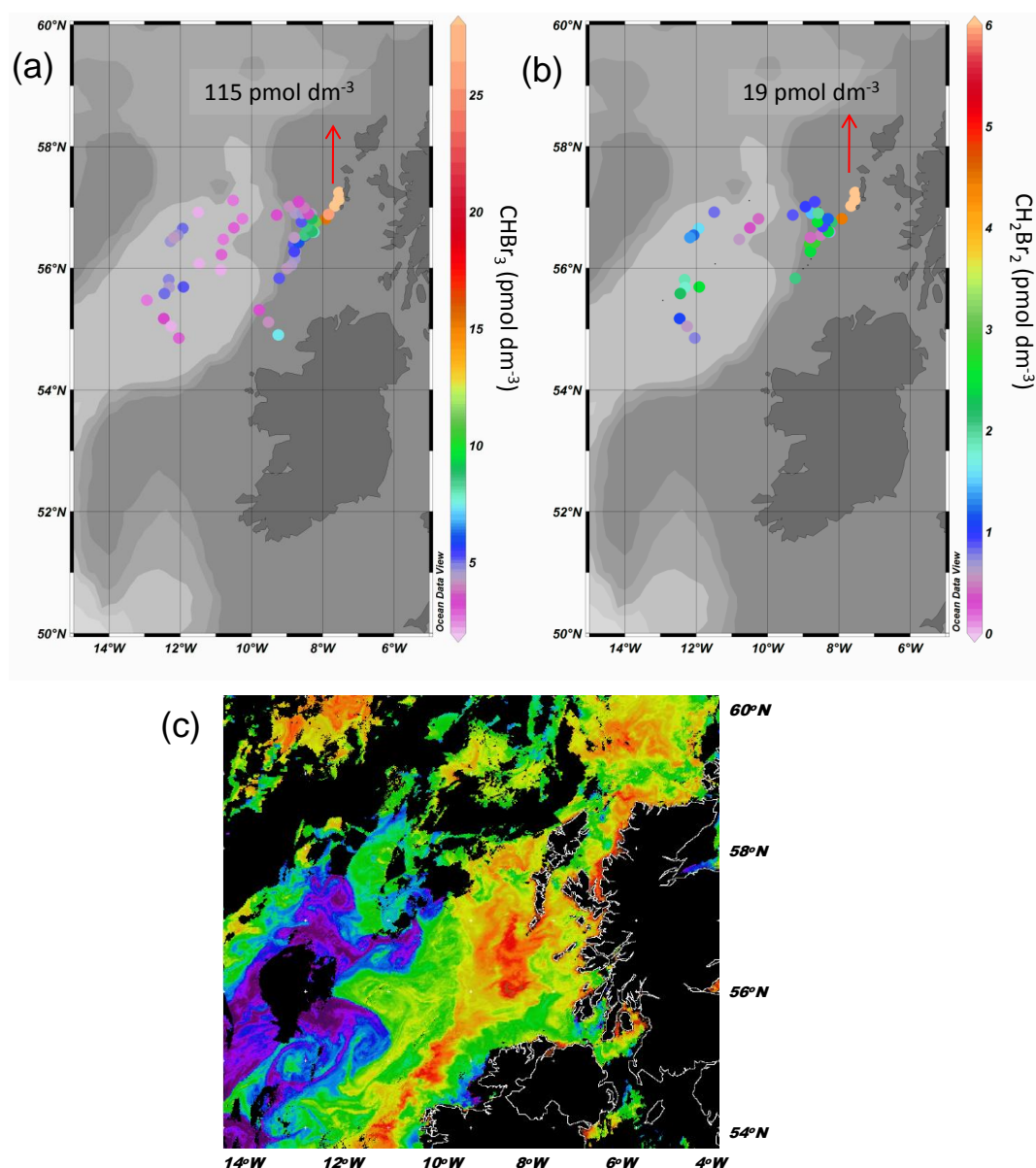


Fig. 4. Surface seawater data for the MAP cruise: (a) CHBr₃ concentrations, (b) CH₂Br₂ concentrations. Concentration scales for CHBr₃ and CH₂Br₂ are the same as for Fig. 1, note that concentrations are off scale near the coast of the Outer Hebrides, (c) Chl-*a* image from MODIS/Aqua ocean colour satellite, weekly composite from 26 June–1 July 2006. See Fig. 1 for more details.

In situ measurements of Chl-*a* were determined during the MAP cruise by fluorescence detection (exciting wavelength: 436 nm, emission wavelength: 680 nm) after filter extraction with acetone. The method is described in Arar and Collins (1997). Elsewhere, Chl-*a* was provided by the NEODAAS Remote Sensing Group, Plymouth Marine Laboratory, from MODIS/Aqua ocean colour satellite data.

3 Results and discussion

3.1 Tropical Atlantic surface seawater and air distributions

The tropical north east Atlantic is characterised by a north-easterly 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

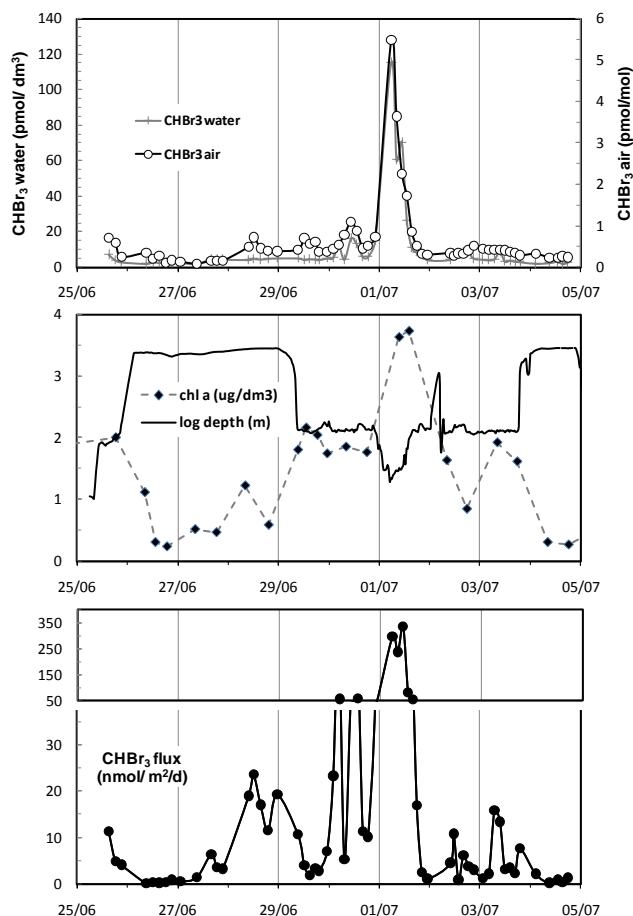


Fig. 5. Time series of CHBr_3 concentrations (air and water), fluxes, ocean depth and Chl-*a* for the MAP cruise.

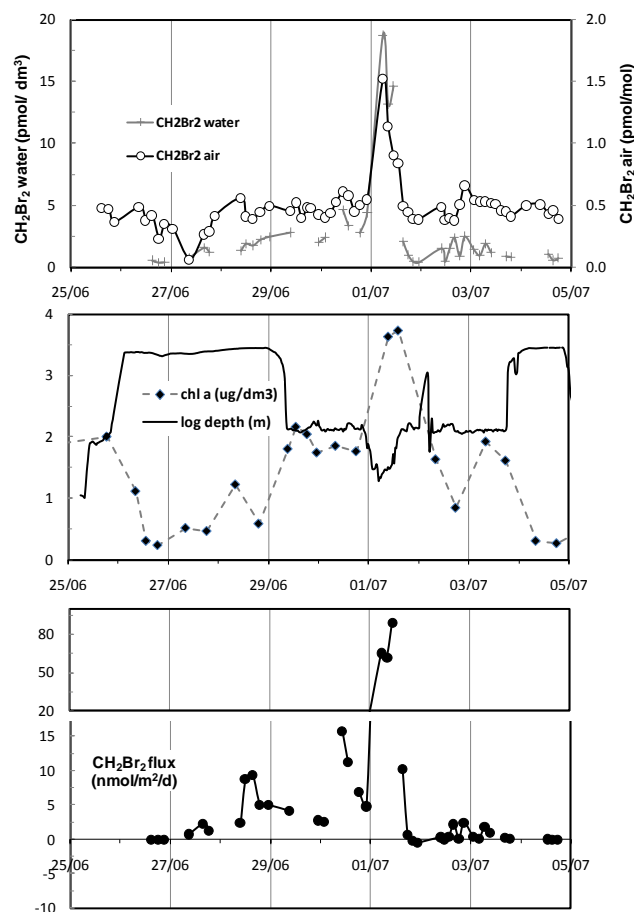


Fig. 6. Time series of CH_2Br_2 concentrations (air and water), fluxes, ocean depth and Chl-*a* for the MAP cruise.

African coastal upwelling zone, located between approximately 25°N and 10°N and between $\sim 20^\circ\text{W}$ to the north-west 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). Tomczak (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 (Peterson et al., 1996).

Samples from the RHAMBLE cruise were collected and analyzed during 22 May–6 June 2007. The ship sailed 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 re-

gion, 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 region $16\text{--}20^\circ\text{N}$, $16\text{--}18^\circ\text{W}$. 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* (satellite data) 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. Unlike previous cruises in the region where very high mixing ratios of CHBr_3 (~ 15 ppt) were observed in air transported from the African continent, attributed to an unknown coastal/continental source (Quack et al., 2004; Carpenter et al., 2007; Quack et al., 2007a), here we observed much lower mixing ratios of 0.5–2 ppt over the upwelling region. We attribute this to the fact that during the RHAMBLE cruise, the air masses were transported from the NE over the upwelling without touching the African continent or coast.

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> mg/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
Upwelling ^a	16–23							
mean		4.1	1.1	11.5	35.6	0.4	3.4	13.3
median		2.5	0.9	9.5	32.1	0.3	3.4	12.7
range (10th–90th %)		2.3–6.6	0.5–2.0	4.7–19.5	10.1–84.1	0.2–0.4	1.5–4.6	4.9–22.0
N		32	32	31	31	26	32	32
Canaries	27–28							
mean		0.1	0.7	14.4	42.9	0.2	3.0	9.2
median		0.1	/	/	/	/	/	/
range (10th–90th %)		0.0–0.1	0.6–0.7	13.1–15.6	9.7–76.1	0.2–0.2	2.9–3.0	2.1–16.3
N		2	2	2	2	2	2	2
Open ocean	25–35							
mean		0.1	0.3	3.5	8.8	0.2	1.4	3.8
median		0.1	0.3	3.7	9.9	0.2	1.1	2.7
range (10th–90th %)		0.1–0.1	0.2–0.5	1.6–5.0	1.0–15.0	0.1–0.2	0.6–2.8	0.4–6.9
N		10	10	10	10	9	10	10
Open ocean	50–60							
mean		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
Shelf ^b	50–60							
mean		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
Coastal ^c	50–60							
mean		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

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

^b Ocean depth 100–200 m

^c Ocean depth <100 m

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). Figure 4 shows CHBr₃ and CH₂Br₂ 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* (in situ) data and depth, are shown in Figs. 5 and 6. Extremely high concentrations of bromocarbons are clearly apparent in and over the shallow coastal waters. Concentrations of CHBr₃ and CH₂Br₂ 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 1).

3.3 Summary of Atlantic bromocarbon concentrations and fluxes

Table 1 summarises the mean, median and ranges of concentrations and fluxes of the bromocarbons in the different regions of the Atlantic. Fluxes were calculated from simultaneous air and water concentration measurements and the wind speed at 10 m according to the parameterization of Nightingale et al. (2000), with temperature-dependent Schmidt numbers for CH_2Br_2 and CHBr_3 estimated according to Yokouchi et al. (2001) and Henry's Law coefficients as reported by Moore et al. (1995).

Both CH_2Br_2 and CHBr_3 exhibited saturations and sea-air fluxes decreasing in the order coastal > upwelling > shelf > open ocean. Outside of coastal regions, Table 1 shows that the average seawater CHBr_3 and CH_2Br_2 concentrations for each region broadly increase with increasing Chl-*a*. However, unaveraged data points show only a weak correlation (e.g. r^2 of 0.39 for the CHBr_3 -Chl-*a* correlation of MAP, excluding coastal data). Coastal CHBr_3 concentrations (mean of 68 pmol dm^{-3} at depths between 20–40 m) were similar to surface water measurements corresponding to depths between 20–45 m 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 $72 \text{ nmol m}^{-2} \text{ d}^{-1}$. These coastal CHBr_3 fluxes are at the low end of the range presented in the review of Quack and Wallace (2003) of $96\text{--}10\,320 \text{ nmol m}^{-2} \text{ d}^{-1}$ (median of $2400 \text{ nmol m}^{-2} \text{ d}^{-1}$), probably because the latter values were derived mainly from measurements made within or very near to macroalgal beds (e.g., Klick and Abrahamsson, 1992; Schall and Heumann, 1993; Carpenter and Liss, 2000). In Swedish coastal waters, Klick and Abrahamsson (1992) measured mean CHBr_3 concentrations of $158 \pm 102 \text{ pmol dm}^{-3}$ in waters within a few 10's of km of the shore, compared to $945 \pm 300 \text{ pmol dm}^{-3}$ within the macroalgal belt. Clearly, there is a need for a common definition of "coastal" and subclasses therein, especially given the potential significance of such regions in contributing short-lived organobromine gases to the atmosphere.

Seawater concentrations in the African upwelling (mean of $11.5 \text{ pmol dm}^{-3}$ CHBr_3 and 3.4 pmol dm^{-3} CH_2Br_2) were similar to the mean concentrations measured by Quack et al. (2007a) of $10.6 \text{ pmol dm}^{-3}$ CHBr_3 (both fresh and aged upwelled waters) and 4.6 pmol dm^{-3} CH_2Br_2 . Class and Ballschmiter (1988) measured $\sim 24 \text{ pmol dm}^{-3}$ CHBr_3 and 6 pmol dm^{-3} CH_2Br_2 in surface waters in this region (25° N , 16° W). As discussed in Sect. 3.1, the air measurements made in this study cannot be directly compared to those measured in the African upwelling region previously (Quack et al., 2004, 2007a; Carpenter et al., 2007) be-

cause these latter measurements were influenced by African coastal/continental air with input from an as yet unidentified but strong source of CHBr_3 (Carpenter et al., 2007; Quack et al., 2007a), whereas in this study, the airmass trajectories did not touch the coast (see Lee et al., 2009).

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 both the warmer waters (mean of 20.4° C for RHaMBLe c.f. 13.7° C for MAP) and higher wind speeds (mean of 9.1 ms^{-1} for RHaMBLe c.f. 6.9 ms^{-1} for MAP) experienced during the RHaMBLe cruise. CH_2Br_2 was near to equilibrium with the atmosphere in some areas, whereas we found that the Atlantic Ocean was always saturated in CHBr_3 , in contrast to Chuck et al. (2005) who found that large areas of the temperate Atlantic were a sink for CHBr_3 . Our mean open ocean CHBr_3 seawater concentration (3.5 pmol dm^{-3} between $25\text{--}60^\circ \text{ N}$) was within the range previously reported in this region. Class and Ballschmiter (1988) measured a mean Atlantic concentration of 3.1 pmol dm^{-3} , Chuck et al. (2005) reported a mean North/South Atlantic ($50^\circ \text{ N}\text{--}65^\circ \text{ S}$) value of 5.1 pmol dm^{-3} and Quack et al. (2004) measured $3\text{--}4 \text{ pmol dm}^{-3}$ in this region (Sect. 6). These CHBr_3 seawater concentrations (and their corresponding fluxes) are slightly higher than the N. Atlantic CHBr_3 averages reported by Butler et al. (2007a), probably because the latter covered a much larger region spanning the North Atlantic central gyre. CH_2Br_2 fluxes, however, are similar in this study and the N. Atlantic data of Butler et al. (2007a), suggesting less variability in the oceanic saturations of this gas.

Our atmospheric North Atlantic open ocean CHBr_3 data, with a mean mixing ratio of 0.3 ppt, agree well with the results of Butler et al. (2007a) who report an average N. Atlantic mean mixing ratio of 0.4 ppt, but are much lower than the Atlantic CHBr_3 observed by Chuck et al. (2005) with a mean of 2.2 ppt between 28° N and 20° S (hence the lower fluxes in the latter study). Our CH_2Br_2 atmospheric mixing ratios (N. Atlantic open ocean average of 0.3 ppt) are rather lower than the data presented by Butler et al. (2007a) (N. Atlantic open ocean average of 1.0 ppt). The high temporal and spatial variability in both gases may explain some of these differences, although calibration differences cannot be ruled out.

3.4 CH_2Br_2 and CHBr_3 correlations and their implications

Covariance between polybromomethanes in air and in seawater (e.g. CHBr_3 , CH_2Br_2 , CH_2BrCl) 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 7 is an x-y plot of the seawater concentrations of CH_2Br_2 and CHBr_3 measured in this study, superimposed on previous measurements. The new data is consistent with previous ratios, which

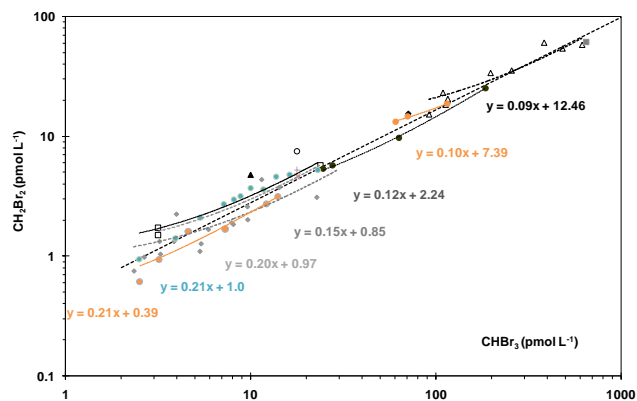


Fig. 7. Correlations of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ measured in surface seawater at different locations. Symbols represent the following: Orange circles, MAP data, separated and binned into coastal (high concentration data) and open ocean (low concentration data); Blue circles, RHaMBLe data, 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, Reifenhäuser 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.

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 $\text{CHBr}_3 < \text{CH}_2\text{Br}_2$. An alternative explanation is that the ratio of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ production (e.g. by phytoplankton) in the open ocean is higher than the production ratio in coastal regions (e.g. by macroalgae).

Atmospheric ratios of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ are often interpreted in the light of their differing 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 bromocarbon 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. 7 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 CH_2Br_2 . This demonstrates that emission ratios deduced from coastal measurements should be treated with caution when inferring “global” average emission ratios.

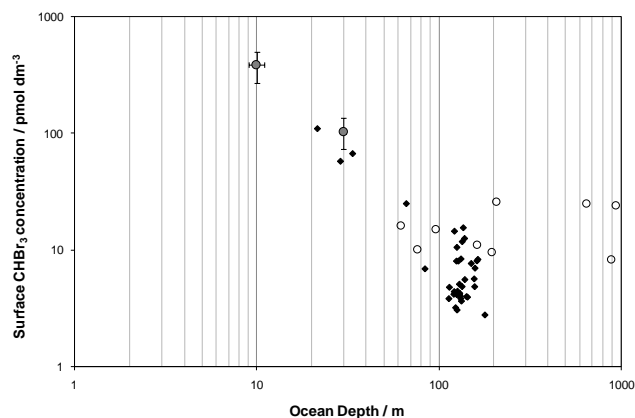


Fig. 8. Surface CHBr_3 concentrations in Atlantic waters of different depths. Filled diamonds – MAP data; open circles – RHaMBLe data; filled circles – average data from Mace Head measured in September 1998 – error bars represent 1σ of the data (Carpenter and Liss, 2000).

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 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). Alternatively, Quack et al. (2007b) suggested that entrainment of thermocline waters, where CHBr_3 may be converted to CH_2Br_2 via reductive hydrogenolysis (Vogel et al., 1987) under anoxic conditions, into the mixed layer could contribute to the ratio shift in open ocean and upwelled waters. Quack et al. (2007b) further point out that, although the volatilisation lifetime of both gases is similar (at a few weeks), CHBr_3 may be lost preferentially from surface waters over time since it tends to have a greater sea-air concentration gradient than CH_2Br_2 .

To a first approximation, assuming that both gases are supersaturated in seawater, the $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ water concentration ratios shown in Fig. 7 can be converted to sea-air emission ratios by taking into account estimated differences in Schmidt numbers for CH_2Br_2 and CHBr_3 (Yokouchi et al., 2001), which increases the water concentration ratio by $\sim 10\%$. (Note that, according to our data, the $\text{CH}_2\text{Br}_2/\text{CHBr}_3$

Table 2. Estimates of global coastal CHBr_3 and CH_2Br_2 fluxes. See text for details.

	% of ocean area	Mean CHBr_3 water concentration (pmol dm^{-3})	Areal CHBr_3 flux Mean and range ($\text{nmol m}^{-2} \text{d}^{-1}$)	Global flux Mean and range (Gmol (Br) yr^{-1})
Coastal (0–50 m)	1.4%	209 ± 89	367 (209–527)	2.0 (1.1–2.9)
Coastally-influenced (50–180 m)	6.1%	11.5 ± 4.8	20.3 (11.9–28.9)	0.5 (0.3–0.7)

flux ratios are on average 7% higher than their equivalent water concentration ratios). This leads to a “coastal” (i.e., macroalgal-rich, since this is the environment of most of the coastal measurements shown in Fig. 7) $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ molar emission ratio of ~ 0.14 (from a molar water concentration ratio of ~ 0.13 at 300 pmol dm^{-3} CHBr_3) and an “open ocean” molar emission ratio of ~ 0.45 (from a molar concentration ratio of ~ 0.41 at 4 pmol dm^{-3} CHBr_3). 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. However, assuming that coastal sources contribute 23–75% of the world’s CHBr_3 and CH_2Br_2 (Quack and Wallace, 2003; Butler et al., 2007a), the global $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ oceanic emission ratio should be in the range 0.21–0.38, which is similar to the range of 0.29–0.38 calculated on the basis of atmospheric sinks (WMO, 2003). We suggest that $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ emission ratios deduced only from coastal data may be significantly biased low.

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. (2007a), 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 35.6 and $13.3 \text{ nmol m}^{-2} \text{d}^{-1}$ for CHBr_3 and CH_2Br_2 , respectively, which are in accordance with the Mauritanian upwelling fluxes of Quack et al., 2007a) and the “tropical” data 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 (0.006–0.3) Gmol (Br) yr^{-1} from CHBr_3 and 0.03 (0.006–0.08) Gmol (Br) yr^{-1} from CH_2Br_2 , comprising on average around 1% of the total global emissions of these compounds (Quack and Wallace, 2003; Butler et al., 2007a).

Although recent studies are in agreement on the total global emissions of CHBr_3 as ~ 10 (3–22) Gmol (Br) yr^{-1} (Quack and Wallace, 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 of open ocean emissions, and suggested that open seawater contributes around $1.9 \text{ Gmol (Br) yr}^{-1}$ CHBr_3 , compared to Quack and Wallace’s estimate of $3 \text{ Gmol (Br) yr}^{-1}$ CHBr_3 . Based on limited data from coastal regions, Butler et al. (2007a) tentatively concluded that coastal sources contribute up to $8 \text{ Gmol (Br) yr}^{-1}$ of the world’s CHBr_3 , whereas Quack and Wallace (2003), from a compilation of data sets, suggested a figure of $2.3 \text{ Gmol (Br) yr}^{-1}$, with $4.7 \text{ Gmol (Br) yr}^{-1}$ 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 8, 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). The data shown in Figure 8 indicate an average concentration of $209 \pm 89 \text{ pmol dm}^{-3} \text{ CHBr}_3$ for waters below 50 m and $11.5 \pm 4.8 \text{ pmol dm}^{-3} \text{ CHBr}_3$ (where ranges indicate observed variability) for waters between 50–180 m depth, assuming a linear distribution of depths between 0–50 and 50–180 m. As discussed in Sect. 3.3, and shown also in Fig. 7 these data are representative of the literature in coastally-influenced waters. Extrapolated to shallower depths, assuming a log-log relationship between depth and concentration, they indicate a maximum CHBr_3 concentration of $1200 \text{ pmol dm}^{-3}$, which is representative of observations in the close vicinity of macroalgal beds (Quack and Wallace, 2003).

Using this data and assuming a mean SST of 15°C and a wind speed of 7 m s^{-1} , we estimate tentatively that coastal and coastally-influenced waters together contribute around 2.5 (1.4–3.5) Gmol Br yr^{-1} (Table 2), neglecting contributions from anthropogenic sources such as coastal power stations (Quack and Wallace, 2003), which are not thought to have affected our study regions. There are various possible flaws in these estimates; not least they are based upon data from only limited regions mainly in the northern hemisphere and they assume a linear distribution of ocean depths rather than a weighted distribution. These different flaws can introduce both positive and negative biases. Nevertheless, we believe the approach offers some improvement to previous approaches because it attempts to integrate data over the coastal zone. Our coastal flux estimate is much less than the $8 \text{ Gmol Br yr}^{-1}$ estimate of Butler et al. (2007a) but close to the near-shore estimate of Quack and Wallace (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} . Refinement of these estimates requires 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 bathymetric data to allow a more accurate assessment and definition of coastal emissions.

4 Conclusions

Simultaneous seawater and air measurements of CHBr_3 and CH_2Br_2 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 CH_2Br_2 in the open ocean. Along with previous studies, we find that macroalgae-rich coastlines are a very significant source of bromocarbons. Surface water bromocarbon concentrations in these regions can be related to ocean depth, i.e. they decrease as the waters are diluted away from the coastline. A crude analysis of coastal CHBr_3 emissions integrated over the coastal zone (0–180 m depth) indicates that coastal con-

tributions to global CHBr_3 emissions are similar to the total open ocean contribution. There is evidence that, outside of these 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 globally, supply at most a few percent of total emissions.

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