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Atmospheric
bromoform at Mace
Head

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Atmospheric bromoform at Mace Head, Ireland: Evidence for a peatland source

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Abstract

In situ atmospheric observations of bromoform ($CHBr_3$) made over a 2.5 year period at Mace Head, Ireland from May 2001–December 2003, including during the NAMBLEX (North Atlantic Marine Boundary Layer Experiment) campaign, show broad maxima from spring until autumn and winter minima, with mixing ratios of 5.3+1.0 pptv (mid March–mid October) and 1.8+0.8 pptv (December–February). This indicates that, unlike $CHCl_3$, which has a summer minimum and winter maximum at Mace Head, local biological sources of $CHBr_3$ have a greater influence on the atmospheric data than photochemical decay during long-range transport. The emission sources are predominantly macroalgal, but we find evidence for a small terrestrial flux from peatland ecosystems, which so far has not been accounted for in the $CHBr_3$ budget. Sharp increases in $CHCl_3$ and $CHBr_3$ concentrations and decreases in O_3 concentrations occurred at night when the wind direction switched from an ocean- to a land-based sector (land breeze) and the wind speed dropped to below 5 ms^{-1}. These observations infer a shallow atmospheric boundary layer with increased O_3 deposition and concentration of local emissions of both $CHCl_3$ and $CHBr_3$. The ratio of $\Delta CHCl_3/\Delta CHBr_3$ varied strongly according to the prevailing wind direction; from 0.6+0.1 in south-easterly (100–170°) air to 1.9+0.8 in north-easterly (40–70°) air. Of these land-sectors, the south-easterly air masses are likely to be strongly influenced by macroalgal beds along the coast and the emission ratios probably reflect those from seaweeds in addition to land sources. The north-easterly airmasses however have a fetch predominantly over land, which locally is comprised of coastal peatland ecosystems (peat bogs and coastal conifer plantations), previously identified as being strong sources of atmospheric $CHCl_3$ under these conditions. Although we cannot entirely rule out other local land or coastal sources, our observations also suggest peatland ecosystem emissions of $CHBr_3$. We use correlations between $CHCl_3$ and $CHBr_3$ during the land breeze events in conjunction with previous estimates of local wetland $CHCl_3$ release to tentatively deduce a global wetland $CHBr_3$ source of 26.9 (0.5–1247) Gg yr^{-1}, which is approximately 10% of the total

global source.

1. Introduction

Bromoform is ubiquitous in the marine environment and is the major natural carrier of organic bromine to the atmosphere. It has a relatively short tropospheric lifetime of ~3 weeks and is believed to make a significant contribution to inorganic bromine in the upper troposphere and lower stratosphere (Sturges et al., 2000; Nielsen and Douglass, 2001; von Glasow et al., 2004). The major sources of $CHBr_3$ have been identified as marine in origin, namely macroalgae, ocean phytoplankton and water chlorination (Gschwend et al., 1985; Carpenter and Liss, 2000; Quack and Wallace, 2003 and references therein). To date, there are only limited and inconclusive studies of production by terrestrial ecosystems. $CHBr_3$ has been found in the air of upper soil of a pristine spruce forest (Haselmann et al., 2000). However, in soil air of rural areas, Hoekstra et al. (1998) found no detectable concentrations of $CHBr_3$, except after in-situ enrichment by KBr. This suggests the potential of soils containing elevated bromide, e.g. coastal soils/peatlands, to produce brominated trihalomethanes. Peat bogs cover approximately 3% of the total continental land mass. They are comprised exclusively of organic matter and in additional coastal bogs are subject to deposition of halides from sea spray, making such sites potentially significant organohalogen producers. Biester et al. (2004) found that the majority of halogens in peat exist in an organically bound form, with concentrations dependent upon peat decomposition processes. Speciated organohalogens were however not identified in this study.

Chloroform concentrations at Mace Head can be substantially influenced by local biological emissions from the pine forests and peat bogs, which cover large parts of Ireland (Dimmer et al., 2001; O'Doherty et al., 2001). Extrapolating from chamber studies made on Irish peatland ecosystems, Dimmer et al. (2001) estimated global annual fluxes of 4.7 (0.1–151.9) $Gg\,yr^{-1}$ of $CHCl_3$ from such systems and 24.1 $Gg\,yr^{-1}$ from total wetlands. $CHBr_3$ measurements were not made in the latter study. Here, we

present over 2.5 years of $CHBr_3$ data measured at Mace Head and use the tracer-ratio technique, in conjunction with the data from Dimmer et al., to estimate the contribution of peatland and wetlands to global $CHBr_3$ emissions.

2. Experimental

2.1. Site description

Mace Head is located on the remote western coast of County Galway, Ireland (53°19′ N, 9°54′ W). The site is well known for background air measurements and receives relatively clean marine air from the prevailing westerly sector associated with the easterly tracking cyclonic systems of the North Atlantic. The surrounding area is sparsely populated and contains a large expanse of peat bogs. The nearest large population centre is Galway, ∼62 miles to the east. Read et al. (2005)[1] give a full description of the site.

2.2. Instrumentation

The York halocarbon measurements were made during the NAMBLEX campaign (2 August–3 September 2002) with a Perkin Elmer Turbomass GC-MS system with electron impact ionisation and operating in selective ion recording mode. Air sampling was from a height of 20 m through a stainless steel 3/4″ manifold, pumped at ∼30 L min^{-1}. Sample volumes of 3 L were pre-concentrated on a two stage carbon-based adsorbent trap held at –10°C before being transferred to the GC by rapid heating to 400°C. Halocarbons were separated on a SGE BPX5 capillary column (50 m×0.32 mm i.d.×3 μm d.f.). Detection limits are between 0.02 and 0.12 pptv for approximately hourly samples of $CHCl_3$, CH_3I, C_2H_5I, $1\text{-}C_3H_7I$, $2\text{-}C_3H_7I$, CH_2ClI, CH_2Br_2,

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[1]Read, K. A., Heard, E., Methven, J., and The NAMBLEX team: The North Atlantic Marine Boundary Layer Experiment (NAMBLEX). Overview of the campaign held at Mace Head, Ireland, in summer 2002, Atmos. Chem. Phys. Discuss., submitted, 2005.

CHBr$_2$Cl, CH$_2$BrI, CHBr$_3$ and CH$_2$I$_2$ with a precision of 3–8% (5% for CHBr$_3$) and complete recovery of all compounds. Our calibration system utilises fixed volume (50 μl) loop injections of the output of thermostatted in-house permeation tubes filled with pure liquids (≥97% purity, Aldrich, UK) into a 100 ml min^{-1} stream of purified nitrogen gas in order to dilute parts per million by volume (ppmv) mixing ratios into low parts per trillion by volume (pptv). The calibration is completely automated, allowing multi-point calibrations during routine operation. The overall accuracy of the measurements is estimated to be ±15%. A full description of the calibration and GC-MS methodology is given in Wevill and Carpenter (2004).

Routine AGAGE (Advanced Global Atmospheric Gases Experiment) GC-MS observations, made by Bristol University, of a range of halocarbons commenced at Mace Head in 1994. A full description of the instrumentation can be found in Prinn et al. (2000) and Simmonds et al. (1995). A nominal, precisely repeatable two liters of ambient air or calibration standard are trapped onto a 3-stage mixed adsorbent contained in a microtrap. The microtrap is located between two thermoelectric coolers maintained at –50°C during sampling. This low temperature enables the small mass of adsorbent material to have the capacity to quantitatively trap the compounds of interest. The trapped sample is purged briefly with clean helium then thermally desorbed (245°C) directly onto a chromatographic capillary column (CPSil-5, 100 m×0.32 mm i.d. ×5 μm d.f.), interfaced to an Agilent benchtop MS. The individual trace components are separated and identified using both their chromatographic retention times, and their characteristic ion masses. Each component is quantified by integrating the response of a selected target ion and where possible, two qualifier ions are used to ensure compound specific ion ratios are maintained. Custom software developed at Scripps Institution of Oceanography (SIO), enables constant monitoring of ion ratios, peak width ratios and many other diagnostic parameters. This enables rapid identification and determination of instrumental problems. At present standard and air analysis are alternated every two hours to provide six calibrated measurements per day. The method of standard preparation and propagation is described in detail in O'Doherty et al. (2004). Briefly,

all working standards are 35 l stainless steel electropolished tanks (Essex Cryogenics, Missouri, USA) filled with either Mace Head "real-air", under baseline conditions, and have a working life of 3–4 months. Calibration of ambient air measurements is achieved by means of bracketing them with measurements from a working standard
5 tank. At present we do not assign a $CHBr_3$ calibration for the ADS-GC-MS data at Mace Head.

2.3. Comparison of York/Bristol measurements and conversion of Bristol $CHBr_3$ relative response to pptv values

An "organic" x-y correlation (i.e. assuming equal errors in x and y data) of York/Bristol
10 $CHCl_3$ data taken within the same 40-min period during the NAMBLEX campaign showed that on average the York measurements were 13% higher than the AGAGE data (with zero offset), with an R^2 value of 0.95 (Fig. 1a). The fact that the instruments were not sampling for the same time periods may explain some or most of the scatter, however there is clearly also a calibration difference although this is within the
15 estimated error of our measurements.

    The same procedure for the correlation of York $CHBr_3$ mixing ratios against the Bristol $CHBr_3$ relative response to a Mace Head reference air sample contained in a 36L electropolished Essex canister) revealed more variance in the linear regression (R^2 value of 0.74) and an offset in the Bristol data (Fig. 1b). Because the York instrument
20 has the same precision for $CHBr_3$ and $CHCl_3$ measurements (Wevill and Carpenter, 2004), we attribute the increased scatter of the correlation compared to Fig. 1a to the shorter lifetime and hence greater natural variability of atmospheric $CHBr_3$. The offset of the Bristol data may be caused by incomplete trapping or recovery of high concentrations of $CHBr_3$ in the microtrap, which was designed for quantitative measurements of
25 the more volatile Halons and CFCs rather than $CHBr_3$. A comparison of the York data with Bristol $CHBr_3$ mixing ratios converted using both the organic regression values and a standard linear least squares regression (with York data on the x axis) is shown in Fig. 2 and reveals the higher dynamic range of the York data. Although the Bristol

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instrument appears to underestimate the highest mixing ratios of $CHBr_3$, nevertheless the average concentrations derived using this approach are equal to the York average concentrations. We chose to use a standard correlation to "correct" the Bristol data to mixing ratios because the organic correlation under-predicted low values and in fact resulted in occasional negative mixing ratios in winter.

2.4. Data selection for local land breeze events

Land breeze events, where the wind direction changes from westerly (ocean sector) in the day to easterly (land sector) at night, are quite commonly observed at Mace Head (e.g. O'Doherty et al., 2001; Biraud et al., 2002). They are accompanied by a rapid decrease in O_3, due to increased deposition over land, and increase in $CHCl_3$, CO_2 and ^{212}Pb concentrations during low wind speeds due to local emissions (Biraud et al., 2002). Here, we select events within the land sector (20–140°) with a > than 40% maximum decrease in $[O_3]$ and >100% change in $[CHCl_3]$. We define the fetch of the land breeze events as the product of their time duration (typically 5–7 h) and the average wind speed recorded during the event (typically 1–5 m s^{-1}) and select events with a fetch of <50 km, i.e. dominated by local continental emissions.

2.5. Tracer-ratio approach

The tracer-ratio technique has been used, in various forms, to estimate trace gas emissions by utilising correlations obtained with a reference compound with a known emission, in this case $CHCl_3$ (e.g. Dunse et al., 2001; Biraud et al., 2002; Carpenter et al., 2003). Visual inspection of the data from Mace Head clearly showed the strong covariance of $CHCl_3$, $CHBr_3$ and O_3 concentrations during land breeze events. For each event, the maximum change in concentration ΔX (where X=$CHCl_3$ or $CHBr_3$) was calculated (the maxima in both species were always coincident temporally), both in units of pptv, yielding one data point for each event. We then use the simple approach of

assuming a linear relationship between the enhancements in mixing ratio,

$$\Delta CHCl_3/\Delta CHBr_3 = E \tag{1}$$

where E is the emission ratio, deduced from the slope of the x-y graph. Here we omit the intercept term, a function of the relative initial concentrations of the trace gases (e.g. Carpenter et al., 2003). The overall approach assumes no atmospheric decay along the trajectory, which in this case should apply, given the short fetches.

3. Results and discussion

3.1. General trends and seasonality

The complete Bristol data set, fixed to the York calibration scale as described in Sect. 2.3, is shown in Fig. 3. Broad spring-autumn maxima, with occasional peaks of over 25 pptv but an average of ~5 pptv, and winter minima are apparent. Figure 4 shows an averaged annual cycle for $CHBr_3$, comprising 2-weekly average data points, with mixing ratios of 5.3±1.0 pptv (mid March–mid October) and 1.8±0.8 pptv (December–February). Also shown is an average UVB (290–320 nm) annual cycle computed for Mace Head. The only other published annual measurements of $CHBr_3$ have been made at the free tropospheric site of Mauna Loa (Atlas and Ridley, 1996, discussed in Nielsen and Douglass, 2001) and at Alert, in the Arctic boundary layer (Yokouchi et al., 1996). Both these studies showed winter maxima and summer minima, suggesting higher reactive loss in summer during long-range transport, but could give little information on the seasonal variation of sources. Thus our data gives a unique insight into the seasonal variation of coastal $CHBr_3$ emissions.

$CHBr_3$ appears to be the most abundant organic halogen compound emitted from macroalgae (e.g. Nightingale et al., 1995; Mtolera et al., 1996; Carpenter et al., 2000) and these emissions are significant on a global scale, comprising probably the dominant source of atmospheric $CHBr_3$ (Carpenter and Liss, 2000). Halocarbon formation

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in macroalgae is initiated by oxidative stress, resulting in H_2O_2 production as part of a defense mechanism (Theiler et al., 1978; Pedersén et al., 1996 and references therein). The formation of polyhalomethanes are initiated by haloperoxidase enzymes produced in the cells, which catalyse the reaction of accumulated halide ions with H_2O_2, forming a hypohalous acid. Halogenated species such as $CHBr_3$ may be subsequently formed in the algal cells and transferred across the cell membrane to seawater (Gschwend et al., 1985). Alternatively, formation may be initiated outside the cell by reaction of the released hypohalous acid with organic matter in seawater (Wever et al., 1991).

Macroalgae exhibit quite constant cover over the course of the year, resulting from the continual recruitment of young plants and the prolific output of spores. Our data indicate that $CHBr_3$ emission occurs all year, with only a short winter period of minimal levels (November–February), when the algal population of the intertidal region is at its lowest. Goodwin et al. (1997) and Klick (1993) reported that $CHBr_3$ release from brown macroalgae maximises in mid summer, probably due to enhanced tissue decay during this period. Further, a number of studies have shown that $CHBr_3$ release from macroalgae is stimulated by light (e.g. Klick, 1993; Nightingale et al., 1995; Mtolera et al., 1996; Goodwin et al., 1997; Carpenter et al., 2000). Light-induced stress, especially at high light intensities, results in increased cellular levels of activated oxygen species including hydrogen peroxide, as by-products of oxygenic photosynthesis, which generally increase the emission of halocarbons. Seaweed incubation experiments reveal an enhancement in $CHBr_3$ release by factors of 2–10 in daylight compared to the dark. Thus, variation in light intensities and/or tissue decay, in conjunction with higher algal coverage from early spring through to late autumn, could explain the seasonal variation of $CHBr_3$ at Mace Head.

It is well established that trace gas emissions from phytoplankton tend to peak in spring (at this latitude around early May), however the contribution of temperate microalgae to atmospheric $CHBr_3$ levels at Mace Head is probably minimal (Carpenter et al., 2003). The highest $CHBr_3$ concentrations are consistently found along coastlines containing macroalgal beds, with coastal and shelf seawater concentrations of $CHBr_3$

of up to 100 times greater than open ocean concentrations (Quack and Wallace, 2003).

3.2. Land breeze events

In total, 28 land breeze events as defined by the selection criteria described in Sect. 2.4 were identified during mid 2001–2003, all occurring during the period 23:00–04:00. These events were characterised by sharp changes in wind direction (from sea to land), $[O_3]$, $[CHCl_3]$ and $[CHBr_3]$, as typified by the event shown in Fig. 5. Only on the 29/30 August 2002 (during the NAMBLEX campaign) were sufficient Bristol and York data available for comparison; the excellent agreement of the (corrected) Bristol and York $\Delta CHCl_3/\Delta CHBr_3$ ratios of 0.62 and 0.61, respectively gives some confidence that both data sets can be used to give an estimate of the emission ratio E in Eq. (1).

Figure 6 shows the $\Delta CHCl_3$ vs. $\Delta CHBr_3$ correlations, separated into events occurring in either south-easterly (100–170°) or north-easterly (40–70°) winds. South-easterly winds travel across the Irish shoreline and are expected to be strongly influenced by local macroalgal emissions. During such events, the $CHCl_3/CHBr_3$ ratio was relatively invariant at ∼0.6 ($R^2=0.73$), indicating that average emission ratios of $CHCl_3/CHBr_3$ from the local coastline are also relatively constant. Both $CHCl_3$ and $CHBr_3$ are known products of macroalgae (e.g. Nightingale et al., 1995; Carpenter et al., 2000 and references therein), with $CHBr_3$ consistently produced in higher amounts across many different genera.

In north-easterly winds, with a fetch inland, the $CHCl_3/CHBr_3$ ratio was much higher at 1.9 and exhibited much greater variance ($R^2=0.17$ and relative standard deviation (RSD) of 42%). The large variance in the regression may be due to a number of factors including different starting concentrations of $CHCl_3$ and $CHBr_3$ along the trajectories during the various events, and different emission ratios from local terrestrial sources, e.g. peat bogs, inland marshes and coastal forests. Although $CHBr_3$ was not measured, Dimmer et al. (2001) found strikingly different emission ratios of $CHCl_3$ to CH_3Br in peatland compared to conifer forest in the vicinity of Mace Head, with greater

variation still within vegetation types. Thus, although our measurements show strong evidence of peatland ecosystem sources of $CHBr_3$ at Mace Head, an absolute emission ratio compared to $CHCl_3$ should be treated with caution, not only because of variation within source, but also because of the short atmospheric lifetimes of $CHCl_3$ and

5   $CHBr_3$, and the instrumental issues potentially affecting the Bristol ratios, as discussed in Sect. 2.3. Nevertheless, it is instructive to approximate source strengths from peatland emissions in order to compare with other known source strengths (which are also highly uncertain). Dimmer et al. (2001) estimated a global $CHCl_3$ flux from peatland soil of 4.7 (0.1–151.9) $Gg\,yr^{-1}$ and from total wetlands of 24.1 $Gg\,yr^{-1}$, calculated simply by

10   extrapolating the measured Irish fluxes to estimated global coverages; $1.04\times10^6\,km^2$ for peatbog (Olson, 1992) and $5.3\times10^6\,km^2$ for wetlands (Matthews and Fung, 1987). We use the 1σ limits of the $CHCl_3/CHBr_3$ ratio determined here of 1.9 (1.1–2.7), together with $CHCl_3$ source estimates to deduce a total global $CHBr_3$ peatland source of 5.2 (0.1–241) $Gg\,yr^{-1}$ and wetlands source of 26.9 (0.5–1247) $Gg\,yr^{-1}$. Any non-

15   peatland ecosystem sources of either $CHCl_3$ or $CHBr_3$ over the north-easterly fetch will add error to our peatland emission estimates. However, despite the large uncertainties involved, it is worth comparing our peatland and wetland source estimates with current estimates for $CHBr_3$ emission of 220 $Gg\,yr^{-1}$ from macroalgae (Carpenter and Liss, 2000) and a total global source of 300 $Gg\,yr^{-1}$ (Dvortsov et al., 1999). Thus, it is

20   possible that peatland and wetland emissions of $CHBr_3$ together are a small (~10%) but significant unaccounted term in the $CHBr_3$ budget.

4. Conclusions

So far, global modelling studies of tropospheric and stratospheric bromine that have specifically included $CHBr_3$ (Dvortsov et al., 1999; Nielsen and Douglass, 2001; von

25   Glasow et al., 2004) have assumed a seasonally invariant ocean source of $CHBr_3$. Our study indicates a much stronger source of $CHBr_3$ in summer than in winter, possibly linked to light levels and macroalgal coverage, and points to an additional coastal ter-

restrial source in the $CHBr_3$ budget of (tentatively) around 10% of the global source. The dual roles of such ecosystems in conjunction with macroalgae indicate the dominance of coastal regions in providing $CHBr_3$ to the atmosphere. Changes in wetland emissions, through man's impact on land use, and in ultraviolet radiation at the earth's surface due to the effect of ozone-depleting substances on stratospheric ozone, show the possibility of anthropogenic effects on the release of $CHBr_3$, which itself is an ozone-depleting substance.

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(a)

(b)
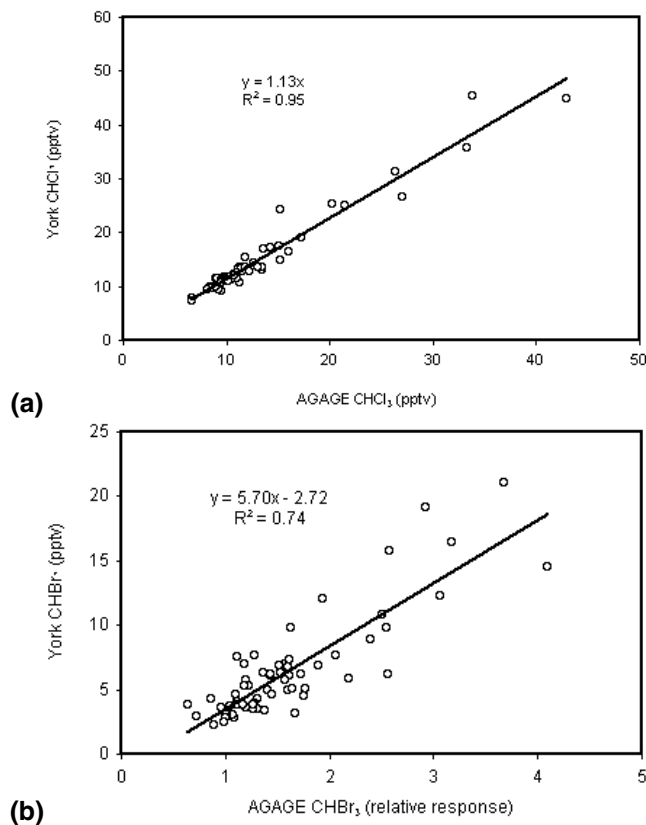
Fig. 1. **(a)** Organic correlation of York and Bristol $CHCl_3$ mixing ratios measured during the NAMBLEX campaign, using data points taken within the same 40-min period. **(b)** Organic correlation of York $CHBr_3$ mixing ratios and Bristol $CHBr_3$ relative response data, using data points taken within same 40-min period.

Atmospheric bromoform at Mace Head

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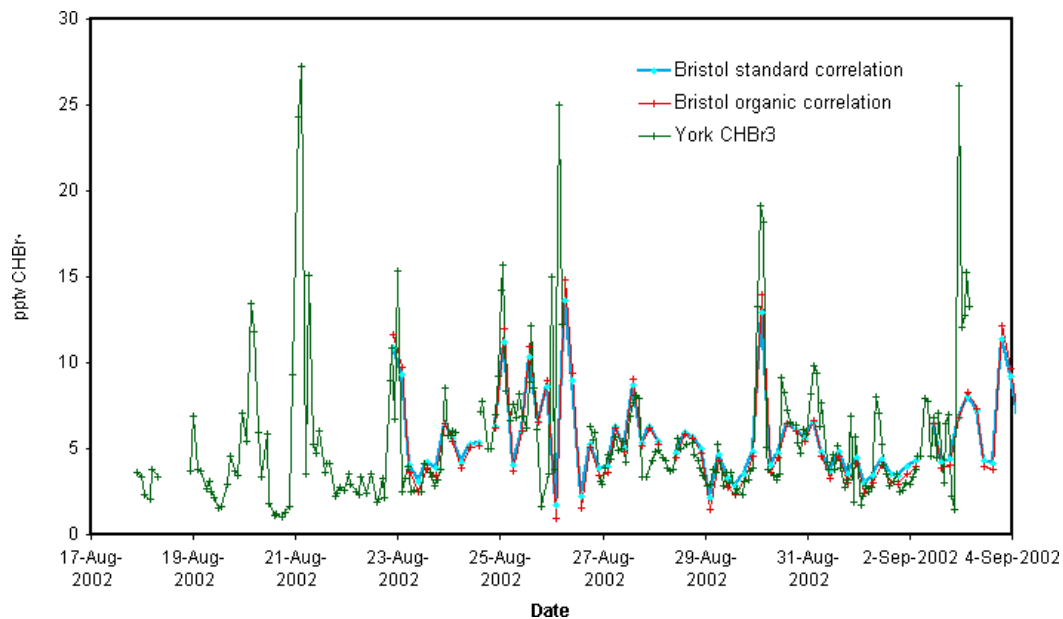
Fig. 2. Comparison of York and Bristol CHBr$_3$ data, the latter converted to mixing ratios using both the organic correlation of Fig. 1b and a standard correlation.

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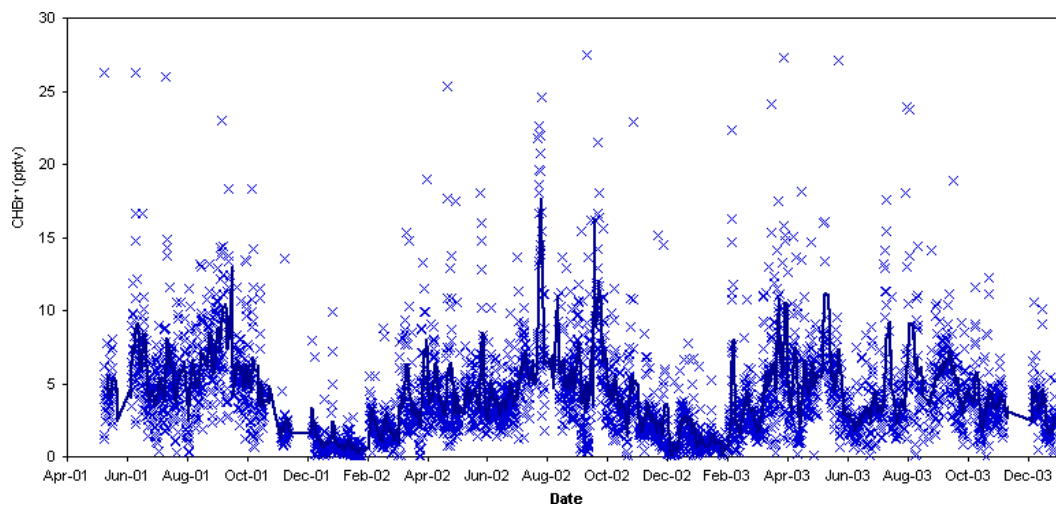
Fig. 3. Bristol $CHBr_3$ data fixed to the York calibration scale. The crosses are individual (approx. 4-hourly) data points and the solid line is a 20-point moving average.

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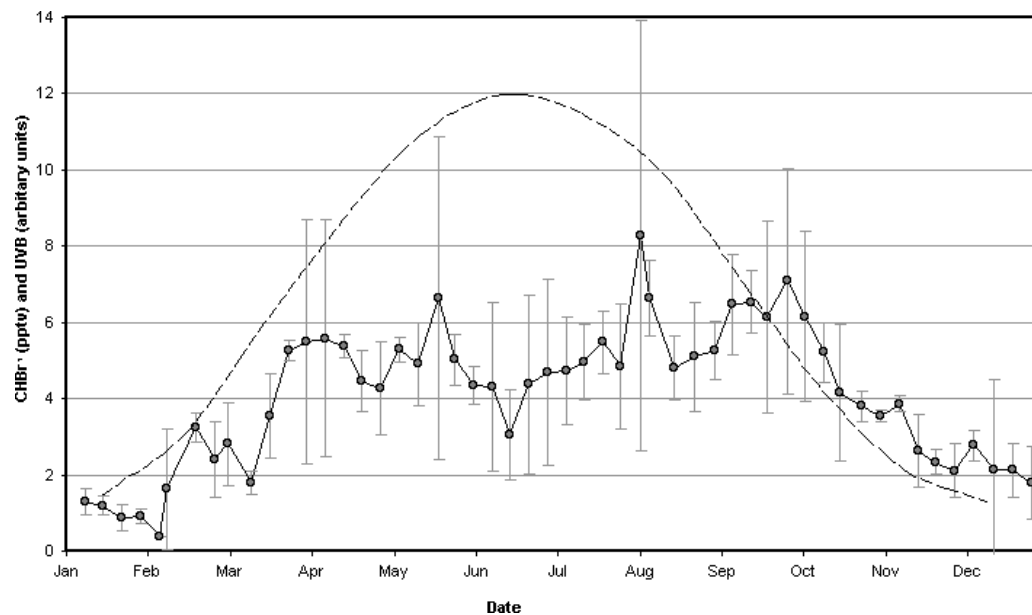
Fig. 4. Mean annual cycle of $CHBr_3$ and UVB at Mace Head. The error bars on the $CHBr_3$ data are the RSDs of the 2-weekly average data points.

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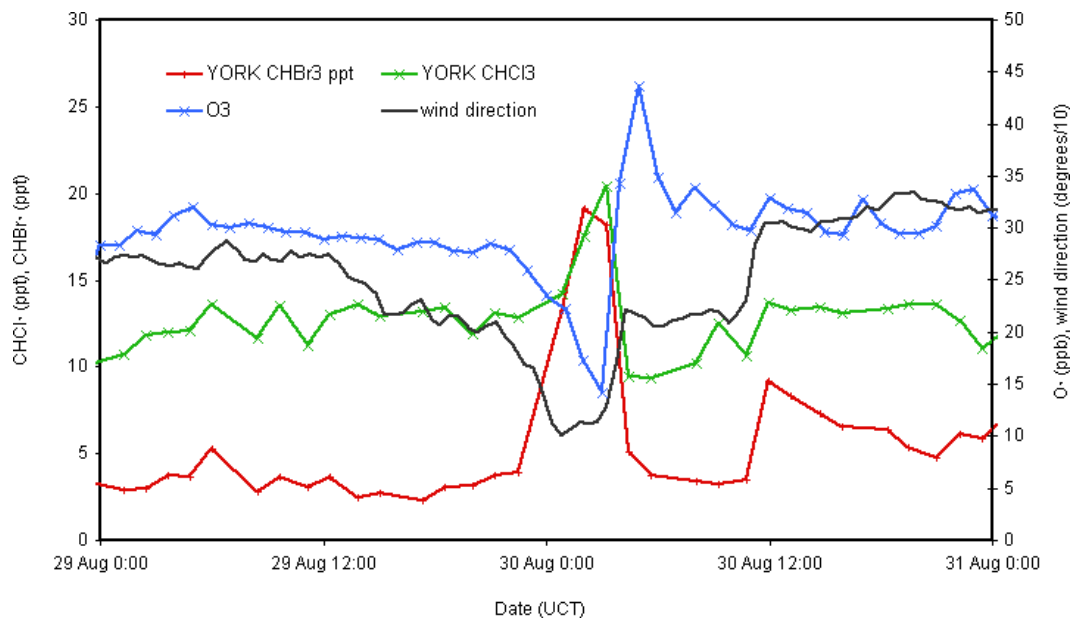
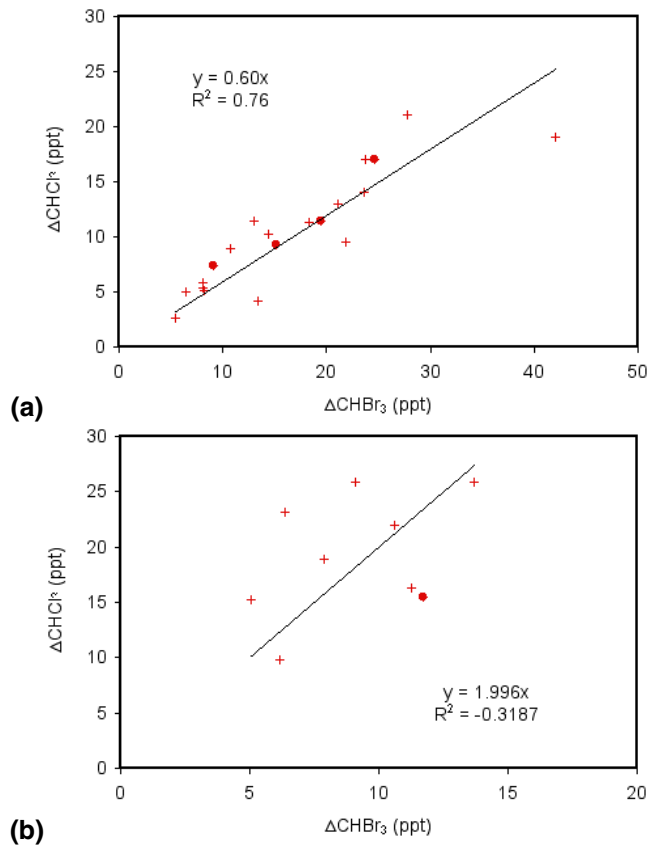**Fig. 5.** Land breeze event during the night of 29/30 August 2002.

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Fig. 6. $\Delta CHCl_3/\Delta CHBr_3$ ratios obtained using both Bristol (crosses) and York (filled circle) data, separated into **(a)** south-easterly (100–170°) and **(b)** north-easterly (40–70°) winds.