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# Coastal measurements of short-lived reactive iodocarbons and bromocarbons at Roscoff, Brittany during the RHaMBLe campaign

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## Abstract

Atmospheric concentrations of the volatile reactive iodocarbons $C_2H_5I$, 1-$C_3H_7I$, 2-$C_3H_7I$, $CH_2ICl$, $CH_2IBr$, $CH_2I_2$ and bromocarbons $CH_2Br_2$ and $CHBr_3$ were determined by GC/MS analysis of marine boundary layer air at Roscoff, Brittany on the northwest coast of France during September 2006. Comparison with other coastal studies suggests that emissions of these trace gases are strongly influenced by site topography, seaweed populations and distribution, as well as tide height. Concentrations of the very short-lived dihalomethanes $CH_2IBr$ and $CH_2I_2$ in particular showed evidence of tidal dependence, with higher concentrations observed at low tide during maximum exposure of seaweed beds. We also present a limited number of halocarbon concentrations in surface seawater and estimate sea-air fluxes based on simultaneous water and air measurements of these gases. $CH_2Br_2$ and $CHBr_3$ were strongly correlated both in air and in seawater, with $CH_2Br_2/CHBr_3$ ratios of 0.19 in air and 0.06 in water. The combined midday I atom flux from the photolabile diahlomethanes $CH_2I_2$, $CH_2IBr$ and $CH_2ICl$ of $\sim 5\times10^3$ molecules cm$^{-3}$ s$^{-1}$ is several orders of magnitude lower than the estimated I atom flux from $I_2$ based on coinciding measurements at the same site, which indicates that at Roscoff the major I atom precursor was $I_2$ rather than reactive iodocarbons.

## 1 Introduction

Emission of iodine- and bromine-containing trace organic compounds into the atmosphere affects the chemical balance of both the troposphere and the stratosphere and has implications for climate. The breakdown of photolabile organic iodine compounds (iodocarbons) to release I atoms and subsequent formation of IO can initiate catalytic ozone depletion cycles and modify $NO/NO_2$ and $OH/HO_2$ cycles with resulting effects on lifetimes of other climatically important trace gases (Vogt et al., 1999; Carpenter, 2003; Bloss et al., 2005; Read et al., 2008) within the marine boundary layer (MBL). In contrast to the iodocarbons which are broken down within the troposphere, it has been suggested that a fraction of the relatively longer lived bromocarbons (e.g. $CH_2Br_2$ and $CHBr_3$) can be transported to the lower stratosphere, and potentially contribute ~20–60% of stratospheric bromine (Sturges et al., 2000; Pfeilsticker et al., 2000; Nielsen and Douglass, 2001).

Short-lived volatile halogenated organic compounds (VHOCs) are produced by marine algae, and although the exact purpose of their production is not fully understood, possible explanations include release of halocarbons by means of a chemical defence mechanism against grazing herbivores (Wever et al., 1991) and as by-products of reactions to scavenge oxidants such as $H_2O_2$, OH and $O_3$ which may cause damage to the plant (Pedersen, 1996). $H_2O_2$ is produced by normal metabolic activity within the plants cells, however when macroalgae (seaweeds) are subjected to oxidative stress, additional $H_2O_2$ is released as part of a defence mechanism, and can reach levels that exceed the plants cellular scavenging capacity (Theiler et al., 1978; Pedersen et al., 1996; Palmer et al., 2005). Iodide and bromide ions are accumulated within macroalgae at concentrations of up to 30 000 times their seawater concentrations (Küpper et al., 1998) and are incorporated into an $H_2O_2$ removal mechanism, catalysed by haloperoxidase enzymes, to produce hypohalous acids (HOI and HOBr), which are thought to subsequently react to form polyhalomethanes such as $CH_2I_2$ and $CHBr_3$ (Wever et al., 1991). There is evidence for increased halocarbon production from intertidal macroalgae during low tide when the plant is exposed and subjected to oxidative stress (Carpenter et al., 1999). The mono-iodinated compounds are believed to be produced by a different pathway involving methyl transferase enzymes (Wuosmaa and Hager, 1990).

The precusors for iodine atoms in coastal areas were initially proposed to be iodine-containing short-lived VHOC (Carpenter et al., 1999). However, more recent studies show that biogenic emission of $I_2$ by macroalgae is one of the most important processes responsible for the observed iodine levels in the coastal MBL (McFiggans et al., 2004; Saiz-Lopez and Plane, 2004; Pirjola et al., 2005; Palmer et al., 2005). The

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source of $I_2$ appears to be the reaction of atmospheric $O_3$ with the iodide accumulated in macroalgae (e.g., *Laminaria digitata*) when the plants are exposed to ambient air at low tide, leading to the direct release of $I_2$ into the atmosphere (Küpper et al., 2008). Mixing ratios of up to 93 ppt $I_2$ have been detected at Mace Head on the west coast of Ireland (Saiz-Lopez et al., 2006), but in contrast, no $I_2$ was observed above the instrument detection limit (~20 ppt) during a study at a French coastal site in Brittany (Peters et al., 2005). In addition, very high concentrations of reactive iodocarbons were measured during the Brittany study, such that it was proposed that the observed levels of IO could be sustained by photolysis of the iodine-containing VHOCs alone (Peters et al., 2005).

Both macroalgae and microalgae (phytoplankton) are thought to initiate release of volatile iodo- and bromocarbons, and consequently the marine environment provides the major source of these trace gases to the atmosphere. Production from macroalgae provides a relatively large localized source to the coastal MBL, and although per unit biomass production from microalgae is considerably less, microalgae have the potential to provide an ocean-wide source and so may be significant in terms of global scale emissions.

There have been a number of attempts to “scale up” halocarbon measurements from a limited number of locations to the global scale in order to calculate global emission estimates for these gases, and hence assess their importance as a halogen source to the atmosphere (e.g. Moore and Groszko, 1999; Quack and Wallace, 2003; Butler et al., 2007). All of these studies have noted that there is considerable uncertainty associated with these estimates, not least as a result of the very limited spatial and temporal range in which concentrations of these very short lived halocarbons have been reported, particularly in coastal and coastally influenced waters (Butler et al., 2007). Consequently, increasing the temporal and spatial resolution of halocarbon measurements is essential, and in this study we contribute to this by reporting the concentrations of a number of short-lived VHOC, including the very short-lived dihalomethanes $CH_2ICl$, $CH_2IBr$ and $CH_2I_2$ as well as $CH_2Br_2$ and $CHBr_3$ in ambient air at a coastal site in Roscoff, Brittany

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during the Reactive Halogens in the Marine Boundary Layer experiment (RHaMBLe) campaign in September 2006.

## 2 Methods

The measurement site on the Atlantic coast of Roscoff in Brittany, France (48.72° N, 3.97° W) was chosen in light of the recent work of Peters et al. (2005) which had found elevated levels of halocarbons and halogen oxides further along the Breton coast at Lilia, a coastline with a high inter-tidal range which results in exposure of a vast area of seaweed beds at low tide. Figure 1 shows the location of the Roscoff site which is surrounded by seaweed beds to the north (between Roscoff and the island Ile be Batz), east (towards the open ocean) and south east, which all become exposed at low tide to some extent, and the town to the south.

### 2.1 Analysis of halocarbons in air

Ambient air measurements were made continuously between the 3 and 27 September 2006, with short breaks in sampling for calibrations and instrument maintenance. Halocarbon concentrations in ambient air were determined using a fully automated Perkin Elmer Turbomatrix gas chromatography-mass spectrometer (GC/MS) with 60 m×0.32 mm internal diameter DB5 capillary column and detection by electron impact ionisation quadrupole mass spectrometry. Volatile gases were pre-concentrated from 3 L air samples (100 ml/min for 30 min) prior to analysis using a Perkin Elmer Turbomatrix thermal desorption unit (TD) with a chemical adsorbent trap (Air Monitoring Trap with carbon-based adsorbent, Perkin Elmer). The trap was held at between −30 and −10°C during sampling, then rapidly heated to 300°C to facilitate desorption to the GC/MS. The sample inlet was located ∼20 m behind the high tide mark, at a height of ∼5 m, and air was pumped through a 60 m Teflon PFA manifold at a rate of ∼30 L/min. A clean metal bellows pump (Senior Aerospace Limited) diverted 100 ml/min from the manifold to the online air trapping system, and air was continuously sampled every ~90 min, 24 h per day.

Iodinated species targeted for analysis were $C_2H_5I$, 1-$C_3H_7I$, 2-$C_3H_7I$, $CH_2ICl$, $CH_2IBr$ and $CH_2I_2$, and the brominated gases monitored were $CH_2Br_2$ and $CHBr_3$. Calibrations were achieved using a permeation oven based dynamic dilution technique (described in detail in Wevill and Carpenter, 2004), in addition to daily analysis of an in-house prepared iodocarbon and bromocarbon gas standard (ppt levels in CP grade nitrogen) to account for any day-to-day drift in instrument sensitivity.

### 2.2 Analysis of halocarbons in seawater

On two days during the campaign an identical Perkin Elmer GC/MS equipped with purge and trap facility was used to analyse surface seawater samples for halocarbon concentrations, alongside the continuous air measurements. 40 ml water samples in air-tight gas syringes were collected from several locations between the site at Roscoff and the island Ile de Batz. The water samples were filtered through Minisart 0.45 $\mu$m cellulose filters and stored in the dark at 3°C for a maximum of 6 hours prior to analysis. Seawater samples were sparged for 50 min at 50°C with zero grade nitrogen gas (BOC) at a flow rate of 50 ml/min in order to extract the volatile components into the gas phase prior to pre-concentration using a Perkin Elmer Turbomatrix thermal desorption unit, identical to the system used for analysis of halocarbons in air. Sparging efficiencies for all halocarbons were >95%.

## 3 Results

### 3.1 Halocarbon ambient air concentrations

Table 1 shows the average and range of halocarbon mixing ratios measured in ambient air during the RHaMBLe campaign at Roscoff. Comparison with previous coastal studies indicates that the iodocarbon concentrations at Roscoff were typically much lower

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than those observed further along the coast of Brittany at Lilia (Peters et al., 2005), and were more comparable with the concentrations observed at Mace Head on the west coast of Ireland (Carpenter et al., 1999, 2003). Both the mean and range of $CH_2ICl$ mixing ratios are in particularly close agreement with those measured at Mace Head, while the other (shorter-lived) dihalomethanes $CH_2IBr$ and $CH_2I_2$ were present at similar mean concentrations, but considerably lower maximum concentrations, at Roscoff. Conversely, the longer lived mono-iodinated $C_2H_5I$ was more concentrated in air at Roscoff compared to Mace Head, and the iodopropanes (which were not reported in the Mace Head study) were detected at levels similar to the lower limit concentrations measured at Lilia. The range of $C_2H_5I$, 1-$C_3H_7I$, 2-$C_3H_7I$ and $CH_2IBr$ concentrations observed at Roscoff were also in reasonable agreement with the equivalent measurements at Dagebüll on the German North Sea coast (Peters et al., 2005), while $CH_2ICl$ and particularly $CH_2I_2$ were lower at Roscoff. The $CH_2ICl$ concentrations measured at Roscoff were however in line with those observed on the coast of the island of Spitzbergen, Norway (Schall and Heumann, 1993).

Since the iodocarbon concentrations at Roscoff were most comparable to those at Mace Head, and unlike many other sites, publications containing detailed descriptions of the topography and distribution of seaweed populations at Mace Head are readily available, the following discussion will focus mainly on a comparison of halocarbon concentrations at these two sites. At Mace Head, air was sampled 5 - 10 m above the ground and ~25 m from the high tide mark while at Roscoff the inlet was located ~5 m above the ground and ~20 m from the high tide mark. Thus the difference in the maximum levels of the very short-lived iodocarbons at Roscoff compared to Mace Head cannot be explained by differences in the distance between the seaweed beds and the sampling point at the two sites. However, the higher maximum concentrations of the short-lived dihalomethanes observed at Mace Head could be due to differences in the topography and seaweed taxonomy and spatial distribution at the two sites. The coastlines of Roscoff and Mace Head are both north European rocky shores, however at Roscoff the inter-tidal zone is relatively shallow while at Mace Head the shoreline slopes steeply towards the sea. The *Laminaria* species of macroalgae (e.g. *Laminaria digitata*, *Laminaria saccharina*, *Laminaria hyperborea*) accumulate more iodine than other macroalgae and are thought to be prolific iodocarbon producers (Küpper et al., 1998; Laturnus, 1996; Pedersen et al., 1996; Carpenter et al., 2000). These plants typically inhabit the relatively deeper coastal waters of the lower littoral / sublittoral zones, since they have a substantial root system which requires support, whereas other species of macroalgae such as the *Fucus* family are typically found in the shallower waters of the inter-tidal zone where the light penetration is greater (Barnes, 1986; Yonge, 1949). Species from the order Laminariales have been identified at both Mace Head (Carpenter et al., 1999) and at Roscoff (McFiggans et al., 2009). At Mace Head *Laminaria digitata* is the dominant species close to the shore, while *Laminaria hyperborea* is present in the deeper waters further from the coast (Hornsby et al., 2009). At Roscoff, the distribution of seaweed species is less uniform than at Mace Head, and the inter-tidal zone is mainly dominated by *Fucus*, however there is also a small amount of *Laminaria digitata*, *Laminaria saccharina* and *Laminaria ochroleuca* in the channel between the site and the island Ile de Batz, and large *Laminaria* (mainly *hyperborea*) beds to the north of Ile de Batz (McFiggans et al., 2009). In incubation studies Pedersen et al. (1996) found that *Laminaria digitata* produced around 13 times more $CH_2I_2$ than *Laminaria saccharina*, and so given the abundance of *Laminaria digitata* close to the shoreline at Mace Head it follows that higher levels of $CH_2I_2$ would be observed here compared to Roscoff.

In addition to the seaweed speciation, topographical differences between the two sites may also influence iodocarbon production to some extent. The steep shelving shoreline at Mace Head provides optimum conditions for iodocarbon emissions, since *Laminaria* are present in deep water close to the shore at high tide, but become exposed (and consequently subjected to oxidative stress) at low tide. Conversely the very shallow inter-tidal zone at Roscoff means that the waters closest to the shoreline are too shallow for *Laminaria*, so although a larger horizontal surface area of seaweed beds becomes exposed at low tide, this mainly consists of *Fucus*. The *Laminaria* order mainly inhabit deeper waters outside the inter-tidal zone, and as such there is only very limited exposure of *Laminaria*, even during low tide, at Roscoff. There is only limited information available on the distribution of seaweed species present at Lilia, however Peters et al. (2005) do report “extended fields of macroalgae” including *Laminaria*, *Fucus vesicolosus* and *Ascophyllum nodosum*.

There were good correlations between the concentrations of several iodocarbons in air during the RHaMBLe campaign at Roscoff (see Figure 2), in particular $CH_2I_2$ and $CH_2IBr$ were well correlated (Spearman’s rank correlation coefficient, $\rho$=0.84, which indicates a correlation significant at 99% confidence level) as were the iodopropanes ($\rho$=0.61, significant at 99 % confidence level) and $C_2H_5I$ and 1-$C_3H_7I$ ($\rho$=0.83, significant at 99% level).

The maximum $CH_2Br_2$ and $CHBr_3$ concentrations at Roscoff were below the minimum concentrations observed at Lilia by Peters et al. (2005), and like the iodocarbons are more comparable with concentrations measured at Mace Head (see Table 1). Strong correlations between brominated organohalogens in both air and seawater have been reported in several other studies (Carpenter and Liss, 2000; Carpenter et al., 2003, 2009; Zhou et al., 2008) and are thought to be the result of a common (most likely macroalgal) source of these trace gases. Figure 3 shows that there was a strong correlation between $CH_2Br_2$ and $CHBr_3$ throughout the campaign at Roscoff ($R^2$=0.85, $\rho$=0.91, which corresponds to a correlation that is significant at 99% confidence level), and in addition there was also some degree of correlation (albeit considerably weaker) between $CH_2Br_2$ and $CH_2IBr$ ($R^2$=0.40, $\rho$=0.72). Although the concentrations of $CH_2Br_2$ and $CHBr_3$ vary considerably with location, their relative concentrations have been found to remain fairly consistent. The $CH_2Br_2$ concentration at Roscoff was typically a factor of 0.19 times that of the $CHBr_3$ concentration (as shown by the slope of the $CH_2Br_2$ vs. $CHBr_3$ plot in Fig. 3). This ratio is in good agreement with the slope of 0.15 derived from measurements of these bromocarbons at Mace Head (Carpenter et al., 2003) and is within the range of 0.08–0.21 observed in a number of previous studies (Zhou et al., 2008; Carpenter and Liss, 2000; Carpenter et al., 2009 and ref-

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erences therein). Since the bromocarbons have reasonably long atmospheric lifetimes of ~0.29 years for $CH_2Br_2$ (Zhang et al., 1997) and ~20 days for $CHBr_3$ (Bilde et al., 1998), the ratio of $CH_2Br_2/CHBr_3$ concentrations measured within a few tens of metres of the source may be considered to directly reflect the ratio of the source strength of these gases (Carpenter et al., 2003). The reasonably consistent $CH_2Br_2/CHBr_3$ ratio therefore suggests a direct link between emissions of these bromocarbons, implying a common source(s). A further discussion of $CH_2Br_2/CHBr_3$ ratios in air and in seawater is presented in Carpenter et al. (2009).

### 3.2 Correlations between halocarbons and tide height

Figure 4 shows the $CH_2I_2$ and $CH_2IBr$ concentrations in air during the RHaMBLe campaign overlaid with the tide height. On a number of occasions there was a significant increase in the $CH_2IBr$ (and to a lesser extent $CH_2I_2$) concentration which coincided with low tide i.e. when the surface footprint around the site contained the most exposed macroalgae. Table 2 shows the ratios of mean low tide to mean high tide halocarbon concentrations. For these purposes low tide concentrations were taken to be those measured made while the tide height was <4.25 m and high tide concentrations are the concentrations observed while the tide height was >6.5 m. A statistical t-test was carried out on the high tide and low tide data sub-sets for each halocarbon to determine whether there were significant differences in their concentrations during the two periods (see Table 2).

The only halocarbons which showed statistically significant elevated ambient air concentrations during periods of low tide relative to high tide were those with the shortest tropospheric lifetimes, i.e. $CH_2I_2$ and $CH_2IBr$. The most significant difference between low tide and high tide concentrations of these dihalomethanes occurred during the period from the 5–14 September, when the site was subjected to easterly winds over the channel between Roscoff and Ile de Batz (see Figs. 4 and 6). This period includes the spring tides on the 9 and 10 September when the inter-tidal range was greatest. As discussed above, the prolific iodocarbon producing seaweeds *Laminaria*

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*digitata*, *Laminaria saccharina* and *Laminaria ochroleuca* were present in the channel between Roscoff and Ile de Batz and were only exposed at low tide during the most extreme inter-tidal range. Figures 4 and 5 show that the site consistently experienced easterly winds between the 7 and 10 September, which coincided with moderate tide-related variability in the $CH_2IBr$ and $CH_2I_2$ concentrations. Between the 5–7 and 10–13 September the wind speed was lower, the wind direction was more variable, and the difference in $CH_2I_2$ and $CH_2IBr$ concentrations at high tide compared to low tide became more pronounced (although it should be noted that during periods of maximum dihalomethane concentrations around low tide the wind typically returned to an easterly direction). The lower wind speeds result in less rapid mixing with surrounding air masses and therefore local sources of short-lived dihalomethanes are less rapidly diluted by regional air, and hence the difference in their concentrations during low and high tide is more accentuated. It is also evident from Fig. 4 that there was no increase in $CH_2I_2$ or $CH_2IBr$ coinciding with low tide on the 13 September when the wind speed increased again and the wind direction became predominantly south westerly. There were also statistically significant differences in the mean high tide and low tide concentrations of $CH_2I_2$ and $CH_2IBr$ from the 14–21 September when the site received south easterly to north easterly air masses, despite the fact that this period incorporates neap tides with minimum amount of seaweed exposure at low tide.

The difference between high tide and low tide concentrations of $CH_2I_2$ and $CH_2IBr$ was less significant during the period from the 21–27 September when the winds were predominantly southerly across the town of Roscoff and not crossing the seaweed beds. There was also no significant tide dependent concentration difference apparent in any halocarbon during the 3–5 September when the site received mainly westerly air masses, however it should be noted that there were only a very limited number of measurements made during this period.

In contrast to $CH_2I_2$ and $CH_2IBr$, $CH_2ICl$ was present at significantly higher concentrations at high tide relative to low tide during the 5–14 September and throughout the campaign as a whole, suggesting an alternative/additional production process for this gas other than biosynthesis from seaweeds experiencing oxidative stress. The increase in $CH_2ICl$ at high tide suggests a production mechanism within the water rather than from exposed seaweed beds, and is consistent with a photochemical source of $CH_2ICl$ resulting from photolysis of $CH_2I_2$ in seawater (Jones and Carpenter, 2005, 2006; Martino et al., 2005). An alternative source/production mechanism for $CH_2ICl$ may also explain the absence of any apparent correlation between observed levels of $CH_2ICl$ in air with either the other dihalomethanes or the mono-iodinated gases.

### 3.3 Halocarbon seawater concentrations and sea-air fluxes

During the 11 and 25 September a limited number of seawater samples were analysed for halocarbons, alongside the ambient air measurements. Samples were taken from a range of locations between the site and Ile de Batz, at a range of tide heights. The observed halocarbon concentrations are summarised in Table 3. All halocarbons exhibited elevated concentrations in seawater during low tide compared to high tide and, with the exception of $CH_3I$, the highest concentrations were consistently observed in water directly over kelp beds approximately mid-way between the site and the island, a region characterised by the presence of the seaweeds *Laminaria digitata*, *Laminaria saccharina* and *Laminaria ochroleuca* (McFiggans et al., 2009). Conversely, seawater closer to the site and to the southern shore of Ile de Batz contained relatively lower levels of halocarbons.

On the whole, the seawater concentrations at Roscoff (typically a few pmol $dm^{-3}$ of most halocarbons and up to several hundred pmol $dm^{-3}$ $CHBr_3$) were comparable with other coastal water measurements of these gases (Klick, 1992; Carpenter and Liss, 2000; Carpenter et al., 2000), and the ratio of $CH_2Br_2$ to $CHBr_3$ in seawater is not dissimilar to the slope of 0.09 determined by Carpenter and Liss (2000) for higher concentrations of these bromocarbons (slope=0.063, see Fig. 8).

Figure 8 shows correlations between the seawater concentrations of several bromocarbons and iodocarbons. $CHBr_3$ and $CH_2Br_2$ are exceptionally well correlated, supporting the theory of a common source for these gases. $CH_2I_2$ and $CH_2IBr$ were less well correlated in seawater than in air ($R^2$=0.68, and at lower concentrations there was no strong relationship at all), however the correlation observed between these dihalomethanes broadly supports the hypothesis of related emission rates for these gases. Unlike in the MBL, $CH_2ICl$ in seawater was found to correlate well with both iodocarbons and bromocarbons, in particular $CH_2IBr$ ($R^2$=0.87) and $C_2H_5I$ (an apparent polynomial relationship with $R^2$=0.95). Incubation studies have demonstrated that while *Laminaria digitata* appears to be the most prolific producer of $CH_2I_2$ and $CH_2IBr$, *Laminaria saccharina* produces the highest concentrations of both $C_2H_5I$ and $CH_2ICl$ (Carpenter et al., 2000). As such, although these gases were not well correlated within the MBL, this could potentially be explained by differences in their gas phase photolytic lifetimes and the apparent correlation between $C_2H_5I$ and $CH_2ICl$ in seawater implies that these gases may possess a common source in coastal waters.

Sea-air fluxes based on these seawater concentrations and simultaneously measured halocarbon concentrations in air have been calculated using the Nightingale (2000) approximation for the gas transfer coefficient $k$ ($\{0.222\,u^2+0.333\,u\}\{S_C/660\}^{-1/2}$), the dimensionless Henry's law coefficients from Moore et al. (1995) and the Khalil et al. (1999) approximation for the temperature dependent Schmidt numbers. Mean average sea-air fluxes for each halocarbon based on our limited number of seawater measurements are given in Table 3.

## 3.4 Contribution to I atom flux

The rate of atmospheric I atom production from the most photolabile iodocarbons - the dihalomethanes $CH_2I_2$, $CH_2IBr$ and $CH_2ICl$, have been calculated using the simple equation $d[\mathrm{I}]/dt=n\,J(CH_2IX)\,[CH_2IX]$, where $J(CH_2IX)$ is the respective dihalomethane photolysis rate constant ($s^{-1}$) and $n$ is the number of I atoms released (i.e. $n$=1 for $CH_2IBr$ and $CH_2ICl$ and $n$=2 for $CH_2I_2$). Instantaneous I atom fluxes have been determined from each individual dihalomethane concentration measurement and the relevant $J(CH_2I_2)$, $J(CH_2IBr)$ and $J(CH_2ICl)$ values determined from the on-site spectral

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radiometer measurements (University of Leicester). The diurnal average I atom fluxes over the whole measurement period from the 3–27 September (incorporating data during both spring and neap tides) are shown in Fig. 7. It is apparent that due to its very short photolytic lifetime and yield of 2 I atoms per molecule photolysed, $CH_2I_2$ accounts for the majority of I atom production from dihalomethane photolysis, even though it was present in lower concentrations than $CH_2IBr$ and $CH_2ICl$. We calculate a combined average midday (11:00 a.m.–02:00 p.m. local time) I atom flux from dihalomethanes of around $4.7\times10^3$ molecules cm$^{-3}$ s$^{-1}$, which is considerably lower than the rate of I atom production from photolysis of $I_2$, which we estimate to be roughly $7\times10^7$ molecules cm$^{-3}$ s$^{-1}$ (based on a mean $I_2$ concentration between 11:00 a.m.–02:00 p.m. of 13 ppt, determined by long path DOAS measurements during the RHaMBLe campaign at Roscoff, Mahajan et al., 2009).

Due to the rapid removal of photolabile I atom precursors during the daytime (photolysis lifetimes were ∼10 s and ∼4 min for $I_2$ and $CH_2I_2$, respectively) it is likely that a significant fraction of these trace gases would have been removed before the point of measurement (Mahajan et al., 2009). As such, it may be appropriate to use average night time concentrations in conjunction with midday photolysis rate constants to estimate upper limit I atom fluxes from these species, which would increase the I atom flux from $I_2$ to $\sim3\times10^8$ molecules cm$^{-3}$ s$^{-1}$ (assuming a concentration of 60 ppt, Mahajan et al., 2009). However, unfortunately the same approximation cannot be made for the iodocarbons, since this assumes a constant emission rate between day and night, and the maximum observed concentrations of the dihalomethanes typically coincided with daytime low tide (see Fig. 4), with lower concentrations at night, which implies that emissions of these gases exhibit some level of light-dependence. This is consistent with incubation experiments which have demonstrated that the rate of halocarbon production from *Laminaria digitata* is between 2 and 10 times higher in the light compared to the dark (Carpenter et al., 2000).

## 4 Conclusions

Both iodocarbon and bromocarbon concentrations in the MBL at Roscoff were in good agreement with the values previously reported at Mace Head in Ireland (Carpenter et al., 1999, 2003), but were considerably lower than the concentrations measured further along the Breton coast at Lilia (Peters et al., 2005). It is apparent that site topography, seaweed speciation and distribution greatly influence emissions of reactive halocarbons, and as such caution should be taken in any attempt to scale up coastal measurements from any one site in order to infer global coastal halocarbon emission terms.

It is clear that the iodocarbon and $I_2$ measurements made at Roscoff support previous studies which identified $I_2$ as the dominant source of I atoms to the MBL, rather than reactive iodocarbons. It should be noted, however, that given the substantially shorter lifetime of $I_2$ compared to the iodocarbons, the relative contribution from $I_2$ will be greatest closest to the source, and the relative importance of I atom release from the dihalomethanes compared to $I_2$ will increase with distance from the point of emission. As such, although directly over seaweed beds I atom production from iodocarbons may be considered insignificant in light of greater production from $I_2$, the iodocarbons do have the potential to increase the spatial extent of I atom release over a broader area compared to a source from $I_2$.

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**Table 1.** The mean and range (10th and 90th percentiles) of halocarbon mixing ratios (all ppt) measured in air during the RHaMBLe campaign, and compared to mixing ratios observed in previous studies. $^{*}$ denotes Mace Head data from Carpenter et al. (1999) and $^{\#}$ corresponds to data from Carpenter et al. (2003).

| | Roscoff (RHaMBLe, this work) Range (mean in brackets) | Lilia (Peters et al., 2005) Range | Mace Head (Carpenter et al., 1999$^{*}$, 2003$^{\#}$) Range (mean in brackets) | Dagebull (Peters et al., 2005) Range | Spitzbergen (Schall and Heumann, 1993) Range |
|---|---|---|---|---|---|
| $CH_2ICl$ | 0.03–0.17 (0.10) | 0.35–12.4 | <0.02–0.21 (0.11)$^{*}$ | 0.1–3.0 | <0.004–0.18 |
| $CH_2I_2$ | 0.01–0.07 (0.03) | 0.11–19.8 | 0.02–0.36 (0.05)$^{*}$ | 0.3–3.1 | <0.08–1.02 |
| $CH_2IBr$ | 0.01–0.13 (0.06) | 0.55–9.90 | <0.02–0.32 (0.08)$^{*}$ | 0.04–0.2 | – |
| $C_2H_5I$ | 0.21–0.82 (0.46) | 2.22–96.9 | 0.02–0.21 (0.06)$^{*}$ | 0.3–0.7 | <0.02–2.28 |
| 1-$C_3H_7I$ | 0.08–0.36 (0.18) | 0.35–34.8 | – | 0.01–1.0 | – |
| 2-$C_3H_7I$ | 0.29–0.74 (0.47) | 0.20–9.10 | – | 0.1–0.3 | – |
| $CH_3I$ | – | 7.6–1830 | 0.12–1.47 (0.43)$^{*}$ | 4.7–23.5 | <0.004–2.12 |
| $CH_2Br_2$ | 0.28–1.36 (0.75) | 2.36–262 | 0.28–3.39 (1.44)$^{\#}$ | 0.4–2.0 | – |
| $CHBr_3$ | 0.56–5.35 (2.73) | 10.5–393 | 1.9–16.3 (6.27)$^{*}$ | 1.1–11.2 | – |

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**Table 2.** The low tide to high tide ratio of each species. [a], [b] and [c] correspond to the difference between low tide and high tide concentrations being significant at the 99.9, 99.0 and 95.0% confidence levels respectively; [d] indicates no significant tidal dependence, or a difference with less than 95% confidence.

| Date<br>Air mass | All data | 3–5 Sep<br>A | 5–14 Sep<br>B | 14–21 Sep<br>C | 21–27 Sep<br>D |
|---|---|---|---|---|---|
| $CH_2ICl$ | 0.79[c] | 0.79[d] | 0.77[c] | 0.97[d] | 0.71[d] |
| $CH_2I_2$ | 2.17[a] | 1.96[d] | 2.36[b] | 3.70[b] | 1.94 [d] |
| $CH_2IBr$ | 2.31[a] | 1.32[d] | 2.55[a] | 2.11[b] | 2.60[c] |
| $C_2H_5I$ | 0.97[d] | – | 0.98[d] | 1.03[d] | 1.11[d] |
| 1-$C_3H_7I$ | 0.99[d] | – | 1.12[d] | 1.00[d] | 1.01[d] |
| 2-$C_3H_7I$ | 0.79[d] | – | 0.83[d] | – | – |
| $CH_2Br_2$ | 1.07[d] | 1.02[d] | 1.15[d] | 1.01[d] | 1.04[d] |
| $CHBr_3$ | 1.10[d] | 0.95[d] | 1.19[d] | 1.01[d] | 1.05[d] |

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**Table 3.** Range of halocarbon concentrations measured in seawater, high tide (>6.5 m) and low tide (<4.25 m) average concentrations, mean low tide to high tide ratio and mean sea-air fluxes. * due to lack of ambient air $CH_3I$ measurements in this work the $CH_3I$ flux was calculated using a mixing ratio of 0.43 ppt (based on Mace Head measurements from Carpenter et al., 1999).

| | Range of seawater concentrations (pmol $dm^{-3}$) | Mean high tide concentration (pmol $dm^{-3}$) | Mean low tide concentration (pmol $dm^{-3}$) | Mean low tide/high tide ratio | Mean sea-air flux (nmol $m^{-2}$ $d^{-1}$) |
|---|---|---|---|---|---|
| $CH_2ICl$ | 2.0–7.8 | 2.5 | 4.5 | 1.8 | 20.3 |
| $CH_2I_2$ | 0.1–4.5 | 0.8 | 1.2 | 1.6 | 7.5 |
| $CH_2IBr$ | 1.9–18.9 | 2.9 | 7.3 | 2.5 | 28.0 |
| $C_2H_5I$ | 1.1–3.9 | 2.0 | 2.8 | 1.4 | 22.4 |
| 2-$C_3H_7I$ | 0.8–4.2 | 1.5 | 2.7 | 1.8 | 13.1 |
| $CH_3I$ | 9.0–31.8 | 12.9 | 18.3 | 1.4 | 31.5* |
| $CH_2Br_2$ | 8.3–34.4 | 11.8 | 22.0 | 1.9 | 18.0 |
| $CHBr_3$ | 142.8–519.4 | 217.4 | 343.2 | 1.6 | 1800.0 |

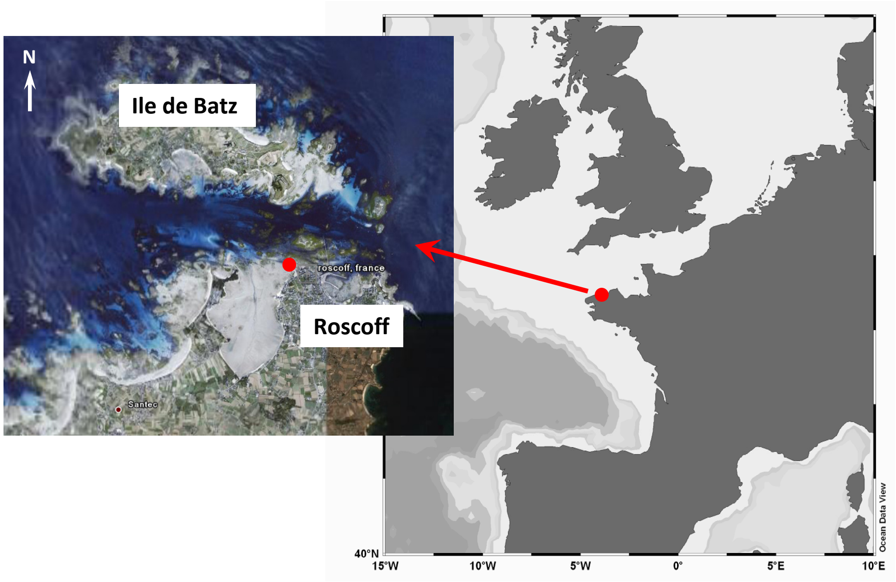

**Fig. 1.** The measurement site for the RHaMBLe experiment at Roscoff on the coast of Brittany is indicated by the red dot on both maps. The inset shows the local topography, with seaweed beds to the south east exposed at low tide and the island Ile de Batz to the north.

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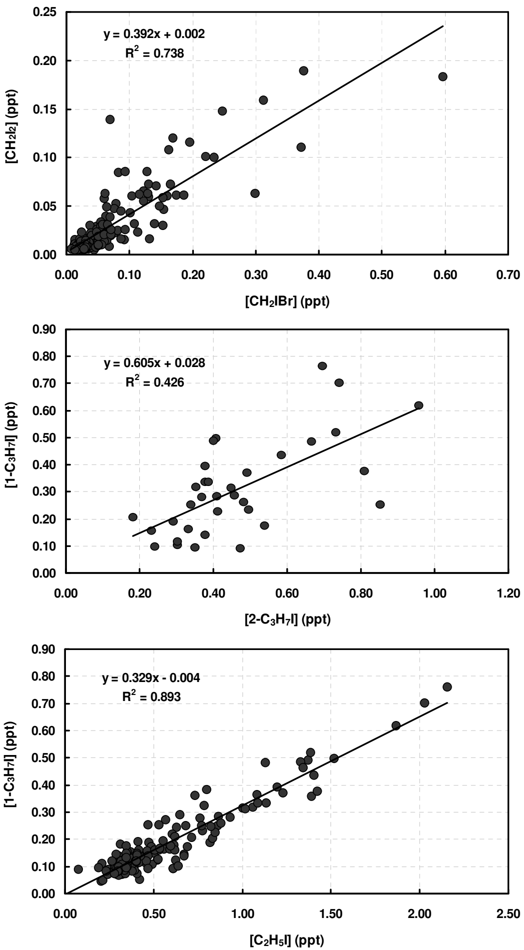

**Fig. 2.** Correlations between concentrations of iodocarbons in the MBL at Roscoff from 3–27 September 2006 inclusive.

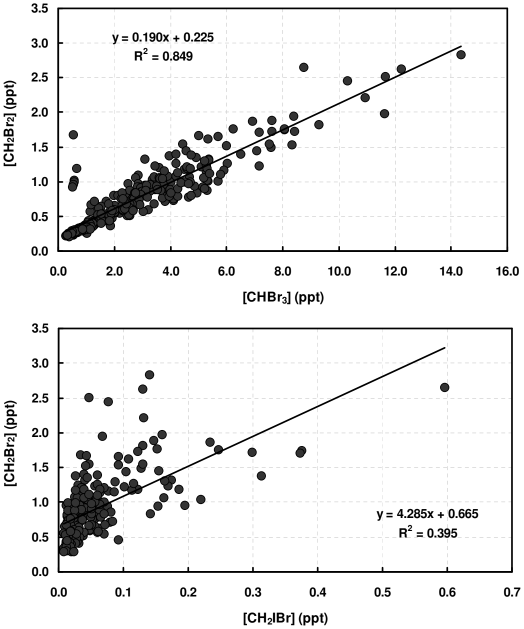

**Fig. 3.** Correlations between bromocarbons in ambient air at Roscoff from 3–27 September 2006 inclusive.

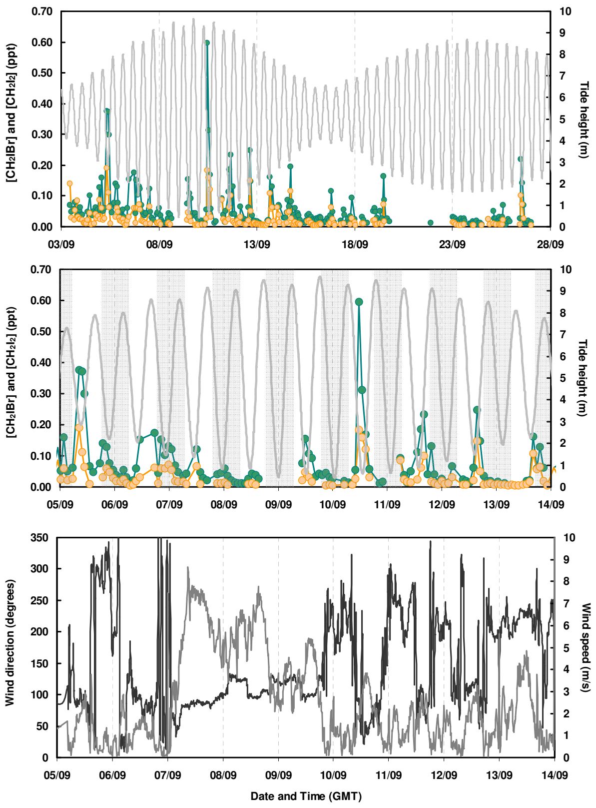

**Fig. 4.** $CH_2I_2$ (orange) and $CH_2IBr$ (green) mixing ratios overlaid with tidal height. Grey shaded areas highlight night time measurements (SZA>90°). Top panel shows data for the whole campaign, middle panel is the period from 5–14 September expanded to illustrate variations in concentrations from low to high tide, and the bottom panel shows wind speed (light grey) and wind direction (dark grey) from 5–14 September.

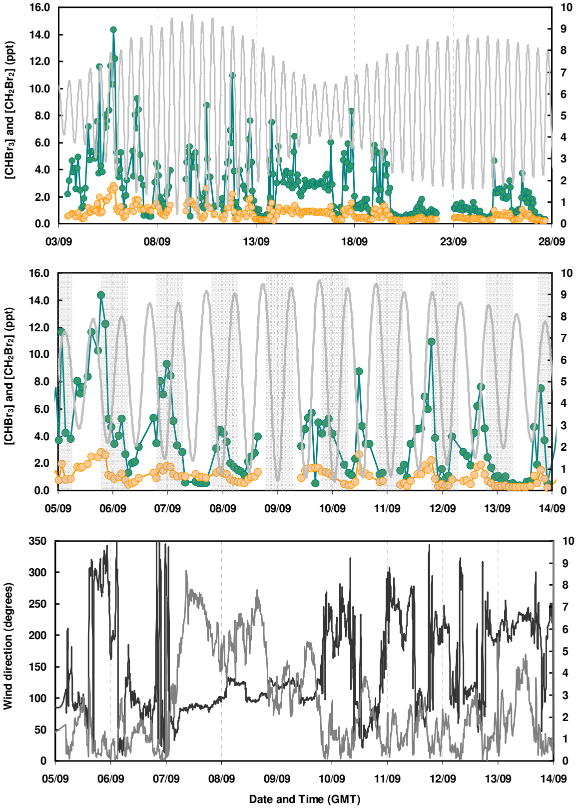

**Fig. 5.** $CH_2Br_2$ (orange) and $CHBr_3$ (green) mixing ratios overlaid with tidal height. Grey shaded areas highlight night time measurements (SZA>90°). Top panel shows data for the whole campaign, middle panel is the period from 5–14 September expanded to illustrate variations in concentrations from low to high tide and the bottom panel shows wind direction (dark grey) and wind speed (light grey) from 5–14 September.

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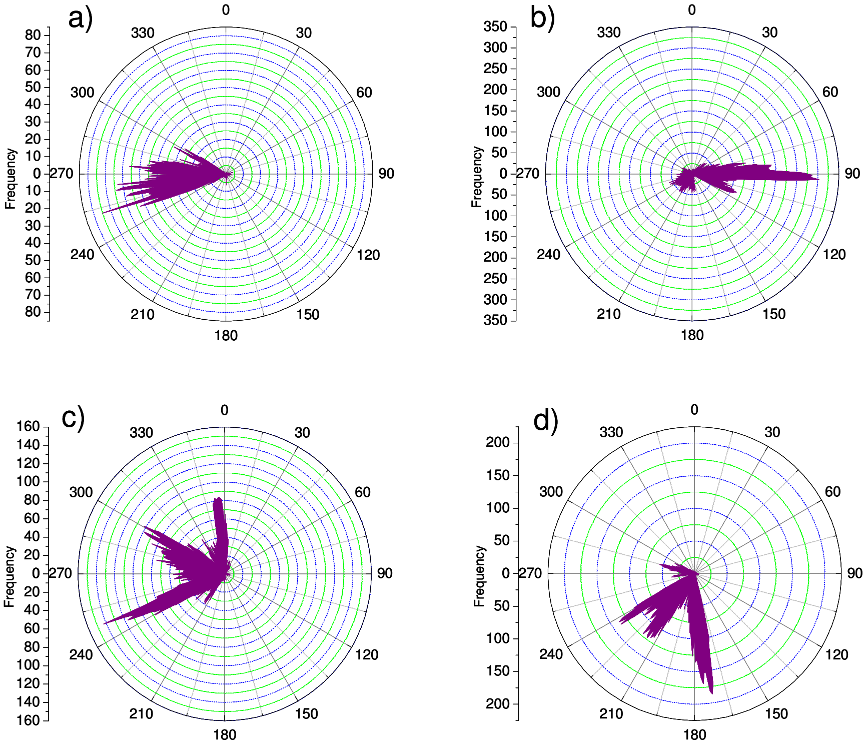

**Fig. 6.** Wind roses to illustrate the wind direction at the site during four distinct periods; **(a)** 3–5 September, **(b)** 5–14 September, **(c)** 14–21 September and **(d)** 21–27 September.

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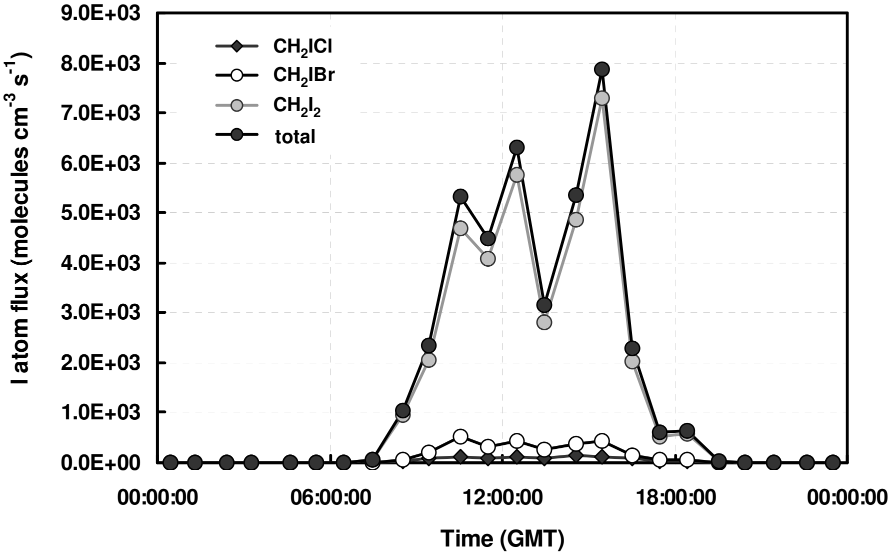

**Fig. 7.** Diurnal average I atom fluxes from CH$_2$ICl, CH$_2$IBr, CH$_2$I$_2$ and the total combined I atom flux from the three dihalomethanes.

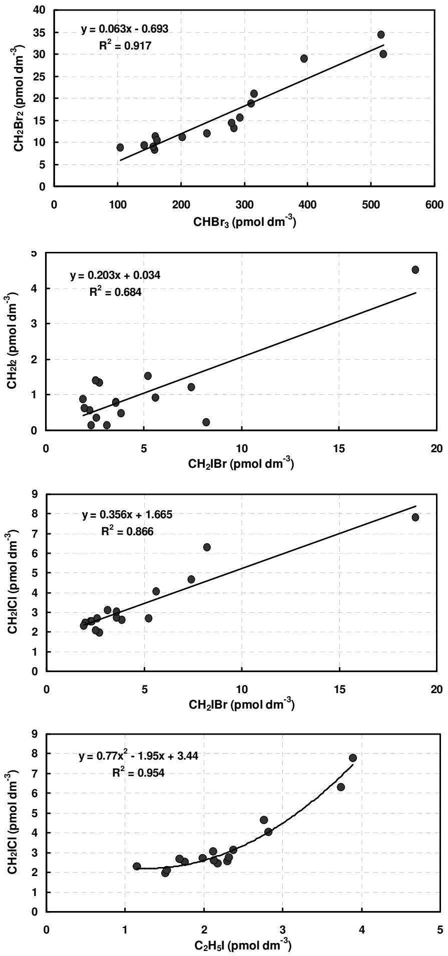

**Fig. 8.** Correlation plots between halocarbon concentrations in seawater during the 11 and 25 September.