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Emission of atmospherically significant halocarbons by naturally occurring and farmed tropical macroalgae

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Abstract

Current estimates of global halocarbon emissions highlight the tropical coastal environment as an important source of very short-lived (VSL) biogenic halocarbons to the troposphere and stratosphere. This is due to a combination of assumed high primary productivity in tropical coastal waters and the prevalence of deep convective transport potentially capable of rapidly lifting surface emissions to the upper troposphere/lower stratosphere. However, despite this perceived importance direct measurements of tropical coastal biogenic halocarbon emissions, notably from macroalgae (seaweeds), have not been made. In light of this, we provide the first dedicated study of halocarbon production by a range of 15 common tropical macroalgal species and compare these results to those from previous studies of polar and temperate macroalgae. Variation between species was substantial; $CHBr_3$ measured at the end of a 24 h incubation varied from 1.4 to 1129 pmol g FW^{-1} h^{-1} (FW = fresh weight of sample). We used our laboratory-determined emission rates to estimate emissions of $CHBr_3$ and CH_2Br_2 (the two dominant VSL precursors of stratospheric bromine) from the coastlines of Malaysia and South East Asia. We compare these values to previous top-down model estimates of emissions from these regions, and conclude that the contribution of coastal $CHBr_3$ emissions is likely to be lower than previously assumed. The contribution of tropical aquaculture to current emission budgets is also considered. Whilst the current aquaculture contribution to halocarbon emissions in this regional is small, the potential exists for substantial increases in aquaculture to make a significant contribution to regional halocarbon budgets.

1 Introduction

Over the past 30 years a number of incubation studies have investigated the production and emission of volatile low molecular weight halocarbons including the methyl halides (e.g. methyl iodide, CH_3I) and polyhalogenated compounds (e.g. bromoform, $CHBr_3$)

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from polar and temperate macroalgae (seaweeds) (e.g. Baker et al., 2001; Carpenter et al., 2000; Goodwin et al., 1997; Gschwend et al., 1985; Laturnus, 1995; Manley and Dastoor, 1988; Marshall et al., 1999). Such studies have helped to quantify the production of halocarbons by macroalgae and develop our understanding of the complexity and variability involved in these biogenic processes. The broad suite of halogenated compounds found in, and released from, algae are thought to act as a defence mechanism. They help protect macroalgae from grazing; control microalgal epiphytes and limit fungal and bacterial infection (La Barre et al., 2010; Paul and Pohnert, 2010; Weinberger et al., 2007). Of these compounds, the volatile organic bromo- and iodocarbons, alongside inorganic iodine species such as molecular iodine (I_2), act as antioxidants by removing harmful active oxygen species produced by macroalgae (Küpper et al., 2008; Palmer et al., 2005). This is consistent with previous work which suggests that environmental stresses such as desiccation, salinity and nutrient depletion influence halocarbon emission rates (Bondu et al., 2008; Mata et al., 2011; Nightingale et al., 1995).

Field campaigns in temperate regions have demonstrated the potential importance of halogenated products emitted from macroalgae. In particular, organic and inorganic iodine emissions (e.g. I_2, CH_3I and diiodomethane, CH_2I_2) influence local atmospheric chemistry (Ball et al., 2010; Chance et al., 2009; Seitz et al., 2010). Biogenic iodinated species in the troposphere have three important impacts; they provide a route for iodine, an essential element for human health, to reach land; they contribute to the production of ultrafine aerosol particles and so potentially contribute to the number and distribution of cloud condensation nucleii and the atmospheric radiation balance; and they alter the balance of oxidising radicals in the troposphere, thereby changing the oxidising capacity of the atmosphere and its ability to processes other gases, including pollutants and greenhouse gases (Saiz-Lopez et al., 2012 and references therein). The inorganic bromine-containing compounds (Br_y) found in the stratosphere were once thought to be derived entirely from long-lived anthropogenic compounds such as halons and methyl bromide. Recent model and measurement studies, however, have

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provided evidence that Br_y from short-lived biogenic sources contribute to stratospheric as well as tropospheric ozone chemistry. The potential contribution of such gases to stratospheric bromine is estimated to be in the range of 1–9 ppt, a substantial amount compared to the total stratospheric Bry abundance of around 20–25 ppt (Dorf et al., 2008; Yang et al., 2005). Due to their shorter atmospheric lifetime iodocarbons are believed to contribute only to tropospheric boundary layer chemistry (Montzka et al., 2010).

The short atmospheric lifetime of biogenic halocarbons, on the order of days to months, alongside geographical variation in biogenic sources leads to temporal and spatial heterogeneity in biogenic production and atmospheric mixing ratios. Current hypotheses suggest tropical emissions may be particularly important due to deep stratospheric convective systems. These systems may provide a rapid transport mechanism delivering short-lived halocarbons and their product gases to the upper troposphere/lower stratosphere (Quack et al., 2004; Salawich, 2006). Within the tropics the coastal zone has been identified as a potentially strong source region. Yokouchi et al. (2005) measured up to 40 ppt of atmospheric $CHBr_3$ along the coast of tropical islands and a decreasing abundance relative to longer-lived halocarbons such as dibromomethane (CH_2Br_2) away from the coast; a pattern indicative of a localised coastal source such as macroalgae.

Research cruises in tropical waters, however, have tended to consider emissions from oceanic, shelf sea and upwelling areas (Quack and Suess, 1999; Quack et al., 2004, 2007), and no study to date has focused on emissions from coastal tropical macroalgae. Previous temperate and polar research has consistently shown large variations in emissions both between and within macroalgal species, highlighting the need for species-specific measurements in different geographical regions. Different macroalgae species are found in different climatic regions, which could lead to differences in halocarbon production and emission rates. The ratio of rhodophytes (red algae) relative to phaeophytes (brown algae) and chlorophytes (green algae) is greater in tropical regions, and kelps, which are common in temperate regions, are absent in the tropics

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(Santelices et al., 2009). Aquaculture is common in the tropics, and is set to increase (see Sect. 3.5.4). Seaweed farms perturb the natural diversity and biomass of certain macroalgal species, potentially altering halocarbon emissions. Environmental conditions also vary, for example the occurrence and rate of herbivory is believed to be greater in the tropics (Cronin et al., 1997).

In this paper we present the first dedicated study of halocarbon production by a range of tropical macroalgae. Incubations of 15 species from the intertidal zone of peninsular Malaysia were conducted to determine production rates for a range of halocarbons with known biogenic sources. We investigated the effect of incubation time and compared the production rates obtained with existing data from temperate and polar species. Calculated production rates were used to estimate $CHBr_3$ and CH_2Br_2 emissions for Malaysian and South East Asian coastal zones, these estimates were then compared to published values. The current and potential future impact of tropical aquaculture on emissions of $CHBr_3$ was also considered.

2 Methods

2.1 Sample collection

In September and October 2011, 15 tropical macroalgae species were collected from several sites on the western coast of Peninsular Malaysia; including an intertidal reef, an aquaculture site and a mangrove stand (Fig. 1). *Kappaphycus alvarezii* was purchased from a small aquaculture site at Pangkor Island, *Ulva reticulata* was collected from a shrimp farm and *Gelidium elegans* was obtained from the University of Malaya (UM) hatchery where it is cultivated for use in aquaculture experiments. All other species were naturally occurring in the coastal environment and obtained from rock pools exposed at low tide or by snorkeling in water up to 1m deep (see full details in Table 1). Care was taken to select intact, healthy looking specimens with a minimum of epiphytes. Species attached via a holdfast were removed by carefully cutting the

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holdfast from the substrate, ensuring minimal damage. One to four species were collected during each sampling trip and returned to the UM hatchery facility where they were stored in large tanks of aerated seawater which were changed about every 3 days. Samples were used within a week of collection. Prior to each incubation replicates of an individual species were chosen, again, only undamaged specimens were selected. In most cases triplicate samples were chosen, but for several incubations the quantity of collected material only allowed duplicate measurements (see Table 1). As previous experiments have shown that different sections of some of the larger algae release different amount of halocarbons (Laturnus, 1996) single whole plants, or multiple smaller plants for filamentous or mat forming algae, were used. In each case, samples of similar mass and appearance were selected. *Cladophora* sp., a mat forming alga, was removed in small sections maintaining the mud substrate to minimise disturbance, and a separate control containing mud and seawater was used for this incubation. Samples from Cape Rachado often had small sea anemones attached, these were gently removed. An individual incubation on anemones alone (species unknown) showed no appreciable halocarbon production (data not shown).

2.2 Incubation protocol

Gas-tight incubation vessels comprised modified 500 mL Erlenmeyer flasks and Dreschel tops as described by Hughes et al. (2011). The Dreschel outlets were capped with 0.2 µm Minisart filters (Sartorius, UK) and plastic Luer-type taps. During incubations all Luer taps were closed and during sample removal one was opened to allow the flask to re-equilibrate to atmospheric pressure, the filter preventing the ingress of bacteria, dust or other foreign matter. Filtered seawater (400 mL, 0.2 µm filtered sterilised) collected from a coastal site near to Kuala Lumpur was added to each flask leaving a 300 mL headspace. Seawater from this site was used for each incubation for standardisation. Algal samples were gently blotted dry and weighed before they were added to the flasks to obtain fresh weight values for use in production calculations. Two control flasks containing filtered seawater only were used for each incubation.

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Flasks were transferred to an incubator at 35 °C which provided 120–130 µmol photons s^{-1} m^{-2} constant light via fluorescent tubes (Philips). Incubations lasted 24 h, 40 mL samples were removed for analysis after 4 (t4) and 24 h (t24). Samples were removed directly into 100 mL gas-tight syringes using a Luer tap port near the base of each flask, taking care to prevent ingress of air. Samples were analysed immediately. After t4 the 40 mL removed for sampling was not replenished to avoid dilution or nutrient addition effects. After t24 macroalgae samples were re-weighed but no significant changes were noted for any of the incubations. Dry weight was calculated by drying samples for 3 days in an oven at 60 °C followed by 24 h in a desiccator; a method used extensively by the UM algal lab. Losses to the headspace were estimated by calculating the solubility of each halocarbon with data from Sander (1999) and using this to compute partitioning between seawater and headspace. Percentage losses to the headspace at t24 varied between 3 and 13.5 % for all gases with the exception of CH_3I, for which the calculated loss was 30 %.

2.3 Halocarbon analysis

Analysis was carried out via purge and trap pre-concentration followed by gas chromatography mass spectrometry (GC-MS) as described in Hughes et al. (2006). Briefly, samples were passed through 0.7 µm WhatmanTM GF/F filters directly into a purpose-built purge system. Here they were purged for 15 min in a 40 mL min^{-1} flow of oxygen-free nitrogen gas and trapped on a stainless steel trap held at −150 °C in the headspace of a dewar of liquid nitrogen. Desorption at 100 °C by immersion of the trap into boiling water transferred the sample in a flow of helium carrier gas along a short transfer line held at 96 °C to an Agilent 6890 GC fitted with a 60 m DB-VRX capillary column (J&W Ltd.; 0.32 mm diameter, film thickness 1.8 µm). A 5973 Agilent MS in electron impact single ion mode provided quantification of halocarbons via comparisons with commercial methanolic solution standards that were diluted gravimetrically in high purity methanol to provide a concentration range similar to that seen experimentally. Identification of each halocarbon was via retention time comparison with a known standard

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using at least two known mass fragments. Regular multi-point calibrations were used to determine experimental concentrations. Two internal standards (deuterated methyl iodide, CD_3I, and ^{13}C-dibromoethane, $^{13}C_2H_4Br_2$) were added to each sample to monitor and correct for sensitivity drift in the system. The internal standard was checked at the start of each incubation to ensure they were free of target halocarbons which may contaminate the samples. The 1 SD (standard deviation) precision of the system was around 13 %. The detection limit of the complete system, at 1–6 pmol L^{-1} (halocarbon dependant) was below the background halocarbon concentrations seen in the seawater control. Compounds investigated were CH_3I, bromochloromethane (CH_2BrCl), CH_2Br_2, bromochloromethane (CH_2BrCl) chloroiodomethane (CH_2ClI), dibromochloromethane ($CHBr_2Cl$), bromoiodomethane (CH_2BrI), $CHBr_3$ and CH_2I_2. Due the analytical set up methyl chloride and methyl bromide could not be measured, but previous studies have suggested that production of these methyl halides from macroalgae is small and unlikely to contribute greatly to global emission budgets (Baker et al., 2001).

3 Results and discussion

3.1 The effect of incubation time on production

Production rates for 10 of the 15 species were calculated at t4 and t24 (see Supplementary Table 1). Table 2 shows the ratio between these values for each species. Over 50 % of measurements were significantly higher at t4 compared to t24 (Student's t-test, $p = 0.05$, on data which was first log-normalised to pass Kolmogorov-Smirnov tests of normality at $p = 0.05$). Exceptions were the two *Caulerpa* species, both of which showed low overall production rates of less than 5 pmol g FW^{-1} h^{-1} for all halocarbons. Both time periods show the same trends, with strong and significant correlations ($R^2 = 0.43$–0.98, $p = 0.05$) between individual halocarbon and species datasets at t4 and t24 (Fig. 2). No individual halocarbon displayed a distinctive trend that may have indicated non-biogenic loss or production processes, this will be discussed in more

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detail later. As the t4 and t24 datasets both show the same patterns, from here on only the t24 dataset, which contains data for a greater number of species, will be discussed.

3.2 Halocarbon production by tropical macroalgae

T24 production values for each species are represented graphically in Fig. 3. Panels in Fig. 3 are ranked in order, with the highest individual halocarbon emission rate at the top. CH_2BrCl emission was low for all species and non was detected from *Bryopsis* sp., *Sargassum siliquosum*, *U. reticulata*. *Padina australis* and *Sargassum baccularia*. *U. reticulata* and *Caulerpa racemosa* showed no discernible production of CH_3I and $CHBrCl_2$, respectively. Otherwise, all other species produced all halocarbons. The bromocarbons, CH_2Br_2 and $CHBr_3$, were produced ubiquitously. Generally $CHBr_3$ was produced in the highest quantities, followed by CH_2Br_2. The exceptions to this were the chlorophytes, *Caulerpa* sp., *C. racemosa*, and *Cladophora* sp., which produced CH_2Br_2 at a similar or faster rate than $CHBr_3$. A third *Caulerpa* species, *Caulerpa lentillifera*, is not included in this study, but also produced higher quantities of CH_2Br_2.

The rhodophyte *Gracilaria changii* was the strongest $CHBr_3$ producer with an average $CHBr_3$ production rate of 1129 pmol g FW^{-1} h^{-1}. Another *Gracilaria* species, *Gracilaria salicornia* was also a strong halocarbon producer. *G. salicornia* was incubated twice, using specimens collected from two different sites within a month of each other (Table 1). Mean $CHBr_3$ production in September (*G. salicornia* 1) was 478 pmol g FW^{-1} h^{-1} but variability was high, with individual incubations revealing rates ranging from 82–875 pmol g FW^{-1} h^{-1}. The second incubation (*G. salicornia* 2) also demonstrated high production with a mean $CHBr_3$ rate of 595 pmol g FW^{-1} h^{-1} and a range of 298–791 pmol g FW^{-1} h^{-1}. Overall, the rhodophytes we tested tended to be the strongest producers, with both *G. elegans* and *K. alvarezii* showing high production rates.

Generally species that were strong bromocarbon producers also produced relatively high levels of other halocarbons. This was demonstrated by assigning each species

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a rank (1 lowest, 15 highest) for $CHBr_3$ production. They were then ranked again, independently, for CH_2Br_2 production, then for CH_3I and so on. The resulting spread of ranks are displayed as box and whisker plots in Fig. 4. Separate groups can be seen; prolific producers include the rhodophytes and *Turbinaria conoides*, phaeophytes are in the middle and chlorophytes are generally weaker producers. The strongest bromocarbon producer in this study, *G. changii*, also showed considerable production of other halocarbons, with CH_2I_2 production up to 300 times greater than most of the chlorophytes and CH_2Br_2 production 2–30 times greater than many of the other species studied. Some species, however, displayed a wide range of ranks. *Bryopsis*, for example, was one of the strongest producers of CH_2ClI with a rank of 13/15 but the weakest producer of $CHBrCl_2$ with a rank of 1/15.

Whilst the rhodophytes produced large quantities of bromocarbons, some of the phaeophytes ranked highly for iodocarbon production. To investigate further, the proportions of bromine, chlorine and iodine produced by each species was calculated and Table 3 shows the results with species ranked in order of decreasing total halide emissions. *T. conoides* was the strongest producer of all iodine-containing compounds, with a CH_2I_2 production rate almost double that for $CHBr_3$. Another phaeophyte, *P. australis*, showed a stronger production rate for CH_3I than for the bromocarbons. The phaeophytes in general showed a stronger propensity towards production of iodinated compounds, the mean percentage iodine emission for phaeophytes was 35 % compared to 8 % for rhodophytes. This corresponds to temperate studies which reported strong iodocarbon emissions from temperate macroalgae such as *Laminaria* (kelp) (Carpenter and Liss, 2000; Küpper et al., 2008). Chlorophtes also produced a higher percentage of iodine (18 %) compared to the rhodophytes, but as overall production rates were lower for these species their contribution to local iodine chemistry is probably of less importance. In temperate regions kelps and other phaeophytes often dominate the algal biomass (de Vooys, 1979) but in tropical regions rhodophytes and chlorophytes are often more common (Santelices et al., 2009), potentially shifting the balance of emissions towards brominated species.

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With the exception of *Bryopsis,* the chlorophytes were the weakest producers, with production rates for all halocarbons below 30 pmol g FW^{-1} h^{-1}. Bromocarbons were still produced in the highest quantities, but production rates for iodinated and mixed bromochloro- compounds were generally less than 1 pmol g FW^{-1} h^{-1} for *Ulva*, *Caulerpa*, and *Cladophora* spp. In common with many chlorophytes, *Bryopsis* species are fast growing and opportunistic, with the potential to rapidly colonise an area. It has been suggested that halogenated metabolites within algal tissues help protect against epiphytes or grazers (Paul and Pohnert, 2010), perhaps the stronger halocarbon emissions from these species helps protect the algae, facilitating their rapid growth.

Potential triggers for halocarbon emissions, such as grazing or oxidative stress, do not help to explain why different species found in the same environment and subjected to similar environmental conditions show such high variability in their halocarbon production rates. It is possible that some species may rely on other metabolites, for example some tropical *Caulerpa* species are reported to use high concentrations of sesquiterpenoid metabolites to deter herbivores (Paul et al., 1987). The *Caulerpa* species we studied all showed low halocarbon production but no other metabolites were investigated. *T. conoides* also stood out from the general pattern of rhodophyte > phaeophyte > chlorophyte in terms of production rates. *T. conoides* is in the same phylogenetic family (Sargassaceae) as the weaker producing *Sargassum* species reported here. Variations between class, genus and species are not unexpected; despite the overarching terms seaweeds or macroalgae they are a diverse and evolutionary distant group, and the evolution and genetic control of halocarbon production is poorly understood.

In the literature to date halocarbon production has been expressed as production in picomoles or nanograms per unit of fresh weight (FW), dry weight (DW) or sometimes both, per unit of time. Fresh weight may provide a more accurate basis for scaling up to emission estimates whereas dry weight potentially provides easier comparisons between algal species as some algae contain much higher water content than others. The ranking procedure used for Fig. 4 was repeated using production expressed per gram

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of DW instead of FW. FW and DW derived ranks are displayed alongside FW/DW ratios in Table 4. Despite the range of FW/DW ratios seen in this study the ranks assigned to each species and the overall pattern of weak or strong producers remains the same whether fresh or dry weight is used.

3.3 Correlations between biogenic halocarbons

Halocarbon correlations from incubation studies could improve our understanding of biological links between halocarbons and their production mechanisms. All log-normalised production values for each halocarbon (except $CHBrCl_2$ which failed normality tests even after log-normalisation) were correlated against one another (Fig. 5) and tested using Pearson's correlation coefficient. Significant correlations ($p \leq 0.05$) were common for the polyhalogenated halocarbons but the mono-halide CH_3I correlated only with two other iodinated compounds, CH_2ClI and CH_2I_2. The strongest correlations were seen for the bromine-containing halocarbons, especially $CHBr_3$, CH_2Br_2 and $CHBr_2Cl$ with R^2 values between 0.79–0.94 ($p \leq 0.001$). The weakest correlations that passed the Pearson's correlation coefficient test included correlations between several of the bromine and iodine containing species, for example $CHBr_3$ and CH_2I_2 ($R^2 = 0.48$, $p = 0.004$) and CH_2ClI and $CHBr_2Cl$ ($R^2 = 0.32$, $p = 0.027$). Our correlations support previous work to define the biochemical production of halocarbons. Methyl halides, in this case CH_3I, are produced via a methyltransferase-mediated reaction between halides and S-adenosyl-L-methionine (SAM), whereas the production of di- and tri-halogenated compounds involves vanadium-dependent haloperoxidases (Bravo-Linares et al., 2010; Goodwin et al., 1997). Manley (2002), summarising his own and others' research, concluded that polyhalomethane production is functional, with polyhalogenated compounds acting as antioxidants, but that methyl halide production does not seem to serve a function and is possibly a by-product of normal metabolism. This difference in functionality supports the lack of correlation we observe between these two groups of halocarbons. However, despite the lack of statistical correlations

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between the production rates of CH_3I and the majority of other halocarbons, strong producers (e.g. *Gracilaria* spp.) produced large quantities of CH_3I and polyhalogenated compounds. This suggests that links may exist between these two production mechanisms. Further research into potential linkages between these two production pathways and the mechanisms that control or trigger them is needed.

The highest correlation ($R^2 = 0.94$, $p < 0.001$) is between $CHBr_3$ and $CHBr_2Cl$. Tokarczyk and Moore (1994) suggested that $CHBr_2Cl$ could be formed from $CHBr_3$ in laboratory cultures of diatoms, although their study did not see a time lag between $CHBr_3$ and $CHBr_2Cl$ production. Some evidence for the formation of $CHBr_2Cl$ from $CHBr_3$ may be seen in this study; although both compounds are present at t4 and t24 the ratio of $CHBr_2Cl : CHBr_3$ decreases from $\sim 18:1$ at t4 to $\sim 11:1$ at t24. This could be indicative of conversion occurring during this time. However, nucleophilic substitution should also lead to further conversion of $CHBr_2Cl$ to $CHBrCl_2$ and this is not seen in our data, the ratio of $CHBrCl_2 : CHBr_2Cl$ remains $\sim 15:1$ at both t4 and t24. Production of CH_2ClI from CH_2I_2 has also been proposed on the basis of data from incubations and the natural environment (Jones and Carpenter, 2005; Tokarczyk and Moore, 1994). Here CH_2I_2 and CH_2ClI have a relatively strong correlation ($R^2 = 0.64$, $p < 0.001$) but we did not see a change in ratio between t4 and t24. Overall, it seems that direct biogenic influence, either through direct biogenic halocarbon production or extracellular production via the emission of hypohalous acids which react with organic matter (Manley, 2002), is the important factor determining halocarbon concentrations in these incubations.

Ratios between emissions of pairs of halocarbon gases have been used in the literature to estimate regional and global oceanic halocarbon fluxes. Atmospheric abundance ratios, typically from research cruises, are plotted in pairs against one another. The emissions are scaled to the measured gas for which the absolute emission rate is believed to be known with some degree of confidence, CH_2Br_2 in most studies. Such plots normally take a compact linear form, where the gradient reflects a combination of dilution/mixing and atmospheric photochemical removal. The point at which the mixing

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and chemical loss lines intersect with the correlation between the ratios is deemed to be representative of the source emission ratio. By this method Yokouchi et al. (2005) arrived at "global" emission ratios from seawater for $CHBr_3/CHBr_2Cl$, $CHBr_3/CH_2Br_2$ and $CHBr_2Cl/CH_2Br_2$ of 13, 9 and 0.7, respectively, with a 35 % combined error. Using a similar approach, but with measurements at the Cape Verde coast, O'Brien et al. (2009) arrived at similar emission ratios for $CHBr_3/CH_2Br_2$ and $CHBr_2Cl/CH_2Br_2$ of 9 and 0.46, respectively, based on 95th percentiles, and 13 and 0.53, respectively based on 99th percentiles.

These values can be compared with the halocarbon emission rates determined here for tropical macroalgae. If macroalgae are fully submerged then the emissions are first to seawater, and then to the atmosphere, so the observed emissions will be modified according to the relative solubility of the gases. Using the Henry's Law coefficients for halocarbons in seawater from Moore et al. (1995) gives relative solubilities for $CHBr_3/CHBr_2Cl$, $CHBr_3/CH_2Br_2$ and $CHBr_2Cl/CH_2Br_2$ of 1.9, 1.5 and 0.8, respectively. Correcting this for equilibrium partitioning between water and gas phases results in atmospheric emission ratios of 6, 3 and 0.4, respectively for the same halocarbon pairs averaged across all macroalgal species measured. If the seaweeds are exposed, and assuming that this exposure does not in itself alter the plant's production or emission, then the corresponding emission ratios would be 11, 4 and 0.3. From our field collection activities we observed that the seaweeds were mostly submerged, with little exposure at low tide. The exceptions to this were mangrove seaweeds and farmed seaweeds during harvesting. In general, the ratios from the incubations are surprisingly consistent with the open ocean and coastal observations of Yokouchi et al. and O'Brien et al. mentioned above. These similarities do, however, belie a wide range of values for individual seaweed species; the ratio of $CHBr_3/CH_2Br_2$ emission to seawater, for example, varied from 5 to 21. We therefore caution that in using such "source" ratios to scale regional or global emissions of halocarbons, the uncertainty in the likely range of source emission ratios should be taken in to account.

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3.4 Comparison with temperate and polar halocarbon production

Given that this is the first dedicated study of halocabon production by tropical macroalgae it seemed pertinent to compare these results with existing data for temperate and polar macroalgae. $CHBr_3$ and CH_3I were selected as case studies and production values assimilated from 21 existing papers. Of these, 5 papers expressed results only per gram of DW and so were removed. The rest were either expressed as pmol g FW^{-1} h^{-1} or converted to this unit. The resulting production value ranges are displayed alongside the results from our study in Fig. 6. Determining error or variability from other studies was not always possible, but Carpenter et al. (2000) also reported considerable intra-species variability, citing differences between the environmental history (grazing pressure, stress, age) of different samples despite attempts to select specimens from a close geographical location. An example of the effect of age can be seen in Mairh et al. (1989) who reported increasing internal iodine concentrations in mature chlorophytes. Gschwend et al. (1985) also quantified their intra-species variation as within a factor of 2, this is similar to the variation between replicates in this study and it therefore likely that errors on other data from the literature are also similar to the standard deviation error bars shown for our values in Fig. 6.

The results of the literature comparison (Fig. 6) show a large range of production values, spanning from negligible or no production to 100 pmol g FW^{-1} h^{-1} for CH_3I and 6000 pmol g FW^{-1} h^{-1} for $CHBr_3$. Phaeophytes displayed the highest mean production rates for CH_3I, followed by rhodophytes. The chlorophytes showed a considerably lower mean rate; 0.3 pmol g FW^{-1} h^{-1} compared to around 10 and 4 pmol g FW^{-1} h^{-1} for phaeophytes and rhodophytes respectively. Conversely, chlorophytes were, on average, the strongest $CHBr_3$ producers, with a production range of 0–6000 pmol g FW^{-1} h^{-1} (mean 307) compared to 0–3000 (mean 160) for phaeophytes and 0–5000 (mean 288) for rhodophytes. These differences between classes may provide assistance in creating emissions budgets if the distribution of chlorophytes, phaeophytes and rhodophytes in an area is known. Species that were recorded as producing

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no CH_3I or $CHBr_3$ are not displayed in Fig. 6, but the percentage of species that did not produce CH_3I was higher than for $CHBr_3$ at ~26 % compared to ~10 %. The percentage standard deviation was similar for both halocarbons.

Sequential measurements from the same incubation flask in this study have highlighted the effect incubation time may have on calculated production. The incubation times used by the studies included in Fig. 6 vary from 30 min to 48 h, so the incubation time could explain some of the variability between studies investigating the same or similar species. Marshall et al. (1999) and Itoh et al. (1997) observed decreases in halocarbon concentrations between 3–48 h in incubations conducted both in light and dark conditions, both papers proposed biological loss processes. Marshall et al. (1999) conducted further experiments and attributed losses to microbial breakdown whilst Itoh et al. (1997) suggested re-adsorption of the halocarbons onto the algal surface followed by degradation. Our results, which show higher mean production at t4 compared to t24 support these previous findings. The higher values at t4 may also be attributed to incubation preparation, a "burst" of halocarbon emissions upon immersion into the incubation flask due to stress/exposure when the samples are weighed and checked may be unavoidable. Manley and Dastoor (1987) suggested that iodine limitation in the incubation seawater could account for decreases in CH_3I production as incubations progress. However, as macroalgae can accumulate iodine to far greater concentrations that seawater, up to 30 000 times greater for some *Laminaria* sp., (Küpper et al., 1998 and refs. within) this seems unlikely in our 24 h incubations. Results from several other studies report the opposite effect, with increasing production seen in longer incubations (e.g. Bravo-Linares et al., 2010). It is possible that longer incubation times in enclosed systems may subject the algae to physiological stresses, such as nutrient depletion, build up of exudates or pH shifts, which may cause increases in halocarbon emissions (Mtolera et al., 1996). These varying results suggest that incubation effects may be species or incubation set up specific.

Our production rates for CH_3I and $CHBr_3$ were within the range of values quoted in the existing literature. For CH_3I and $CHBr_3$ all but one to two species (*Papenfusiella*

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kuromo (Itoh et al., 1997), *Gracilaria cornea* (Ekdahl et al., 1998), *Bryopsis* sp. and *Caulerpa* sp. (this study)) fell within ± 1 SD around the mean for each class (red, brown, green). Methodological differences could have affected the emission rates recorded; for example Itoh et al. (1997) cut disks out of some algae samples for use in incubations which may have triggered defensive emissions leading to the high CH_3I production observed.

Three genera which had been intensively studied, *Fucus*, *Laminaria* and *Ulva*, are highlighted in Fig. 6 to show variability within these groups. The spread of results recorded for species from these three genera measured from different locations and under different conditions is considerable. This variability is probably due to two factors. Firstly, differences in measurement techniques, such as incubation times, could impact calculated production, as discussed previously. Secondly, it is possible that species which share evolutionary traits, and so are grouped in the same genus, can demonstrate differences in physiology. Several studies have measured species from the same genus using the same experimental technique and seen large differences in $CHBr_3$ production between species from the same or similar locations (Carpenter et al., 2000; Laturnus, 1996). Thereby, it seems possible that similar species from different locations could show differences in production rates beyond that which may be attributable to different experimental protocols.

3.5 A semiquantitative analysis of the halocarbon flux from macroalgae

The tropical region, especially the Pacific, has often been considered an important source region with regards to the global halocarbon budget. Tropical fluxes have been proposed as globally important on the basis of observed high atmospheric mixing ratios and surface seawater concentrations and a proposed strong macroalgal source (Butler et al., 2007; Pyle et al., 2011; Yokouchi et al., 2005). As this study provides the first direct measurements of tropical macroalgal halocarbon production it is worthwhile to use the incubation-derived halocarbon production values to estimate regional fluxes of $CHBr_3$ and compare these values to existing estimates. Papers referred to multiple

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times are abbreviated after first use for brevity. All data used in these estimates, alongside any assumptions or calculations made, are summarised in Supplementary Table 2 and a comparison with other studies is made in Supplementary Table 3.

3.5.1 Determining macroalgal biomass

To estimate macroalgal biomass along the Malaysian coastline, biomass transects conducted by the UM at Port Dickson (Fig. 1) were used (Keng et al., 2012) [Keng12]. Biomass evaluations were made several times over an 18 month period between March 2010 and June 2011. During each visit triplicate 100–130 m long transects each comprising 10 to 13 quadrats were conducted. All seaweed in each 0.3 m^2 quadrat was collected and returned to the laboratory to determine total fresh and dry biomass as well as species abundance. Average biomass values during this 18 month period were 7.0, 5.2 and 0.1 kg FW m^{-2} for phaeophytes, chlorophytes and rhodophytes, respectively. No other published biomass data for the tropics was available for comparison, however Hameed and Ahmed (1999) [HA99] measured localised biomass on the Pakistan coast and provide mean annual biomass values of 13.6, 11.0 and 4.1 kg FW m^{-2} for phaeophytes, chlorophytes and rhodophytes. Both studies show the same distribution of biomass: phaeophyte > chlorophyte > rhodophyte. However, total biomass per square kilometre from HA99 is roughly double that of Keng12. Previous studies estimating the contribution made by macroalgae to the global halocarbon flux (Gschwend et al., 1985; Nightingale et al., 1995) used biomass values determined from a 1975 FAO report (Michanek, 1975 – out of print, summary in Naylor, 1976) [Mich75] which estimated a global standing stock of phaeophyte and rhodophyte biomass of 1.5×10^{10} and 2.7×10^{9} kg FW, respectively. There are no data for chlorophytes in the Mich75 dataset, and it is biased to species that are harvested or farmed for commercial purposes. A comprehensive discussion of the Mich75 estimation and the errors attached to it, with regard to temperate coastlines, can be found in Carpenter and Liss (2000) [CL2000] who conclude that it is an underestimation. Attempts to distribute the global standing stock given by Mich75 over the potential coastal area inhabited

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by macroalgae (Charpy-Roubaud and Sournia, 1990) results in biomass estimates of $\sim 2.2 \times 10^{-3}$ kg FW m^{-2} for phaeophytes and 3.9×10^{-4} kg FW m^{-2} for rhodophytes. These are much lower than both the Keng12 and HA99 estimates. This is not unexpected as seaweed distribution is variable and errors would arise from scaling in either direction. On one hand, individual biomass studies are likely conducted in areas of high macroalgae biomass and therefore enhanced research potential. On the other, global standing stock estimates are difficult to reduce to regional biomass estimates, especially in the tropics where much of the current data is based on temperate and/or economic species. An example of a potential source of error when estimating halocarbon emissions can be seen in the significantly lower proportion of rhodophytes in the Keng12 database compared with both HA99 and Mitch75. We have shown tropical rhodophytes to be prolific producers of halocarbons and an overestimation of rhodophyte biomass could therefore lead to an overestimation in emission budgets. For these reasons, our ability to use local biomass data is of distinct benefit to the following estimates.

3.6 Determining regional fluxes and annual emissions

To calculate the potential $CHBr_3$ flux from tropical macroalgae we assume that the coastal area covered by macroalgae extends 200 m from the shore with a constant gradient to a water depth of 6 m. Whilst the Keng12 biomass study extended to a maximum of 130 m, for safety reasons only, visual confirmation of seaweed extending out past this point was made. We then defined three potential coastal scenarios. Within each scenario the following assumptions remained constant:

A1: We assume that seaweeds are distributed evenly within the base of the coastal zone in the same amount per square metre as recorded in the Port Dickson transects.

A2: We averaged production rates for phaeophytes, rhodophytes and chlorophytes from our incubations and multiplied this by the Keng12 biomass data to give a production rate of 378 nmol $CHBr_3$ m^{-2} h^{-1}.

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A3: Taking into account results from Carpenter et al. (2000) [Car2000] who show average diel production over a 24 h light : dark cycle to be only 60 % of that under constant illumination we reduce our production values, which were determined under constant light, by the same amount.

A4: Where emissions are into seawater we assume instant mixing within this volume of water. We assume that the flux to the atmosphere is the major loss process for $CHBr_3$ in seawater since it has a long lifetime in seawater relative to all other known loss processes i.e. hydrolysis, biotic and abiotic reductive dehalogenation, halogen substitution and photolysis (see CL2000; Quack and Wallace, 2003 [QW03] and references therein).

A5: Flux calculations are made using mean seawater concentrations calculated in each scenario and Eqs. (1) and (2) below; where K_w is the transfer velocity expressed from the liquid phase and ΔC is the concentration difference between the liquid (C_w) and gaseous (C_a) phases. A mean atmospheric concentration of 3.2 ppt was determined from air samples taken over coastal seawater as part of the EU SHIVA project. The SHIVA field campaign, which took place in Malaysian Borneo in November 2011, used a small boat to take air samples directly above the ocean surface along transects out to 20 km from the shore. Air samples were returned to UEA for analysis via GC-MS. The range of $CHBr_3$ concentrations measured was 0.9–6 ppt. The dimensionless Henry's Law constant (H) was calculated using a mean 10° S-10° S latitudinal water temperature of 26.8 °C and a mean oceanic surface wind speed of 5.47 m s^{-1} (QW03) and the procedure described in Johnson (2010).

$$\text{Flux} = -K_w \Delta C \quad (1)$$

$$\Delta C = \frac{C_a}{H} - C_w \quad (2)$$

A6: To estimate annual emissions from Malaysia and the South East Asian (SEA) region we assume that, as our calculations included both a mean annual seaweed biomass and a correction for reduced halocarbon production during darkness, our

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fluxes remain constant throughout the year. We use coastal lengths from the World Resources Institute (WRI, 2012) who provide comparable data for all countries discussed in this study. Our definition of SEA includes the coastline of the following countries: Brunei, Burma, Cambodia, Christmas Island, Indonesia, Malaysia (both peninsular and eastern), the Philippines, Singapore, Thailand, Timor-Leste and Vietnam. No detailed information is available on the percentage of shoreline that supports seaweed, but based on our own visual estimates from sites around Malaysia we cautiously assume that 40 % of the Malaysian and SEA coastline supports seaweed out to 200 m. We assume that an even distribution of macroalgae exists within this area, in the density reported by Keng12.

Scenario 1:

Seaweeds are never exposed at low tide and emit constantly into the "wedge" of water extending 200 m from the shore to a maximum depth of 6 m, a volume of 6×10^5 dm^3 for every metre of coastline. We assume the volume of seawater remains constant but refer to the Car2000 methodology whose calculations suggest that, due to tidal flushing, daily mean $CHBr_3$ concentration in the seawater wedge is similar to that which would be seen after 6 h of constant emissions into the seawater. Following this technique we estimate a mean daily $CHBr_3$ concentration of 755 pmol dm^{-3}. This is within the range of coastal values given by QW03 of 36–2000 pmol dm^{-3}. It is higher than preliminary measurements we made in 2010 which showed concentrations up to 410 pmol dm^{-3} over seaweed beds at Port Dickson, as well as the 388 pmol dm^{-3} mean reported by Car2000 from measurements at Mace Head, Ireland (Supplementary Table 3). However, their assumption was that a depth of 10 m was reached 200 m from the shore. Increasing our water depth to 10 m would reduce our seawater concentration to 454 pmol dm^{-3}, closer to the Car2000 value.

The resulting mean $CHBr_3$ flux from Malaysian coastal seawater influenced by seaweed beds to the atmosphere is 45 nmol $CHBr_3$ m^{-2} h^{-1}. Scaling this up to cover

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Malaysia and SEA (using A6) we calculate an annual flux of 1 Mmol Br yr^{-1} for Malaysia and 15 Mmol Br yr^{-1} for SEA (Mmol is 10^6 moles).

Scenario 2:

In this scenario a tidal cycle is applied to the coastal wedge. Between 0–50 m from the shore macroalgae beds are periodically exposed and submerged during a semi-diurnal tidal cycle. Between 50–200 m the macroalgae remain constantly submerged. The volume of water within the entire 200 m wedge fluctuates with the tidal cycle, with a maximum tidal range of 1.7 m. We assume that, when exposed, the average production rate of 378 nmol $CHBr_3$ m^{-2} h^{-1} (A2) is emitted directly to the atmosphere and when submerged a flux rate is calculated using A5. Scaling up this flux rate using A6 gives an annual emission from Malaysia and SEA of 2 and 40 Mmol Br yr^{-1}, respectively.

Scenario 3:

In Scenarios 1 and 2 an assumption is made that $CHBr_3$ flushed from the coastal wedge during the tidal cycle is effectively lost and does not reach the atmosphere. However, as the lifetime of $CHBr_3$ in seawateris on the order of several years (see Carpenter et al., 2009 [Car09]; Hense and Quack, 2009) $CHBr_3$ flushed from this coastal wedge may still evade to the atmosphere. With this in mind, Scenario 3 assumes all emissions from seaweed (at a rate of 378 nmol $CHBr_3$ m^{-2} h^{-1} (A2)) enters the atmosphere without an intermediate step via seawater. We believe this represents an upper limit estimation and that both scenarios provide a flux rate range with which to compare to other studies. The annual emissions from Scenario 3 for Malaysia and SEA are 7 and 140 Mmol Br yr^{-1}, respectively.

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3.6.1 A comparison of estimated fluxes and emissions

We believe that the idealised scenarios described above place bounds on the likely coastal emissions from the SEA region and can be compared to previous estimates. Comparisons between flux rate estimates should be made with caution as different studies use different flux calculations. Numerous factors can affect calculated fluxes, including approximations of wind speed, Schmidt number and $CHBr_3$ diffusivity. However, if we compare our flux rate range of 45–378 nmol $CHBr_3$ m^{-2} h^{-1} to the median global coastal flux derived by QW03 of 101 nmol $CHBr_3$ m^{-2} h^{-1} and their global range of 4–430 nmol $CHBr_3$ m^{-2} h^{-1} our values fit within their range. The QW03 data were heavily biased towards measurements in temperate and polar regions, and many were taken within the Atlantic, so this comparison suggests that tropical coastlines are not outliers in terms of global coastal fluxes. Comparisons can also be made with Car09 who give a temperate (50–60° N) coastal flux rate of 10 (5–13) nmol $CHBr_3$ m^{-2} h^{-1} and Butler et al. (2007) [BTL07] who provide an average global coastal flux rate of 9 (< 0.1–21) nmol $CHBr_3$ m^{-2} h^{-1}. These flux rates both fall below our Scenario 1 lower estimate, however both datasets are from research cruises which are unlikely to represent waters directly influenced by macroalgae emissions. The potential importance of macroalgae in determining coastal fluxes can be seen in a comparison with observations from the Cape Verde observatory (16.8N, 24.9 W, tropical Atlantic) where intertidal seaweeds are not noticeably abundant. A localised flux rate of 7 nmol m^{-2} h^{-1} given by O'Brien et al. (2009) from model studies attempting to replicate local sources of observed high atmospheric $CHBr_3$ concentrations at Cape Verde is also lower than our range. Our flux rates are also higher than a range of open ocean $CHBr_3$ flux rates of 0.1–0.5 nmol $CHBr_3$ m^{-2} h^{-1} (BTL07; QW03; Tegtmeier et al., 2012) (Supplementary Table 3). Our calculations suggest that in the tropics, as in temperate regions, there is a higher flux rate in a narrow coastal region compared to the open ocean.

A collection of flux rates should be accompanied by estimates of total annual emissions for meaningful comparisons; a high flux in a narrow coastal band may contribute

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less than a lower open ocean flux covering a large area. Previous work (e.g. Warwick et al., 2006) has estimated that tropical coastlines act as an important global, as well as regional, halocarbon source, so we estimate regional $CHBr_3$ emissions based on our flux rates to allow comparisons with regional and global emission estimates. No other nation-specific data is available for comparison, but Pyle et al. (2011) [Pyle11] used atmospheric $CHBr_3$ measurements from inland and coastal sites with back trajectory and chemical transport models to estimate SEA regional emissions. They calculated an annual emission from this region of between 180–350 Mmol Br yr^{-1} (assuming their Scenario 5 emissions are distributed evenly between coastal and open ocean regions). These values are lower than original estimates using a similar model with a coarser spatial resolution (Warwick et al., 2006) which predicted ~ 7050 Mmol $CHBr_3$ yr^{-1} using similar scenarios. This earlier study suggested that the tropics must be a dominant source of halocarbon emissions in order to account for the observed atmospheric distribution of $CHBr_3$. Our SEA annual emission range, 40 (1–140) Mmol Br yr^{-1}, is lower than Pyle11, with our upper limit similar to their lower estimate. However a number of differences between these studies could account for this disparity. Firstly, both studies define SEA differently, the Pyle11 SEA region covers a larger area and includes and more coastline, than ours. Secondly, whilst they do not specify the coastal width used in their model it is likely larger than our 200 m strip (scenarios in Warwick et al., 2006, which remain similar in Pyle11, use data from QW03 who quote a coastal area up to 2 km from the shore). It seems likely that strong seaweed-influenced fluxes are limited to a small coastal zone, and should not be extrapolated to cover a large coastal region. Elevated concentrations in shelf regions are potentially attributable to other sources (see QW03) and may need to be parameterized independently in model scenarios. This result highlights an important point made by Car09; that to compare coastal fluxes and emissions the community needs to create a standardised definition of coastal, shelf and open ocean zones.

If one compares our annual emissions to a wider dataset that provides global coastal annual emission estimates ranging from 1600 (CL2000) to 8100 (BTL07) Mmol Br yr^{-1}

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our upper limit (Scenario 3) SEA value provides between 2–9 % of total coastal $CHBr_3$ emissions. Previous studies have estimated the contribution of tropical oceans to the global halocarbon budget at ∼ 75 % (Palmer and Reason, 2009 (± 46 %), Yang et al., 2005). Our lower value suggests other areas, such as the open oceans, may be important in terms of global $CHBr_3$ emissions. Whilst lower $CHBr_3$ fluxes are seen in the open ocean its large area suggests it may provide a significant contribution to regional emission budgets.

Several potential sources of error could affect our calculations which scale up biomass from one site to cover the SEA region. One example is the percentage of total macroalgae biomass comprised of phaeophytes, rhodophytes and chlorophytes. Data from Keng12 suggests rhodophyte biomass is < 1 % of total seaweed biomass per square metre yet rhodophytes were the dominant halocarbon producers during our incubation studies. For example, increasing rhodophyte biomass to 10 % in Scenario 1 leads to a doubling of the flux rates from 45 nmol $CHBr_3\,m^{-2}\,h^{-1}$ to 93 nmol $CHBr_3\,m^{-2}\,h^{-1}$. This simple test highlights the benefit of conducting localised biomass studies alongside halocarbon production measurements. We also recognise, however, that Port Dickson was selected for this study in part because of prominent macroalgae colonisation. Other coastal areas we inspected along the western Malaysian shore were notably devoid of visible seaweed beds. Species selection was representative of common Malaysian species, including dominant genera such as *Sargassum* and *Gracilaria*, but a wide variety of species remain unquantified in terms of halocarbon emissions. For example, only 3 out of the 39 Malaysian S*argassum* species recorded by Phang et al. (2008) were incubated. It should also be recalled that macroalgae produce CH_2Br_2 and mixed bromochloro- compounds alongside $CHBr_3$. These gases are also atmospherically important. Repeating the calculations made for $CHBr_3$ Sect. 3.5.2 we estimate the annual emission of CH_2Br_2 from SEA to be ∼ 10–75 $Mmol\,Br\,yr^{-1}$. This is not inconsiderable when compared to the same value for $CHBr_3$ (1–140) and when one considers the longer atmospheric lifetime of CH_2Br_2 and, therefore, its potential to

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dominate over $CHBr_3$ in terms of the flux of bromine from very short lived gases to the stratosphere.

Upon consideration of all factors, it seems likely that macroalgae may play an important role, regionally and within a narrow coastal band. However, across a larger coastal area emissions from tropical coastal macroalgae cannot account for all of the annual emissions predicted by models.

3.6.2 The impact of tropical aquaculture

Having established estimates for current Malaysian/SEA emissions it is of interest to consider how these are influenced by seaweed mariculture today, and how this may change in the future. Rhodophyte genera such as *Gracilaria*, *Gelidium* and *Kappaphycus*, which were all found to emit large quantities of bromocarbons in this study, are commonly farmed for food or commercial products in SEA (John et al., 2011; McHugh, 2003).

As the seaweed found at Port Dickson is naturally occurring we assume the parameters used to calculate regional biomass in the flux calculations represent the natural biomass of Malaysia. We also estimate that current farmed seaweed biomass at $\sim 6000\,\mathrm{t\,DW\,yr^{-1}}$ (Neish, 2009; Phang, 2010) is in addition to this. Using these parameters to calculate halocarbon production from natural and farmed biomass we estimate that aquaculture currently makes up 0.7 % of total Malaysian biomass but contributes ~ 2 % of Malaysian $CHBr_3$ macroalgae emissions, due to the fact that farmed seaweeds in this region are all rhodophytes which are strong emitters of bromocarbons. There is a strong interest in increasing the amount of seaweed aquaculture in Malaysia; various studies suggest the potential increase could lead to a 6 to 11-fold increase in the area under cultivation (Goh and Lee, 2010; Neish, 2009; Phang et al., 2010). If we assume naturally produced halocarbon emissions remain constant this increase could lead to a corresponding increase in the relative contribution of $CHBr_3$ emissions from aquaculture, making it responsible for 12–20 % of total macroalgal emissions.

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Clearly caveats must be applied to these calculations. The percentage change estimates for the effects of aquaculture only consider production from macroalgae and not other potential coastal sources such as phytoplankton or mangroves. It is assumed that air-sea gas exchange processes are equal for natural and farmed algae and that the rate of these processes will not change in the future. Accurate emission budgets would also need to include emissions that may occur during harvesting and post-harvest processing. We assume halocarbon production from natural and farmed algae is the same, despite the fact that artificial aquaculture environment places increased physiological stress on the algae due to increased prevalence of pests, disease or herbivores; increased light stress and potential nutrient limitation (Ask and Azanza, 2002). It is also important to consider aquaculture on a global scale. Within the SEA region 94 % of seaweed production occurs in Indonesia and the Philippines (Phang et al., 2010) and market analyses suggest production in all SEA is likely to increase (Neish, 2009), with consequent increases in regional halocarbon emissions. There are also other important non-tropical producers. China is the world leader, harvesting 1.2 million tonnes (DW) of seaweed in 2007, over five times the amount produced in the entire SEA region (Tang et al., 2011). These potentially larger emissions are, however, at a distance from the region of tropical deep convective systems. The range of cultivated species also differs; China produces mainly *Laminaria*, a strong producer of iodinated species, and *Porphyra* (Tang et al., 2011), so the impact on local atmospheric chemistry may also vary between the two regions.

4 Conclusions

1. Incubations of 15 tropical macroalgae species showed variable production rates covering several orders of magnitude. Brominated halocarbons were dominant, and rhodophytes produced the most bromocarbons. Phaeophytes and chlorophytes showed a stronger propensity towards iodocarbon production, although emissions in general were low for the majority of chlorophytes we studied.

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2. Our measurements at two time points during a 24 h incubation demonstrate that incubation time can also have an impact on determined production rates; production rates were higher at t4 compared to t24. For this reason, comparisons between individual studies should be made with caution.

3. Nonetheless, data from previous studies were compared to our tropical data and the range of production values was similar, although statistically significant differences were seen, particularly between polar and tropical species. As the tropical dataset is considerably smaller than that for polar and temperate species we cannot conclude that predictions about halocarbon production potential can be made on the basis of a species' geographical location. It is likely that the main difference in emissions between regions would come from differences in species distribution and abundance. Environmental impacts and geographical distance may play a role in shaping the genetic control of halocarbon production, and therefore differences between geographical groups. However, little is known about the genetic control of halocarbon production and why this varies between species. Future research in this area is needed to better understand these processes.

4. $CHBr_3$ fluxes and corresponding annual emission rates from the SEA coastal environment were investigated and our emission estimates fall at the lower range of published data. It seems likely that the contribution made by macroalgae to the regional SEA coastal halocarbon budget is smaller than previously estimated.

5. Current aquaculture is a minor contribution to Malaysian $CHBr_3$ emissions. However, projected increases in aquaculture could lead to an increasingly important contribution, especially if aquaculture growth is mirrored in neighbouring countries with significant aquaculture industries.

6. The SEA region is one of rapid environmental change; aquaculture, mangrove destruction and urban pollution may all influence coastal biology and therefore halocarbon emissions. Due to the potential importance of this area as a source

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region for stratospheric Br_y quantifying emissions from this area, and understanding how they may change in the future, will make an important contribution to our understanding of global halogen budgets.

Supplementary material related to this article is available online at: http://www.biogeosciences-discuss.net/10/483/2013/bgd-10-483-2013-supplement.zip.

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Table 1. Tropical macroalgae investigated, their collection sites and sample details. *n* = number of replicates used in incubation study.

Species	Collection site	Collection date	Incubation date	Sample composition	*n*
Rhodophyta					
Gelidium elegans	UM culture	17 Oct 11	18 Oct 11	Single specimen	3
Gracilaria changii	Morib mangrove	19 Sep 11	21 Sep 11	Single specimen	3
Gracilaria salicornia 1	Morib mangrove	19 Sep 11	21 Sep 11	Single specimen	3
Gracilaria salicornia 2	Pantai Dickson	17 Oct 11	18 Oct 11	Single specimen	3
Kappaphycus alvarezii	Seaweed farm, Pulau Pangkor	12 Sep 11	15 Sep 11	Single specimen	3
Phaeophyta					
Padina australis	Pantai Purnama	29 Oct 11	1 Nov 11	Selection of small plants	2
Sargassum baccularia	Pantai Purnama	29 Oct 11	1 Nov 11	Single specimen	2
Sargassum binderi	Cape Rachado	6 Oct 11	13 Oct 11	Single specimen	3
Sargassum siliquosum	Pantai Purnama	29 Oct 11	1 Nov 11	Single specimen	2
Turbinaria conoides	Cape Rachado	6 Oct 11	10 Oct 11	Single specimen	3
Chlorophyta					
Bryopsis sp.	Pantai Purnama	29 Oct 11	1 Nov 11	Selection of small plants	2
Caulerpa racemosa	Cape Rachado	6 Oct 11	9 Oct 11	Single specimen	3
Caulerpa sp.	Cape Rachado	6 Oct 11	9 Oct 11	Single specimen	3
Cladophora sp.	Pantai Dickson	5 Oct 11	9 Oct 11	Section of algal mat	3
Ulva reticulata	Shrimp farm, Kuala Selangor	21 Sep 11	23 Sep 11	Selection of small plants	3

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Table 2. Ratio t4 : t24 halocarbon production rates. Production (pmol g FW^{-1} h^{-1}) was higher at t4 for all but one occurrence. nm = not measured, × = at one or both time points compound not detected. Production by *P. australis*, *S. baccularia*, *S. siliquosum* and *Bryopsis* sp. was not measured at t4.

Species	CH_3I	CH_2BrCl	CH_2Br_2	$CHBrCl_2$	CH_2ClI	$CHBr_2Cl$	CH_2BrI	$CHBr_3$	CH_2I_2
G. elegans	2.32	3.05	2.00	5.70	3.65	2.96	6.72	7.83	7.86
G. changii	2.72	16.47	11.80	3.56	7.20	3.25	13.26	3.95	3.16
G. salicornia 1	3.22	5.16	3.34	1.77	8.71	1.26	6.84	3.29	6.85
G. salicornia 2	2.36	12.45	10.87	4.36	13.08	3.71	26.36	5.39	14.72
K. alvarezii	nm	0.51	0.54	0.96	0.57	0.85	1.52	3.38	4.17
S. binderi	1.45	3.04	3.10	0.73	2.95	1.40	7.87	2.61	10.76
T. conoides	0.68	0.91	2.21	3.04	0	1.81	1.15	2.13	1.03
C. racemosa	4.98	×	0.59	×	1.75	1.39	1.51	2.07	1.91
Caulerpa sp.	0.93	×	0.08	×	1.75	1.39	1.51	2.07	1.91
Cladophora sp.	0.57	1.54	3.62	0.71	0.38	2.08	2.22	2.14	0.36
U. reticulata	×	×	2.39	4.99	8.81	6.14	4.39	6.68	6.75

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Table 3. Total mass of halides emitted during incubation and percentage contribution from bromine, chorine and iodine. Species arranged in order of decreasing total halide emissions.

Species	Total halide emitted (ng)	%Br	%Cl	%I
G. changii	138 748	88.9	1.1	10.0
K. alvarezii	114 395	91.8	1.5	6.7
G. salicornia (mean)	65 655	89.1	1.3	9.7
T. conoides	40 895	42.5	0.3	57.2
Bryopsis sp.	8419	81.3	0.3	18.4
S. binderi	4243	92.5	2.3	5.2
G. elegans	2873	92.6	1.6	5.7
S. siliquosum	2843	79.6	1.5	18.9
U. reticulata	2400	96.8	0.7	2.5
S. baccularia	1548	80.1	2.0	17.9
P. australis	1104	35.0	1.0	64.1
C. racemosa	915	69.8	0.4	29.8
Caulerpa sp.	657	83.2	1.0	15.8
Cladophora sp.	370	74.4	1.4	24.2

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Table 4. Changes in mean "production rank" when calculating production using fresh or dry weight. Species are ordered in increasing percentage DW.

Species	t24 mean rank		DW as % FW
	FW	DW	
C. racemosa	2.5	5.6	4.3
Caulerpa sp.	2.7	6.8	4.8
Bryopsis sp.	8.3	8.6	5.9
G. salicornia 1	9.6	11.2	8.0
G. elegans	8.6	6.2	8.7
Cladophora sp.	2.3	1.3	8.9
K. alvarezii	12.4	13.5	9.8
U. reticulata	3.7	2.3	11.4
G. changii	12.3	11.0	11.4
P. australis	6.3	7.1	12.6
S. binderi	8.6	7.4	12.9
S. siliquosum	8.6	7.3	14.3
T. conoides	13.3	12.8	14.4
S. baccularia	6.1	6.0	15.4
G. salicornia 2	10.7	10.0	27.0

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Fig. 1. Location of sampling sites Peninsular Malaysia. ★ = Kuala Lumpur (laboratory), • = sampling sites. 1. Seaweed farm, Pangkor Island, Perak. 2. Shrimp farm, Kuala Selangor, Selangor. 3. Mangroves, Morib, Selangor. 4. Port Dickson, Negeri Sembilan; including Cape Rachardo, Pantai Dickson and Pantai Purnama.

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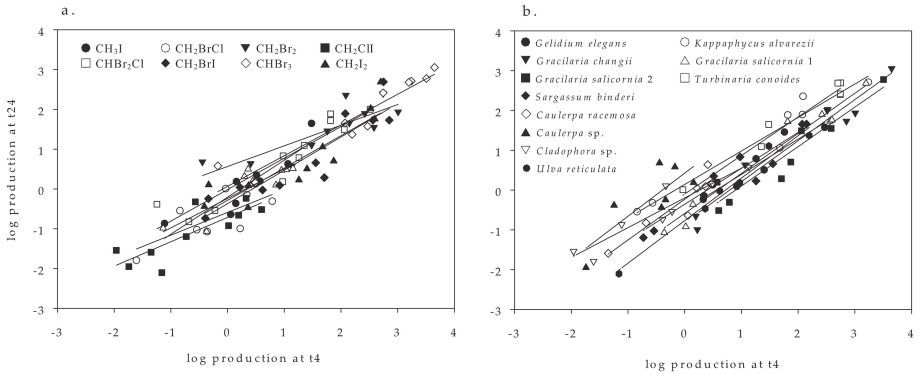

Fig. 2. Correlation between log-normalised production (pmol g FW^{-1} h^{-1}) at t4 and t24 for **(a)** individual halocarbons and **(b)** seaweed species.

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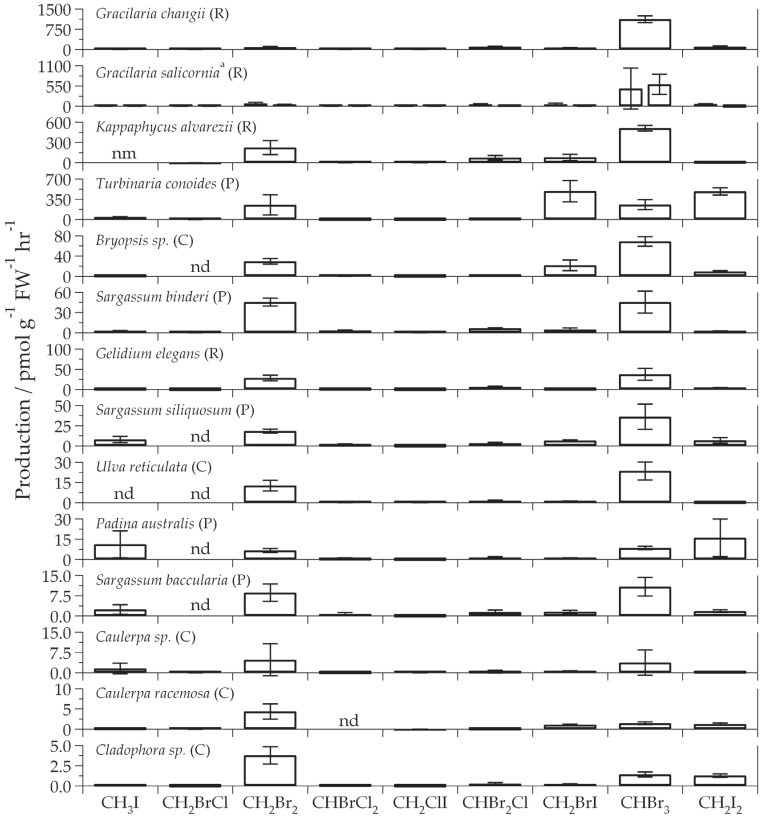

Fig. 3. Halocarbon production by tropical macrophytes measured at t24. Bars are mean production of biological replicates ($n = 2$ or 3, see Table 1) with error bars the 1σ standard deviation. R = rhodophyte, P = phaeophyte, C = chlorophyte. "nm" is "not measured" and "nd" is "not detected". (a) *G. salicornia* was incubated twice (see Table 1).

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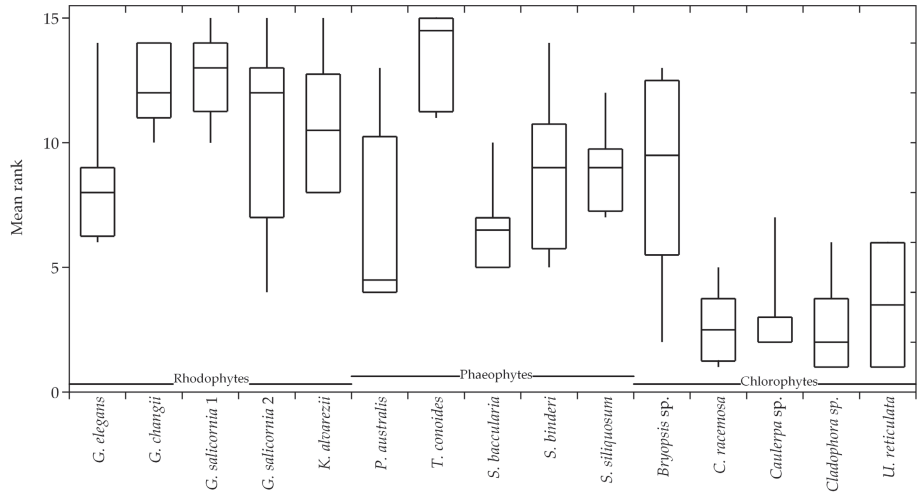

Fig. 4. Production rank box and whisker plots for all halocarbons emitted by each seaweed species. Production data in pmol in g FW^{-1} h^{-1} at t24 were used to rank the seaweeds for their production of each halocarbon. The lower and upper limits of the boxes represent the 25th and 75th percentiles, the horizontal lines are median values and whiskers represent the 10th and 90th percentiles. Species are ordered by class (rhodophyte, phaeophyte, chlorophyte) and alphabetically with these groups.

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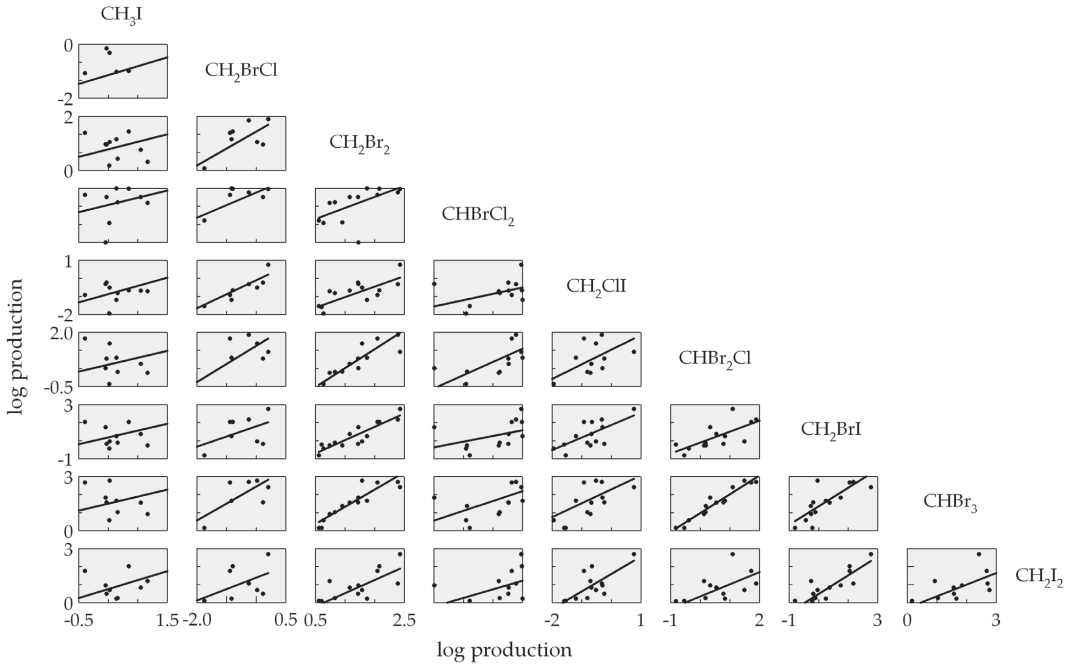

Fig. 5. Halocarbon correlation plots of log-normalised production (pmol g FW^{-1} h^{-1}).

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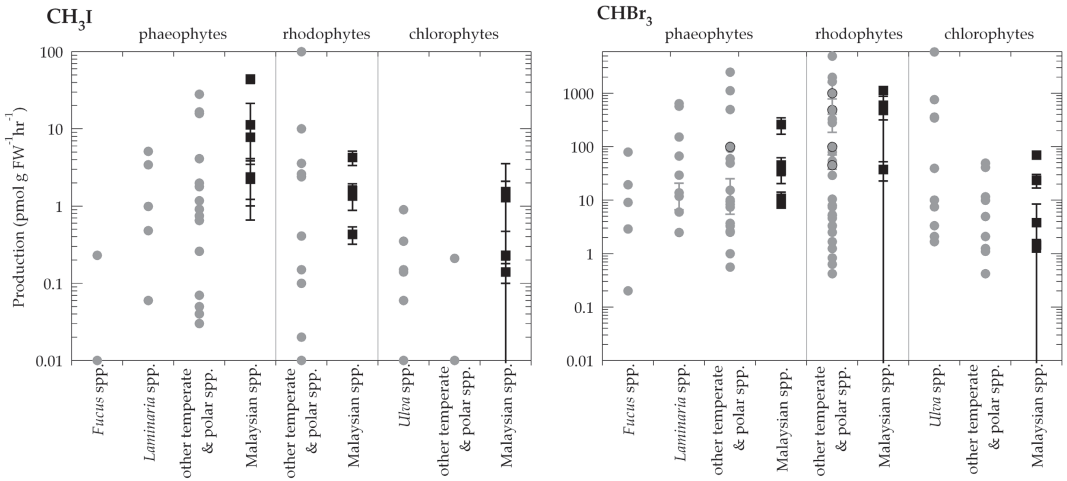

Fig. 6. Halocarbon production reported in this and previous studies for CH_3I and $CHBr_3$. ■ = this study, error bars = 1σ standard deviation. • = previous studies (black outline = study may include subtropical or tropical strains). Published values were from the following sources: Carpenter et al. (2000); Collen et al. (1994); Ekdahl et al. (1998); Giese et al. (1999); Goodwin et al. (1997); Itoh and Shinya (1994); Itoh et al. (1997); Klick (1993); Laturnus (1996); Laturnus et al. (2004); Laturnus et al. (2010); Manley and Dastoor (1987); Manley et al. (1992); Marshall et al. (1999); Pedersen et al. (1996); Schall et al. (1994).

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