

CAN SEAWEED FARMING IN THE TROPICS CONTRIBUTE TO CLIMATE CHANGE THROUGH EMISSION OF SHORT-LIVED HALOCARBONS?

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ABSTRACT Volatile halocarbons form a major source of halogen radicals in the atmosphere, which are involved in the catalytic destruction of ozone. Studies show that marine algae release halocarbons, with 70% of global bromoform produced by marine algae (Carpenter *et al.*, 2000). The role of halocarbons in algae is linked to their use as defense against epiphytes and grazing as well as scavengers of strong oxidants (Nightingale *et al.*, 1995). Halocarbon release rates are higher for tropical algae than temperate species (Abrahamsson *et al.*, 1995). The Maritime Continent is a major contributor to emissions of short-lived halocarbons and their transport to the stratosphere due to deep convection. The Coral Triangle situated in the Maritime Continent, is a centre for seaweed farming. The following discusses the potential impact of tropical seaweed emissions of halogenated compounds to climate change.

ABSTRAK Halokarbon mudah meruap adalah sumber utama radikal halojen dalam atmosfera, yang terlibat dalam pemusnahan lapisan ozon. Kajian menunjukkan bahawa alga melepaskan halokarbon, dan 70% bromoform dihasilkan oleh alga marin (Carpenter *et al.*, 2000). Peranan halokarbon dalam alga berfungsi sebagai pertahanan terhadap epifit dan 'oxidant scavengers' yang kuat (Nightingale *et al.*, 1995). Kadar pengeluaran halokarbon adalah lebih tinggi untuk alga tropika daripada spesies sederhana (Abrahamsson *et al.*, 1995). Benua Maritim adalah pengeluar utama bagi halokarbon jangka hayat pendek dan pengangkutannya ke stratosfera disebabkan perolakan dalam Segitiga Terumbu Karang yang diletak dalam Benua Maritim, adalah pusat pengkulturan rumpai laut. Kertas ini membincangkan impak daripada pengeluaran halokarbon daripada rumpai laut terhadap perubahan iklim.

(**Keywords:** Volatile halocarbons, Marine algae, Seaweed farms, Maritime Continent, Climate change)

INTRODUCTION

Natural and Farmed Seaweeds in the Maritime Continent.

The Maritime Continent as used by meteorologists and oceanographers to describe the interaction between ocean and land, refers to the region between the Indian and Pacific Oceans including the archipelagos of Indonesia, Borneo, New Guinea, the Philippine Islands, the Malay Peninsula, and the surrounding seas (Commonwealth of Australia 2015, Bureau of Meteorology). The Coral Triangle (Figure 1) is a marine area comprising more than 100,000 km coastline and a marine area of 6 million km², situated within the Maritime Continent, and is bordered by six nations, namely Indonesia, Philippines, Malaysia, Solomon Islands and Timor Leste (Phang *et al.*, 2010). The Coral Triangle is situated in one of the mega-diversity regions of the world, especially in terms of marine biodiversity. The long

coastlines together with the abundance of islands support a rich diversity of marine algae. Checklists of the seaweed flora of the region is incomplete but available publications indicate that the Philippines has the highest diversity with 949 taxa including 61 taxa of Cyanobacteria, 522 taxa of Rhodophyta, 154 taxa of Ochrophyta (Phaeophyta) and 212 taxa of Chlorophyta (Ganzon-Fortes *et al.*, 2012). Verheij and Prud'homme van Reine (1993) reported a total of 199 taxa with 80 taxa of Chlorophyta, 36 taxa of Phaeophyta and 83 taxa of non-coralline and 35 taxa of coralline Rhodophyta for the Spermonde Archipelago. An updated checklist (Pham *et al.*, 2011) of Singapore algae comprised a total of 1,054 species, varieties and forms of algae, both freshwater and marine. Lewmanomont and Ogawa (1995) published a photographic guide to the common seaweeds and seagrasses of Thailand, comprising 49 taxa of Rhodophyta, 41 taxa of Chlorophyta, 26 taxa of Phaeophyta and 2 taxa of Cyanophyta. Updated records for Malaysia give a total of 355 taxa

belonging to the Cyanophyta (8 taxa), Chlorophyta (87), Rhodophyta (156) and the Phaeophyta (90) (Phang 2015 unpublished data). A total of 827 species comprising 180 Chlorophyta, 147 Phaeophyta, 412 Rhodophyta and 88 Cyanophyta were compiled from various published sources for Vietnam (Nguyen *et al.*, 2013). In general the red seaweeds dominate in terms of diversity followed by the brown and green seaweeds.

The Coral Triangle also represents an excellent example of a tropical region where intensive seaweed farming takes place (Hurtado *et al.*, 2014). More than 120 million people live within the Coral Triangle but these populations are amongst the poorest in the region, and seaweed farming is an important contributor to poverty eradication (WWF, 2015). Seaweed farming is one of three priority development areas for the agriculture sector in Malaysia, and the main seaweeds farmed in the Coral Triangle, belong to the red seaweed genera *Kappaphycus* Doty and *Euचेuma* J. Agardh, with minor contributions from *Gracilaria* farmed in Indonesia. In 2007, the global production of the carrageenophytes (*Kappaphycus* and *Euचेuma*) was more than 200,000 metric tonnes (MT) dry weight (DW) (Neish, 2008), which sold for between USD800 to 1200 per MT DW. In 2009, the total production of *Kappaphycus* within the Coral Triangle was 200,000 MT DW, and Papua New Guinea joined in

with trial plots in the Alatau area in August 2010 (Phang *et al.*, 2010). In 2010, 5,623,000 MT wet weight (WW) of the carrageenophytes were produced globally, with Indonesia (60.5%), the Philippines (31.9%), Malaysia (3.7%), Tanzania (2.3%) and China (1.1%) taking the lead (Hurtado *et al.*, 2014). Production in the Coral Triangle is set to increase based on the potential cultivable area(s); Indonesia has 17,000 islands with 52,716 km coastline; Philippines has 7000 islands with 36,289 km coastline while in Malaysia, about 8,000 ha is under cultivation, with another 43,000 ha allocated for future farms. In 2012, the top carrageenophyte producers were Indonesia (6,514,864 MT WW; USD 1,348 million); Philippines (1,751,971 MT WW; USD 231.8 million), Malaysia (331,490 MT WW; USD 64.4 million); Solomon Islands (13,000 MT WW.; USD 530,000) and Timor Leste (15,000 MT WW; USD 113,000) (FAO, 2014). Vietnam produced 234,600 MT WW worth USD 117.3 million). In 2012, Tanzania produced 15,088 MT DW with a value of USD 4.25 million (Msuya *et al.*, 2014). *Kappaphycus* sold for USD 0.51 per kg DW, twice that for *Euचेuma*. Latin America, comprising Argentina, Brazil, Chile, Mexico and Peru, with a total marine area of about 59,591 km², produce mainly *Gracilaria* species, with *Kappaphycus* and *Euचेuma* being trial planted (Hayashi *et al.*, 2014). Other seaweeds like *Sarcothalia*, *Mazzaela*, *Gigartina*, *Chondracanthus* and *Gelidium* are harvested from natural populations.

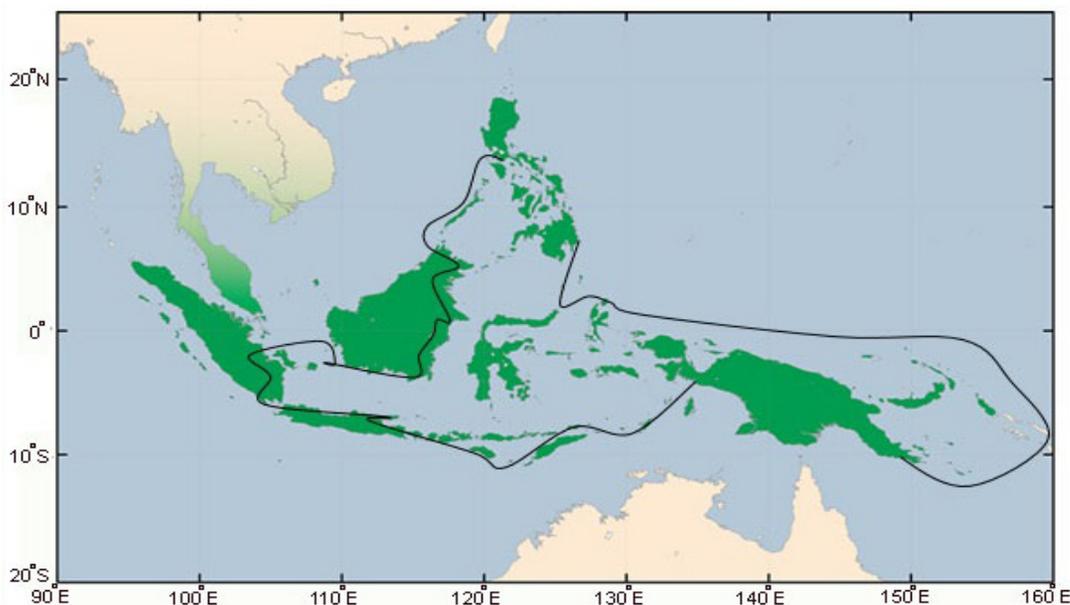


Figure 1. The Maritime Continent and the Coral Triangle (bordered in black)
(Source: <http://www.bom.gov.au/climate/about/tropics/maritime-continent.shtml>)

Marine Emissions of Halogenated Compounds in the Tropics

The tropics, including Southeast Asia, have rapidly industrialised, resulting in increased contributions to air pollution. Natural and anthropogenic emissions influence atmospheric composition, climate and air quality. Climate change may in turn affect natural emissions especially those from the terrestrial and marine ecosystems. It has been shown that halogens in the form of very short-lived halocarbons (VSLH) and volatile organic compounds (VOC) may affect the oxidizing capacity of the troposphere. These compounds when transported up into the troposphere and stratosphere, undergo photolysis and the halogens which are released, result in ozone depletion in the stratosphere and influence climate change (Aschmann *et al.*, 2009). Examples are brominated and chlorinated halocarbons which indirectly affect temperature (Forster and Joshi, 2005) by ozone depletion. High sea surface temperatures coupled with high bioproductivity in tropical oceans lead to deep convection forces which transfer these compounds to the atmosphere (Levine *et al.*, 2007). While the tropical and sub-tropical Pacific Ocean has been shown to be an important source of VSLH, information in the tropical Southeast Asian region is currently being gathered through active multinational collaborations (Pfeilsticker *et al.*, 2013). This is important as the transport of the short-lived species to the tropical tropopause is very rapid over the Maritime Continent (Levine *et al.*, 2008). Of the VSLH compounds, the reactive bromine and iodine species originate mainly from organic halocarbons from macroalgae (seaweeds) (Carpenter and Liss, 2000). Chloroform (CHCl_3) is also produced naturally by seaweeds (Nightingale *et al.*, 1995). Rainforests may also contribute to the emissions. Pyle *et al.* (2011a) reported that levels of bromoform (CHBr_3) differed between two monitoring sites in Sabah, one in the rainforest at Danum Valley and the second at Kunak, a coastal town. Levels at Kunak were higher and analysis confirmed that the air had traversed biologically rich oceanic and coastal areas. A survey showed that natural seaweed populations at Kunak comprised species of brown seaweeds (*Sargassum*, *Dicyota*, *Hormophysa* and *Padina*), red seaweeds (*Amphiroa*, *Laurencia*, *Gracilaria*, *Hypnea*) and green seaweeds (*Caulerpa*, *Halimeda*, *Anadymene*, *Neomeris*) (Pyle *et al.*, 2011b). *Sargassum siliquosum* and *Sargassum myriocystum* were dominant. Seaweed farms of *Eucheuma* and *Kappaphycus* are

abundant in the region (Phang *et al.*, 2010). It has been shown that *Eucheuma denticulatum* produces the halocarbons CHBr_3 and diiodomethane (CH_2I_2) (Mtolera *et al.*, 1996).

Halocarbon Production

Halocarbons comprise compounds consisting of a carbon atom bonded to one or more halogens. While long-lived halocarbons contribute significantly to the stratospheric halogen load, it may be the short-lived halocarbons with lifetimes of six months or less that are important in the contribution of free halogen radicals to the stratosphere (Laube *et al.*, 2008). Examples of long-lived halocarbons include the chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons, carbon tetrachloride (CCl_4), methyl chloroform (CH_3CCl_3) and methyl chloride (CH_3Cl). These gases are predominantly anthropogenic (WMO, 2007). Although natural processes such as volcanic eruption could release some of these long-lived compounds e.g. CCl_4 , CH_3Cl (Frische *et al.*, 2006), the contribution of CFCs and few other long-lived compounds through natural processes are negligible (Martinerie *et al.*, 2009). In an attempt to minimize and prevent further loss of the stratospheric ozone, the Montreal Protocol on Substances that Deplete the Ozone Layer (1987) and its subsequent amendments saw the complete phase-out of CFCs, halons, and carbon tetrachloride. As a result of such treaties, there were significant declines in the surface concentrations of the CFCs and carbon tetrachloride globally (WMO, 2011). However, due to the long atmospheric lifetime of these compounds, a time lag exists between the decline in the source gas emissions and the actual concentration of such gases existing in the atmosphere (Martinerie *et al.*, 2009). This would mean that the 'complete loss' of such compounds in the atmosphere would take up years and even centuries depending on the lifetime of gases, which in turn rely on the oceanic and terrestrial uptakes, photolysis and hydroxyl radical oxidation of the particular compound (WMO, 2011). The majority of iodinated short-lived compounds are released through natural processes especially from the ocean (WMO, 2011) but anthropogenic release of several iodinated compounds including CH_3I through biomass burning (Mead *et al.*, 2008) and for use as fumigant (UNEP/TEAP, 2010) had been reported. Enhanced emissions of methyl iodide (CH_3I) could be caused by increased sea surface temperature (Yokouchi *et al.*,

2008) and abiotic chemical mechanism stimulated by dust deposition (Williams *et al.*, 2007), oceanic sources may include phytoplankton (Hughes *et al.*, 2006) and seaweeds (Carpenter *et al.*, 2000). Carpenter *et al.* (2000) reported CH_2I_2 as the dominant iodocarbon released by temperate brown species, namely *Laminaria digitata*, *Laminaria saccharina*, *Ascophyllum nodosum*, *Fucus vesiculosus* and *Fucus serratus* that were studied. The Laminarias were reported as the strongest accumulators of iodide - the accumulated form of iodine, among all living organisms to date (Ar Gall *et al.*, 2004). This iodide was also found to be the simplest inorganic form of antioxidant (Küpper *et al.*, 2008). Terrestrial sources of chlorinated and brominated compounds include vegetation, soil production, biomass burning, mangroves, fungal processes, salt marshes, rice paddies and peatlands which also contribute to the emission of short-lived halocarbons (Montzka *et al.*, 2010; LTURNUS *et al.*, 2002).

The role of halocarbons in algae is linked to their use as defense against epiphytes and grazing as well as scavengers of strong oxidants (Paul *et al.*, 2006; Ohsawa *et al.*, 2001; Manley, 2002). Halocarbons emitted by macroalgae have anti-herbivory (McConnell and Fenical, 1977) and antibacterial activities (Neidleman and Geigert, 1986). Bromoform (CHBr_3) emissions in seawater comparable with the amount usually emitted by coralline red algae have been found to inhibit growth of microscopic marine algae, specifically the diatoms. Further investigation showed that the surface of coralline algae that produced CHBr_3 and CH_2Br_2 were void of diatoms whereas the surface of dead corallines which did not have any halocarbon emission were filled with epiphytic diatom populations (Ohsawa *et al.*, 2001). Choo *et al.* (2004) reported that *Enteromorpha ahneriana* have less epiphytic infestations and grazers on its surface unlike *Cladophora glomerata*, due to higher production of hydrogen peroxide and emission of brominated volatile halocarbons in the former. Other publications from La Barre (2010), Paul and Pohnert (2010) and Weinberger *et al.* (2007) have further confirmed that a wide range of halogenated compounds are indeed emitted by algae as a defense mechanism; specifically for protection against grazing, oppressing microalgal epiphytes and keeping bacterial infection at a minimal level. How do seaweeds produce halogenated compounds? The production of volatile polyhalogenated compounds is linked to haloperoxidase enzyme

activity in the seaweed (Manley, 2002), responsible for countering the oxidative stress in seaweeds resulting from the build-up of reactive oxygen species from metabolic responses like photosynthesis (Dummermuth *et al.*, 2003). These reactive oxygen species are reduced to produce hydrogen peroxide which is used in the halogenation of organic compounds by the enzymes (Manley, 2002). Haloperoxidases especially the bromoperoxidase, are produced by green, red and brown seaweeds (Butler and Walker, 1993; Carpenter *et al.*, 2000). In the brown seaweeds, haloperoxidases are linked to uptake of seawater iodide, which provides a strong antioxidant defense to the seaweed (Küpper *et al.*, 1998). The emission of methyl halide was suggested to involve the S-adenosylmethionine (SAM): halide ion methyl transferase reactions, which is not dependent on presence of hydrogen peroxide (Ohsawa *et al.*, 2001; Wuosmaa and Hager, 1990).

Halocarbon Emission by Tropical Algae

Lovelock (1975) first reported increased levels of CH_3I over kelp beds. Later studies reported different types of volatile halocarbon compounds released by seaweeds and microalgae (e.g., Hughes *et al.*, 2006; Tokarczyk and Moore, 1994) by temperate and polar seaweeds. *Eucheuma denticulatum*, a tropical red seaweed cultivated as a source of carrageenan, was reported to release bromoform, diiodomethane, dibromochloromethane, perchloroethylene, chloroiodomethane, chloroform, *sec-butyl* iodide, methyl iodide, methylchloroform, carbon tetrachloride, trichloroethylene and butyl iodide (Mtolera *et al.*, 1996). The dominant volatile halocarbons (VHC) were bromoform ($310 \pm 25 \mu\text{g kg DW}^{-1} \text{h}^{-1}$) and diiodomethane ($182 \pm 9 \mu\text{g kg DW}^{-1} \text{h}^{-1}$). High irradiance and carbon dioxide deficiency increased the halocarbon production through induction of hydrogen peroxide synthesis (Mtolera *et al.*, 1995; Mtolera *et al.*, 1996). Another tropical carrageenophyte *Kappaphycus alvarezii* was shown to release hydrogen peroxide into the seawater under stress from high light, low temperature and in the presence of thylakoid electron transport system inhibitor (Barros *et al.*, 2006). This occurred to avoid accumulation of the harmful peroxide that leads to oxidative lesions in the tissue. However, this prevented immediate induction of the H_2O_2 -scavenging activities of catalases and ascorbate peroxidases, but is useful for long-term adaptation to a stressed environment. Species of the red agarophytes, *Gracilaria*, release volatile halogenated organic compounds (VHOC)

involving vanadium-dependent haloperoxidases (Weinberger *et al.*, 2007). While *Gracilaria* sp. produces iodo-bromoperoxidases releasing brominated and iodinated compounds, *Gracilaria chilensis* expresses a selective haloperoxidase to selectively release chlorinated compounds. A commonly found Malaysian red seaweed, *Laurencia* has been reported to produce a variety of halogenated compounds. *Laurencia majuscula* produces elatol, iso-butanol and rogiolol as secondary metabolites that served as antibacterial compounds (Vairappan, 2003; Vairappan and Phang, 2005). *L. similis* produced polybrominated indoles, namely 2,3,5,6-tetrabromoindole and 1-methyl-2,3,5,6-tetrabromoindole (Vairappan *et al.*, 2004), also with antibacterial activities. Other halogenated sesquiterpenes identified from Malaysian *Laurencia* spp. included the brominated metabolites tiomanene, acetyl-majapolene B, majapolene A, majapolene B, three halogenated sesquiterpenes and two halogenated C15 acetogenins (Vairappan *et al.*, 2008).

Marine algae were reported to be significant natural sources of olefins in the oceans. Seaweeds were collected from their natural habitats in tropical, sub-tropical and temperate regions for determination of the production rates of two chlorinated ethenes, trichloroethylene and perchloroethylene (Abrahamsson *et al.*, 1995). The production rates were 0.22 – 3,400 ng g⁻¹ FW h⁻¹ and 0.0026 – 8.2 ng g⁻¹ FW h⁻¹ for trichloroethylene and perchloroethylene respectively. Two species, *Asparagopsis taxiformis* (tropical to sub-tropical) and *Falkenbergia hillebrandtii* (sub-tropical) gave highest production rates. It was further shown that the history and conditioning of an alga prior to analysis are important factors influencing the halocarbon release (Abrahamsson and Pedersén, 2000).

Dimethyl sulphide (DMS) is another trace gas formed in marine waters by biological (algae) and photochemical processes (Liss, 2007). Dimethylsulphoniopropionate (DMSP) serves as an osmolyte and cryoprotectant in marine species and is the precursor to the DMS. DMS affects climate by serving as cloud condensation nuclei. In a survey of corals and benthic algae in the Great Barrier Reef of Australia, DMSP concentrations ranged from 21 – 3831 fmol DMSP zooxanthellae⁻¹ in corals and 0.16 – 2.96 nmol DMSP cm⁻² for benthic seaweeds (Broadbent *et al.*, 2002), indicating the importance of these organisms as reservoirs of DMSP. Another trace gas, isoprene (2-methyl-1,3-butadiene) is pro-

duced by marine phytoplankton (Shaw *et al.*, 2003; Broadgate *et al.*, 1997), with pathway for isoprenoid biosynthesis reported for the green microalgae *Chlorella fusca*, *Chlamydomonas reinhardtii* and *Scenedesmus obliquus*, hot spring *Cyanidium caldarium* and the blue-green alga *Synechocystis* (Disch *et al.*, 1998). In 2004, Broadgate *et al.* reported that marine macroalgae like *Chondrus crispus*, *Asparagopsis armata*, *Ulva intestinalis*, *Laminaria digitata*, *Fucus vesiculosus*, emit isoprene. Production is related to species, temperature as well as irradiance.

Halocarbon release rates are higher for tropical algae than temperate species. The fringing coral reef at Cape Rachado, west coast Peninsular Malaysia, is dominated by Phaeophyta (brown seaweeds). Regular monitoring of the seaweed community revealed that species diversity ranged from 69 to 81 species with biomass ranging from 17 to 104 g.m⁻² (Phang, 1995). The seaweed communities at the intertidal reef are exposed to varying environmental conditions linked to the change of tides and the seasons. The three dominant brown seaweeds, namely *Sargassum binderi* Sonderex (J. Agardh), *Padina australis* (Hauck), and *Turbinaria conoides* (J. Agardh) (Kützing) were shown to emit eight volatile halogenated compounds (iodomethane (CH₃I), diiodomethane (CH₂I₂), bromochloromethane (CH₂BrCl), bromoiodomethane (CH₂BrI), dibromomethane (CH₂Br₂), tribromomethane (CHBr₃), bromodichloromethane (CHBrCl₂), and dibromochloromethane (CHBr₂Cl). Laboratory studies showed that the release of halogenated compounds by the three dominant brown seaweeds, as detected using a purge-and-trap sample preparation system with a gas chromatograph and mass-selective detector, was influenced by irradiance. Correlations were also observed between emissions of certain halocarbons with photosynthetic activity, especially bromo- and iodinated compounds 0.6 < r < 0.9; (p < 0.01) suggesting that environmental factors such as light can affect the release of these volatile halogenated compounds by the seaweeds into the atmosphere (Keng *et al.*, 2013). The influence of irradiance on production of some halocarbons by the seaweeds may be a photosynthesis-related mechanism (Ek Dahl *et al.*, 1998; Goodwin *et al.*, 1997; Laturus *et al.*, 2000), since the halocarbons may be a result of hydrogen peroxide produced by the Mehler reaction or pseudocyclic photophosphorylation during photosynthesis (Manley and Barbero, 2001; Pedersén *et al.*, 1996). Halocarbon production in seaweeds is

also affected by light (Mtolera *et al.*, 1995; Nightingale *et al.*, 1995; Laturus *et al.*, 2000); pH (Mtolera *et al.*, 1995); desiccation (Leedham, 2015; Nightingale *et al.*, 1995); oxidative stress (Abrahamsson *et al.*, 2003); tissue age (Nightingale *et al.*, 1995); tissue wounding / grazing (Sundström *et al.*, 1996; Nightingale *et al.*, 1995) and photosynthetic activity (Sundström *et al.*, 1996; Goodwin *et al.*, 1997).

Potential Contribution of Seaweed Farms to Halocarbon Emission in the Maritime Continent

Leedham *et al.* (2013) published an excellent report on halocarbon production by 15 tropical seaweeds collected in Malaysia, including the farmed seaweed, *Kappaphycus alvarezii*, and calculated production rates were used to estimate CHBr_3 and CH_2Br_2 emissions for Malaysian and South East Asian coastal zones. Of the seaweeds studied, the farmed species of *Gracilaria changii* (1037–1272 pmol $\text{gFW}^{-1} \text{h}^{-1}$) and *Kappaphycus alvarezii* (479–558 pmol $\text{gFW}^{-1} \text{h}^{-1}$) were shown to be amongst the highest producers of CHBr_3 . Leedham *et al.* (2013) also estimated the annual emissions of CHBr_3 from Malaysia and the Southeast Asian region (SEA, comprising Brunei, Burma, Cambodia, Christmas Island, Indonesia, Malaysia, the Philippines and Singapore) based on the total coastal lengths. The estimated flux rate of 17–610 nmol $\text{CHBr}_3 \text{m}^{-2} \text{h}^{-1}$ for SEA resulted in an estimated annual emission range of 6–224 mmol Br yr^{-1} that was lower than that (180–350 mmol Br yr^{-1}) reported by Pyle *et al.* (2011a), although the definition of SEA was not similar. Robinson *et al.* (2014) provided updated observations, especially of the biogenic short-lived CHBr_3 , CH_2Br_2 and CHI_3 , from a 15-month survey from the rainforest (Danum) and coastal (Kunak) sites first reported by John *et al.* (2011). Robinson *et al.* (2014) reported that contrary to John *et al.* (2011), the bromine detected at both the rainforest and coastal sites were similar, with CHBr_3 and CH_2Br_2 not showing seasonal variations, but short-term variations were evident in the coastal site related to the marine sources including coastal seaweed and both coastal and oceanic phytoplankton. They also stated that the overall bromine values of 8.0 ppt and 6.8 ppt at the coast and inland respectively, were not very different from reported tropical data. Mohd Nadzir *et al.* (2014) used data collected during a research cruise over the Straits of Malacca, the South China Sea and the Sulu-Sulawesi Sea in 2009, estimated a regional emission of 63 $\text{Ggyr}^{-1} \text{CHBr}_3$ for

the Southeast Asian region. CHBr_3 was the most abundant bromocarbon, ranging from 5.2 pmolmol^{-1} in the Straits of Malacca to 0.94 pmolmol^{-1} over the open ocean. Although these figures were based on many assumptions, short-term monitoring or grab samples, they were useful for comparisons with data reported for other regions, indicating the potential importance of the tropics as a dominant source of halocarbons which are transported to the stratosphere by the intense tropical convection.

The red seaweeds *Kappaphycus/Eucheuma* and *Gracilaria* are the dominant species farmed in the Coral Triangle. Seaweed production increased tremendously from 2003 till 2012 in Indonesia (1209% increase), Malaysia (1226%), Vietnam (682%) and the Philippines (77%) (FAO, 2014). China (50% increase) and Korea also recorded increase in seaweed production, although it was based on brown seaweeds, while Japan (-8%) and Taiwan (-72%) recorded great decrease in production. These figures predict upward trends in most of the countries in the Maritime Continent, and it is timely to focus more attention on the emissions of halocarbons arising from seaweed farms in the region. Green seaweeds like *Caulerpa*, *Ulva* harvested from natural populations for use as food, and the brown seaweeds *Sargassum* and *Padina* which dominate coral reefs, may also be significant contributors to the halocarbon load in the region. Keng *et al.* (2013) showed that the Malaysian brown seaweeds, *Sargassum binderi*, *Turbinaria conoides* and *Padina australis* had much higher production rates of CH_3I , CH_2I_2 , CH_2Br_2 , CHBr_3 , CH_2BrI , CHBr_2Cl , CH_3BrCl_2 , CH_2BrCl than the temperate and polar species.

Table 1 summarises the halocarbons emitted by selected seaweed species that are found in tropical/sub-tropical Maritime Continent. The life-times of some of these compounds range from 7 days (CH_3I) to 15–21 days (CHBr_3) and up to 120 days (CH_2Br_2) (Robinson *et al.*, 2014). Dibromomethane (CH_2Br_2) is emitted by all the seaweeds reported and it would be interesting to determine the contributions of farmed versus natural seaweed populations.

More intensive studies have to be carried out, including halocarbon emissions from more seaweed species and the mapping of both natural and farmed seaweed areas to provide better estimates of areas to be used for the estimations. The effects of ocean warming and acidification on marine algae are still

Table 1. Halocarbons produced by selected tropical seaweed species

Halocarbon	CH ₃ I	CH ₂ I ₂	CH ₃ Br ₂	CHBrI ₃	CH ₂ BrI	CHBr ₂ Cl	CHBrCl ₂	CH ₂ BrCl	CH ₂ ClI	CH ₃ CCl ₃	CCl ₄	C ₄ H ₉ I	C ₂ HCl ₃	C ₂ Cl ₄
RHODOPHYTA														
<i>Kappaphycus alvarezii</i> ^a	n/a	4.17	0.54	3.38	1.52	0.85	0.96	0.51	0.57	n/a	n/a	n/a	n/a	n/a
<i>Eucheuma denticulatum</i> ^c	0.50	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	5.00	1.80	0.60	n/a	n/a
<i>Gracilaria changii</i> ^a	2.72	3.16	11.80	3.95	13.26	3.25	3.56	16.47	7.20	n/a	n/a	n/a	n/a	n/a
<i>Gracilaria salicornia</i> ^a	2.36	14.72	10.87	5.39	26.36	3.71	4.36	12.45	13.08	n/a	n/a	n/a	n/a	n/a
<i>Gracilaria chilensis</i> ^d	+	n/a	+	+	+	+	+	n/a	+	n/a	n/a	n/a	n/a	n/a
<i>Gracilaria cornea</i> ^e	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	7.00	-
<i>Laurencia obtusa</i> ^e	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.76	0.003
<i>Hypnea musciformis</i> ^e	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	4.80	-
<i>Corallina officinalis</i> ^e	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	2.20	-
<i>Gelidium elegans</i> ^a	2.32	7.86	2.00	7.83	6.72	2.96	5.70	3.05	3.65	n/a	n/a	n/a	n/a	n/a
PHAEOPHYTA														
<i>Sargassum binderei</i> ^a	1.45	10.76	3.10	2.61	7.87	1.40	0.73	3.04	2.95	n/a	n/a	n/a	n/a	n/a
<i>Sargassum binderei</i> ^b	16.7	0.60	6.20	113.00	1.60	48.50	39.40	0.10	n/a	n/a	n/a	n/a	n/a	n/a
<i>Turbinaria conoides</i> ^a	0.68	1.03	2.21	2.13	1.15	1.81	3.04	0.91	0	n/a	n/a	n/a	n/a	n/a
<i>Turbinaria conoides</i> ^b	4.60	9.70	49.20	407.90	15.40	12.80	1.50	0.80	n/a	n/a	n/a	n/a	n/a	n/a
<i>Padina australis</i> ^b	1.10	1.80	0.00	4.90	0.00	0.50	0.40	0.00	n/a	n/a	n/a	n/a	n/a	n/a
CHLOROPHYTA														
<i>Ulva reticulata</i> ^a	n/a	6.75	2.39	6.68	4.39	6.14	4.99	n/a	8.81	n/a	n/a	n/a	n/a	n/a
<i>Ulva rigida</i> ^e	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.09	-
<i>Caulerpa racemosa</i> ^a	4.98	1.91	0.59	2.07	1.51	1.39	n/a	n/a	1.75	n/a	n/a	n/a	n/a	n/a
<i>Caulerpa</i> ^e	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	5.90	-

a: production rate, pmol gFW⁻¹ h⁻¹ (ratio t4:t24 h) (Emma *et al.* 2013)
 b: production rate, pmol gFW⁻¹ h⁻¹ (Keng *et al.*, 2013)
 c: production rate, µg kgDW⁻¹ h⁻¹ (Mtolera *et al.*, 1996)
 n/a: data not available +: present -: not detected
 d: production rate, pmol g⁻¹ FW min⁻¹ (Weinberger *et al.*, 2007)
 e: production rate, ng g⁻¹ FW h⁻¹ (Abrahamsson *et al.*, 1995)

relatively undetermined, although reports indicate that the environmental stress can cause increased release of halocarbons from seaweeds. Tropical species have adapted to less variable climatic conditions than temperate species, with narrower ranges of temperature and irradiance. Our studies have shown that polar and temperate algae survive at temperatures much higher than their ambient, while the tropical algae grew best at their ambient temperature (28–33 °C). This is probably because the tropical microalgae are already growing at their upper temperature limit (Teoh *et al.*, 2013). Adaptation to temperature changes is related to lipid content as well as the ratio of saturated fatty acid (SFA) to unsaturated fatty acid (UFA) contents. At low temperatures, there is an increase in SFA to maintain membrane fluidity, while at increased temperature, the reverse was observed. How will temperature stress influence halocarbon production and emission in tropical seaweeds, especially under acidifying conditions?

CONCLUDING REMARKS

Recent reports show that the tropics make significant contributions of the short-lived halogenated compounds to the atmosphere, contributing to climate change, but has yet to be confirmed for the west Pacific region. Seaweed production has increased tremendously in the Coral Triangle over the last decade, and if the trend continues, farmed seaweeds may be an important source of these compounds in addition to natural populations. Attempts to estimate the annual emissions of selected compounds are based on many assumptions. To enable better estimations, efforts at profiling halocarbon emissions from the farmed seaweeds as well as dominant species along the coastal and island habitats, under various environmental conditions, have to be combined with extensive survey and mapping of natural seaweed beds to determine the species composition, distribution and relative abundance. Long-term and continuous measurements are important to provide high quality data for understanding the contribution of the tropical marine biogenic sources of the halocarbons to the atmosphere, and implications to global climate change. The atmospheric laboratory at the Institute of Ocean and Earth Sciences (IOES) Bachok Marine Research Station, Kelantan, which faces the South China Sea, has been equipped to serve the purpose of long-term and continuous monitoring of the atmospheric com-

position in the region.

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