Journal of Applied Phycology (2023) 35:3007–3020
https://doi.org/10.1007/s10811-023-03067-z

RESEARCH

Emission of volatile halocarbons from the farming of commercially important tropical seaweeds

Fiona Seh-Lin Keng[1,2] · Siew-Moi Phang[1,3] · Noorsaadah Abd Rahman[2] · Hui-Yin Yeong[1] · Gill Malin[4] · Emma Leedham Elvidge[5] · William Sturges[4] · Choon-Weng Lee[1,6]

Received: 8 May 2023 / Revised: 29 July 2023 / Accepted: 9 August 2023 / Published online: 9 September 2023

Abstract

The emission rates of the atmospherically important halogenated trace gases $CHBr_3$, $CHBr_2Cl$ and $CHBrCl_2$ were measured from two commercially important tropical red seaweed species *Gracilaria manilaensis* Yamamoto and Trono, and *Kappaphycus alvarezii* (Doty) L.M.Liao in a range of environments to investigate the potential impact of seaweed aquaculture on atmospheric halocarbon concentrations. Deep convective transport in the tropics can carry such volatile halocarbons to the upper troposphere and lower stratosphere. In this first study of its kind, emissions from these two seaweed species were measured after growing on an offshore platform, in onshore tanks, and in cages at a river mouth in eastern Peninsular Malaysia. Of the three cultivation systems, the amount of $CHBr_3$ released by *G. manilaensis* was highest from the cage culture at the river mouth (267 ± 13 ppbv), followed by the offshore platform (78 ± 47 ppbv) and onshore tank (69 ± 69 ppbv). Daylight emissions by *G. manilaensis* and *K. alvarezii* from both offshore and onshore cultivations were greater than in the dark. The global production of seaweed is projected to increase further due to the rising demand for seaweed products, the emphasis on clean energy, and climate action. Harvesting of commercial seaweeds could potentially significantly increase local atmospheric abundances of $CHBr_3$; in our study 500 g of these typical seaweeds increased $CHBr_3$ in a 40 L flux chamber by 41–267 ppbv in 30 min; far above usual background amounts. As our study showed that higher temperatures increase seaweed halocarbon emissions, given impending climate change, and the possible extension of seaweed cultivation to subtropical seas as seawater temperatures rise, this might further increase halocarbon emissions. We estimate that the harvesting of *K. alvarezii* in the year 2020 in Malaysia could have released 63–322 mol Br for each hour of harvesting activity.

Keywords Tropical seaweeds · Climate change · Seaweed aquaculture · Atmospheric science · Bromoform · Marine biotechnology · Marine biogeochemistry

✉ Fiona Seh-Lin Keng
fionakeng@um.edu.my

✉ Siew-Moi Phang
phang@um.edu.my

1 Institute of Ocean and Earth Sciences (IOES), Universiti Malaya, 50603 Kuala Lumpur, Malaysia

2 Institute for Advanced Studies, Universiti Malaya, 50603 Kuala Lumpur, Malaysia

3 Faculty of Applied Sciences, UCSI University, 56000 Cheras, Kuala Lumpur, Malaysia

4 Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich Research Park, Norwich NR4 7TJ, UK

5 Faculty of Science, University of East Anglia, Norwich Research Park, Norwich NR4 7TJ, UK

6 Institute of Biological Sciences, Faculty of Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia

Introduction

Since ancient times seaweeds have been grown for food and a variety of chemical constituents. The seaweed sector is currently projected to be worth US$ 6 billion per year (FAO 2022). In 2020, 35.01 million tonnes of seaweed were generated through cultivation, representing 97.45 percent of the total 35.93 million tonnes of seaweed produced worldwide (FAO 2022). Tropical seaweed production in the Coral Triangle has increased from 0.39 to 11 million tonnes of fresh weight from 1990 to 2020. This includes commercially significant algae, including *Eucheuma* spp., *Gracilaria* spp., and *Kappaphycus alvarezii*. The Coral Triangle is one of the world's most biodiverse regions in terms of marine life, spanning six countries in Southeast Asia and the Pacific,

namely Indonesia, the Philippines, Malaysia, Papua New Guinea, the Solomon Islands, and Timor-Leste (Asia Development Bank 2016).

While seaweeds such as *Gracilaria* are grown largely for human consumption, e.g., agar–agar, *Eucheuma* and *Kappaphycus* are mostly cultivated for the manufacturing of carrageenan, a popular ingredient in the cosmetic and food processing industries. Seaweed production in Malaysia increased from 111,298 t in 2008 to 182,061 t in 2020, with a market value of US$ 1.4 billion (FAO 2022). Both the hanging basket and longline methods are cultivation methods commonly adopted by the seaweed industry in Malaysia, especially in the cultivation of *K. alvarezii* (Sade et al. 2006; Phang et al. 2019). Rising demand for cultivated seaweeds in the magnitude of orders greater than the current levels has been anticipated, mainly due to its dietary benefits and capability to generate multiple ecosystem services (Kang et al. 2011; Rizki et al. 2023) in response to the United Nations Sustainability Development Goals (Duarte et al. 2021).

Even though widespread cultivation of seaweeds has been essential to improving the socioeconomic position of coastal communities, the growth in seaweed production in the tropical Coral Triangle might lead to an increase in the region's halocarbon burden (Phang et al. 2015). Coastal seaweeds are recognised as significant sources of volatile halocarbons such as $CHBr_3$ (Keng et al. 2020). Short-lived halocarbons account for 30% of total stratospheric bromine (WMO 2018). Previous research indicated that *K. alvareziii*, *Gracilaria changii*, and *Gracilaria edulis* are among the farmed tropical seaweeds that are capable of emitting significant quantities of such halocarbons (Leedham et al. 2013; Mithoo-Singh et al. 2017). Much of the short-lived halocarbon load emitted from the surface is removed by photolysis and oxidation in the troposphere, but some fraction can enter the stratosphere, notably through rapid convective uplift in the tropics, where photolysis releases reactive inorganic bromine species that destroy ozone (Hossaini et al. 2012a; Liu and Zipser 2015; Pan et al. 2017). These brominated short-lived halocarbons are responsible for significant loss of lower stratospheric ozone and may be 3.6 times more powerful than long-lived halocarbons in exerting a radiative impact through ozone loss (Hossaini et al. 2015).

The emission of volatile halocarbons by seaweeds has been linked to environmental factors such as variations in irradiance, temperature, saltwater nutrients, and salinity (Laturnus et al. 2000; Abrahamsson et al. 2003; Bondu et al. 2008). Along the electron transport chain, harmful reactive oxygen species such as hydrogen peroxide and hydroxyl compounds are often generated in chloroplasts and mitochondria (Manley and Barbero 2001; Dummermuth et al. 2003; Gill and Tuteja 2010). Bromoperoxidases in the seaweeds catalyse the reaction between H_2O_2 and halides to produce hypohalide, which then reacts with either the ketones in the seaweeds or dissolved organic matter (DOM) in the environment to produce $CHBr_3$ (Wever et al. 1991; Opsahl and Benner 1997; Lin and Manley 2012; Wever and van der Horst 2013). Disturbances to the H_2O_2 equilibrium, such as changes in environmental conditions, may have an impact on the emission of halocarbons by seaweed, since the accumulation of reactive oxygen species (Li et al. 2010; Dietz 2016) may result in an increase in the generation of volatile halocarbons (Küpper et al. 2013).

Our previous works investigating the emission of halocarbons by tropical seaweeds, including the effect of environmental factors such as irradiance, pH, and temperature on halocarbon emissions through a series of laboratory-based studies, showed that tropical seaweeds are important coastal sources of halocarbons and could contribute to the regional, if not global, halocarbon pool (Keng et al. 2013; Leedham et al. 2013; Mithoo-Singh et al. 2017; Keng et al. 2021). However, gaps remained in this area as emissions data from the tropics remained limited, and much remained unknown about how environmental changes could affect the emission of halocarbons by the seaweeds during cultivation. The lack of data from oceanic input and the under-representation of coastal and extreme emissions often cause huge variability and uncertainties in the modelling and estimation of global oceanic halogen load (Hossaini et al. 2012b; Ziska et al. 2013, 2017; Fuhlbrügge et al. 2016; WMO 2018). In this study, the emissions of $CHBr_3$, $CHBr_2Cl$, and $CHBrCl_2$ by G. *manilaensis* and the economically important *K. alvarezii* harvested from the various cultivation systems were quantified. The effects of temperature, irradiance, seawater salinity and nutrient levels are also investigated. The emission rate of $CHBr_3$ by *K. alvarezii* from the offshore platform was then used to estimate the release of Br by farmed *K. alvarezii* during harvesting in Malaysia. This study will provide in-depth information on the halocarbon emission by farmed seaweeds in the tropics, which could be useful for future estimation work, particularly with the potential expansion of the seaweed farming industry, considering the vast beneficial properties and the newly explored potential of exploiting the high $CHBr_3$ content in red seaweeds like A*sparagopsis taxiformis* to reduce methane production by ruminants (Glasson et al. 2022).

Materials and methods

Seaweed cultivation

Gracilaria manilaensis Yamamoto and Trono (Gracilariaceae, Rhodophyta; PSM13041) was collected at Tanjung Kupang, Johor, Malaysia (1°20′26″ N 103°36′16″ E), while *Kappaphycus alvarezii* (Doty)

L.M.Liao (Solieriaceae, Rhodophyta; PSM13827) was purchased from a seaweed farm off Tawau, Sabah, East Malaysia (4°18′58″ N 117°46′26″ E). The seaweeds (Fig. 1) were then transported to the Bachok Marine Research Station (BMRS) in Bachok, Kelantan. *Gracilaria manilaensis* and *K. alvarezii* were both grown in the BMRS hatchery's onshore overflow tank cultivation system and on an offshore platform. *Gracilaria manilaensis* was also cultivated in a cage culture system at a river mouth close to the BMRS. The cultivation of *G. manilaensis* was tested in the river, as this seaweed is commonly found in sheltered bays, estuaries, and river mouths with sandy or sandy-mud bottoms.

Fig. 1 The cultivated seaweed species are, from left to right, *Gracilaria manilaensis* and *Kappaphycus alvarezii.* Further descriptions of these seaweeds are provided in the main text

Onshore tank cultivation system

The onshore tank cultivation was made up of several overflow systems. Each of the overflow systems consists of three polypropylene tanks, each measuring 1.3 × 0.9 × 0.5 m, attached to a reservoir tank with a top filter (Fig. 2a). Approximately 1000 L of seawater was used to fill the reservoir and the three tanks, and a continuous flow of seawater within the system was maintained by submersible pumps. About 30% of the seawater in the system was refreshed with fresh natural seawater every three days, and the cultures were maintained at a 28 ± 3 °C seawater temperature and under natural sunlight at the BMRS outdoor hatchery. Two onshore overflow systems were used for *G. manilaensis* and *K. alvarezii* cultures, respectively. The designated tanks were each filled with 1 kg of *G. manilaensis* and 500 g of *K. alvarezii* and these culture studies were carried out for 4 weeks. An initial study was carried out in April 2018 and successive studies in October 2018.

Offshore platform

An offshore platform measuring 5 × 5 m was constructed from wooden planks and 120 L polyethylene drums as floats. The platform was anchored about 600 m offshore in 4.5 – 6 m depth of water, depending on the tide. Fishing net of 2 cm mesh was attached to the underside to protect the seaweed from fish grazing. The seaweeds were cultivated for four weeks; slightly shorter than the typical cycle of 45 days for the cultivation of *G. manilaensis* and *K. alvarezii*. This was because our preliminary investigations had indicated that both *G. manilaensis* and *K. alvarezii* have higher biomass productivities and growth rates in weeks 1–3, with

Fig. 2 The three systems from which seaweed was cultivated were: onshore tanks (**a**), offshore platform (**b**), and cage culture at Sungai Melawi (**c**, **d**)

a decline beginning in week 4. The seaweeds were generally healthy with no visible signs of senescence or bleaching throughout the chosen cultivation period.

In these studies, *G. manilaensis* was cultivated in cuboid baskets, while *K. alvarezii* was tied directly to a monoline system. Cuboid baskets of 0.3 × 0.3 × 0.1 m were made from 1 cm mesh fishing net wound around PVC tubing. Each basket contained 500 g of *G. manilaensis* and three baskets were spaced out along a 50-m nylon monoline and kept floating about 10 cm under the sea surface (Fig. 2b). Bunches of *K. alvarezii,* each weighing 150 g, were tied along a monoline at intervals of 20 cm, with a 15 cm gap between the seaweed bunches and the monoline. All monolines were kept 0.5 m apart from each other. Loggers to collect irradiance and temperature data were tied to the lines. There was a total of three rows of *G. manilaensis* in the hanging baskets and five lines of *K. alvarezii* bunches cultivated at the platform between October 4 and 31, 2018.

River mouth cage culture

A cage culture system measuring 1.5 × 1.0 × 0.5 m with three compartments as replicates was constructed out of the same material as the hanging basket used in the offshore platform cultivation system. The three compartments were each filled with 500 g of *G. manilaensis* (Fig. 2c). The system was then deployed at the river mouth of Sungai Melawi (6º1′23.24″ N, 102º25′3.47″ E), close to the BMRS (Fig. 2d). The water depth at the river mouth ranged from 0.2 to 1.5 m, influenced by tidal fluctuations. The cage culture system, larger than the offshore hanging cuboid basket, allows the seaweed to float at varying tidal levels. This design ensures the seaweeds remained mostly immersed in water while being capable of floating to the surface during high tide.

Sampling and data collection

Four sampling trips were made (Table 1). Seaweeds sampled during trips 2, 3, and 4 were from the same starting batch, resembling a cycle of seaweed cultivation.

Seaweed from the offshore platform was collected by boat: a random rope line with hanging baskets of *G. manilaensis,* and another with bunches of *K. alvarezii,* were brought back to the onshore hatchery. Each trip took between 5 and 10 min. The seaweeds were immersed in a basin containing seawater during transport. All seaweed samples used for incubation in the flux chamber from the onshore tanks and offshore platform were pre-weighed and immersed in an isolated compartment in the onshore tanks for no longer than two hours prior to incubation. At the onshore tanks, approximately 500 g of seaweed biomass were harvested from randomly selected tanks during each sampling event. For the offshore and river culture samples, seaweed from a single bunch or compartment was randomly chosen for sampling. In cases where the biomass was low, seaweed from the next closest bunch or compartment was also harvested to ensure an adequate sample of biomass.

Data loggers (Onset, HOBO) were attached to the three cultivation systems and within the flux chambers to record irradiance and temperature, with the latter being used to correlate with halocarbon emission data during incubation. The temperature and irradiance levels in the flux chamber were within the range experienced by the seaweeds at their various cultivation locations, and is therefore representative of those experienced during growth. Seawater salinity (Master-S38M, ATAGO) was determined during seaweed sampling. Seawater samples were collected and transported back to Kuala Lumpur in a chilled condition for analysis of nutrient content. The seawater nutrient levels were determined using the HACH DR 3900 spectrophotometer and the salicylate (Reardon et al. 1966), diazotization (USEPA 1979), cadmium reduction (APHA 1998), and ascorbic acid (APHA 1998) methods (Hach 2001).

Flux chamber air sample collection

A custom-made flux chamber (Fig. 3) was used to sample the halocarbon emissions from the seaweed. The 40-L flux chamber was designed and modified according to the EPA-recommended flux chamber (Eklund 1992) and that described by Sartin et al. (2002). A small axial fan unit powered by a 12 V battery was built in to help move air around in the chamber.

Flux chamber measurements on seaweeds cultivated from the onshore tank and the offshore platform were made at the onshore hatchery, whilst measurements on samples from the cage culture system were made on shore near the river mouth to minimise changes in emissions during transport. All emission measurements on seaweeds from the offshore platform and river mouth were carried out during daylight, whilst seaweeds from the onshore tanks were also sampled after sunset to determine their emissions in the dark. The seaweeds were only removed from the isolated compartments of the tanks, or from the river mouth, immediately before incubation in the flux chamber.

Whole seaweeds were blotted dry for weighing and around 500 g were placed in the flux chamber in which the seaweeds were re-moistened by sprinkling 100 mL of seawater or river water, depending on the locations where the seaweeds were sampled. This was done to prevent complete drying-out of the seaweed during the 30 min incubation period and to better mimic that from freshly harvested seaweed. The same steps were repeated for the control sample, with the same amount of river or seawater used, but no seaweed. The seaweeds and controls were left for 30 min in the flux chamber prior to the collection of the air samples. The temperature within the flux chamber was

Table 1 The sampling dates, the culture age of the seaweed from which air samples were collected (via flux chamber and air canisters), the sampling conditions, i.e., daylight and darkness, the number of air samples (*n*) collected, and the net emission of $CHBr_3$, $CHBr_2Cl$, and $CHBrCl_2$ (average ± standard deviation of biological replicates; minimum to maximum; ppbv) by *G. manilaensis* and *K. alvarezii* from the three cultivation systems

Sampling Trip		Seaweed Culture Age	Sampling Condition / Number of samples collected/ Net emission										
			Onshore tank						Offshore platform			Cage culture	
			Daylight			Dark			Daylight			Daylight	
No	Date		C	GM	KA	C	GM	KA	C	GM	KA	C	GM
1	4–5 Apr 2018	1 week	1	2	1	2	1	1					
2	8 – 10 Oct 2018	< 3 days	1*	3	3	1	3		1*	3	2		
3	18 Oct 2018	2 weeks							1	3	3	1	2
4	30 – 31 Oct 2018	4 weeks	1**	2	2	1	3	2	1**	3	2		
$CHBr_3$													
1	4–5 Apr 2018	1 week		128 ± 119 (38 – 206)	61		17	17					
2	8 – 10 Oct 2018	< 3 days		19 ± 13 (6 – 32)	88 ± 13 (80 – 102)		4 ± 1 (3.4 – 4.9)			76 ± 34 (55 – 114)	23 ± 3 (21 – 25)		
3	18 Oct 2018	2 weeks								115 ± 60 (70 – 183)	29 ± 10 (18 – 38)		267 ± 13 (258 – 276)
4	30 – 31 Oct 2018	4 weeks		89 ± 10 (82 – 97)	71 ± 49 (37 – 106)		7 ± 2 (5 – 9)	26 ± 20 (12– 40)		43 ± 16 (24 – 53)	78 ± 21 (63 – 93)		
Overall				69 ± 69 (6 – 206)	78 ± 25 (37 – 106)		7 ± 5 (3 – 17)	23 ± 15 (12 – 40)		78 ± 47 (24 – 183)	41 ± 27 (18 – 93)		267 ± 13 (258 – 276)
$CHBr_2Cl$													
1	4–5 Apr 2018	1 week		3 ± 3 (1 – 5)	3.0		0.7	0.4					
2	8 – 10 Oct 2018	< 3 days		0.5 ± 0.3 (0.2 – 0.7)	1.4 ± 0.3 (1.2 – 1.7)		0.2 ± 0.0 (0.1 – 0.2)			5.3 ± 1.7 (3.8 – 6.8)	2.5 ± 0.0 (2.4 – 2.5)		
3	18 Oct 2018	2 weeks								3.8 ± 0.0 (3.8 – 3.8)	0.6 ± 0.0 (0.6 – 0.7)		5.2 ± 0.6 (4.7 – 5.6)
4	30 – 31 Oct 2018	4 weeks		8 ± 6 (4 – 12)	1.9 ± 1.2 (1.0 – 2.8)		0.2 ± 0.0 (0.1 – 0.2)	0.5 ± 0.4 (0.2 – 0.8)		1.5 ± 0.6 (0.9 – 2.0)	1.5 ± 0.0 (1.5 – 1.5)		
Overall				3.3 ± 4.3 (0.2 – 12)	1.8 ± 0.8 (1.0 – 3.0)		0.2 ± 0.2 (0.1 – 0.7)	0.5 ± 0.3 (0.2 – 0.8)		3.9 ± 2.2 (0.9 – 7.3)	1.4 ± 0.8 (0.6 – 2.5)		5.2 ± 0.6 (4.7 – 5.6)
$CHBrCl_2$													
1	4–5 Apr 2018	1 week		0.1 ± 0.1 (0 – 0.2)	0.17		0.01	0.01					
2	8 – 10 Oct 2018	< 3 days		0.1 ± 0.0 (0.0 – 0.1)	0.3 ± 0.09 (0.3 – 0.45)		0.04 ± 0.01 (0.03 – 0.04)			0.9 ± 0.5 (0.4 – 1.4)	0.3 ± 0.2 (0.2 – 0.5)		
3	18 Oct 2018	2 weeks								0.8 ± 0.3 (0.5 – 1.0)	0.1 ± 0.0 (0.1 – 0.1)		0.4 ± 0.1 (0.3 – 0.5)
4	30 – 31 Oct 2018	4 weeks		0.9 ± 0.8 (0.3 – 1.5)	0.1 ± 0.1 (0.1 – 0.2)		0.02 ± 0.00 (0.01 – 0.02)	0.04 ± 0.04 (0.02 – 0.07)		0.11 ± 0.04 (0.07–0.15)	0.08 ± 0.01 (0.08 – 0.09)		
Overall				0.3 ± 0.5 (0.0 – 1.5)	0.25 ± 0.14 (0.05 – 0.45)		0.03 ± 0.03 (0.01 – 0.09)	0.03 ± 0.03 (0.01 – 0.07)		0.6 ± 0.5 (0.07 – 1.4)	0.2 ± 0.1 (0.1 – 0.5)		0.4 ± 0.1 (0.3 – 0.5)

C Control (without seaweeds); *, ** shared control between onshore tank and offshore platform samples for the same sampling day; *GM* = *G. manilaensis*, *KA* = *K. alvarezii*

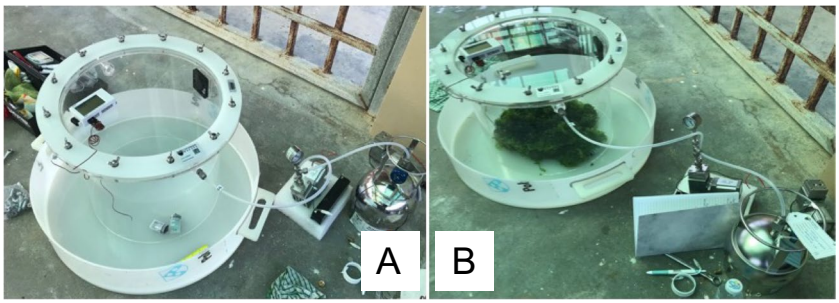

Fig. 3 The flux chamber connected to a canister via an air pump: (**a**) the collection of control air; (**b**) the collection of air sample containing halocarbon emissions from seaweeds

recorded at the start and at the end of the incubation, while two to three readings of irradiance levels were also recorded.

Air samples from the flux chamber were collected using SilcoCan canisters (Entech Instruments). Canisters with volumes of 2.7 L and 3.2 L were cleaned prior to sampling through repeated baking (at 90 °C) and flushing with high-purity nitrogen gas (Linde Malaysia) for six cycles before evacuating (Canister Cleaning System, Entech).

Air from the flux chambers was drawn into the canisters through PFA transfer tubing connected to a 12 V battery-powered pump (Air Dimensions Inc.) to a final pressure of 10 psig after flushing once with the same air to the same pressure. Samples were transported back to the laboratory for analysis within three weeks.

Air samples, with or without seaweeds, collected after sunrise and before sunset were classified as 'daylight' samples, while air samples collected after sunset were classified as 'dark'. Control air samples in daylight ($n=5$) and dark ($n=4$) without seaweed were collected for comparison to the air samples containing seaweed. Net emissions by seaweeds were then determined by subtracting the mixing ratios of compounds in the flux chamber containing seaweeds from the controls, which were taken prior to the sampling of the seaweeds on the same day, either during daylight or darkness. All halocarbon mixing ratios (ppbv) measured from the flux chambers represent the emissions from 500 g of seaweed biomass in 30 min, standardised from the actual measured weight of biomass in each.

Sample analysis

Filled canisters were attached to the inlet of an Entech pre-concentrator (7200 Sample Preconcentrator, Entech Instruments) coupled to an Agilent GCMS (7890B/5977B, Agilent Technologies). The pre-concentrator uses a three-stage trapping process known as 'Extended Cold Trap Dehydration' to improve the sensitivity of the analyses. This includes passing 100 cm^3 air samples through an empty Silonite-D treated trap (M1) pre-cooled to − 40 °C, eliminating water from the samples. The analytes were then transferred to a second-stage Tenax trap (M2) at − 50 °C for trapping. This was followed by back-desorption of the Tenax trap to the final focusing trap (M3) prior to injection into the GCMS system (Markle et al. 2017). Further details on the pre-concentration parameters are summarised in Supplementary Table S1.

The GC system was fitted with a 60-m capillary column (J&W DB-VRX; film thickness 1.40 µm, internal diameter 0.25 mm). The GC oven was programmed to hold the temperature at 35 °C for 10 min, ramp up to 220 °C at a rate of 8 °C min^{-1} and hold for 3 min (Markle et al. 2017). The analyte concentrations were then determined by comparing the peak areas or target ion masses against the peak areas of the same in a standard gas. A standard gas containing volatile organic compounds was diluted to a concentration of 10 ppbv (courtesy of Entech Instruments) with a calibration volume of 10 cm^3. Of these, three compounds, $CHBr_3$, $CHBr_2Cl$, and $CHBrCl_2$, were chosen for monitoring.

A total of three technical replicates were analysed from each canister containing air samples, and the mean value was represented as a single data entry for each of the control and biological replicates (n), therefore, all standard deviations mentioned in the text represent values from the biological replicates. The detection limit of < 1 ppbv for all three compounds was determined from the sum of three times the standard deviation and the blank mean of the system (Kaiser 1970).

Statistical analysis

Data collection, figure constructions and initial analyses were performed in Microsoft Excel. Following initial data processing, statistical analyses were performed on the dataset using SPSS Statistics Version 22 (IBM).

The following statistical tests were performed:

- To compare halocarbon emissions during daylight and darkness at the onshore tank cultivation system, the dataset ($n=7$) for daylight and dark emissions by *G. manilaensis;* and $n=6$, 3 for daylight and dark emissions by *K. alvarezii* was analysed using the Mann–Whitney U test.
- One-way ANOVA was performed to compare the halocarbon emissions from *G. manilaensis* ($n=7$, 9, 2 for onshore tank, offshore platform, and river mouth culture respectively) and the means between seawater nutrient and salinity levels from different cultivation sites ($n=15$, 16, 2, and $n=24$, 16, 2 for the readings of nutrients and salinity levels at the onshore, offshore, and cage cultivation systems).

- An independent sample t-test was used to test the difference in the transformed emission data by *K. alvarezii* between the onshore tank ($n=6$) and offshore platform ($n=7$).
- To compare *G. manilaensis* and *K. alvarezii* halocarbon emissions at various temperatures and irradiance during incubation in the flux chamber, Pearson's bivariate ($n=25$, 14) and Pearson's partial correlation ($n=22$, 13) were run on temperature and irradiance data collected during each flux chamber incubation. The latter was done to eliminate the effect of irradiance. The linear relationships between these factors were assessed by scatterplots and partial regression plots. The normality of transformed data was assessed by Shapiro–Wilk's test ($p>0.05$), and there were no univariate or multivariate outliers, as assessed by boxplots and Mahalanobis Distance, respectively.
- The Pearson Product-Moment Correlation was used to look at the relationships between the transformed daylight emission data of *G. manilaensis* ($n=15$, 17) and *K. alvarezii* ($n=12$, 13), which was pooled from all daylight measurements from the three cultivation systems, and the measured levels of nutrients and salinity of the seawater data collected during the sampling of the seaweeds. The significance levels (2-tailed) were determined. Preliminary analyses showed the relationship to be linear with both variables normally distributed, as assessed by Shapiro–Wilk's test ($p>0.05$), and there were no outliers.

Estimation of emissions from the harvesting of *K. alvarezii* in Malaysia and the Coral Triangle

To estimate the bromine emission from the harvesting of *K. alvarezii* in Malaysia and the Coral Triangle, the emission range of halocarbon per kg fresh weight of *K. alvarezii* per hour (ppbv kg FW^{-1} h^{-1}) was estimated from the emission range of 500 g of *K. alvarezii* incubated in the flux chamber for 30 min (ppbv). The estimated range (ppbv kg FW^{-1} h^{-1}) was then extrapolated to the respective countries' total biomass production in 2020 using the following formula, assuming a one-hour average harvesting period and field conditions similar to those in the flux chamber:

$$\text{Estimated emission in 2020 (mol Br)} = X \times \text{mixing ratio of halocarbon (ppbv per kg FW per h)} \times 1.5956 \times 10^{-9} \times \text{biomass (kg FW)} \times 1\text{h}$$

where 1.5956 is the mol of air, derived from the ideal gas law in the 40 L flux chamber at an average temperature of 32.35 °C; X = 3, 2, and 1 for the number of bromine atoms in $CHBr_3$, $CHBr_2Cl$, and $CHBrCl_2$, respectively.

Results

Halocarbon emissions by seaweeds from the three cultivation systems

Throughout the sampling period, net halocarbon emissions by *G. manilaensis* and *K. alvarezii* collected from the cultivation systems showed that the seaweeds released a higher amount of $CHBr_3$, followed by $CHBr_2Cl$ and $CHBrCl_2$ (Fig. 4). The emissions of $CHBr_3$ were influenced by the cultivation of *G. manilaensis* and *K. alvarezii* in different systems, possibly due to the varying environmental conditions present in each system. The comparison of halocarbon mixing ratios by *G. manilaensis* among the three cultivation systems showed that the emission of $CHBr_3$ was enhanced in the river mouth cage culture system (267 ± 13 ppbv) compared to the onshore tanks and offshore platform, which exhibited mixing ratios of 69 ± 69 ppbv and 78 ± 47 ppbv, respectively (Table 1). An independent t-test showed that both onshore and offshore cultivation systems did not affect the emissions of either $CHBr_2Cl$ or $CHBrCl_2$, but $CHBr_3$ emitted by *K. alvarezii* was statistically higher at the onshore tanks ($t(11)=2.59$, $p=0.025$; Supplementary Table S2).

Between daylight data from the two seaweed species at the onshore tanks, higher mixing ratios were observed in *G. manilaensis,* e.g., $CHBr_3$ (128 ± 119 ppbv), $CHBr_2Cl$ (8 ± 6 ppbv), and $CHBrCl_2$ (0.9 ± 0.8 ppbv) compared to *K. alvarezii*, which showed $CHBr_3$ (88 ± 13 ppbv), $CHBr_2Cl$ (3.0 ± 0.0 ppbv), and $CHBrCl_2$ (0.3 ± 0.09 ppbv; Table 1).

At the offshore platform, higher mixing ratios of $CHBr_3$ (115 ± 60 ppbv) were observed during the second week of cultivation *G. manilaensis* compared to the first (76 ± 34 ppbv) and fell to 43 ± 16 ppbv during the fourth week of cultivation (Fig. 5). The emissions of $CHBr_2Cl$, remained rather low and decreased from the first to the fourth week of cultivation. Emissions of $CHBr_3$ from *K. alvarezii* increased throughout the cultivation period from week one, from 23 ± 3 ppbv to 29 ± 10 ppbv and reached 78 ± 21 ppbv in the fourth week of cultivation (Fig. 5). The recorded emissions of $CHBr_2Cl$ and $CHBrCl_2$ were around one and three magnitudes lower than $CHBr_3$, which, similar to *G. manilaensis*, showed a general decreasing trend throughout the cultivation period (Fig. 5). Also, throughout the cultivation period, we observed mechanical grazing of *K. alvarezii* by rabbit fish.

Difference in emissions during daylight and dark at the onshore tanks

A Mann–Whitney U test result from the onshore cultivation system showed that the median net mixing ratios of both

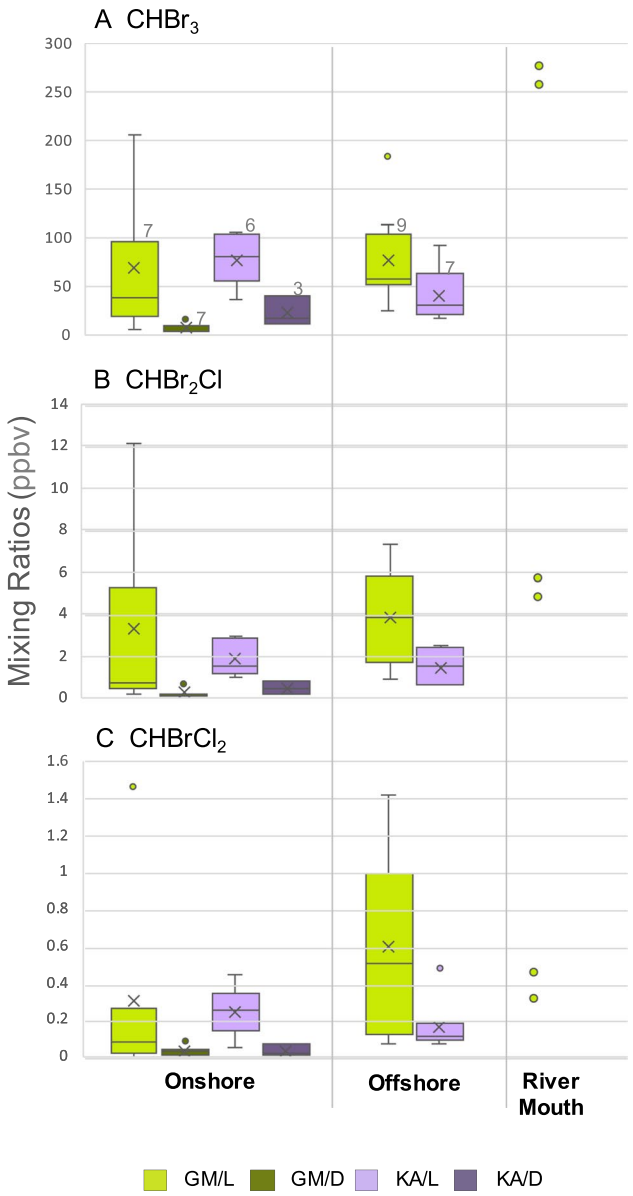

Fig. 4 The net mixing ratios of $CHBr_3$, $CHBr_2Cl$, and $CHBrCl_2$ released during incubation by 500 g of *G. manilaensis* (GM) and *K. alvarezii* (KA) cultivated at the onshore cultivation tank, offshore platform, and river mouth cage culture, respectively. Daylight (L) and dark (D) measurements were taken for the onshore cultivated seaweed. In this, the horizontal bars of the onshore and offshore box plots represent the median values, the boxes give the upper and lower quartile ranges, and the error bars show the spread of the data. Outlier data (between 1.5 and 3 box lengths from the box edges) and extreme cases (> 3 box lengths from the box edges) are denoted by circles. Sample numbers, *n,* are included at the top right corner of the $CHBr_3$ box plot and remained the same for $CHBr_2Cl$ and $CHBrCl_2$. Since there were only 2 replicates for daylight *G. manilaensis* samples cultivated at the river mouth cage culture, these are represented as individual points in the graph

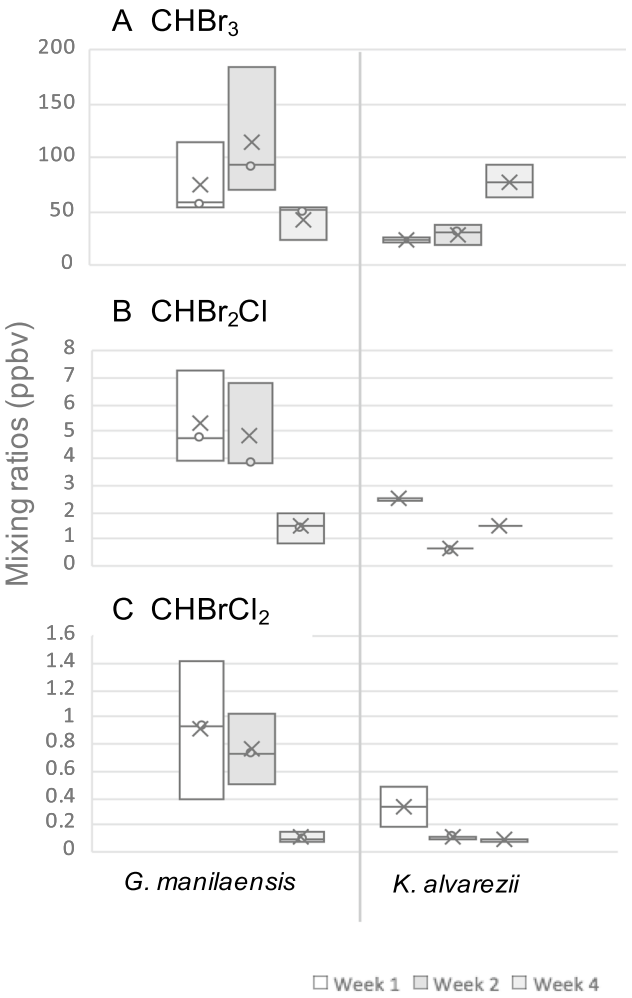

Fig. 5 Net mixing ratios (ppbv) of $CHBr_3$, $CHBr_2Cl$, and $CHBrCl_2$ released by 500 g of *G. manilaensis* and *K. alvarezii* cultivated at the offshore platform throughout the cultivation cycle. The horizontal bar represents the median value, the box gives the upper and lower quartile ranges, and the error bar shows the spread of the data; $n = 2$ or 3 (denoted by circles at the median)

$CHBr_3$ and $CHBr_2Cl$ by *G. manilaensis,* and $CHBr_3$, $CHBr_2Cl$, and $CHBrCl_2$ released by *K. alvarezii* were significantly higher during daylight than in the dark (Supplementary Table S3), while insignificant changes ($p = 1.0$) were observed in the controls for all three compounds between daylight and dark. The changes in emissions between daylight and darkness could only be attributed to the presence of seaweeds since no significant difference was noted between the daylight and dark reading of control samples (Supplementary Table S3).

The mean daylight to dark (L:D) ratios showed that halocarbon emissions by *G. manilaensis* in the day could be around a magnitude (13–16 times) higher than in the dark and

could reach an upper bound ratio of 82–100. *K. alvarezii* from this study reported an average increase of three to six times the emissions of the investigated halocarbons during daylight relative to the dark, with a maximum ninefold increase observed in the emission of $CHBr_3$ (Supplementary Table S4).

Correlations between halocarbon emissions and environmental parameters

During cultivation, *G. manilaensis* at the river mouth cage culture experienced the greatest variation in temperature, ranging from 24 to 43 °C (Table 2). The onshore system experienced the least fluctuation in temperature compared to the other two systems. Irradiance levels were between 0–3466 µmol photons m^{-2} s^{-1} at the cultivation sites. Seawater phosphate level was particularly elevated at the river mouth, with a significantly lower salinity level of 4 ± 0 ppt compared to the other two cultivation systems (Table 3).

To further determine the relationship between environmental factors and halocarbon emissions by *G. manilaensis,* the emissions data from *G. manilaensis* grown at all three cultivation systems was pooled and plotted against the irradiance and temperature readings at the time of measurement in the flux chamber (Table 4), and all daylight emission data against the seawater nutrients and salinity where the seaweeds were grown.

Positive correlations were recorded between temperature and the emissions ($r(23) = 0.7–0.8$; $p < 0.01$; Table 4), and between irradiance and the emissions of all halocarbons ($r(23) = 0.5–0.6$; $p < 0.01$). The correlations between temperature and emission became weaker ($r_{partial}(22) = 0.5–0.6$; $p < 0.01$; Table 4) when the influence of irradiance was eliminated statistically, while correlations between temperature and the emission of $CHBr_3$ by *K. alvarezii* became stronger when the influence of irradiance was eliminated. Of all the correlations between the daylight emission data and the seawater nutrients and salinity, only the emission of $CHBr_3$ by *G. manilaensis* was found to be positively correlated to seawater phosphate levels ($r(15) = 0.54$; $p < 0.05$).

Discussion

Halocarbon emissions from seaweeds at the three cultivation systems

In this study data from the onshore tank arises from two different batches of seaweeds due to the separate surveys conducted, while data from the offshore and river mouth cultures were generated from the same (second) batch of seaweeds. The first survey was conducted in April 2018 as a preliminary trial, while the second survey was conducted in October 2018 to compare the different cultivation systems. The inclusion of the April data provides a better overview of the emissions from the tank culture in general, where the range of emissions is comparable to those recorded from the other two cultivation systems (Fig. 4). The cultivation of seaweeds for both batches lasted for a month.

Among the different cultivation systems, the highest data point of $CHBr_3$ came from the river mouth where *G. manilaensis* was cultivated (Fig. 4). It was believed that the production of mixed halocarbons such as $CHBr_2Cl$ and $CHBrCl_2$ resulted from the nucleophilic substitution of $CHBr_3$ (Tokarczyk and Moore 1994; Leedham et al. 2013). As such, there is a possibility that the effect of environmental changes could be more evident in the emission of $CHBr_3$ relative to $CHBr_2Cl$ and $CHBrCl_2$. The higher $CHBr_3$ could be due to the significantly higher level of phosphorus (0.39 ± 0.01 mg L^{-1}, $F(2,30) = 20.71$, $p < 0.001$) and a rather low salinity level (4 ± 0 ppt, $F(2,39) = 19.36$, $p < 0.001$) at the river where the cage cultures located (Table 3). There were also greater temperature fluctuations (Table 2) of up to 19 °C (24.2–43.2 °C) at the river mouth compared with the offshore system (24.7–40.3 °C) and the onshore tank system (24.6–35.7 °C) and could have been due to tidal changes in the river. Although the bromide load in seawater is higher and therefore might lead to higher in situ production of $CHBr_3$, factors such as the spatial differences in the distribution of dissolved organic matter

Table 2 Temperature and irradiance data collected from the various cultivation systems and within the flux chamber

Parameters		Onshore tanks	Offshore platform	Cage culture	Flux chamber
Temperature (°C)	Mean ± S. D	29.21 ± 1.81	30.73 ± 2.38	29.48 ± 2.60	31.13 ± 1.83
	Range	24.64 – 35.65	24.73 – 40.30	24.16 – 43.24	27.81 – 33.60
	Difference in range	11.01	15.56	19.08	5.79
Irradiance (µmol photons m^{-2} s^{-1})	Range	0–1019	0–3466	0–1478	0–352

Table 3 Nutrient contents and salinity readings (mean ± standard deviation) at the various seaweed cultivation systems at Bachok, Kelantan, tested using one-way ANOVA

Nutrients	Onshore tanks	Offshore platform	Cage culture	Statistical results
Phosphate (mg L^{-1})	0.05 ± 0.07^{a}	0.10 ± 0.07^{a}	0.39 ± 0.01^{b}	$F(2,30) = 20.71$, $p < 0.001$
Nitrogen, Ammonia (mg L^{-1})	0.05 ± 0.09^{a}	0.10 ± 0.12^{a}	0.20 ± 0.02^{a}	$F(2,30) = 1.74$, $p = 0.192$
Nitrate (mg L^{-1})	1.0 ± 0.8^{a}	1.9 ± 0.7^{a}	1.4 ± 0.1^{a}	$F(2,30) = 6.44$, $p = 0.005$
Nitrite (mg L^{-1})	0.057 ± 0.079^{a}	0.103 ± 0.104^{a}	0.007 ± 0.000^{a}	$F(2,30) = 1.60$, $p = 0.218$
Salinity (ppt)	25 ± 7^{b}	29 ± 2^{b}	4 ± 0^{a}	$F(2,39) = 19.36$, $p < 0.001$

[a, b]denotes homogeneous group among the cultivation systems based on Tukey's post-hoc test ($p < 0.05$); $n = 15$, 16, 2 and $n = 24$, 16, 2 for the readings of nutrients and salinity levels at the onshore, offshore and cage cultivation systems.

Table 4 Bivariate Pearson's correlations (r) and Pearson's Partial correlations ($r_{partial}$) when irradiance was controlled for between the pooled halocarbon emissions by *G. manilaensis* with the temperature and irradiance at the time of incubation in the flux chamber

Control Variables		df	$CHBr_3$	$CHBr_2Cl$	$CHBrCl_2$	
G. manilaensis						
-none-[a]	Temperature	r	23	0.75 (0.00)	0.78 (0.01)	0.69 (0.00)
	Irradiance	r	23	0.63 (0.00)	0.61 (0.01)	0.53 (0.01)
Irradiance	Temperature	$r_{partial}$	22	0.53 (0.01)	0.62 (0.00)	0.53 (0.01)
K. alvarezii						
-none-[a]	Temperature	r	14	0.59* (0.02)		0.59* (0.02)
	Irradiance	r	14			0.54* (0.03)
Irradiance	Temperature	$r_{partial}$	13	0.76 (0.00)		

Cells contain zero-order (Pearson) correlations; data for temperature (27.81–33.60 °C) and irradiance (0–353 µmol photons m^{-2} s^{-1}) were collected during incubation in the flux chamber; only correlations with $p < 0.05$ are reported; all correlations are significant at the 0.01 level (2-tailed) except * where correlations are significant at the 0.05 level (2-tailed); df = degree of freedom; bracketed values indicate significance levels, *p*.

could also affect the formation of $CHBr_3$ (Liu et al. 2015; Shah et al. 2015). These, together with the physiological changes exerted by the different environmental parameters on the seaweeds throughout the cultivation period, may be interactive and thereby affect the ability of the seaweeds to produce bromoform. There is, however, a low sample number for the river mouth study, this is a potential area for further exploration.

At the offshore platform, where *K. alvarezii* was grown using the most common (monoline) cultivation method used in the Coral Triangle, mechanical grazing by rabbit fish may have contributed to the increased $CHBr_3$ emissions observed throughout the cultivation period. The effect of mechanical stresses such as grazing and wounding on enhancing halocarbon emissions in the seaweeds had been previously reported by Nightingale et al. (1995). As *K. alvarezii* was tethered to the rope at the offshore platform, as opposed to *G. manilaensis*, which was cultivated in woven poly net baskets, rabbit fish were able to freely access and feed on the cultivated *K. alvarezii*. In addition, *K. alvarezii* has a softer texture than G. *manilaensis*, which may make it a more desirable diet for the fish. Lower emissions by *G. manilaensis* during Week 4 of culture may have been attributable to reduced stress responses to the environment as a result of adaptation.

Difference in emissions during daylight and dark at the onshore tanks

The significantly higher amounts of halocarbons released by *G. manilaensis* and *K. alvarezii* during daylight than darkness at the onshore tank systems (except $CHBrCl_2$ by *G. manilaensis*) suggests a strong link between light and light-related activities. Reactive oxygen species (ROS) are commonly produced during physiological activities such as photosynthesis and respiratory electron transport (Rutherford et al. 2012; Wever and van der Horst 2013) and could be enhanced by environmental stresses (Nightingale et al. 1995). With more ROS present, more halocarbons are produced (Wever and van der Horst 2013; Abrahamsson et al. 2018). Lower temperatures in the dark could also affect the emissions by reducing enzymatic activities or slow down fluxes (Punitha et al. 2018; Macdonald et al. 2020).

The higher emissions of $CHBr_2Cl$, and $CHBrCl_2$ by *K. alvarezii* during daylight could be due to the higher amount of $CHBr_3$ produced by the seaweed (Fig. 4). Strong correlations had been observed between the emission of $CHBr_3$ with $CHBr_2Cl$, and to a lesser extent, $CHBr_2Cl$ with $CHBrCl_2$ in seaweeds (Leedham et al. 2013). During the production of halocarbons by haloperoxidase, $CHBr_3$ is produced as a result

of halide oxidation by H_2O_2, which increases in stressful conditions. This is followed by the reaction with ketones or dissolved organic matter (DOM) in the environment (Wever et al. 1991; Opsahl and Benner 1997; Lin and Manley 2012; Wever and van der Horst 2013; Liu et al. 2015). Brominated compounds such as $CHBr_2Cl$ and $CHBrCl_2$ could possibly be formed through the same enzymatic pathway or through subsequent nucleophilic substitution of $CHBr_3$ (Abrahamsson et al. 2018).

Carpenter et al. (2000) reported a tenfold increase in $CHBr_3$ during daylight compared to dark emissions by the temperate brown seaweed *Laminaria digitata*. This was the largest increase of all halocarbons investigated in that study, with most of the other compounds, including $CHBr_2Cl$, reporting at least a two-fold increase during the day. The quantification was derived from seawater measurements of the compounds (Carpenter et al. 2000). Although calculations from the previous study were based on seawater contents of halocarbons, the values were still within the range of L:D ratios observed in *G. manilaensis* and *K. alvarezii*. These ratios could provide details on the changes in emissions between dark and illuminated conditions by farmed seaweeds in the tropics, reducing the uncertainty in macroalgal halocarbon emissions arising from diurnal changes.

Correlations between halocarbon emissions and environmental parameters

There is evidence that both temperature and irradiance have an impact on halocarbon emissions. This study indicates a stronger correlation between temperature change in the flux chamber and halocarbon emissions ($r(23) = 0.7–0.8$; $p < 0.01$) compared to irradiance ($r(23) = 0.5–0.6$; $p < 0.01$). A direct correlation between seawater salinity and halocarbon emissions could not be established, even though higher $CHBr_3$ emissions were observed at the river mouth, where phosphate levels were higher and salinity lower (Fig. 4; Supplementary Table S1). The positive correlation between seawater phosphate levels ($r(15) = 0.54$; $p < 0.05$) and the $CHBr_3$ emission by *G. manilaensis* could indicate that a higher phosphate level at the river mouth could be exerting a dominant effect in driving higher emissions of $CHBr_3$ instead of the salinity change, since *G. manilaensis* is tolerant to a wide range of salinity, e.g., being able to grow in fishponds at lower salinities between 23–28 ppt and was found to grow well at a salinity of 15 ppt (Mohamad Hidayat et al. 2021). However, there is an underrepresentation of low salinity river samples ($n = 2$) in this study.

Estimated emissions from the harvesting of *K. alvarezii* in Malaysia and the Coral Triangle

While data on *G. manilaensis* production is limited, a recent statistic from FAO (2022) showed a total production of 182,061 t (FW) of *K. alvarezii* in Malaysia in 2020. A simple extrapolation based on this biomass data could give an estimate of the potential contribution of *K. alvarezii* farming in Malaysia in terms of its halocarbon emissions. The estimated range of bromine contribution based on the release of the dominant compound, $CHBr_3$, during the harvesting of *K. alvarezii* alone is between 63 and 322 mol Br for each hour of harvesting activity (Table 5). This was based on the mixing ratios of $CHBr_3$ emitted from *K. alvarezii* collected from the offshore platform (Fig. 5), as this method of cultivation closely resembles the mass cultivation of *K. alvarezii* in Malaysia and the Coral Triangle (Lim et al. 2021). As the air samples from this study were collected from fresh and moistened *K. alvarezii*, this estimate may provide relevance to the potential increase in halocarbon load into the atmosphere during harvesting of the seaweeds at the *K. alvarezii* farms in Malaysia. However, this estimation deriving from the abundance in a closed flux chamber may not directly align with the open layer of the

Table 5 Estimation of halocarbon emissions by farmed *K. alvarezii* in Malaysia, the Philippines, Indonesia, and the Coral Triangle based on total production in the year 2020

	Mixing ratios (ppbv)	Estimated Range* (ppbv kg^{-1} FW h^{-1})	Biomass production (kg FW)	Estimated Range (mol Br)
Malaysia				
$CHBr_3$	18.3–92.6	73–370	182,061,000	63–322
$CHBr_2Cl$	0.6–2.5	2.4–10		1.4–5.8
$CHBrCl_2$	0.1–0.5	0.4–2.0		0.1–0.6
Estimation based on the emission of $CHBr_3$				
Philippines	18.3–92.6	73–370	1,404,743,000	491–2488
Indonesia			8,080,796,000+	2823–14,311
Coral Triangle			9,667,600,000	3378–17,122

*Scaled-up from the mixing ratios measured when 500 g of *K. alvarezii* was incubated in the 40L flux chamber for 30 min; conversion to mol Br was calculated based on a mean air temperature of 32.35 °C; + combined data of *Eucheuma* and *Kappaphycus* was used due to the unavailability of single-species data

surface atmosphere due to various factors including wind, temperature and humidity, which influence the dispersal and distribution of gases in the open environment.

To further explore the contribution of *Kappaphycus* farming to the regional halogen pool, the biomass production data from Indonesia and the Philippines were used to extrapolate the rate of halogen released by *K. alvarezii* during harvesting. With this, a combined emission of 3378–17,122 mol Br for an hour of harvesting activity was estimated from the harvesting of *Kappaphycus* in the Coral Triangle in 2020 alone (Table 5). This estimate was based on an hour of harvesting activity and the condition of the field being similar to the flux chamber within an hour. In addition to the cultivation and harvesting of seaweeds, further downstream processing, such as the post-harvest drying necessary to produce carrageenan, also contributes to the emission of volatile halocarbons such as $CHBr_3$ (Leedham Elvidge et al. 2015).

The estimated harvesting emissions from this study could be the first estimate of halocarbon emissions of farmed seaweed in the tropics, which is an important region for the convective transport of reactive bromines into the upper troposphere and lower stratosphere. In the tropics, both *G. manilaensis* and *K. alvarezii* are red seaweeds with high $CHBr_3$ emission rates (Keng et al. 2020). In light of the recently debated proposal to mass cultivate seaweeds with high $CHBr_3$ emissions as livestock feed to counter the production of enteric methane, this could provide an insight into the need to balance the environmental impact of $CHBr_3$ emissions while addressing the methane crisis (Glasson et al. 2022).

Conclusion

Measurements of cultivated seaweeds showed higher emissions of $CHBr_3$, $CHBr_2Cl$, and $CHBrCl_2$ during daylight than in the dark. Daylight emissions from the farmed *G. manilaensis* were found to be 13 to 16 times higher than dark emissions on average, while emissions from *K. alvarezii* were between three and six times higher during the day. The emission of halocarbons by *G. manilaensis* in the different cultivation systems was affected by changes in temperature, irradiance, and possibly seawater phosphate levels as seen in the river culture, while the emission of $CHBr_3$ by *K. alvarezii* was affected by temperature. Predicted values from this study showed that the harvesting activity of *K. alvarezii* in Malaysia in 2020 could have released 63–322 mol Br for each hour of harvesting activity, and in the Coral Triangle, 3378–17,122 mol Br.

This study provides an estimate of the halocarbon emission from farmed seaweed in the tropics, shedding light on its environmental impact. The findings underscore the need for further exploration of factors like salinity, dissolved organic matter, and emissions during cultivation, especially in mass-cultivated regions, to better assess the potential of seaweed farming-related policy as climate solutions, and enhance the prediction of climate change's impact on halocarbon emissions by seaweeds.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10811-023-03067-z.

Acknowledgements Acknowledgements are due to Ahmad Nurhakim Sabri, Shahizam Mohd Hasan, and Ahamad Kamil Sabuti for their assistance during sample collection, culture, and logistics.

Authors' contributions F.S.-L. Keng: Conceptualization, Methodology, Data curation, Original draft preparation, Reviewing and Editing; S.-M. Phang: Conceptualization, Methodology, Reviewing and Editing, Funding acquisition, Supervision; N. Abd Rahman: Reviewing and Editing, Supervision; H.-Y. Yeong: Conceptualization, Methodology, Reviewing and Editing; Gill Malin: Reviewing and editing, Supervision; E. Leedham Elvidge: Methodology, Data curation, Reviewing and editing, Supervision; William Sturges: Methodology, Data curation, Reviewing and editing, Supervision; C.-W. Lee: Reviewing and Editing, Funding acquisition.

Funding The research is funded by the Higher Institution Centre of Excellence (HICoE) Phase II Fund, Ministry of Higher Education Malaysia (IOES-2014F & HICoE IOES-2023D), UM Research University Fund (RU003-2022), Postgraduate Research Grant, PPP (PG300-2016A), and the University of Malaya Grand Challenge Fund (GC002B-15SBS).

Data availability The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests The authors declare no conflict of interest.

References

Abrahamsson K, Choo KS, Pedersén M, Johnsson G, Snoeijs P (2003) Effects of temperature on the production of hydrogen peroxide and volatile halocarbons by brackish water algae. Phytochemistry 6:725–734

Abrahamsson K, Granfors A, Ahnoff M, Cuevas CA, Saiz-Lopez A (2018) Organic bromine compounds produced in sea ice in Antarctic winter. Nat Commun 9:5291

APHA (1998) Standard methods for the examination of water and wastewater, twentieth. American Public Health Association, Washington DC

Asia Development Bank (2016) The Coral Triangle: An ecosystem under threat. Retrieved from https://www.adb.org/multimedia/coral-triangle/

Bondu S, Cocquempot B, Deslandes E, Morin P (2008) Effects of salt and light stress on the release of volatile halogenated organic compounds by *Solieria chordalis*: A laboratory incubation study. Bot Mar 51:485–492

Carpenter LJ, Malin G, Liss PS, Küpper FC (2000) Novel biogenic iodine-containing trihalomethanes and other short-lived halocarbons in the coastal East Atlantic. Global Biogeochem Cycles 14:1191–1204

Dietz KJ (2016) Thiol-based peroxidases and ascorbate peroxidases: Why plants rely on multiple peroxidase systems in the photosynthesizing chloroplast? Mol Cells 39:20–25

Eklund B (1992) Practical guidance for flux chamber measurements of fugitive volatile organic emission rates. J Air Waste Manag Assoc 42:1583–1591

Duarte CM, Bruhn A, Krause-Jensen D (2021) A seaweed aquaculture imperative to meet global sustainability targets. Nat Sustain 5:185–193

Dummermuth AL, Karsten U, Fisch KM, König GM, Wiencke C (2003) Responses of marine macroalgae to hydrogen-peroxide stress. J Exp Mar Biol Ecol 289:103–121

FAO (2022) Fishery and Aquaculture Statistics. Global aquaculture production 1950–2020 (FishStatJ). FAO Fisheries and Aquaculture Division, Rome. www.fao.org/fishery/statistics/software/fishstatj/en

Fuhlbrügge S, Quack B, Tegtmeier S, Atlas E, Hepach H, Shi Q, Raimund S, Krüger K (2016) The contribution of oceanic halocarbons to marine and free tropospheric air over the tropical West Pacific. Atmos Chem Phys 16:7569–7585

Gill SS, Tuteja N (2010) Reactive oxygen species and antioxidant machinery in abiotic stress tolerance in crop plants. Plant Physiol Biochem 48:909–930

Glasson CRK, Kinley RD, de Nys R, King N, Adams SL, Packer MA, Svenson J, Eason CT, Magnusson M (2022) Benefits and risks of including the bromoform containing seaweed *Asparagopsis* in feed for the reduction of methane production from ruminants. Algal Res 64:102673

Hach (2001) Instruction manual for Odyssey DR/2500 spectrophotometer. Hach Company, Colorado, United States of America

Hossaini R, Chipperfield MP, Feng W, Breider TJ, Atlas E, Montzka SA, Miller BR, Moore F, Elkins J (2012a) The contribution of natural and anthropogenic very short-lived species to stratospheric bromine. Atmos Chem Phys 12:371–380

Hossaini R, Chipperfield MP, Dhomse S, Ordonez C, Saiz-Lopez A, Abraham NL, Archibald A, Braesicke P, Telford P, Warwick N, Yang X, Pyle J (2012b) Modelling future changes to the stratospheric source gas injection of biogenic bromocarbons. Geophys Res Lett 39:L20813

Hossaini R, Chipperfield MP, Montzka SA, Rap A, Dhomse S, Feng W (2015) Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone. Nat Geosci 8:186–290

Kaiser H (1970) Part II Quantitation in Elemental Analysis. Anal Chem 42:26A-59A

Kang OL, Ramli N, Said M, Ahmad M, Md Yasir S, Ariff A (2011) *Kappaphycus alvarezii* waste biomass: A potential biosorbent for chromium ions removal. J Environ Sci 23:918–922

Keng FSL, Phang SM, Abd Rahman N, Leedham EC, Hughes C, Robinson AD, Harris NRP, Pyle JA, Sturges WT (2013) Volatile halocarbon emissions by three tropical brown seaweeds under different irradiances. J Appl Phycol 25:1377–1386

Keng FSL, Phang SM, Abd Rahman N, Leedham Elvidge EC, Malin G, Sturges WT (2020) The emission of volatile halocarbons by seaweeds and their response towards environmental change. J Appl Phycol 32:1377–1394

Keng FSL, Phang SM, Abd Rahman N, Yeong HY, Malin G, Leedham Elvidge EC, Sturges W (2021) Halocarbon emissions by selected tropical seaweeds exposed to different temperatures. Phytochemistry 190:112869

Küpper FC, Carpenter LJ, Leblanc C, Toyama C, Uchida Y, Maskrey BJ, Robinson J, Verhaeghe EF, Malin G, Luther GW III, Kroneck PMH, Kloareg B, Meyer-Klaucke W, Muramatsu Y, Megson IK, Potin P, Feiters MC (2013) In vivo speciation studies and antioxidant properties of bromine in *Laminaria digitata* reinforce the significance of iodine accumulation for kelps. J Exp Bot 64:2653–2664

Laturnus F, Giese B, Wiencke C, Adams FC (2000) Low-molecular-weight organoiodine and organobromine compounds released by polar macroalgae – The influence of abiotic factors. Fresenius J Anal Chem 368:297–302

Leedham EC, Hughes C, Keng FSL, Phang SM, Malin G, Sturges WT (2013) Emission of atmospherically significant halocarbons by naturally occurring and farmed tropical macroalgae. Biogeosciences 10:3615–3633

Leedham Elvidge EC, Phang SM, Sturges WT, Malin G (2015) The effect of desiccation on the emission of volatile bromocarbons from two common temperate macroalgae. Biogeosci Discuss 11:10673–10701

Li LX, Zhao JQ, Tang XX (2010) Ultraviolet irradiation induced oxidative stress and response of antioxidant system in an intertidal macroalgae *Corallina officinalis* L. J Environ Sci 22:716–722

Lim PE, Poong SW, Tan J, Assim A, Gachon C, Brodie J, Cottier-Cook E (2021) A practical guide to the aquaculture of *Kappaphycus* and *Eucheuma* in Malaysia. Retrieved from https://www.globalseaweed.org/wp-content/uploads/2021/11/Bilingual-Practical-Guide-Ebook.pdf

Lin CY, Manley SL (2012) Bromoform production from seawater treated with bromoperoxidase. Limnol Oceanogr 57:1857–1866

Liu Y, Thornton DCO, Bianchi TS, Arnold WA, Shields MR, Chen J, Yvon-Lewis SA (2015) Dissolved organic matter composition drives the marine production of brominated very short-lived substances. Environ Sci Technol 49:3366–3374

Liu C, Zipser EJ (2015) The global distribution of largest, deepest, and most intense precipitation systems. Geophys Res Lett 42:3591–3595

Markle D, Casteel C, Robinson T, Cardin D (2017) Improved performance and dynamic range for EPA Method TO-15 using the Entech 7200 and Thermo Scientific ISQ QD GCMS. Entech Instruments Inc. Retrieved from https://gcms.cz/labrulez-bucket-strapi-h3hsga3/paper/ImprovedPerformance_Thermo_LowRes.pdf

Manley SL, Barbero PE (2001) Physiological constraints on bromoform (CHBr3) production by *Ulva lactuc*a (Chlorophyta). Limnol Oceanogr 46:1392–1399

Macdonald ML, Wadham JL, Young D, Lunder CR, Hermansen O, Lamarche-Gagnon G, O'Doherty S (2020) Consumption of CH_3Cl, CH_3Br, and CH_3I and emission of $CHCl_3$, CHBr3, and C_H2B_r2 from the forefield of a retreating Arctic glacier. Atmos Chem Phys 20:7243–7258

Mithoo-Singh PK, Keng FSL, Phang SM, Leedham Elvidge EC, Sturges WT, Malin G, Abd Rahman N (2017) Halocarbon emissions by selected tropical seaweeds: species-specific and compound-specific responses under changing pH. PeerJ 5:e2918

Mohamad Hidayat NS, Mohammad-Noor N, Mohamad MAN, Abdullah NSA, Sariyathul Rusly SA, Saad S, Mukai Y, Susanti D (2021) Growth of *Gracilaria manilaensis* Yamamoto et Trono (Rhodophyta) under different light intensities, salinities and pH. Borneo J Mar Sci Aquacult 5:53–56

Nightingale PD, Malin G, Liss PS (1995) Production of chloroform and other low molecular-weight halocarbons by some species of macroalgae. Limnol Oceanogr 40:680–689

Opsahl S, Benner R (1997) Distribution and cycling of terrigenous dissolved organic matter in the ocean. Nature 6:480–482

Pan LL, Atlas EL, Salawitch RJ, Honomichl SB, Bresch JF, Randel WJ, Apel EC, Hornbrook RS, Weinheimer AJ, Anderson DC, Andrews SJ, Baidar S, Beaton SP, Campos TL, Carpenter LJ, Chen D, Dix B, Donets V, Hall SR, Hanisco TF, Homeyer CR, Huey LG, Jensen JB, Kaser L, Kinnison DE, Koenig TK, Lamarque JF, Liu C, Luo J, Luo ZJ, Montzka DD, Nicely JM, Pierce RB, Riemer DD, Robinson T, Romashkin P, Saiz-Lopez A, Schauffler S, Shieh O, Stell MH, Ullmann K, Vaughan G, Volkamer R, Wolfe G (2017) The convective transport of active species in the tropics (CONTRAST) experiment. Bull Am Meteorol Soc 98:106–128

Phang SM, Keng FSL, Mithoo-Singh PK, Lim YK, Abd Rahman N, Leedham EC, Robinson AD, Harris NRP, Pyle JA, Sturges WT (2015) Can seaweed farming in the tropics contribute to climate change through emission of short-lived halocarbons? Malaysian J Sci 34:7–18

Phang SM, Yeong HY, Lim PE (2019) The seaweed resources of Malaysia. Bot Mar 62:265–273

Punitha T, Phang S-M, Juan JC, Beardall J (2018) Environmental control of vanadium haloperoxidases and halocarbon emissions in macroalgae. Mar Biotechnol 20:282–303

Reardon J, Foreman JA, Searcy RL (1966) New reactants for the colorimetric determination of ammonia. Clin Chim Acta 14:403–405

Rizki IN, Klaypradit W, Patmawati (2023) Utilization of marine organisms for the green synthesis of silver and gold nanoparticles and their applications: A review. Sustain Chem Pharm 31:100888

Rutherford AW, Osyczka A, Rappaport F (2012) Back-reactions, short-circuits, leaks and other energy wasteful reactions in biological electron transfer: Redox tuning to survive life in O_2. FEBS Lett 586:603–616

Sade A, Ismail A, Ariff MRM (2006) The seaweed industry in Sabah, East Malaysia. JATI 11:97–107

Sartin JH, Halsall C, Hayward S, Hewitt CN (2002) Emission rates of C_8–C_{15} VOCs from seaweed and sand in the inter-tidal zone at Mace Head. Atmos Environ 36:5311–5321

Shah A, Liu ZQ, Salhi E, Höfer T, Werschkun B, von Gunten U (2015) Formation of disinfection by-products during ballast water treatment with ozone, chlorine, and peracetic acid: influence of water quality parameters. Environ Sci: Water Res Technol 1:465–480

Tokarczyk R, Moore M (1994) Production of volatile organohalogens by phytoplankton cultures. Geophys Res Lett 21:285–288

USEPA (1979) USEPA approved for wastewater analysis. Fed Reg 44:25505

WMO (World Meteorological Organization) (2018) Scientific assessment of ozone depletion: 2018, Global Ozone Research and Monitoring Project–Report No.58, World Meteorological Organisation, Geneva

Wever R, Tromp MGM, Krenn BE, Marjani A, Van Toi M (1991) Brominating activity of seaweed *Ascophyllum nodosum*: Impact on the biosphere. Environ Sci Technol 25:446–449

Wever R, van der Horst M (2013) The role of vanadium haloperoxidases in the formation of volatile brominated compounds and their impact on the environment. Dalton Trans 42:11778–11786

Ziska F, Quack B, Abrahamsson K, Archer SD, Atlas E, Bell T, Butler JH, Carpenter LJ, Jones CE, Harris NRP, Hepach H, Heymann KG, Hughes C, Kuss J, Krüger K, Liss P, Moore RM, Orlikowska A, Raimund S, Reeves CE, Reifenhäuser W, Robinson AD, Schall C, Tanhua T, Teghmeier S, Turner S, Wang L, Wallace D, Williams J, Yamamoto H, Yvon-Lweis S, Yokouchi Y (2013) Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide. Atmos Chem Phys 13:8915–8934

Ziska F, Quack B, Tegtmeier S, Stemmler I, Krüger K (2017) Future emissions of marine halogenated very-short lived substances under climate change. J Atmos Chem 74:245–260