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Bromocarbons in the tropical coastal and open ocean atmosphere during the Prime Expedition Scientific Cruise 2009 (PESC 09)

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Abstract

Atmospheric concentrations of very short-lived species (VSLS) bromocarbons, including $CHBr_3$, CH_2Br_2, $CHCl_2Br$, $CHClBr_2$, CH_2BrCl, were measured in the Strait of Malacca and the South China and Sulu-Sulawesi Seas during a two month research cruise in June/July 2009. The highest bromocarbon concentrations were found in the Strait of Malacca, with smaller enhancements in coastal regions of Northern Borneo. $CHBr_3$ was the most abundant bromocarbon, ranging from 5.2 $\mathrm{pmol\,mol^{-1}}$ in the Strait of Malacca to 0.94 $\mathrm{pmol\,mol^{-1}}$over the open ocean. Other bromocarbons showed lower concentrations, in the range of 0.8–1.3 $\mathrm{pmol\,mol^{-1}}$ for CH_2Br_2, 0.1–0.5 $\mathrm{pmol\,mol^{-1}}$ ($CHCl_2Br$) and 0.1–0.4 $\mathrm{pmol\,mol^{-1}}$ ($CHClBr_2$). There was no significant correlation between bromocarbons and in situ chlorophyll *a*. Together the short-lived bromocarbons contribute an average of 8.9 $\mathrm{pmol\,mol^{-1}}$ (range 5.2–21.4 $\mathrm{pmol\,mol^{-1}}$) to tropospheric bromine load, which is similar to that found in previous studies (Montzka et al., 2011). Statistical tests showed strong Spearman correlations amongst brominated compounds suggesting a common source. Log-log plots of $CHBr_3/CH_2Br_2$ vs. $CHBr_2Cl/CH_2Br_2$ show that both chemical reactions and dilution into the background atmosphere contribute to the composition of these halocarbons at each sampling point. We have used the correlation to make a crude estimate of the regional emissions of $CHBr_3$ and derive a value of 63 $\mathrm{Gg\,yr^{-1}}$ for the South East (S.E.) Asian region (10° N–20° S, 90–150° E). Finally, we note that satellite-derived chlorophyll *a* (chl *a*) products do not always agree well with in situ measurements, particularly in coastal regions of high turbidity, meaning that satellite chl *a* may not always be a good proxy for marine productivity.

1 Introduction

In recent years there has been a growing interest in the role of short-lived halocarbons in atmospheric chemistry, in particular their potential involvement in stratospheric ozone depletion. The term VSLS has been coined to represent halogen-containing compounds with lifetimes of typically less than six months. Bromine-containing VSLS and their atmospheric degradation products are believed to account for around a quarter of total bromine entering the lower stratosphere (Dorf et al., 2006; Salawich et al., 2006; Montzka et al., 2011) and almost certainly contribute to the “missing” bromine (6 $\mathrm{pmol\,mol^{-1}}$, range 3–8 $\mathrm{pmol\,mol^{-1}}$) required to maintain the levels of inorganic bromine (BrO) measured in the stratosphere (Montzka et al., 2011).

The main brominated VSLS identified to date include bromoform ($CHBr_3$), dibromomethane (CH_2Br_2), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and bromochloromethane (CH_2BrCl). Biogenic sources are significant contributors of these gases to the atmosphere, and the oceans have been identified as one of the main natural sources, where organisms such as macroalgae (seaweeds) and microalgae (phytoplankton) can release large quantities of halocarbon gases to the atmosphere (Sturges et al., 1993; Moore et al., 1996; Laturnus and Adams, 1998). Previous ship and coastal measurements have produced bromocarbon data for many different global regions. A good summary can be found in Montzka et al. (2011). These studies show large temporal and spatial variability in both seawater and atmospheric concentrations, emphasizing the importance of localized emissions of these gases.

Because of their short atmospheric lifetimes, the region where VSLS are emitted into the atmosphere becomes significant and their O_3 depletion potentials (ODPs) vary accordingly (Ko et al., 2003). Tropical regions are believed to be the most important location for rapid transport of air from the surface to the upper troposphere and lower stratosphere. In the tropics, deep convection provides a potential pathway for rapid transport of insoluble gases from the lower to the upper troposphere. Convection is particularly strong over the western Pacific (Gettelman et al., 2002; Fueglistaler et al., 2004) and tropical region (Fueglistaler et al., 2009). The southern part of the South China Sea is believed to be the maximum precipitation region compared to other East Asia regions (Yihui and Chan, 2005) and could be a particularly important location for transport (deep convection) for halocarbons from the surface to the upper atmosphere.

Furthermore, the warm, shallow waters of the tropical warm pool make them potentially important source regions for biologically-produced halocarbons. Therefore, this region has the potential to supply a proportion of the "missing" ~ 6 $\mathrm{pmol\,mol^{-1}}$ of bromine, thought to be related to VSLS, to the stratosphere.

Yokouchi et al. (1997) were the first to report bromocarbon measurements in the Straits of Malacca and the South China Sea. During a cruise between Japan and the Bay of Bengal they measured mean concentrations of 0.77 $\mathrm{pmol\,mol^{-1}}$ (max 1.42 $\mathrm{pmol\,mol^{-1}}$) and 1.2 $\mathrm{pmol\,mol^{-1}}$ (max 7.1 $\mathrm{pmol\,mol^{-1}}$) for $CH_2Br_2$and $CHBr_3$, respectively. The highest levels were seen in harbour regions of Singapore and Penang and the authors suggested a link between high $CHBr_3$ concentrations and high chlorophyll *a* (chl *a*) and the influence of algae sources. Values for bromoform (mean 1.2 $\mathrm{pmol\,mol^{-1}}$; range 0.38–10.67 $\mathrm{pmol\,mol^{-1}}$) during a cruise from in the South China Sea were observed by Quack and Suess (1999): in the South China Sea values were between 0.8 and 1.6 $\mathrm{pmol\,mol^{-1}}$.

A second cruise reported in Yokouchi et al. (1997) was in the western Pacific (Japan–SE Australia), and atmospheric mixing ratios were observed to be in the range of 0.13–2.9 $\mathrm{pmol\,mol^{-1}}$ ($CHBr_3$) and 0.14–1.58 $\mathrm{pmol\,mol^{-1}}$ (CH_2Br_2). More recently, Yokouchi et al. (2005) reported larger variations of bromocarbon concentrations, with $CHBr_3$ ranging from ~ 1 $\mathrm{pmol\,mol^{-1}}$ over the open ocean to ~ 40 $\mathrm{pmol\,mol^{-1}}$ in the vicinity of tropical islands in the western Pacific region. Butler et al. (2007) amalgamated data from seven open ocean cruises spanning a ten-year period and much of the world's oceans. Their tropical mean mixing ratios for $CHBr_3$ and CH_2Br_2 were 1 $\mathrm{pmol\,mol^{-1}}$ (0.4–2.1 $\mathrm{pmol\,mol^{-1}}$) and 0.9 $\mathrm{pmol\,mol^{-1}}$ (0.6–1.3 $\mathrm{pmol\,mol^{-1}}$) respectively.

Despite these measurements collected over the last 10–20 yr, the seas and coastlines of SE Asia are still vastly underrepresented. This knowledge gap introduces uncertainties in our understanding of the global distributions and fluxes of bromocarbons and therefore in our ability to predict future changes in global fluxes and their impact on stratospheric ozone and climate. Pyle et al. (2011) reported measurements of bromocarbons from two land-based sites in Borneo covering a short period in 2008. The coastal measurements were characterised by large variability, from a background of between 2 and 5 pmol mol^{-1} of $CHBr_3$ to occasional measurements of hundreds of pmol mol^{-1}. Measurements around the island were generally much lower and less variable, more consistent with the background of about 1 pmol mol^{-1}. The data were used to make an estimate of the regional emission strength of $CHBr_3$ which, depending on assumptions, ranged between 21 and 50 Gg yr^{-1} in SE Asia (10° N to 20° S, 90 to 150° E). For purpose of comparison we will also consider tetrachloroethylene (C_2Cl_4), which is a predominantly industrial compound used as a metal degreasing solvent, for dry cleaning and so can be considered a tracer of anthropogenic activity (Pyle et al., 2011).

How representative these Borneo measurements are of the whole region is an important question and one that was addressed by the *Prime Expedition Scientific Cruise* in 2009 (PESC 09). Selected halocarbons, including the five bromomethanes detailed above, were measured in air samples collected in three different ocean areas: the Strait of Malacca (SM), the South China Sea (SCS) and the Sulu-Sulawesi Seas (SSS). Samples were collected at both coastal and open ocean locations, including locations close to the sites mentioned in Pyle et al. (2011). The cruise and measurement details are presented in Sect. 2 whilst results are presented and discussed in Sect. 3.

2 Experimental

2.1 Cruise details

The PESC-09 cruise was conducted by the Malaysian Royal Navy and Malaysian Ministry of Science and Technology Innovation (MOSTI) and involved local government, private research agencies and public universities in Malaysia. The vessel used was the Kapal Diraja (Royal Ship) Perantau, which is designed and equipped for hydrographic surveying and for conducting meteorological and oceanographic observations. The cruise started from Port Klang (2°57′ N, 101°20′ E) in the Straits of Malacca, on

18th June and ended at, Kota Kinabalu (6°11′ N, 116°10′ E) on 31 July. These paths were separated into four different legs which are leg one (Port Klang-Labuan), leg two (Labuan-Layang-layang Island-Kota Kinabalu), leg three (Kota Kinabalu-Tawau) and leg four (Tawau- Kota Kinabalu). Figure 1 shows the ship's route together with the location of the 27 air sampling stations.

During the seven week cruise, several different oceanic regions were covered, including SM, SCS and SSS seas, and coastal regions of western and northern Borneo. Mangrove forest, sea grass beds and coral reefs dominate much of the coastline and, in northern Borneo in particular, there are areas of cultivated macroalgal beds along the coastline at sites such as Semporna, Kunak and Lahad Datu. The sampling locations were chosen to represent a variety of coastal and open ocean sites.

2.2 Sampling and measurements

Air was sampled through a 1/4″ OD PFA tube located on the upper deck with the inlet ~ 10 m above the ocean surface and adjusted at each sampling time to point into the prevailing wind. Air was pulled into a pre-evacuated 3 L canister (Restek SilcoCan™) using a compact, battery-operated diaphragm pump (Rasmussen) until the canisters were approximately two atmospheres over pressure (approximately five minutes of sampling). Canisters were filled and vented at least three times, before a final fill which was kept for analysis. A total of 27 air samples were collected during the cruise, and these were shipped to the University of East Anglia, UK for halocarbon analysis by GC-MS (gas chromatography-mass spectroscopy).

The samples were processed within four months of collection using a commercial thermal desorption system (Markes UNITY™/Air Server). The analytical technique was similar to that described by Worton et al. (2008). Air samples (1000 mL) were dried with a Nafion™ counter-flow dryer prior to collection and pre-concentration on a 2-bed adsorbent trap at −15 °C. The desorbed analytes were separated on a capillary column (Restek 100 m × 0.32 mm RTX 102) using a temperature programme of 30 °C (2 min), 8 °C min^{-1} to 150 °C (16 min), 20 °C min^{-1} to 220 °C (5 min). The mass spectrometer was operated in negative ion, chemical ionisation (NICI) mode using methane (≥ 99.99 %) as the reagent gas. The quadrupole detector was run in single ion mode, monitoring m/z 35/37 for chlorinated, m/z 79/81 for brominated and m/z 127 for iodinated compounds. Samples were normally analysed twice and referenced to a working standard. The working standard was an aluminium cylinder containing dried ambient air at high pressure. The mole fractions of halocarbons in the working standard were determined by repeat comparison to calibrated gas standards supplied by NOAA-ESRL in electropolished stainless steel canisters (Essex Industries). These comparisons are performed periodically and allow an assessment of any potential changes in the absolute mole fractions of halocarbons in our working standard over time. From comparisons with three separate NOAA standards: SX-3546 (comparison performed in 2008); SX-3570 (2010); and SX-3568 (2012) we believe the concentration of $CHBr_3$ in the working standard has declined by approximately 40 % over the period October 2008–September 2012, whilst that of CH_2Br_2 has remained essentially unchanged (1.23 ± 0.07 pmol mol^{-1}, or 5.6 %, 1σ). NOAA calibration data for the three mixed bromochloromethanes were only available for the 2010 and 2012 comparisons, but our analysis shows that the concentrations of CH_2ClBr and $CHClBr_2$ in the working standard have remained approximately constant (0.28 ± 0.004 pmol mol^{-1}, or 1.5 %; and 1.18 ± 0.04 pmol mol^{-1}, 3.2 % respectively) whilst that of $CHCl_2Br$ may have increased by around 15 % (1.56 ± 0.17 pmol mol^{-1}, or 10.6 %). The calibration factors applied to the PESC-09 data have been time-corrected as appropriate. This drift analysis makes the underlying assumption that the five bromocarbons are reliably stored in the Essex stainless steel cylinders.

The mole fractions reported here are therefore on the latest NOAA scales for CH_2Br_2 (2004) and $CHBr_3$ (2003), and on a preliminary NOAA scale for CH_2BrCl, $CHBrCl_2$ and $CHBr_2Cl$ (B. Hall, personal communication). The uncertainty in the absolute mole fractions in the working standard, based on combined uncertainties associated with the standard comparisons and NOAA's stated uncertainties was ±6.5 % for CH_2Br_2, ±7.1 % for $CHBr_3$, ±7.5 % for CH_2ClBr, ±5.9 % for $CHCl_2Br$ and ±6.8 % for $CHClBr_2$.

Mean analytical precision of the actual PESC-09 samples was $< 3\,\%$ for CH_2Br_2 and $CHBr_3$, $< 5\,\%$ for $CHBrCl_2$ and $CHBr_2Cl$, and $\sim 15\,\%$ for CH_2BrCl (due to its low abundance and low response in NICI).

Chl *a* in the surface seawater was measured using the Kapal Diraja (KD) Perantau's in-situ fluorometer attached to Sea-Bird SBE-911plus CTD system at all 27 sampling locations. CTD equipment was performed with a package consisting of a 24-place, 10 L rosette frame (AOML's grey frame), a 24-place water sampler (SBE32) and 24, 10 L Niskin bottles sampler. This package was deployed on all stations. Several fluorometers sensor for turbidity and pH measurements were attached to the CTD. The CTD instrument was run and calibrated automatically each time before sampling by the Malaysian Navy supporting scientist. The chl *a* concentration was measured from 1 m to 20 m depth. The values were taken at approximately 5 m depth and have been compared with satellite-derived chl *a* data from SeaWIFS (Sea-Viewing Wide Field-of-view Sensor) and MODIS (Moderate Resolution Imaging Spectroradiometer). Chl *a* derived from ocean colour measurements made during overpasses of the SeaWIFS and Aqua-MODIS satellite sensors were used to determine apparent chl *a* values in the nearest 9 km × 9 km grid square to each sampling point. The corresponding monthly average chl *a* values (i.e. those for either June or July) were used; these being obtained from the NASA Goddard "Giovanni" on-line database (http://oceancolor.gsfc.nasa.gov/SeaWiFS/). Shorter averaging periods are available (e.g. 8 day) but were found to be insufficient for full coverage of the cruise track given the width of the viewing swath, the level of missing data on several overpasses, and differences between satellite sensors in ocean colour-derived chl *a*. Plainly there is a substantial difference in both the temporal and spatial scales between the monthly-averaged and 9 km × 9 km grid-box averaged satellite measurements and the near-instantaneous in situ "spot" measurements. As an indication of the level of uncertainty (at least that related to spatial scales) the standard deviation of satellite-determined chl *a* was calculated for the eight to ten grid boxes surrounding the target grid box depending on the values (negative values were not considered), and the target box itself, at each location.

3 Results and Discussion

In the following sections we will, first, present an overview of the halocarbon data collected during PESC09 (Sect. 3.1). We then discuss possible causes of any observed variability, focussing on an analysis of air parcel trajectories, to understand air mass origins, and in situ measurements of chl *a*, which are a possible proxy for biological activity (Sect. 3.2). In Sect. 3.3 we explore correlations between the measured species and provide a rough estimate of regional bromoform emissions. Finally (Sect. 3.4) we use the data to investigate the potential contribution of VSLS to stratospheric bromine loading.

3.1 Halocarbon measurements

Mean and standard deviation values of the measured halocarbon concentration at each site are given in Table 1 along with some comparison with data from the literature. Figure 2 shows the concentrations of brominated compounds ($CHBr_3$, CH_2Br_2, $CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl) at each of the cruise sampling sites, whose locations are marked on Fig. 1. Figure 2 also shows the anthropogenic tracer C_2Cl_4. The most abundant bromine compound was $CHBr_3$, with mean concentrations from around 1 $pmol\,mol^{-1}$ to more than 5 $pmol\,mol^{-1}$ (mean = 1.85 $pmol\,mol^{-1}$, max = 5.2 $pmol\,mol^{-1}$). Most measurements are between 1 and 2 $pmol\,mol^{-1}$. The mean mixing ratio of $CH_2Br_2$was 1.23 $pmol\,mol^{-1}$(max = 2.21), with the minor species $CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl having mixing ratios in the mean 0.1 to 0.9 $pmol\,mol^{-1}$. For the anthropogenic tracer C_2Cl_4, mixing ratios varied only between 0.9 and 1.0 $pmol\,mol^{-1}$. The PESC-09 measurements are generally within the range of previous measurements in tropical regions.

3.2 Regional analysis

3.2.1 Straits of Malacca (Stations 1–4)

PESC-09 took place during the South West Monsoon (SWM) when sea surface temperatures are slightly warmer (28–32 °C, May/June) than in the North West Monsoon (NWM) (25–29 °C, December/January). Tan et al. (2006) report that chl *a* in the Straits of Malacca shows seasonal variability with concentrations increased by as much as a factor of two ($0.57\,\text{mg}\,\text{m}^{-3}$ in August and $1.38\,\text{mg}\,\text{m}^{-3}$ in January 1992–2002 monthly average) during NWM compared to SWM.

The highest concentrations of $CHBr_3$ were observed at the beginning of the cruise in the Strait of Malacca (SM). The mean concentration in samples 2–4 was $4.4\,\text{pmol}\,\text{mol}^{-1}$. which is similar to the levels in the same region reported by Yokouchi (1997). The enhanced levels may be related to the high population of macro and micro algae such as phytoplankton and seaweeds at coastal areas, especially in the region of 1–2° N, 102–103° W. Previous studies on chl *a* in the SM were influenced by highly mixing of nutrients input from rivers of Sumatra (Tan et al., 2006). CH_2Br_2, $CHCl_2Br$, $CHClBr_2$ and $CHCl_3$ were also enhanced in samples 2–4, which is indicative of similar sources. SM is one of the world's busiest shipping lanes, connecting the Indian Ocean to the Pacific (Tan et al., 2006). With the close proximity of Singapore and the numerous oil and gas platforms in the area, it is also possible that, for some halocarbons, concentrations here might be strongly influenced by anthropogenic sources. For example, Yokouchi et al. (1997) measured anthropogenic short-lived C_2Cl_4 increased near Singapore and the affects suggested to be very local. However, of the anthropogenic compounds measured (CFCs, halons and C_2Cl_4) none were enhanced in samples 2–4.

3.2.2 South China Sea (Stations 5–14)

Measurements in the SCS show fairly uniform and relatively low mixing ratios for all the brominated compounds. For example, the mean values for $CHBr_3$, CH_2Br_2 and

$CHBr_2Cl$ were 1.46, 1.12 and 0.35 pmol mol^{-1} respectively, with no significantly enhanced values. The prevailing wind direction for most samples collected along this section of the cruise was westerly, so the influence of any local coastal emissions would likely be low.

3.2.3 Sulawesi and Sulu Seas (Stations 15–27)

Slightly higher concentrations of bromocarbons were observed during the cruise through the SSS, especially at Station 22 and 24 where $CHBr_3$ concentrations were 2.37 and 2.60 pmol mol^{-1} respectively. During this period the ship passed near to coastal sites at Semporna (Station 22), Kunak (19, 20, 21, 27) and Tawau (24, 26). The coastal areas near to Semporna and Kunak have significant seaweed biomass, with cultivated *Kappaphycus* and *Eucheuma* at Semporna and *Sargassum* and other brown algae at Kunak. Samples 17 and 21 had slightly elevated levels of C_2Cl_4, suggesting a possible influence from local anthropogenic sources.

Pyle et al. (2011) measured $CHBr_3$ concentrations at Kunak ranging from a typical background of 2–5 pmol mol^{-1}, but with excursions up to 60 pmol mol^{-1} (the latter attributed to measurement very close to local emissions). During their short measurement period in July 2008 the air flow was predominantly from the south east, with back-trajectories showing air having travelled from northern Australia, over the Timor and East Java Seas and up the eastern coast of Borneo. The authors speculated that these are areas of high biological activity, with both the warm ocean and extensive coastline providing significant sources of halocarbons. Despite similar air mass back-trajectories and sampling in similar locations, we did not measure the very high levels of $CHBr_3$ reported by Pyle et al. (2011). For example, at Station 27, back-trajectories did not show air flow passed any seaweed or high nutrient area.

3.3 Drivers of variability

The data collected during PESC-09 show relatively small variability, consistent with the ship data reported by Yokouchi et al. (1997) over western Pacific, East and South East Asia. For example, they observed high mixing ratio of $CHBr_3$ over Strait of Malacca where chl *a* were higher than those observed in other areas in their cruise. In contrast to the data reported by, for example, Yokouchi et al. (2005), which had wide geographical coverage in the Pacific, or by Pyle et al. (2011) for two sites in Borneo. It seems likely that these latter studies both included data collected close to emission sources.

Atmospheric variability is driven by various factors including wind direction, atmospheric lifetime, proximity to local sources and temporal variation of flux rates. Changes in VSLS emissions could arise from a number of complex factors. Emissions of VSLS bromocarbons are predominantly biogenic, with the ocean the most important source (Baker et al., 2000; Quack et al., 2004). Proximity to local seaweed beds (including seaweed farms) is likely to be an important influence in coastal regions. In the case of microalgae, their abundance and distribution in seawater are affected by nutrient supplies and sea surface temperatures, while sea-air fluxes of VSLS are determined by meteorological parameters including wind speed. Chl *a* can be used as a simple proxy for biological activity, possibly producing halocarbons, which may be emitted into the atmosphere, depending on concentrations and wind speed.

3.3.1 Meteorological variability

A major factor controlling the halocarbon measurements during the cruise is likely to have been the wind direction. Figure 7 shows selected 10 day air mass back trajectories for seven of the cruise sampling locations calculated from the NOAA HYSPLIT model (R. R. Draxler and G. D. Rolph, HYSPLIT- Hybrid Single-Particle Lagrangian Integrated Trajectory model 2011, available at http://www.arl.noaa.gov/ready.html). In all cases the large-scale structure is consistent. Air masses arrive at the sampling locations from the south east and have likely been influenced by emissions from shallow, warm seas, including the South Java Sea. There is therefore likely to be little variability associated with transport from different large-scale emission regions, although local emissions close to the sampling locations could still be important in driving local variability. For example, the trajectories arriving at site 22, near Sipadan Island, or at Station 19, near Kunak, are very likely to have been influenced by the seaweed beds in that area. A similar conclusion was reached by Pyle et al. (2011) based on their coastal Kunak measurements in June 2008, made one year earlier than the PESC cruise. In particular, the origins of the measured air masses are very similar in both years.

3.3.2 Biological activity

Chl *a* was also measured at 60 sites including 27 sites where halocarbons are measured during the cruise, both in situ from the ship and remotely from satellite sensors, and has been compared with the halocarbon data to explore possible biological drivers of variability. Figure 1 plots the monthly average chl *a* across the region from SeaWiFS for June 2009 over layed with the sampling stations. High apparent chl *a* is seen around the coastlines, which intuitively might be expected to relate to phytoplankton abundance and hence to the bromocarbon emission strength. Indeed high apparent satellite-derived chl *a* values were evident in the Strait of Malacca, where the highest $CHBr_3$ was measured. However, a plot of ocean colour-derived chl *a* from the two satellite sensors vs. in situ chl *a* (Fig. 5) shows significant disagreement between the remotely-sensed and in situ measurements. The standard deviation between eight to ten grid box surrounding the target grid box are in the range of 1.1 to 32.4 $\mathrm{mg\,m^{-3}}$ for MODIS and 0.1 to 18.2 $\mathrm{mg\,m^{-3}}$ for SeaWiFS. The filled symbols denote samples in which the turbidity was > 0.5 FTU, whereas open symbols denote lower turbidity. It is apparent that the lower turbidity samples display a relatively compact relationship between remotely-sensed and in situ chl *a* and with absolute values that are in good quantitative agreement. Indeed a linear regression on the lower turbidity samples yields a gradient of 1.0 (standard error of 0.1) and an r^2 value of 0.88. The points that fall above this line are all in samples with turbidities greater than 0.5 FTU, implying that the satellite sensors over-estimate chl *a* under such conditions. Indeed the in situ measurements showed that ship-board measurements of chl *a* are no higher than those made in the open ocean.

Plots of halocarbons vs. in situ chl *a* (Fig. 6) show no correlation with satellite's chl *a*, with the highest mixing ratios of $CHBr_3$ and CH_2Br_2 associated with below average chl *a* values ($< 0.2\,mg\,m^{-3}$). Only $CHCl_3$ appeared to display a weak positive relationship with chl *a*. The above finding is not necessarily surprising even if phytoplankton are a source of such gases, since a connection between halocarbons measured in the marine atmospheric boundary layer and sub-surface biology may be dependent on other factors including wind speed. Furthermore, the observed halocarbon concentrations might originate over a wide geographic area and not necessarily driven solely by localised emissions. In this context, satellite-derived chl *a* may potentially be more relevant than in situ measurements. However, even filtering the satellite-derived chl *a* for turbidities of less than 0.5 FTU, did not reveal any significant correlations with halocarbon concentrations (not shown). Similarly, there were no obvious correlations between the halocarbons and turbidity. Although turbidity measurements in the Strait of Malacca (average of 3.3 FTU) were significantly higher than those in the South China Sea (average of 0.3 FTU; Table 1), coinciding with high $CHBr_3$, the turbidity was almost as high close to land near Semporna (average of 2.1 FTU for Stations 24–27), but with little evidence of substantially enhanced halocarbons in the latter region. We conclude that halocarbon concentrations are generally somewhat higher close to land, and also higher in the Strait of Malacca, thus a connection to the coastal zone is suspected, but there is little evidence to connect this directly to open ocean microorganisms.

3.4 Emission ratios

Significant correlations between brominated halocarbons have been observed during coastal measurements suggesting that these gases have come from the same sources (Yokouchi et al., 2005; O'Brien et al., 2009; Carpenter et al., 2009). Several studies have exploited these correlations to explore the possible source strengths of the individual species. Carpenter et al. (2003), Yokouchi et al. (2005) and O'Brien et al. (2009) all show that a plot of $CH_2Br_2/CHBr_3$ vs. $CHBr_3$ often shows a straight line with the ratio $CH_2Br_2/CHBr_3$ increasing with decreasing $CHBr_3$. Atmospheric ratios of $CH_2Br_2/CHBr_3$ are often interpreted in the light of their differing atmospheric lifetimes, which are about 24 days for $CHBr_3$ and 120 days for CH_2Br_2 (Montzka et al., 2011). (The relationship between $CHBr_3$ and other somewhat longer-lived brominated halocarbons such as $CHBr_2Cl$ also showed similar patterns, for example $CHBr_2Cl/CHBr_3$ would be higher at lower concentration of $CHBr_3$.) Since $CHBr_3$ has the shorter lifetime of the two species, an increase in the ratio would be consistent with more aged air masses, in which $CHBr_3$ has been preferentially removed. Yokouchi et al. (2005) used the minimum ratio of $CH_2Br_2/CHBr_3$ to define the ratio of the emission sources by assuming that the emissions came from the common sources and are constant on a regional scale. If the global emission of CH_2Br_2 is known, then that of $CHBr_3$ can be inferred. An alternative explanation, however, is that the emission ratio for $CH_2Br_2/CHBr_3$ in the open ocean is different (i.e. higher) to that in coastal areas and so the assumption of a single characteristic seawater ratio is invalid, along with the extrapolation of source strength.

Figure 3 shows the relationships between CH_2Br_2 and $CHBr_3$ and between $CHBr_2Cl$ and $CHBr_3$ for each data set. Correlations are strong between CH_2Br_2 and $CHBr_3$ (correlation coefficient, $r = 0.9$), $CHBr_3$ and $CHBr_2Cl$ ($r = 0.7$) and $CHBr_3$ and $CHBrCl_2$ (correlation coefficient $r = 0.5$). Figure 4a and b shows the concentration ratios of $CH_2Br_2/CHBr_3$ and $CHBr_2Cl/CHBr_3$ plotted against $CHBr_3$on log-log scale, with both ratios increasing linearly as $CHBr_3$ decreases; $CHBr_3$, with its shorter lifetime is a possible measure of time since co-emission. These figures are consistent with those reported by Yokouchi et al. (2005).

Yokouchi et al. (2005), following McKeen and Liu (1993), used plots of pairs of ratios, e.g. $CHBr_3/CH_2Br_2$ vs. $CHBr_2Cl/CH_2Br_2$, where CH_2Br_2 has the longest lifetime, to explore the possible emission strengths of the individual species. Making a number of assumptions, in such a plot the location of individual points in ratio space is determined by the emission ratio at an (assumed) common regional source and by the ratio of the rates of chemical removal and mixing into the "background" atmosphere. Assuming that the emission source strength of one species is known, that of the others can be obtained using the ratio determined from the plot. Using this method, O'Brien et al. (2009) estimated a global emission of bromoform of 823–1404 $\mathrm{Gg\,yr^{-1}}$ (values depend inter alia on the assumed CH_2Br_2 emissions) using data collected at Cape Verde in June 2006. This emission is much higher than estimates in Ko et al. (2003), or in Warwick et al. (2006). However, Pyle et al. (2011) suggest that it is not reasonable to derive global emission estimates from regional data for a short-lived species such as bromoform. They showed that data from Borneo could instead only be used to constrain regional emissions.

Using data from the cruise, $CHBr_3/CH_2Br_2$ is plotted against $CHBr_2Cl/CH_2Br_2$ in Fig. 4b. The left side of the triangle is the "dilution line" (the 1 : 1 slope for mixing into a zero background) and the "chemical decay line", defined by the ratio of lifetimes of individual species due to photochemistry, is the right hand line. The intersection of these 2 lines defines the emission ratios. Nearly all the data falls into a triangle whose vertex for $CHBr_3/CH_2Br_2$ takes a value of 5 (point D on the figure). This is about half the value reported by Yokouchi et al. (2005) and O'Brien et al. (2009) but very similar to the result obtained by Brinckmann et al. (2012) based on data collected in a recent western Pacific cruise. If we assume that this emission ratio of 5 is appropriate to the SE Asian Region, (10° N to 20° S, 90 to 160° E, as used by Pyle et al., 2011) and recalling that the air mass histories in the two periods of these two studies are quite similar, then we could derive an emission estimate for $CHBr_3$ from the regional CH_2Br_2 emission. That value is not observationally constrained; instead we can use the SEA regional CH_2Br_2 emission from Warwick et al. (2006), which assumed spatially uniform ocean emissions of CH_2Br_2 in the tropics. In that case, with a CH_2Br_2 emission of 12.6 $\mathrm{Gg\,yr^{-1}}$, we obtain a regional emission, based on point D from Fig. 4b, of about 63 $\mathrm{Gg\,yr^{-1}}$ of $CHBr_3$. This value is within a factor of about two of the value obtained by Pyle et al. (2011), where estimates the global emissions of $CHBr_3$ are in the ranged between 21 and 50 $\mathrm{Gg\,yr^{-1}}$ (and both are much less than the regional value in Warwick et al., 2006). To be more confident about this emission value would require, amongst other things, improved estimates of the CH_2Br_2 emission. However, the consistency of the calculations does suggest that useful constraints on regional estimates can be obtained based on McKeen and Liu (1993) plots.

3.5 Total bromine

The cruise data can be used to give an upper limit on the amount of bromine which could potentially reach the stratosphere, i.e. by summing the measured bromine mixing ratios and weighting by the number of bromine atoms. The mean VSLS-derived bromine ($[\mathrm{Br}]_{\mathrm{VSLS}}$) in the 27 samples was $8.9 \pm 3.7\,\mathrm{pmol\,mol^{-1}}$. There is some regional variability as discussed earlier, with SM having the highest $[\mathrm{Br}]_{\mathrm{VSLS}}$ (mean = $17.8\,\mathrm{pmol\,mol^{-1}}$) compared to other sampled areas. Of this $8.9\,\mathrm{pmol\,mol^{-1}}$, $CHBr_3$ contributes ~ 65 % and CH_2Br_2 25 %. This is similar to results compiled by Montzka et al. (2011) for which an average total bromine from the same gases in the tropical marine boundary layer (mostly from open ocean measurements) is given as $8.4\,\mathrm{pmol\,mol^{-1}}$ with a range of $3.6–13.3\,\mathrm{pmol\,mol^{-1}}$. With the exception of the Strait of Malacca, there does not appear to be a large regional enhancement of $[\mathrm{Br}]_{\mathrm{VSLS}}$ in our data, despite the cruise having taken place mostly within 50 km of the coast. The data do not suggest that this part of SE Asia is a “hot spot” for emissions.

The $[\mathrm{Br}]_{\mathrm{VSLS}}$ measured during the PESC cruise are likely to account for some of the “missing” bromine entering the stratosphere, assuming conservative transport of the constituent bromine either in the form of the source gas itself, or as brominated product gases.

4 Conclusions

We report in situ halocarbon and ancillary data obtained during a research cruise of the Perantau in June and July 2009. The cruise covered the Straits of Malacca, the South China Sea and the Sulu and Sulawesi Seas. These are warm, shallow ocean areas and contain conditions suspected likely to support high halocarbon production and emission to the atmosphere. The region is also important as the location of the strongest convection world wide; it thus represents potentially a very important source region for the transport of marine boundary layer concentrations of VSLS to the upper troposphere and stratosphere.

Data were collected at 27 sites during the cruise. High bromoform concentrations (4–5 $\mathrm{pmol\,mol^{-1}}$) were measured in the nutrient rich Straits of Malacca. Otherwise concentrations were generally between 1 and 2 $\mathrm{pmol\,mol^{-1}}$. This is consistent with an earlier cruise reported by Yokouchi et al. (1997). Slightly higher concentrations were measured close to seaweed farms in Semporna but nowhere on the cruise did we find very high concentrations similar to those reported by Pyle et al. (2011) at a coastal site at Kunak, believed to be close to emission sources. Further, there is no evidence from the cruise data that local emission sources in this region lead to widespread, elevated concentrations ("hotspots") which might make a contribution to stratospheric input out of proportion to the area of the region.

Measurements of other bromocarbons were in the expected ranges with typical concentrations as indicated, CH_2Br_2 ~1 $\mathrm{pmol\,mol^{-1}}$, $CHBr_2Cl$ ~ 0.2–0.4 $\mathrm{pmol\,mol^{-1}}$, $CHBrCl_2$ ~ 0.2–0.3 $\mathrm{pmol\,mol^{-1}}$ and CH_2BrCl ~ 0.1–0.2 $\mathrm{pmol\,mol^{-1}}$. The bromocarbons were well correlated, suggesting common sources. Previously, such relationships have been used to obtain global emission estimates. For short-lived gases like bromoform, with an atmospheric lifetime of perhaps 15 to 20 days, we do not think this approach is suitable; the footprint sampled by the cruise is regional at most. Instead, we used a plot an approach as applied by Yokouchi et al. (2005) to provide a very rough estimate of the regional (S.E. Asia) emission ration of bromoform to dibromomethane of about 5.

Using the dibromomethane emissions from Warwick et al. (2006) leads to bromoform emissions of 63 $\mathrm{Gg\,yr^{-1}}$ for S.E. Asia (10° N to 20° S, 90° E to 160° E) in reasonable agreement with the recent estimates from Pyle et al. (2011). Much more data, not least on CH_2Br_2 emissions, would be required to confirm this estimate but the use of species correlations for regional emission estimate looks to a promising approach.

Chl−*a* was measured on the cruise. There was little obvious correlation between this and the measured atmospheric halocarbon concentrations. Satellite measurements of chl *a* suggested high values in the Straits of Malacca, coinciding with high turbidity and high halocarbon concentrations. However, it seems likely that the satellite data were affected by the high turbidity in these waters, and the underway in situ chl *a* measurements were the same as those observed in the open sea. This is inconsistent with earlier work suggesting significant correlation between bromoform emissions and marine biological activity. The reasons for this are not clear, although it seems likely that the higher halocarbon concentrations in the Straits maybe be as a result of some influence of the nearby coastal areas and land masses.

The seas around South East Asia are important for a number of atmospheric processes, including both convection and the emission of halocarbons. Measurements of halocarbons are sparse; despite the new measurements reported here, the region remains data poor.

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Table 1. Mean, standard deviation (in brackets) and range (in bold) values of the measured halocarbon concentrations in this work and values from the literature based on tropical ocean areas (n.m. not mentioned).

		Bromocarbon's Mixing ratios						
Area	Author	$CHBr_3$ Mean (std) **range**	$CHBr_2Cl$ Mean (std) **range**	CH_2Br_2 Mean (std) **range**	$CHBrCl_2$ Mean (std) **range**	CH_2BrCl Mean (std) **range**	**Chl** *a* (mg m^{-3}) (std)	Turbidity (FTU)
Strait of Malacca								
coastal	This study	3.69 (1.54) **1.85–5.25**	0.32 (0.09) **0.19–0.39**	1.38 (0.37) **1.05–1.92**	0.12 (0.02) **0.19–0.39**	0.12 (0.04) **0.1–0.14**	0.19 (0.3)	3.33 (1.22)
South China Sea								
Open ocean	This study	1.51 (0.4) **1.07–2.02**	0.21 (0.05) **0.15–0.27**	1.01 (0.19) **0.88–1.29**	0.22 (0.07) **0.17–0.32**	0.10 (0.01) **0.09–0.11**	0.17 (0.09)	0.19 (0.07)
coastal	This study	0.90 (0.32) **0.82–1.02**	0.15 (0.08) **0.12–0.2**	0.90 (0.09) **0.82–1.02**	0.18 (0.03) **0.15–0.22**	0.10 (0.03) **0.07–0.15**	0.22 (0.12)	0.15 (0.07)
Sulu-Sulawesi seas								
coastal	This study	1.60 (0.5) **1.07–2.61**	0.23 (0.08) **0.15–0.44**	1.04 (0.16) **0.89–1.36**	0.3 (0.08) **0.22–0.52**	0.15 (0.04) **0.12–0.28**	0.32 (0.2)	1.54 (0.92)
Previous study over tropical ocean								
South east Asia 100–105° E	Youkouchi et al. (1995)	1.2 (n.m) **0.3–7.0**		0.77 (n.m) **0.38–1.42**				
Western Pacific 43° N, 150° E and 4° N, 113° E	Quack and Suess. (1994)	1.2 (n.m) **0.38–10.67**	0.2 (n.m) **0.07–1.34**		0.28 (n.m) **0.08–2.96**			
San Cristobal Island (Loberia)	Yokouchi et al. (2005)	14.2 (10.1) **4.2–43.6**	1.5 (1.0) **0.5–4.1**	3.2 (1.5) **1.8–7.6**				
Christmas Island (Topono)	Yokouchi et al. (2005)	23.8 (10.7) **16.3–31.4**	2.0 (0.7) **1.5–2.4**	3.0 (1.0) **2.3–3.7**				
Java Island	Yokouchi et al. (2005)	0.9 (0.4) **0.4–1.6**	0.2 (0.2) **0.1–0.6**	0.9 (0.2) **0.6–1.5**				
Pacific Equator	Yokouchi et al. (2005)	1.9 (0.9) **0.8–3.5**	0.3 (0.1) **0.1–0.6**	1.3 (0.5) **0.2–0.5**				

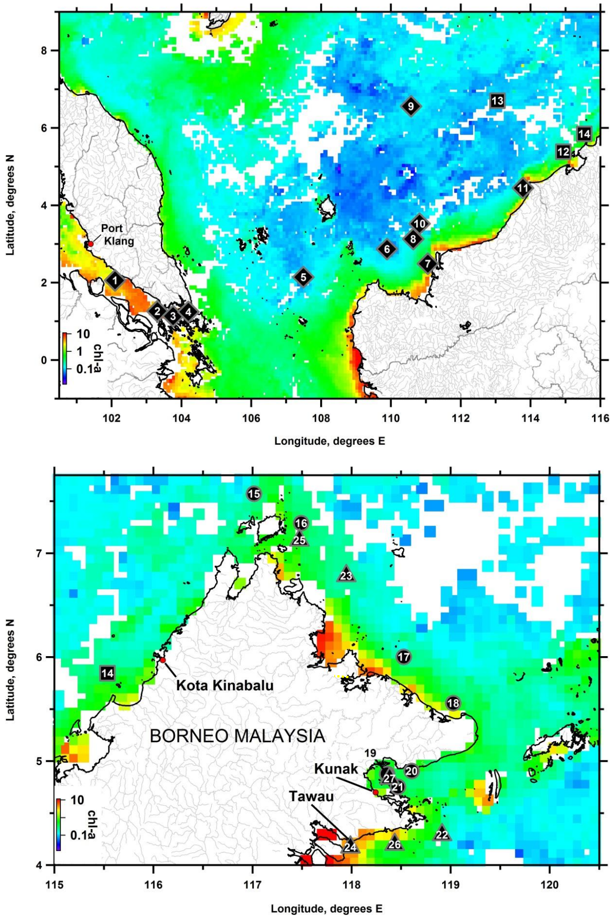

Fig. 1. Sampling locations overlay with SeaWiFS chl *a* during PESC 2009 (labels: diamond = 1st leg, square = 2nd leg, circle = 3rd leg and triangle = 4th leg).

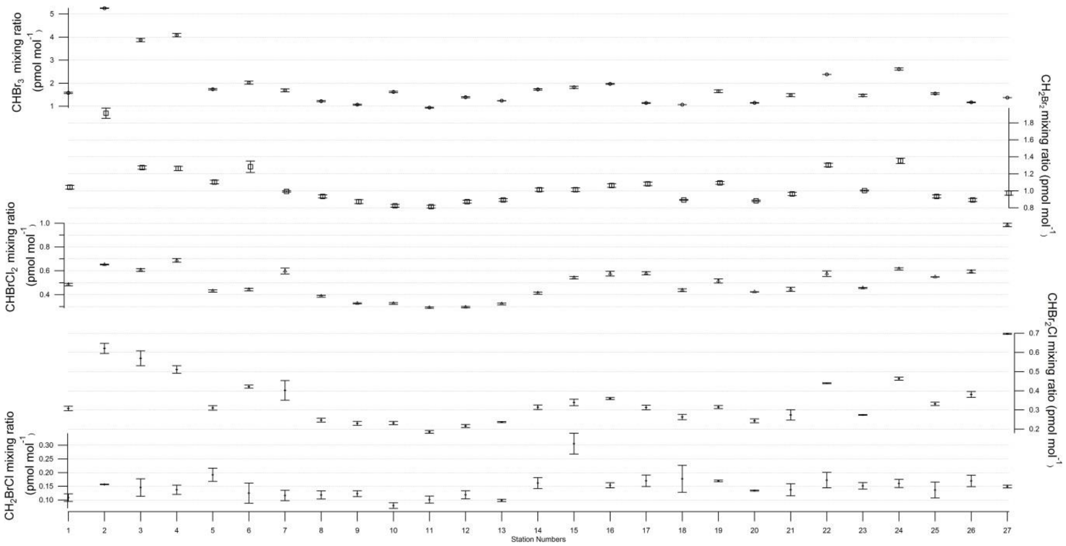

Fig. 2. Bromocarbons mixing ratios for each station during PESC 2009.

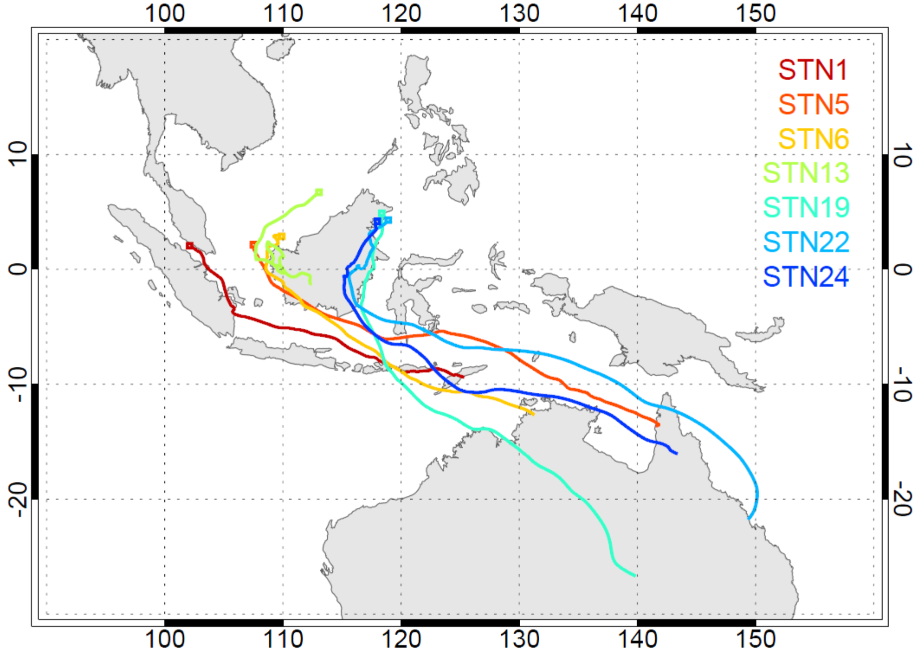

Fig. 3. 10 days air distribution backward trajectories calculated from the NOAA HYSPLIT model for each selected stations.

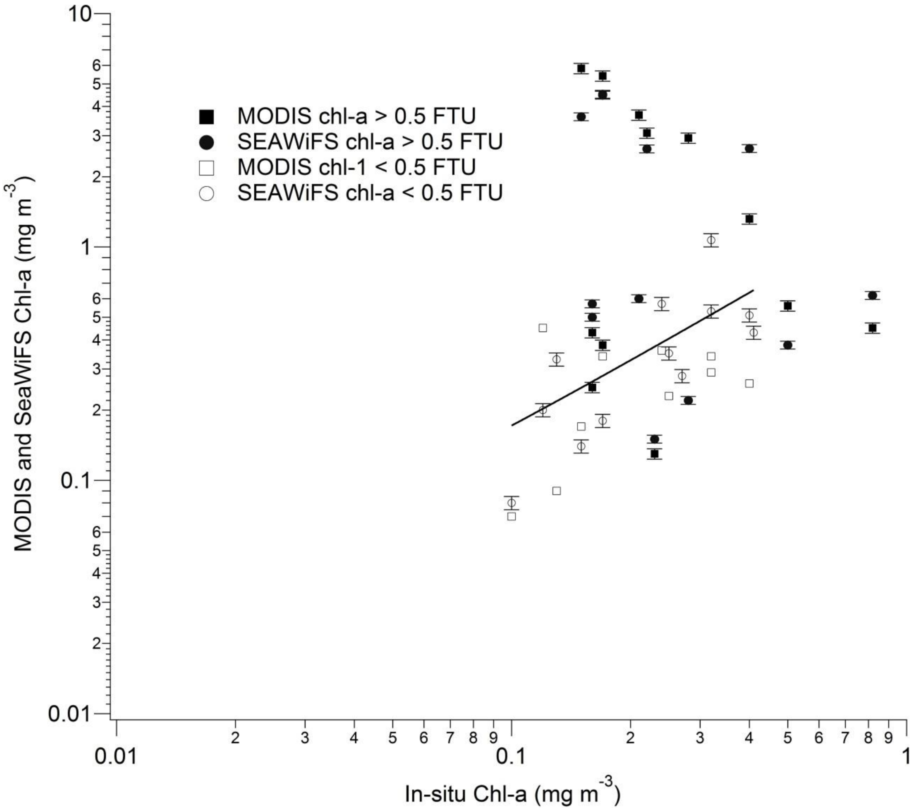

Fig. 4. Chl *a* concentration from the satellite data against in-situ chl *a*. The solid symbols represent samples where turbidity was > 0.5 FTU, and open symbols for turbidities < 0.5 FTU. The line is a linear fit to the lower turbidity samples.

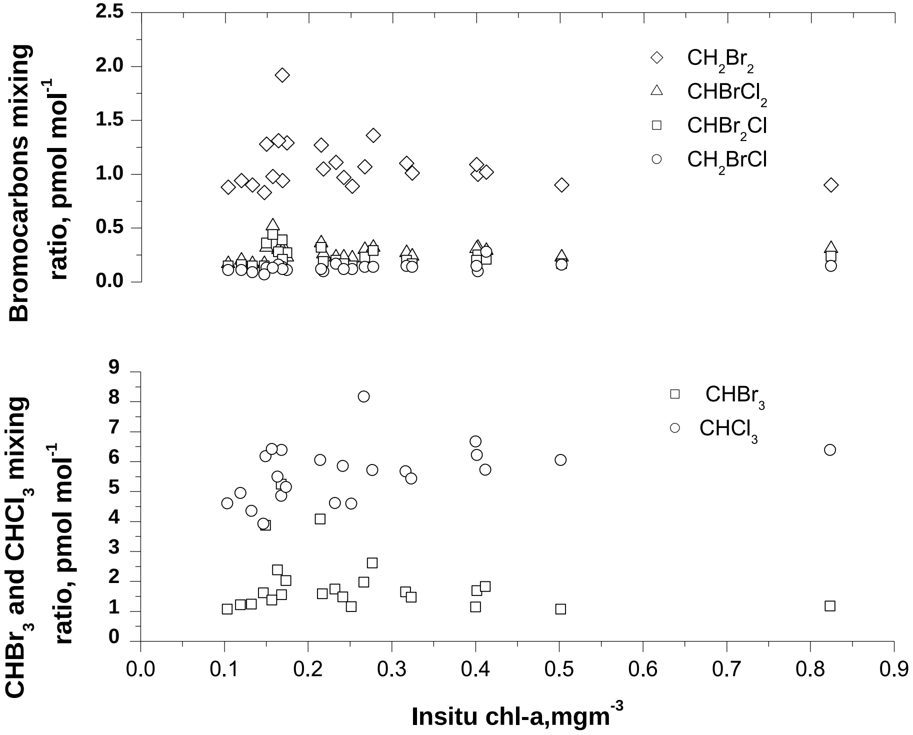

Fig. 5. Halocarbon concentrations as a function of in situ measurements of chl *a* in the water column.

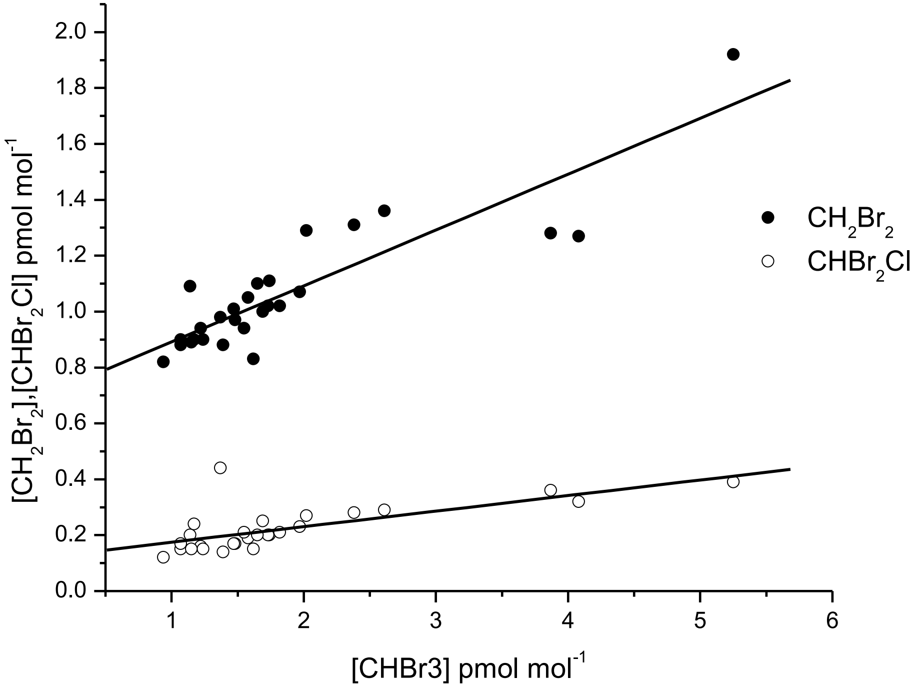

Fig. 6. Log-log plot for correlations of CH_2Br_2 and $CHBr_2Cl$ vs. $CHBr_3$ concentrations.

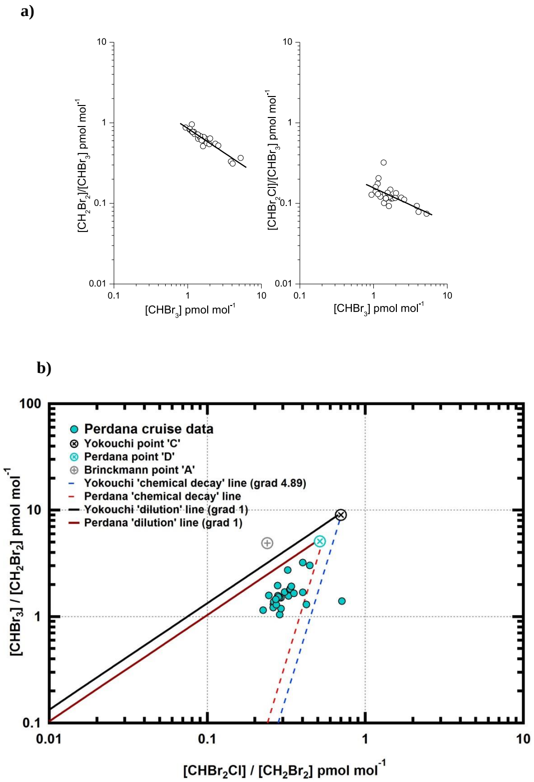

Fig. 7. **(a)** Log-log plot $CH_2Br_2/CHBr_3$ and $CHBr_2Cl/CHBr_3$ against $CHBr_3$ and **(b)** log-log plots of $CHBr_3/CH_2Br_2$ against $CHBr_2Cl/CH_2Br_2$ for all stations during Perdana Cruise, following Yokouchi et al. (2005) and Brinckmann et al. (2011). The solid line is the dilution line 1 : 1 and the solid dash line is the chemical decay line which estimated from the lifetime of the 3 species in the atmosphere. In this case, we have followed the example of Yokouchi et al. (2005) by using the lifetimes of 26 days ($CHBr_3$), 69 days ($CHBr_2Cl$) and 120 days (CH_2Br_2). Thus the decay line has a slope of 4.89. The black point at the top of the data set is the point C in Yokouchi et al. (2005) and grey point is the point A in Brinckmann et al. (2011) log-log plots where $CHBr_3/CH_2Br_2$ to be around 9 and $CHBr_2Cl/CH_2Br_2$ to be around 0.7 from Yokouchi et al. (2005) and around 5 for $CHBr_3/CH_2Br_2$ and 0.2 for $CHBr_2Cl/CH_2Br_2$ from Brinckmann et al. (2011).