



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

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Abstract. Atmospheric concentrations of very short-lived species (VLS) bromocarbons, including CHBr_3 , CH_2Br_2 , CHCl_2Br , CHClBr_2 , and 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 $5.2 \text{ pmol mol}^{-1}$ in the Strait of Malacca to $0.94 \text{ pmol mol}^{-1}$ over the open ocean. Other bromocarbons showed lower concentrations, in the range of $0.8\text{--}1.3 \text{ pmol mol}^{-1}$ for CH_2Br_2 , $0.1\text{--}0.5 \text{ pmol mol}^{-1}$ for CHCl_2Br , and $0.1\text{--}0.4 \text{ pmol mol}^{-1}$ for CHClBr_2 . There was

no significant correlation between bromocarbons and in situ chlorophyll *a*, but positive correlations with both MODIS and SeaWiFS satellite chlorophyll *a*. Together, the short-lived bromocarbons contribute an average of $8.9 \text{ pmol mol}^{-1}$ (range $5.2\text{--}21.4 \text{ pmol mol}^{-1}$) to tropospheric bromine loading, which is similar to that found in previous studies from global sampling networks (Montzka et al., 2011). Statistical tests showed strong Spearman correlations between brominated compounds, suggesting a common source. Log–log plots of $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ versus $\text{CHBr}_2\text{Cl}/\text{CH}_2\text{Br}_2$ 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 to derive a value of 32 Gg yr^{-1} for the Southeast (SE) Asian region ($10^\circ \text{ N} - 20^\circ \text{ S}$, $90 - 150^\circ \text{ E}$). 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 very short-lived substances (VSLs) has been used to represent halogen-containing compounds with lifetimes of less than six months (WMO, 2007). Bromine-containing VSLs and their atmospheric degradation products are believed to account for around a quarter of the total bromine entering the lower stratosphere (Dorf et al., 2006; Salawich et al., 2006; Montzka et al., 2011), and contribute to the “missing” bromine (6 pmol mol^{-1} , range $3 - 8 \text{ pmol mol}^{-1}$) required for the levels of inorganic bromine Br_y and 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 emissions from 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 into the atmosphere (Sturges et al., 1993; Moore et al., 1996; Laturmus and Adams, 1998). Previous ship and coastal measurements have collected bromocarbon data for many different global regions, summarised in Montzka et al. (2011). These studies show large temporal and spatial variability in both seawater and atmospheric concentrations, emphasising the importance of localised emissions of these gases.

Because of their short atmospheric lifetimes, the region where VSLs are emitted into the atmosphere is 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 major pathway for rapid transport of insoluble gases from the lower to the upper troposphere. Importantly, such convective transport appears to be particularly strong over the western Pacific (Gettelman et al., 2002; Fueglistaler et al., 2004). 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 sup-

ply a portion of the “missing” $\sim 6 \text{ pmol mol}^{-1}$ of bromine, thought to be related to VSLs, to the stratosphere.

Yokouchi et al. (1997) were the first to report atmospheric bromocarbon measurements in the Strait of Malacca and the South China Sea. During a cruise between Japan and the Bay of Bengal, they measured mean concentrations of $0.77 \text{ pmol mol}^{-1}$ (max $1.42 \text{ pmol mol}^{-1}$) and $1.2 \text{ pmol mol}^{-1}$ (max $7.1 \text{ pmol mol}^{-1}$) 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 algal sources. During a cruise in the South China Sea, Quack and Suess (1999) observed mean ambient air concentrations for bromoform of $1.2 \text{ pmol mol}^{-1}$ (range $0.38 - 10.6 \text{ pmol mol}^{-1}$).

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

Despite these measurements collected over the last two decades, the seas and coastlines of SE Asia are still vastly under-represented. This knowledge gap introduces uncertainties into our understanding of the global distributions and fluxes of bromocarbons and therefore into 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 3 weeks in June and July 2008. The coastal measurements were characterised by large variability, from a background of 2 to 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 a 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 ($10^\circ \text{ N} \times 20^\circ \text{ S}$, 90° E to 160° E). For the purpose of comparison we will also consider tetrachloroethylene (C_2Cl_4), which has predominantly industrial uses as a metal degreasing solvent, and dry cleaning, and can be considered to be a tracer of anthropogenic activity (Pyle et al., 2011).

How representative these Borneo measurements are of the whole SE Asia 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 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, sometimes close to the sites mentioned in Pyle et al. (2011). The cruise and measurement details are presented in Sect. 2. Results are presented and discussed in Sect. 3.

2 Measurements

2.1 Cruise details

The PESC-09 cruise was conducted by the Malaysian Royal Navy and the 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 ($2^{\circ}57' N$, $101^{\circ}20' E$) in the Strait of Malacca on 18 June and ended at Kota Kinabalu ($6^{\circ}11' N$, $116^{\circ}10' E$) on 31 July. These paths were separated into four different legs: 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 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 face the prevailing wind. Air was pumped into a pre-evacuated 3 L canister (Restek SilcoCan™) using a compact, battery-operated diaphragm pump (Rasmussen) until the canisters were approximately two atmospheres above ambient 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 was 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

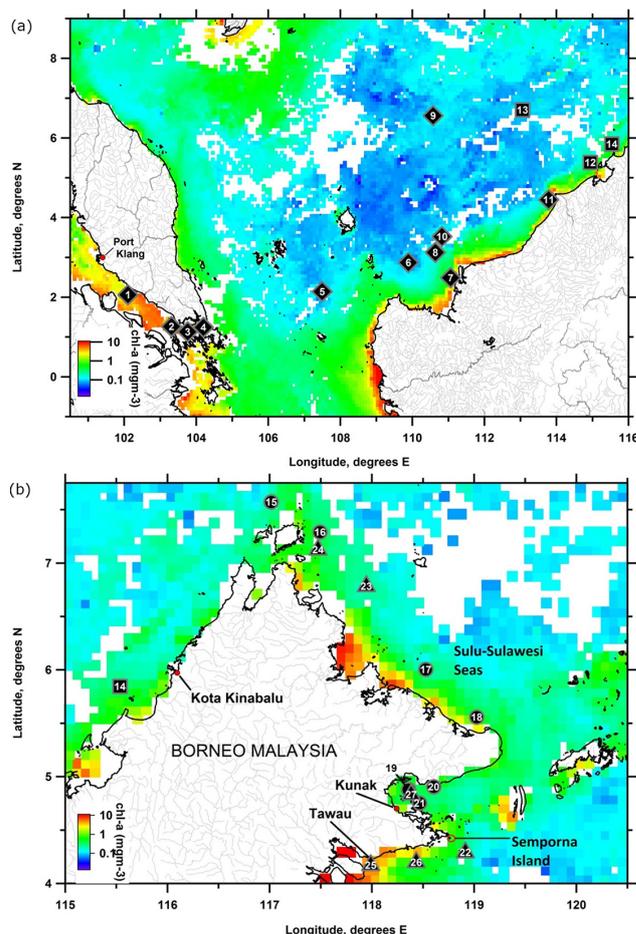


Figure 1. Sampling locations overlaid with SeaWiFS chl *a* during PESC 2009 (labels: the diamond is the 1st leg, the square is the 2nd leg, the circle is the 3rd leg, and the triangle is the 4th leg).

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 two-bed adsorbent trap at $-15^{\circ} C$. The desorbed analytes were separated on a capillary column (Restek $100\text{ m} \times 0.32\text{ mm}$ RTX 102) using a temperature programme of $30^{\circ} C$ (2 min), $8^{\circ} C\text{ min}^{-1}$ to $150^{\circ} C$ (16 min), and $20^{\circ} C\text{ min}^{-1}$ to $220^{\circ} C$ (5 min). The mass spectrometer was operated in negative ion, chemical ionisation (NICI) mode using methane ($\geq 99.99\%$) 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 to 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 ($1.23 \pm 0.07 \text{ pmol mol}^{-1}$, 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 ($0.28 \pm 0.004 \text{ pmol mol}^{-1}$, or 1.5 % and $1.18 \pm 0.04 \text{ pmol mol}^{-1}$; 3.2 % respectively), whilst that of CHCl_2Br may have increased by around 15 % ($1.56 \pm 0.17 \text{ pmol mol}^{-1}$, 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 stored reliably in the Essex stainless steel cylinders.

The mole fractions reported here are 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 (Brad 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 $\pm 6.5\%$ for CH_2Br_2 , $\pm 7.1\%$ for CHBr_3 , $\pm 7.5\%$ for CH_2ClBr , $\pm 5.9\%$ for CHCl_2Br , and $\pm 6.8\%$ for CHClBr_2 . The 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 a Sea-Bird SBE-911plus CTD (conductivity, temperature, depth) system at all 27 sampling locations. The CTD equipment was operated together with a package consisting of a 24-place, 10L rosette frame, a 24-place water sampler (SBE32) and a 24 10L Niskin bottle sampler. This package was deployed at all stations. Several fluorometers, turbidity sensors and pH measurements were attached to the CTD. The CTD instrument was run and calibrated automatically at each station before sampling. The chl *a* concentration was measured from 1 m to 20 m depths, with 5 m intervals. Readings were taken at the sea surface at approximately 1 m in depth and have been compared to 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 $9 \times 9 \text{ km}$ grid square nearest to each sampling point. The corresponding monthly average chl *a* values (i.e. those

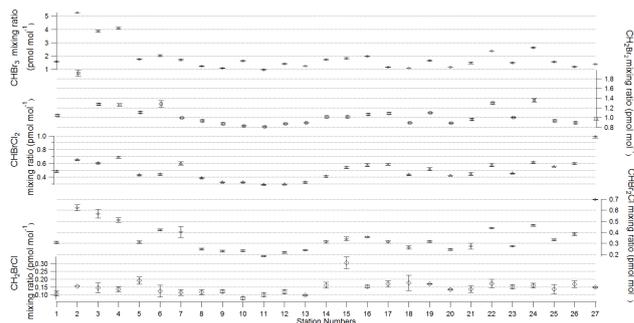


Figure 2. Bromocarbon mixing ratios for each station during PESC 2009.

for either June or July) were used, obtained from the NASA Goddard “Giovanni” online database (<http://oceancolor.gsfc.nasa.gov/SeaWiFS/>). Shorter (e.g. eight-day) averaging periods are available, but were found to be insufficient for full coverage of the cruise track, given the width of the viewing swath, the number of missing data on several overpasses, and differences between satellite sensors in ocean colour-derived chl *a*. There is a substantial difference in both the temporal and spatial scales between the monthly averaged and $9 \times 9 \text{ km}$ 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 and including the target grid box, depending on the values at each location (negative values were not considered).

3 Results and discussion

In the following sections we will, first, present an overview of the halocarbon data collected during PESC-09 (Sect. 3.1). We then discuss possible causes of any observed variability, focussing on an analysis of air parcel trajectories 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 VLSL to stratospheric bromine loading.

3.1 Halocarbon measurements

Mean and standard deviation of the measured halocarbon concentration at each site are given in Table 1 along with some comparison to 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 in Fig. 1. The most abundant bromine compound was CHBr_3 , with mean concentrations from around 1 pmol mol^{-1} to

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).

Area	Author	Bromocarbon mixing ratios					Chl <i>a</i> (mg m ⁻³) (std)	Turbidity (FTU)
		CHBr ₃ Mean (std) range	CHBr ₂ Cl Mean (std) range	CH ₂ Br ₂ Mean (std) range	CHBrCl ₂ Mean (std) range	CH ₂ BrCl Mean (std) range		
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 the tropical ocean								
Southeast 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				

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 CH₂Br₂ was 1.23 pmol mol⁻¹ (max = 2.21), with the minor species CHBr₂Cl, CHBrCl₂ and CH₂BrCl having mixing ratios in the mean 0.1 to 0.9 pmol mol⁻¹. For the anthropogenic tracer C₂Cl₄, 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 Strait of Malacca (stations 1–4)

PESC-09 took place during the Southwest Monsoon (SWM), when sea surface temperatures are slightly warmer (28–32 °C, May/June) than in the Northwest Monsoon (NWM) (25–29 °C, December/January). Tan et al. (2006) report that chl *a* in the Strait of Malacca shows seasonal variability, with concentrations increasing by as much as a factor of 2 (0.57 mgm⁻³ in August and 1.38 mgm⁻³ in January 1992–2002 on a monthly average) during the NWM compared to the SWM.

The highest concentrations of CHBr₃ were observed at the beginning of the cruise in the Strait of Malacca (SM). The mean concentration in samples 2–4 was 4.4 pmol 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 seaweed in coastal areas, especially in the region of 1–2° N, 102–103° W. Previous studies on chl *a* in the SM were influenced by nutrient input from rivers of Sumatra (Tan et al., 2006). CH₂Br₂, CHCl₂Br, CHClBr₂ and CHCl₃ were also enhanced in samples 2–4, which is indicative of similar sources.

3.2.2 South China Sea (stations 5–14)

Measurements in the SCS show fairly uniform and relatively low mixing ratios for all brominated compounds. For example, the mean values for CHBr₃, CH₂Br₂ and CHBr₂Cl 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 stations 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 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 high concentrations of up to 60 pmol mol^{-1} (the latter were attributed to measurement very close to local emissions). During their short measurement period in July 2008, the air flow was predominantly from the southeast, with back trajectories showing air travelling 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, backward trajectories did not indicate that air flow had 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 the western Pacific and SE Asia (see Table 1). For example, Yokouchi observed mixing ratios of CHBr_3 of 0.32 to 7.1 pmol mol^{-1} , which is similar to our study, with a range of 1.85–5.25 pmol mol^{-1} for CHBr_3 . This contrasts with the study of Yokouchi et al. (2005) over the western Pacific and Java Island, who observed high mixing ratios with a range of 16.3 to 31.4 pmol mol^{-1} at Christmas Island, and 4.2 to 43.6 pmol mol^{-1} at San Cristobal Island. Pyle et al. (2011) also observed high mixing ratios of CHBr_3 in Malaysian Borneo (near to stations 21 and 27 in this study), with a range of 2 to 60 pmol mol^{-1} . 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 in flux rates. Changes in VSLs emissions could arise from a number of complex factors. Emissions of VSLs are predominantly biogenic, with the ocean being 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 influ-

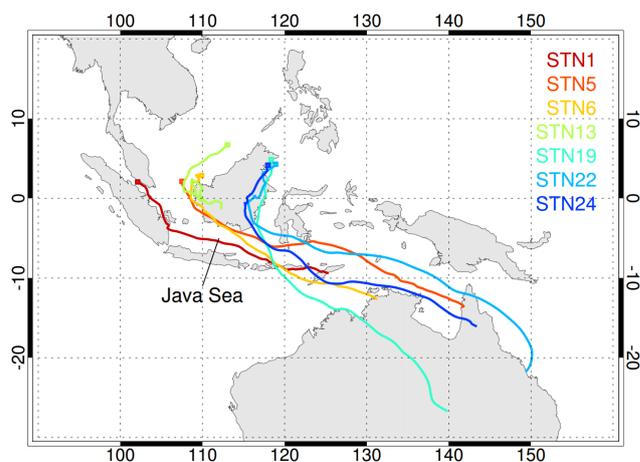


Figure 3. Ten-day air distribution backward trajectories calculated from the NOAA HYSPLIT model for each selected station.

ence 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 variability of the halocarbon concentrations during the cruise is the wind direction. Figure 3 shows selected ten-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), available at <http://www.arl.noaa.gov/ready.html>. In all cases the large-scale structure is consistent. Air masses arriving at the sampling locations originated from the southeast 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-09 cruise, and the origins of the measured air masses were very similar in both years.

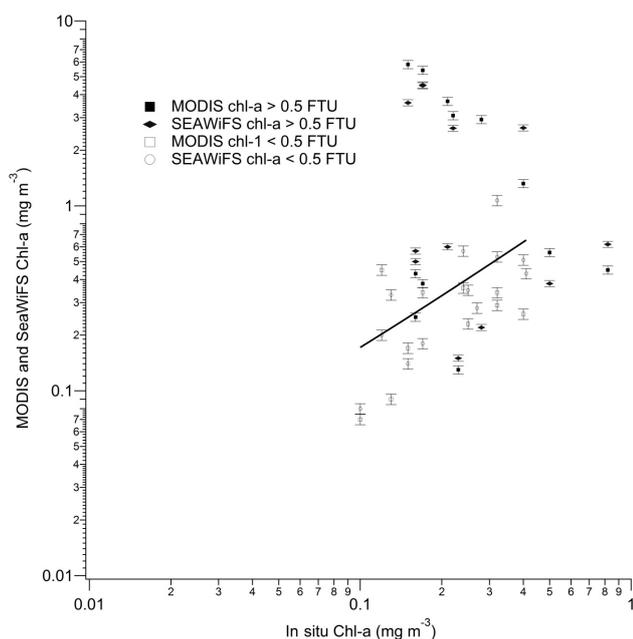


Figure 4. chl *a* concentrations from the satellite data plotted against in situ chl *a*. The solid symbols represent samples where turbidity was >0.5 FTU, and open symbols for turbidities <0.5 FTU. The line is a linear fit to the lower turbidity samples.

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. We compare the chl *a* measurements to 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 overlaid with the sampling stations. High chl *a* levels are commonly observed along the coastlines, seemingly indicating high phytoplankton abundance. Indeed, high satellite-derived chl *a* values were evident in the Strait of Malacca, where the highest CHBr₃ was measured. However, a plot of ocean colour-derived chl *a* from the two satellite sensors versus in situ chl *a* (Fig. 4) shows significant disagreement between the remotely sensed and in situ measurements. The standard deviations from the target grid box and those surrounding it are in the range of 1.1 to 32.4 mgm⁻³ for MODIS and 0.1 to 18.2 mgm⁻³ for SeaWiFS.

In Fig. 4, the filled symbols denote samples in which the turbidity was >0.5 FTU (Formazin turbidity unit), whereas the open symbols denote low turbidity (<0.5 FTU). It is apparent that the low 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 do not follow the positive linear regression line are characterised by satellite chl *a*

concentrations greater than 1 mg m⁻³ and turbidities greater than 0.5 FTU, implying that the satellite sensors overestimate chl *a* under such conditions. Indeed, the in situ measurements showed that ship-board measurements of chl *a* are lower than those made in the open ocean. We reiterate (refer back to Sect. 2.2) that there are difficulties in comparing coarse satellite data to in situ measurements, but believe that this type of comparison still provides valuable information from a data-sparse region.

Plots of bromocarbon air concentration versus satellite chl *a* concentration (Fig. 5) show a positive correlation, with the highest mixing ratios of CHBr₃ and CH₂Br₂ associated with above-average chl *a* values (> 5 mgm⁻³) for the MODIS and SeaWiFS satellites. Both satellite chl *a* products show *r*² values >0.6 against CHBr₃ and CH₂Br₂ (also CHBr₂Cl for MODIS), but other species show little correlation for both satellite chl *a* products. In situ chl *a* concentrations show a negative correlation for all bromocarbons species, with *r*² = -0.26 (*p* > 0.01) and *r*² = -0.21 (*p* > 0.01) for CHBr₃ and CH₂Br₂, respectively (see Fig. 5). The exact reason for the weak correlation of the bromocarbons and the in situ chl *a* data is unclear.

The above finding is not necessarily surprising even if phytoplankton are a source of such gases, since a connection between bromocarbons 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 are not necessarily driven solely by localised emissions. In this context, satellite-derived chl *a*, also providing information from a wider area, may potentially be more relevant than in situ measurements. 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 CHBr₃, 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 due to the lower marine productivity, especially in the coastal and open ocean regions of SCS (Fig. 1). We conclude that halocarbon concentrations are generally somewhat higher close to land and also higher in the Strait of Malacca; a connection to the coastal zone is thus 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 in coastal air 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

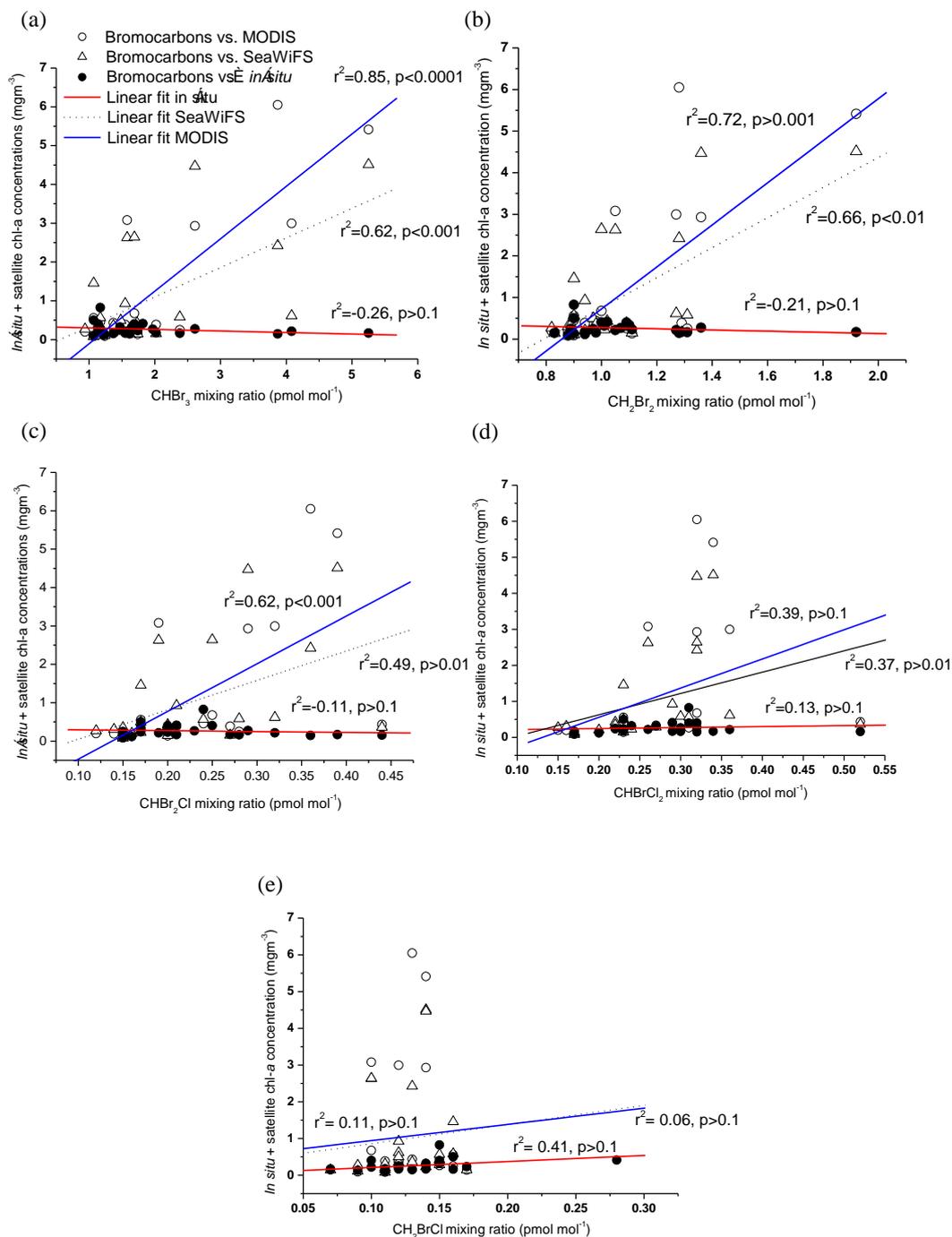


Figure 5. Monthly June–July 2009 in situ and satellite chl *a* concentrations as a function of VLS bromocarbon mixing ratios: (a) CHBr_3 , (b) CH_2Br_2 , (c) CHBr_2Cl , (d) CHBrCl_2 , and (e) CH_2BrCl .

al. (2009) all show that a log–log plot of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ versus CHBr_3 often shows a straight line, with the ratio $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ increasing with decreasing CHBr_3 . Atmospheric ratios of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ are often interpreted in the light of their differing atmospheric lifetimes, which are about 26 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, $\text{CHBr}_2\text{Cl}/\text{CHBr}_3$ would be higher at a 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

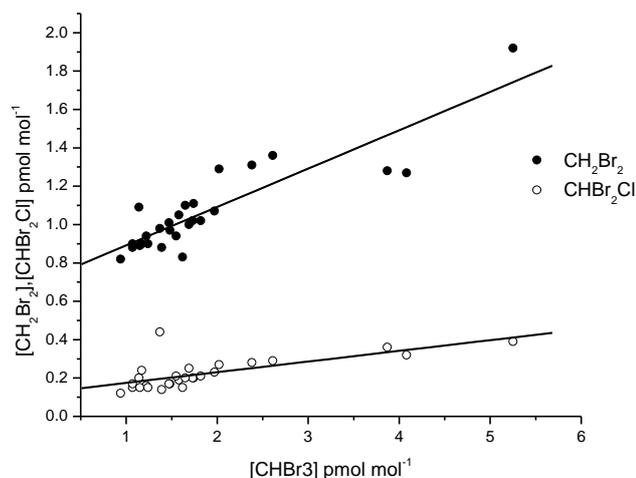


Figure 6. Plot for correlations of CH_2Br_2 and CHBr_2Cl versus CHBr_3 concentrations.

which CHBr_3 has been removed at a faster rate. Yokouchi et al. (2005) used the minimum ratio of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ 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. However, the emission ratio for $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ in the open ocean is different to (i.e. higher than) that in coastal areas, and so the assumption of a single characteristic seawater ratio is invalid, along with the extrapolation of source strength.

Figure 6 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 $r^2 = 0.9$), CHBr_3 and CHBr_2Cl ($r^2 = 0.7$), and CHBr_3 and CHBrCl_2 (correlation coefficient $r^2 = 0.5$) (not shown in the figure). These variations in correlation are consistent with the relationships observed in recent studies of the strength of emission of these different compounds from a range of Malaysian seaweeds (Leedham et al., 2013; Seh-Lin Keng et al., 2013). Figures 7a and b show the concentration ratios of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ and $\text{CHBr}_2\text{Cl}/\text{CHBr}_3$ plotted against CHBr_3 on a 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. $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ versus $\text{CHBr}_2\text{Cl}/\text{CH}_2\text{Br}_2$, 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 in the “background” atmosphere. Assuming that the emis-

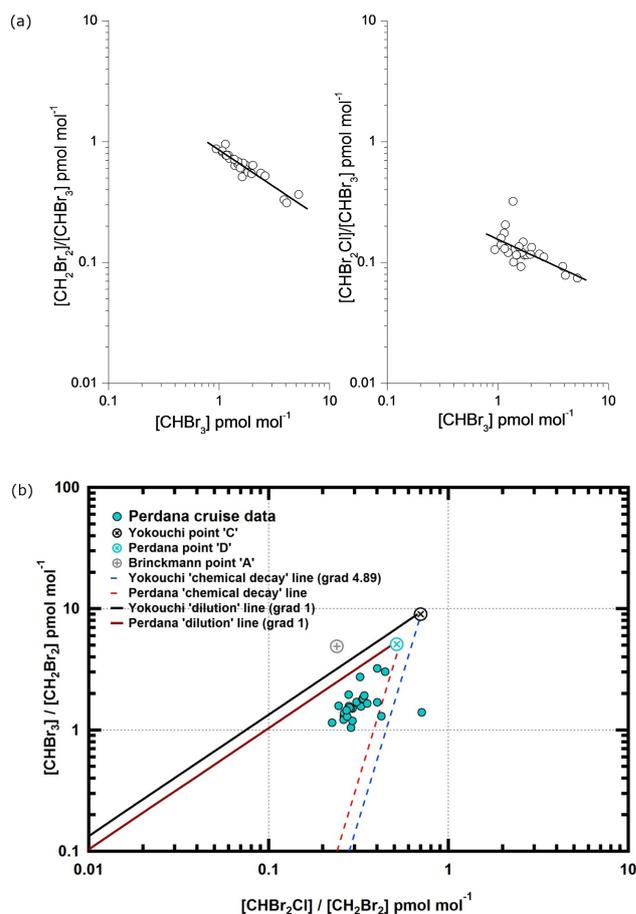


Figure 7. (a) Log–log plot $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ and $\text{CHBr}_2\text{Cl}/\text{CHBr}_3$ against CHBr_3 , and (b) log–log plots of $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ against $\text{CHBr}_2\text{Cl}/\text{CH}_2\text{Br}_2$ for all stations during the Perdana cruise, following Yokouchi et al. (2005) and Brinckmann et al. (2011). The solid line is the dilution line 1:1 and the solid dashed line is the chemical decay line estimated from the lifetime of the three 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). The decay line thus 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 the grey point is the point A in the Brinckmann et al. (2011) log–log plots where $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ is around 9 and $\text{CHBr}_2\text{Cl}/\text{CH}_2\text{Br}_2$ is around 0.7 from Yokouchi et al. (2005), and around 5 for $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ and 0.2 for $\text{CHBr}_2\text{Cl}/\text{CH}_2\text{Br}_2$ from Brinckmann et al. (2011).

sion 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 $823\text{--}1404\text{ Gg yr}^{-1}$ (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, $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ is plotted against $\text{CHBr}_2\text{Cl}/\text{CH}_2\text{Br}_2$ in Fig. 7b. 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 two lines, a point typically chosen to allow the lines to encompass the majority of the data, defines the emission ratios. Nearly all the data falls into a triangle whose vertex for $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ takes a value of 5 (point D in the figure). This is about half the value reported by Yokouchi et al. (2005) and O’Brien et al. (2009), but similar to the result obtained by Brinckmann et al. (2012) based on data collected on a recent western Pacific cruise. If we assume that this emission ratio of 5 is appropriate for the SE Asian region, (10° N to 20° S, 90° E 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 use the SEA regional CH_2Br_2 emission from an updated version of the Warwick et al. (2006) inventory (as used by Yang et al., 2014). As before, spatially uniform ocean emissions of CH_2Br_2 are assumed in the tropics, but emissions are halved, so that the global total of 57 Gg $\text{CH}_2\text{Br}_2/\text{yr}$ is more consistent with the recent studies of Liang et al. (2010) and Ordonez et al. (2012). In that case, with a SEA CH_2Br_2 emission of 6.4 Gg yr^{-1} , we obtain a regional emission, based on point D from Fig. 7b, of about 32 Gg yr^{-1} of CHBr_3 . This value is within the range obtained by Pyle et al. (2011), who estimated emissions of CHBr_3 for the same area to be between 21 and 50 Gg yr^{-1} . It is also consistent with the recent work of Ashfold et al. (2014), who estimated a total tropical CHBr_3 emission of 225 Gg yr^{-1} ; simply scaling this tropical number down (using the ratio of areas) to the SEA region considered here implies a CHBr_3 emission of 33 Gg yr^{-1} . Our estimates, and those of Pyle et al. (2011) and Ashfold et al. (2014), are all much less than the regional value in Warwick et al. (2006). To be more confident about our 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 the McKee 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 VLSL-derived bromine ($[\text{Br}]_{\text{VLSL}}$) in the 27 samples

was $8.9 \pm 3.7 \text{ pmol mol}^{-1}$. There is some regional variability, as discussed earlier, with SM having the highest $[\text{Br}]_{\text{VLSL}}$ (mean = $17.8 \text{ pmol mol}^{-1}$) compared to other sampled areas. Of this $8.9 \text{ pmol mol}^{-1}$, 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 $8.4 \text{ pmol mol}^{-1}$, with a range of 3.6–13.3 pmol mol^{-1} . With the exception of the Strait of Malacca, there does not appear to be a large regional enhancement of $[\text{Br}]_{\text{VLSL}}$ 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 “hotspot” for emissions.

The $[\text{Br}]_{\text{VLSL}}$ measured during the PESC-09 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 Strait of Malacca, the South China Sea and the Sulu and Sulawesi seas. These are warm, shallow ocean areas, and contain conditions likely to support high halocarbon production and emission into the atmosphere. The region is also important as a location of the strongest convection; therefore it represents potentially an important source region for the transport of marine boundary layer concentrations of VLSL to the upper troposphere and stratosphere.

Data were collected at 27 sites during the cruise. High bromoform concentrations ($4\text{--}5 \text{ pmol mol}^{-1}$) were measured in the nutrient-rich Strait of Malacca. Otherwise, concentrations were generally between 1 and 2 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. Furthermore, 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.

Our measurements of other compounds, including the less often reported mixed chloro-bromocarbons, are also reasonably consistent with the few other studies in the region (e.g. Quack and Suess, 1999 and Yokouchi et al., 1997; see Table 1). Our typical concentrations of $\text{CH}_2\text{Br}_2 \sim 1 \text{ pmol mol}^{-1}$, $\text{CHBr}_2\text{Cl} \sim 0.2\text{--}0.4 \text{ pmol mol}^{-1}$, $\text{CHBrCl}_2 \sim 0.2\text{--}0.3 \text{ pmol mol}^{-1}$ and

$\text{CH}_2\text{BrCl} \sim 0.1\text{--}0.2 \text{ pmol mol}^{-1}$ lead to a $[\text{Br}]_{\text{VLS}}$ of $8.9 \text{ pmol mol}^{-1}$. This is close to values obtained by Sala et al. (2014) from measurements collected in the planetary boundary layer of the same region during the SHIVA campaign (7.8 and $9.1 \text{ pmol mol}^{-1}$ using two separate instruments). The similarity suggests that boundary-layer VLS mixing ratios in this important region are beginning to be better characterised.

The bromocarbons were well correlated, suggesting common sources. Previously, such relationships were used to obtain global emission estimates. For a short-lived gas like bromoform, with an atmospheric lifetime of ~ 26 days, we do not think this approach is suitable; the footprint sampled by the cruise is regional at most. Instead, we used an approach as applied by Yokouchi et al. (2005) to provide a very rough estimate of the regional (SE Asia) emission ratio of bromoform to dibromomethane of about 5. Using an updated version of the Warwick et al. (2006) dibromomethane emissions leads to bromoform emissions of 32 Gg yr^{-1} for SE Asia (10° N to 20° S , 90° E to 160° E), which is in reasonable agreement with the recent estimates from Pyle et al. (2011) and Ashfold et al. (2014). Many 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 estimates looks to be a promising approach.

$\text{Chl } a$ was also measured on the cruise. There was little obvious correlation between this and the measured atmospheric halocarbon concentrations. Satellite measurements of $\text{chl } a$ suggested high values in the Strait 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 underwater in situ $\text{chl } a$ measurements were similar to those observed in the open sea. It seems likely that the higher halocarbon concentrations in the Strait maybe result from the local influence of the nearby coastal areas and land masses.

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

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