

1 **Bromocarbons in the tropical coastal and open ocean atmosphere during the 2009**

2 **Prime Expedition Scientific Cruise (PESC-09)**

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Abstract

32 Atmospheric concentrations of very short-lived species (VSLS) bromocarbons, including
33 CHBr_3 , CH_2Br_2 , CHCl_2Br , CHClBr_2 , CH_2BrCl , were measured in the Strait of Malacca, the
34 South China and Sulu-Sulawesi Seas during a two month research cruise in June-July 2009.

35 The highest bromocarbon concentrations were found in the Strait of Malacca, with smaller
36 enhancements in coastal regions of Northern Borneo. CHBr_3 was the most abundant
37 bromocarbon, ranging from $5.2 \text{ pmol mol}^{-1}$ in the Strait of Malacca to $0.94 \text{ pmol mol}^{-1}$ over
38 the open ocean. Other bromocarbons showed lower concentrations, in the range of 0.8-1.3
39 pmol mol^{-1} for CH_2Br_2 , 0.1-0.5 pmol mol^{-1} for CHCl_2Br and 0.1-0.4 pmol mol^{-1} for CHClBr_2 .

40 There was no significant correlation between bromocarbons and *in situ* chlorophyll-*a* but
41 positive correlations with both MODIS and SeaWiFS satellite's chlorophyll-*a*. Together the
42 short-lived bromocarbons contribute an average of $8.9 \text{ pmol mol}^{-1}$ (range $5.2\text{-}21.4 \text{ pmol mol}^{-1}$)
43 to tropospheric bromine loading, which is similar to that found in previous studies from
44 global sampling networks (Montzka et al., 2011). Statistical tests showed strong Spearman
45 correlations amongst brominated compounds, suggesting a common source. Log-log plots of
46 $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ versus $\text{CHBr}_2\text{Cl}/\text{CH}_2\text{Br}_2$ show that both chemical reactions and dilution into
47 the background atmosphere contribute to the composition of these halocarbons at each
48 sampling point. We have used the correlation to make a crude estimate of the regional
49 emissions of CHBr_3 and derive a value of 32 Gg yr^{-1} for the South East (SE) Asian region
50 ($10^\circ\text{N}\text{-}20^\circ\text{S}$, $90^\circ\text{E}\text{-}150^\circ\text{E}$). Finally, we note that satellite-derived chlorophyll-*a* (chl-*a*)
51 products do not always agree well with *in situ* measurements, particularly in coastal regions

52 of high turbidity, meaning that satellite chl-*a* may not always be a good proxy for marine
53 productivity.

54

55 **1 Introduction**

56 In recent years there has been a growing interest in the role of short-lived halocarbons in
57 atmospheric chemistry, in particular their potential involvement in stratospheric ozone
58 depletion. The term very short-lived substances (VSLS) has been used to represent halogen-
59 containing compounds with lifetimes less than six months (WMO, 2007). Bromine-
60 containing VSLS and their atmospheric degradation products are believed to account for
61 around a quarter of total bromine entering the lower stratosphere (Dorf et al., 2006; Salawich
62 et al., 2006; Montzka et al., 2011) and contribute to the ‘missing’ bromine (6 pmol mol⁻¹,
63 range 3-8 pmol mol⁻¹) required to the levels of inorganic bromine Br_y and BrO measured in
64 the stratosphere (Montzka et al., 2011).

65 The main brominated VSLS identified to date include bromoform (CHBr₃),
66 dibromomethane (CH₂Br₂), dichlorobromomethane (CHCl₂Br), dibromochloromethane
67 (CHClBr₂) and bromochloromethane (CH₂BrCl). Biogenic emissions from the oceans have
68 been identified as one of the main natural sources, where organisms such as macroalgae
69 (seaweeds) and microalgae (phytoplankton) can release large quantities of halocarbon gases
70 to the atmosphere (Sturges et al., 1993; Moore et al., 1996; Laturus and Adams, 1998).
71 Previous ship and coastal measurements have collected bromocarbon data for many different
72 global regions, summarised in Montzka et al. (2011). These studies show large temporal and
73 spatial variability in both seawater and atmospheric concentrations, emphasizing the
74 importance of localised emissions of these gases.

75 Because of their short atmospheric lifetimes, the region where VSLS are emitted into
76 the atmosphere is significant and their O₃ depletion potentials (ODPs) vary accordingly (Ko
77 et al., 2003). Tropical regions are believed to be the most important location for rapid
78 transport of air from the surface to the upper troposphere and lower stratosphere. In the
79 tropics, deep convection provides a major pathway for rapid transport of insoluble gases from
80 the lower to the upper troposphere. Importantly, such convective transport appears to be
81 particularly strong over the western Pacific (Gettelman et al., 2002; Fueglistaler et al., 2004).
82 Furthermore, the warm, shallow waters of the tropical warm pool make them potentially
83 important source regions for biologically-produced halocarbons. Therefore, this region has
84 the potential to supply a proportion of the 'missing' ~6 pmol mol⁻¹ of bromine, thought to be
85 related to VSLS, to the stratosphere.

86 Yokouchi et al. (1997) were the first to report atmospheric bromocarbon
87 measurements in the Strait of Malacca and the South China Sea. During a cruise between
88 Japan and the Bay of Bengal they measured mean concentrations of 0.77 pmol mol⁻¹ (max
89 1.42 pmol mol⁻¹) and 1.2 pmol mol⁻¹ (max 7.1 pmol mol⁻¹) for CH₂Br₂ and CHBr₃,
90 respectively. The highest levels were seen in harbour regions of Singapore and Penang and
91 the authors suggested a link between high CHBr₃ concentrations and high chlorophyll-*a* (chl-
92 *a*) and the influence of algal sources. During a cruise in the South China Sea, Quack and
93 Suess (1999) observed mean ambient air concentrations for bromoform of 1.2 pmol mol⁻¹
94 (range 0.38-10.67 pmol mol⁻¹).

95 A second cruise reported in Yokouchi et al. (1997) was made in the western Pacific
96 (Japan-SE Australia) where atmospheric mixing ratios were observed in the range of 0.13-
97 2.9 pmol mol⁻¹ for CHBr₃ and 0.14-1.58 pmol mol⁻¹ for CH₂Br₂. More recently, Yokouchi et
98 al. (2005) reported a larger range of bromocarbon concentrations, with CHBr₃ ranging from

99 ~1 pmol mol⁻¹ over the open ocean to ~40 pmol mol⁻¹ in the vicinity of tropical islands in the
100 western Pacific region. Butler et al. (2007a) collected data from seven open ocean cruises
101 spanning a ten-year period, covering much of the world's oceans. Their tropical air mean
102 mixing ratios for CHBr₃ and CH₂Br₂ were 1 pmol mol⁻¹ (0.4-2.1 pmol mol⁻¹) and 0.9 pmol
103 mol⁻¹ (0.6-1.3 pmol mol⁻¹) respectively.

104 Despite these measurements collected over the last two decades, the seas and
105 coastlines of SE Asia are still vastly under-represented. This knowledge gap introduces
106 uncertainties in our understanding of the global distributions and fluxes of bromocarbons and
107 therefore in our ability to predict future changes in global fluxes and their impact on
108 stratospheric ozone and climate. Pyle et al. (2011) reported measurements of bromocarbons
109 from two land-based sites in Borneo covering 3 weeks in June and July 2008. The coastal
110 measurements were characterised by large variability, from a background of 2 to 5 pmol mol⁻¹
111 of CHBr₃ to occasional measurements of hundreds of pmol mol⁻¹. Measurements around the
112 island were generally much lower and less variable, more consistent with the background of
113 about 1 pmol mol⁻¹. The data were used to make an estimate of the regional emission strength
114 of CHBr₃ which, depending on assumptions, ranged between 21 and 50 Gg/yr in SE Asia
115 (10°N x 20°S, 90°E to 160°E). For the purpose of comparison we will also consider
116 tetrachloroethylene (C₂Cl₄), which has predominantly industrial uses as a metal degreasing
117 solvent, and dry cleaning and can be considered as a tracer of anthropogenic activity (Pyle et
118 al., 2011).

119 How representative these Borneo measurements are of the whole SE Asia region is an
120 important question and one that was addressed by the *Prime Expedition Scientific Cruise* in
121 2009 (PESC-09). Selected halocarbons, including the five bromomethanes detailed above,
122 were measured in air samples collected in three different areas: the Strait of Malacca (SM),

123 the South China Sea (SCS) and the Sulu-Sulawesi Seas (SSS). Samples were collected at
124 both coastal and open ocean locations, sometimes close to the sites mentioned in Pyle et al.
125 (2011). The cruise and measurement details are presented in section 2. Results are presented
126 and discussed in section 3.

127

128 **2 Measurements**

129 **2.1 Cruise details**

130 The PESC-09 cruise was conducted by the Malaysian Royal Navy and Malaysian Ministry of
131 Science and Technology Innovation (MOSTI) and involved local government, private
132 research agencies and public universities in Malaysia. The vessel used was the Kapal Diraja
133 (Royal Ship) Perantau, which is designed and equipped for hydrographic surveying and for
134 conducting meteorological and oceanographic observations. The cruise started from Port
135 Klang ($2^{\circ}57' N 101^{\circ}20' E$) in the Strait of Malacca, on 18th June and ended at, Kota Kinabalu
136 ($6^{\circ}11' N 116^{\circ}10' E$) on 31st July. These paths were separated into four different legs: leg one
137 (Port Klang-Labuan); leg two (Labuan-Layang-layang Island-Kota Kinabalu); leg three (Kota
138 Kinabalu-Tawau) and leg four (Tawau- Kota Kinabalu). Figure 1 shows the ship's route
139 together with the location of the 27 air sampling stations.

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

146 2.2 Sampling and measurements

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

156 The samples were processed within four months of collection using a commercial
157 thermal desorption system (Markes UNITY™/Air Server). The analytical technique was
158 similar to that described by Worton et al. (2008). Air samples (1000 ml) were dried with a
159 Nafion™ counter-flow dryer prior to collection and pre-concentration on a 2-bed adsorbent
160 trap at -15°C. The desorbed analytes were separated on a capillary column (Restek 100 m x
161 0.32 mm RTX 102) using a temperature programme of 30°C (2 min), 8°C/min to 150 °C (16
162 min), 20°C/min to 220°C (5min). The mass spectrometer was operated in negative ion,
163 chemical ionisation (NICI) mode using methane (≥99.99%) as the reagent gas. The
164 quadrupole detector was run in single ion mode, monitoring m/z 35/37 for chlorinated, m/z
165 79/81 for brominated and m/z 127 for iodinated compounds. Samples were normally analysed
166 twice and referenced to a working standard. The working standard was an aluminium
167 cylinder containing dried ambient air at high pressure. The mole fractions of halocarbons in
168 the working standard were determined by repeat comparison to calibrated gas standards
169 supplied by NOAA-ESRL in electropolished stainless steel canisters (Essex Industries).

170 These comparisons are performed periodically and allow an assessment of any potential
171 changes in the absolute mole fractions of halocarbons in our working standard over time.
172 From comparisons with three separate NOAA standards: SX-3546 (comparison performed in
173 2008); SX-3570 (2010); and SX-3568 (2012) we believe the concentration of CHBr_3 in the
174 working standard has declined by approximately 40% over the period October 2008-
175 September 2012, whilst that of CH_2Br_2 has remained essentially unchanged (1.23 ± 0.07
176 pmol mol^{-1} , or 5.6%, 1σ). NOAA calibration data for the three mixed bromochloromethanes
177 were only available for the 2010 and 2012 comparisons, but our analysis shows that the
178 concentrations of CH_2ClBr and CHClBr_2 in the working standard have remained
179 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%
180 respectively) whilst that of CHCl_2Br may have increased by around 15% ($1.56 \pm 0.17 \text{ pmol}$
181 mol^{-1} , or 10.6%). The calibration factors applied to the PESC-09 data have been time-
182 corrected as appropriate. This drift analysis makes the underlying assumption that the five
183 bromocarbons are reliably stored in the Essex stainless steel cylinders.

184 The mole fractions reported here are on the latest NOAA scales for CH_2Br_2 (2004)
185 and CHBr_3 (2003), and on a preliminary NOAA scale for CH_2BrCl , CHBrCl_2 and CHBr_2Cl
186 (Brad Hall, personal communication). The uncertainty in the absolute mole fractions in the
187 working standard, based on combined uncertainties associated with the standard comparisons
188 and NOAA's stated uncertainties was $\pm 6.5\%$ for CH_2Br_2 , $\pm 7.1\%$ for CHBr_3 , $\pm 7.5\%$ for
189 CH_2ClBr , $\pm 5.9\%$ for CHCl_2Br and $\pm 6.8\%$ for CHClBr_2 . Mean analytical precision of the
190 actual PESC-09 samples was $<3\%$ for CH_2Br_2 and CHBr_3 , $<5\%$ for CHBrCl_2 and CHBr_2Cl ,
191 and $\sim 15\%$ for CH_2BrCl , due to its low abundance and low response in NICI).

192 *Chl-a* in the surface seawater was measured using the Kapal Diraja (KD) Perantau's
193 in-situ fluorometer attached to Sea-Bird SBE-911plus CTD (conductivity, temperature,

194 depth) system at all 27 sampling locations. The CTD equipment was operated together with a
195 package consisting of a 24-place, 10-liter rosette frame, a 24-place water sampler (SBE32)
196 and 24, 10-liter Niskin bottles sampler. This package was deployed at all stations. Several
197 fluorometers, turbidity sensors and pH measurements were attached to the CTD. The CTD
198 instrument was run and calibrated automatically at each station before sampling. The chl-*a*
199 concentration was measured from 1 m to 20 m depth with 5 m intervals. Readings were taken
200 at the sea surface approximately 1 m depth and have been compared with satellite-derived
201 chl-*a* data from SeaWiFS (Sea-Viewing Wide Field-of-view Sensor) and MODIS (Moderate
202 Resolution Imaging Spectroradiometer). Chl-*a* derived from ocean colour measurements
203 made during overpasses of the SeaWiFS and Aqua-MODIS satellite sensors were used to
204 determine apparent chl-*a* values in the nearest 9x9 km grid square to each sampling point.
205 The corresponding monthly average chl-*a* values (i.e. those for either June or July) were
206 used, obtained from the NASA Goddard ‘Giovanni’ on-line database
207 (<http://oceancolor.gsfc.nasa.gov/SeaWiFS/>). Shorter averaging periods are available (e.g. 8-
208 day) but were found to be insufficient for full coverage of the cruise track given the width of
209 the viewing swath, the level of missing data on several overpasses, and differences between
210 satellite sensors in ocean colour-derived chl-*a*. There is a substantial difference in both the
211 temporal and spatial scales between the monthly-averaged and 9x9 km grid-box averaged
212 satellite measurements and the near-instantaneous *in situ* ‘spot’ measurements. As an
213 indication of the level of uncertainty (at least that related to spatial scales) the standard
214 deviation of satellite-determined chl-*a* was calculated for the eight to ten grid boxes
215 surrounding and including the target grid box, depending on the values at each location
216 (negative values were not considered).

217

218 3. Results and Discussion

219 In the following sections we will, first, present an overview of the halocarbon data collected
220 during PESC-09 (section 3.1). We then discuss possible causes of any observed variability,
221 focussing on an analysis of air parcel trajectories and *in situ* measurements of chl-*a*, which
222 are a possible proxy for biological activity (section 3.2). In section 3.3 we explore
223 correlations between the measured species and provide a rough estimate of regional
224 bromoform emissions. Finally (section 3.4) we use the data to investigate the potential
225 contribution of VSLS to stratospheric bromine loading.

226

227 3.1 Halocarbon measurements

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

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240

241 3.2 Regional analysis

242 3.2.1 Strait of Malacca (Stations 1-4).

243 PESC-09 took place during the South West Monsoon (SWM) when sea surface temperatures
244 are slightly warmer (28-32°C, May/June) than in the North West Monsoon (NWM) (25-29°C,
245 December/January). Tan et al. (2006) report that chl-*a* in the Strait of Malacca shows
246 seasonal variability with concentrations increased by as much as a factor of two (0.57 mgm⁻³
247 in August and 1.38 mgm⁻³ in January 1992-2002 monthly average) during NEM compared to
248 SWM.

249 The highest concentrations of CHBr₃ were observed at the beginning of the cruise in the
250 Strait of Malacca (SM). The mean concentration in samples 2-4 was 4.4 pmol mol⁻¹, which is
251 similar to the levels in the same region reported by Yokouchi (1997). The enhanced levels
252 may be related to the high population of macro and micro algae such as phytoplankton and
253 seaweeds at coastal areas, especially in the region of 1-2°N, 102-103°W. Previous studies on
254 chl-*a* in the SM were influenced by nutrient input from rivers of Sumatra (Tan et al., 2006).
255 CH₂Br₂, CHCl₂Br, CHClBr₂ and CHCl₃ were also enhanced in samples 2-4, which is
256 indicative of similar sources.

257

258 3.2.2 South China Sea (Stations 5 to 14)

259 Measurements in the SCS show fairly uniform and relatively low mixing ratios for all
260 brominated compounds. For example, the mean values for CHBr₃, CH₂Br₂ and CHBr₂Cl were
261 1.46, 1.12 and 0.35 pmol mol⁻¹ respectively, with no significantly enhanced values. The
262 prevailing wind direction for most samples collected along this section of the cruise was
263 westerly, so the influence of any local coastal emissions would likely be low.

264 3.2.3 Sulawesi and Sulu Seas (Stations 15-27)

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

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

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287 3.3 Drivers of variability

288 The data collected during PESC-09 show relatively small variability, consistent with the ship
289 data reported by Yokouchi et al. (1997) over the western Pacific and South East Asia (see
290 Table 1). For example, Yokouchi observed mixing ratios of CHBr_3 of 0.32 to 7.1 pmol mol^{-1}
291 which is similar to our study, with a range of 1.85-5.25 pmol mol^{-1} for CHBr_3 . This contrasts
292 with the study of Yokouchi et al. (2005) over western Pacific and Java Island, who observed
293 high mixing ratios with a range of 16.3 to 31.4 pmol mol^{-1} at Christmas Island, and 4.2 to
294 43.6 pmol mol^{-1} at San Cristobal Island. Pyle et al. (2011) also observed high mixing ratios of
295 CHBr_3 in Malaysian Borneo (near to station 21 and 27 in this study), with a range of 2 to 60
296 pmol mol^{-1} . It seems likely that these latter studies both included data collected close to
297 emission sources.

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

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309

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311 **3.3.1 Meteorological variability**

312 A major factor controlling the variability of the halocarbon concentrations during the cruise is
313 the wind direction. Figure 3 shows selected 10-day air mass back trajectories for seven of the
314 cruise sampling locations calculated from the NOAA HYSPLIT model (R. R. Draxler and G.
315 D. Rolph, HYSPLIT- Hybrid Single-Particle Lagrangian Integrated Trajectory), available at
316 <http://www.arl.noaa.gov/ready.html>). In all cases the large-scale structure is consistent. Air
317 masses arriving at the sampling locations originated to the south east and have likely been
318 influenced by emissions from shallow, warm seas, including the South Java Sea. There is
319 therefore likely to be little variability associated with transport from different large-scale
320 emission regions, although local emissions close to the sampling locations could still be
321 important in driving local variability. For example, the trajectories arriving at site 22, near
322 Sipadan Island, or at station 19, near Kunak, are very likely to have been influenced by the
323 seaweed beds in that area. A similar conclusion was reached by Pyle et al. (2011) based on
324 their coastal Kunak measurements in June 2008, made one year earlier than the PESC-09
325 cruise and the origins of the measured air masses were very similar in both years.

326

327 **3.3.2 Biological activity**

328 Chl-*a* was also measured at 60 sites including 27 sites where halocarbons are measured
329 during the cruise, both *in situ* from the ship and remotely from satellite sensors. We compare
330 the chl-*a* measurements with the halocarbon data to explore possible biological drivers of
331 variability. Figure 1 plots the monthly average chl-*a* across the region from SeaWiFS for
332 June 2009 overlaid with the sampling stations. High chl-*a* levels are commonly observed
333 along the coastlines, seemingly indicating high phytoplankton abundance. Indeed high
334 satellite-derived chl-*a* values were evident in the Strait of Malacca, where the highest CHBr₃

335 was measured. However, a plot of ocean colour-derived chl-*a* from the two satellite sensors
336 versus *in situ* chl-*a* (Figure 4) shows significant disagreement between the remotely-sensed
337 and *in situ* measurements. The standard deviations from the target grid box and those
338 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
339 SeaWiFS.

340 In Figure 4, the filled symbols denote samples in which the turbidity was >0.5 FTU
341 (Formazin turbidity unit), whereas open symbols denote low turbidity (<0.5 FTU). It is
342 apparent that the low turbidity samples display a relatively compact relationship between
343 remotely-sensed and *in situ* chl-*a* and with absolute values that are in good quantitative
344 agreement. Indeed a linear regression on the lower turbidity samples yields a gradient of 1.0
345 (standard error of 0.1) and an r^2 value of 0.88. The points that do not follow the positive
346 linear regression line are characterised by satellite chl-*a* concentrations greater than 1 mg m⁻³,
347 and turbidities greater than 0.5 FTU, implying that the satellite sensors over-estimate chl-*a*
348 under such conditions. Indeed the *in situ* measurements showed that ship-board
349 measurements of chl-*a* are lower than those made in the open ocean. We reiterate (refer back
350 to Section 2.2) that there are difficulties in comparing coarse satellite data with *in situ*
351 measurements, but believe this type of comparison still provides valuable information from a
352 data-sparse region.

353 Plots of bromocarbon air concentration versus satellite chl-*a* concentration (Figure 5)
354 show a positive correlation, with the highest mixing ratios of CHBr₃ and CH₂Br₂ associated
355 with above average chl-*a* values (> 5 mgm⁻³) for MODIS and SeaWiFS satellites. Both
356 satellite chl-*a* products show R values > 0.6 against CHBr₃ and CH₂Br₂ (also CHBr₂Cl for
357 MODIS) but other species show little correlation for both satellite chl-*a* products. *In situ* chl-
358 *a* concentrations show negative correlation for all bromocarbons species with $r=-0.26$

359 ($p > 0.01$) and $r = -0.21$ ($p > 0.01$) for CHBr_3 and CH_2Br_2 , respectively (see figure 5). The exact
360 reason for the weak correlation of the bromocarbons and the *in situ* chl-*a* data is unclear.

361 The above finding is not necessarily surprising even if phytoplankton are a source of
362 such gases, since a connection between bromocarbons measured in the marine atmospheric
363 boundary layer and sub-surface biology may be dependent on other factors including wind
364 speed. Furthermore, the observed halocarbon concentrations might originate over a wide
365 geographic area and are not necessarily driven solely by localised emissions. In this context,
366 satellite-derived chl-*a*, also providing information from a wider area, may potentially be more
367 relevant than *in situ* measurements. Although turbidity measurements in the Strait of Malacca
368 (average of 3.3 FTU) were significantly higher than those in the South China Sea (average of
369 0.3 FTU; Table 1), coinciding with high CHBr_3 , the turbidity was almost as high close to land
370 near Semporna (average of 2.1 FTU for Stations 24-27), but with little evidence of
371 substantially enhanced halocarbons in the latter region due to the lower marine productivity
372 especially at the coastal and open ocean region of SCS (Figure 1). We conclude that
373 halocarbon concentrations are generally somewhat higher close to land and also higher in the
374 Strait of Malacca, thus a connection to the coastal zone is suspected, but there is little
375 evidence to connect this directly to open ocean microorganisms.

376

377 **3.4 Emission ratios**

378 Significant correlations between brominated halocarbons have been observed in coastal air
379 measurements suggesting that these gases have come from the same sources (Yokouchi et al.,
380 2005; O'Brien et al., 2009; Carpenter et al., 2009). Several studies have exploited these
381 correlations to explore the possible source strengths of the individual species. Carpenter et al.

382 (2003), Yokouchi et al. (2005) and O'Brien et al. (2009) all show that a log-log plot of
383 $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ versus CHBr_3 often shows a straight line with the ratio $\text{CH}_2\text{Br}_2/\text{CHBr}_3$
384 increasing with decreasing CHBr_3 . Atmospheric ratios of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ are often interpreted
385 in the light of their differing atmospheric lifetimes, which are about 26 days for CHBr_3 and
386 120 days for CH_2Br_2 (Montzka et al., 2011). The relationship between CHBr_3 and other
387 somewhat longer-lived brominated halocarbons such as CHBr_2Cl also showed similar
388 patterns, for example $\text{CHBr}_2\text{Cl}/\text{CHBr}_3$ would be higher at lower concentration of CHBr_3 .
389 Since CHBr_3 has the shorter lifetime of the two species, an increase in the ratio would be
390 consistent with more aged air masses, in which CHBr_3 has been removed at a faster rate.
391 Yokouchi et al. (2005) used the minimum ratio of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ to define the ratio of the
392 emission sources by assuming that the emissions came from the common sources and are
393 constant on a regional scale. If the global emission of CH_2Br_2 is known, then that of CHBr_3
394 can be inferred. However the emission ratio for $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ in the open ocean is different
395 (i.e. higher) to that in coastal areas and so the assumption of a single characteristic seawater
396 ratio is invalid, along with the extrapolation of source strength.

397 Figure 6 shows the relationships between CH_2Br_2 and CHBr_3 and between CHBr_2Cl
398 and CHBr_3 for each data set. Correlations are strong between CH_2Br_2 and CHBr_3 (correlation
399 coefficient, $r = 0.9$), CHBr_3 and CHBr_2Cl ($r = 0.7$) and CHBr_3 and CHBrCl_2 (correlation
400 coefficient $r = 0.5$) (not shown in the figure). These variations in correlation are consistent
401 with the relationships observed in recent studies of the strength of emission of these different
402 compounds from a range of Malaysian seaweeds (Leedham et al., 2013; Seh-Lin Keng et al.,
403 2013). Figures 7a and 7b show the concentration ratios of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ and
404 $\text{CHBr}_2\text{Cl}/\text{CHBr}_3$ plotted against CHBr_3 on a log-log scale, with both ratios increasing linearly

405 as CHBr_3 decreases; CHBr_3 , with its shorter lifetime, is a possible measure of time since co-
406 emission. These figures are consistent with those reported by Yokouchi et al. (2005).

407 Yokouchi et al. (2005), following McKeen and Liu (1993), used plots of pairs of
408 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
409 explore the possible emission strengths of the individual species. Making a number of
410 assumptions, in such a plot the location of individual points in ratio space is determined by
411 the emission ratio at an (assumed) common regional source and by the ratio of the rates of
412 chemical removal and mixing into the ‘background’ atmosphere. Assuming that the emission
413 source strength of one species is known, that of the others can be obtained using the ratio
414 determined from the plot. Using this method, O’Brien et al. (2009) estimated a global
415 emission of bromoform of 823-1404 Gg/yr (values depend *inter alia* on the assumed CH_2Br_2
416 emissions) using data collected at Cape Verde in June 2006. This emission is much higher
417 than estimates in Ko et al. (2003), or in Warwick et al. (2006). However, Pyle et al. (2011)
418 suggest that it is not reasonable to derive global emission estimates from regional data for a
419 short-lived species such as bromoform. They showed that data from Borneo could instead
420 only be used to constrain regional emissions.

421 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
422 Figure 7b. The left side of the triangle is the ‘dilution line’ (the 1:1 slope for mixing into a
423 zero background) and the ‘chemical decay line’, defined by the ratio of lifetimes of individual
424 species due to photochemistry, is the right hand line. The intersection of these 2 lines, a point
425 typically chosen to allow the lines to encompass the majority of the data, defines the emission
426 ratios. Nearly all the data falls into a triangle whose vertex for $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ takes a value
427 of 5 (point D on the figure). This is about half the value reported by Yokouchi et al. (2005)
428 and O’Brien et al. (2009) but similar to the result obtained by Brinckmann et al. (2012) based

429 on data collected in a recent western Pacific cruise. If we assume that this emission ratio of 5
430 is appropriate to the SE Asian Region, (10°N to 20°S, 90°E to 160°E, as used by Pyle et al.
431 (2011)) and recalling that the air mass histories in the two periods of these two studies are
432 quite similar, then we could derive an emission estimate for CHBr_3 from the regional CH_2Br_2
433 emission. That value is not observationally constrained; instead we use the SEA regional
434 CH_2Br_2 emission from an updated version of the Warwick et al. (2006) inventory (as used by
435 Yang et al., 2014). As before, spatially uniform ocean emissions of CH_2Br_2 are assumed in
436 the tropics, but emissions are halved so that the global total of 57 Gg CH_2Br_2 /yr is more
437 consistent with the recent studies of Liang et al. (2010) and Ordonez et al. (2012). In that
438 case, with a SEA CH_2Br_2 emission of 6.4 Gg/yr, we obtain a regional emission, based on
439 point D from figure 7b, of about 32 Gg/yr of CHBr_3 . This value is within the range obtained
440 by Pyle et al (2011), who estimated emissions of CHBr_3 , for the same area, to be between 21
441 and 50 Gg/yr. It is also consistent with the recent work of Ashfold et al. (2014), who
442 estimated a total tropical CHBr_3 emission of 225 Gg/yr; simply scaling this tropical number
443 down (using the ratio of areas) to the SEA region considered here implies a CHBr_3 emission
444 of 33 Gg/yr. Our estimates, and those of Pyle et al. (2011) and Ashfold et al. (2014), are all
445 much less than the regional value in Warwick et al. (2006). To be more confident about our
446 emission value would require, amongst other things, improved estimates of the CH_2Br_2
447 emission. However, the consistency of the calculations does suggest that useful constraints on
448 regional estimates can be obtained based on McKeen and Liu (1993) plots.

449

450 **3.5 Total bromine**

451 The cruise data can be used to give an upper limit on the amount of bromine which could
452 potentially reach the stratosphere, i.e. by summing the measured bromine mixing ratios and

453 weighting by the number of bromine atoms. The mean VSLs-derived bromine ($[\text{Br}]_{\text{VSLs}}$) in
454 the 27 samples was $8.9 \pm 3.7 \text{ pmol mol}^{-1}$. There is some regional variability as discussed
455 earlier, with SM having the highest $[\text{Br}]_{\text{VSLs}}$ (mean = $17.8 \text{ pmol mol}^{-1}$) compared to other
456 sampled areas. Of this $8.9 \text{ pmol mol}^{-1}$, CHBr_3 contributes ~65% and CH_2Br_2 25%. This is
457 similar to results compiled by Montzka et al. (2011) for which an average total bromine from
458 the same gases in the tropical marine boundary layer (mostly from open ocean
459 measurements) is given as $8.4 \text{ pmol mol}^{-1}$ with a range of 3.6–13.3 pmol mol^{-1} . With the
460 exception of the Strait of Malacca, there does not appear to be a large regional enhancement
461 of $[\text{Br}]_{\text{VSLs}}$ in our data, despite the cruise having taken place mostly within 50 km of the
462 coast. The data do not suggest that this part of SE Asia is a ‘hot spot’ for emissions.

463 The $[\text{Br}]_{\text{VSLs}}$ measured during the PESC-09 cruise are likely to account for some of
464 the ‘missing’ bromine entering the stratosphere, assuming conservative transport of the
465 constituent bromine either in the form of the source gas itself, or as brominated product
466 gases.

467

468 **4. Conclusions**

469 We report *in situ* halocarbon and ancillary data obtained during a research cruise of
470 the Perantau in June and July 2009. The cruise covered the Strait of Malacca, the South China
471 Sea and the Sulu and Sulawesi Seas. These are warm, shallow ocean areas and contain
472 conditions likely to support high halocarbon production and emission to the atmosphere. The
473 region is also important as a location of the strongest convection, therefore it thus represents
474 potentially an important source region for the transport of marine boundary layer
475 concentrations of VSLs to the upper troposphere and stratosphere.

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

485 Our measurements of other compounds, including the less often reported mixed
486 chloro-bromocarbons, are also reasonably consistent with the few other studies in the region
487 (e.g. Quack and Suess, 1999; Yokouchi et al., 1997, see table 1). Our typical concentrations
488 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
489 $\text{CH}_2\text{BrCl} \sim 0.1\text{-}0.2 \text{ pmol mol}^{-1}$ lead to a $[\text{Br}]_{\text{VSLs}}$ of $8.9 \text{ pmol mol}^{-1}$. This is close to values
490 obtained by Sala et al., (2014) from measurements collected in the planetary boundary layer
491 of the same region during the SHIVA campaign (7.8 and $9.1 \text{ pmol mol}^{-1}$ using two separate
492 instruments). The similarity suggests boundary layer VSLs mixing ratios in this important
493 region are beginning to be better characterised.

494 The bromocarbons were well correlated, suggesting common sources. Previously,
495 such relationships have been used to obtain global emission estimates. For a short-lived gas
496 like bromoform, with an atmospheric lifetime of ~ 26 days, we do not think this approach is
497 suitable; the footprint sampled by the cruise is regional at most. Instead, we used an approach
498 as applied by Yokouchi et al. (2005) to provide a very rough estimate of the regional (S.E.
499 Asia) emission ratio of bromoform to dibromomethane of about 5. Using the

500 dibromomethane emissions from Liang et al. (2010) leads to bromoform emissions of 32 Gg
501 yr⁻¹ for S.E. Asia (10°N to 20°S, 90°E to 160°E), which is in reasonable agreement with the
502 recent estimates from Pyle et al. (2011) and Ashfold et al. (2014). Much more data, not least
503 on CH₂Br₂ emissions, would be required to confirm this estimate, but the use of species
504 correlations for regional emission estimates looks to be a promising approach.

505 Chl-*a* was also measured on the cruise. There was little obvious correlation between
506 this and the measured atmospheric halocarbon concentrations. Satellite measurements of chl-
507 *a* suggested high values in the Strait of Malacca, coinciding with high turbidity and high
508 halocarbon concentrations. However, it seems likely that the satellite data were affected by
509 the high turbidity in these waters, and the underwater *in situ* chl-*a* measurements were similar
510 to those observed in the open sea. It seems likely that the higher halocarbon concentrations in
511 the Strait maybe result from local influence of the nearby coastal areas and land masses.

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

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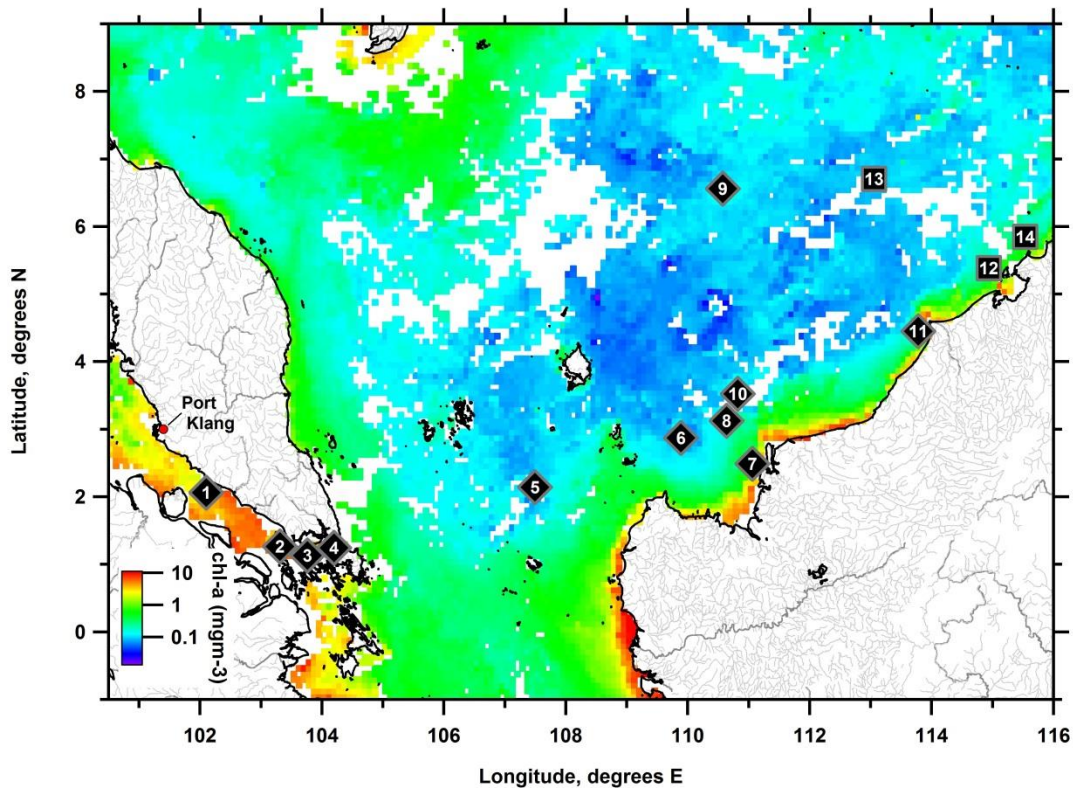
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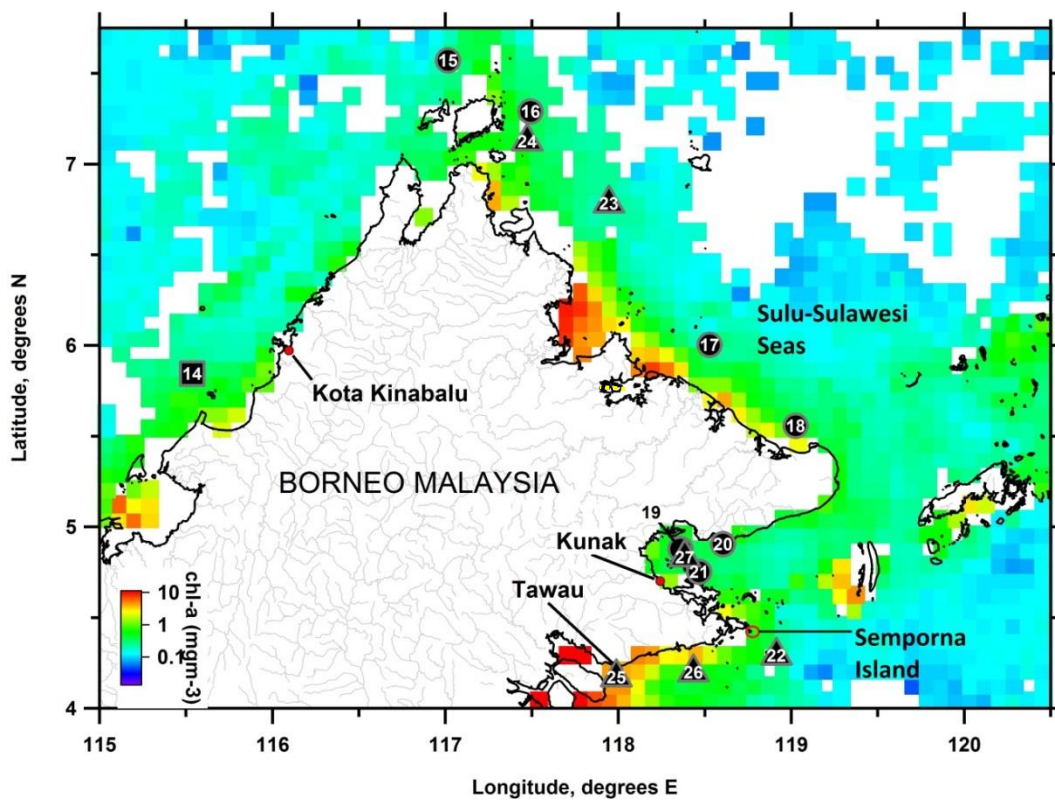
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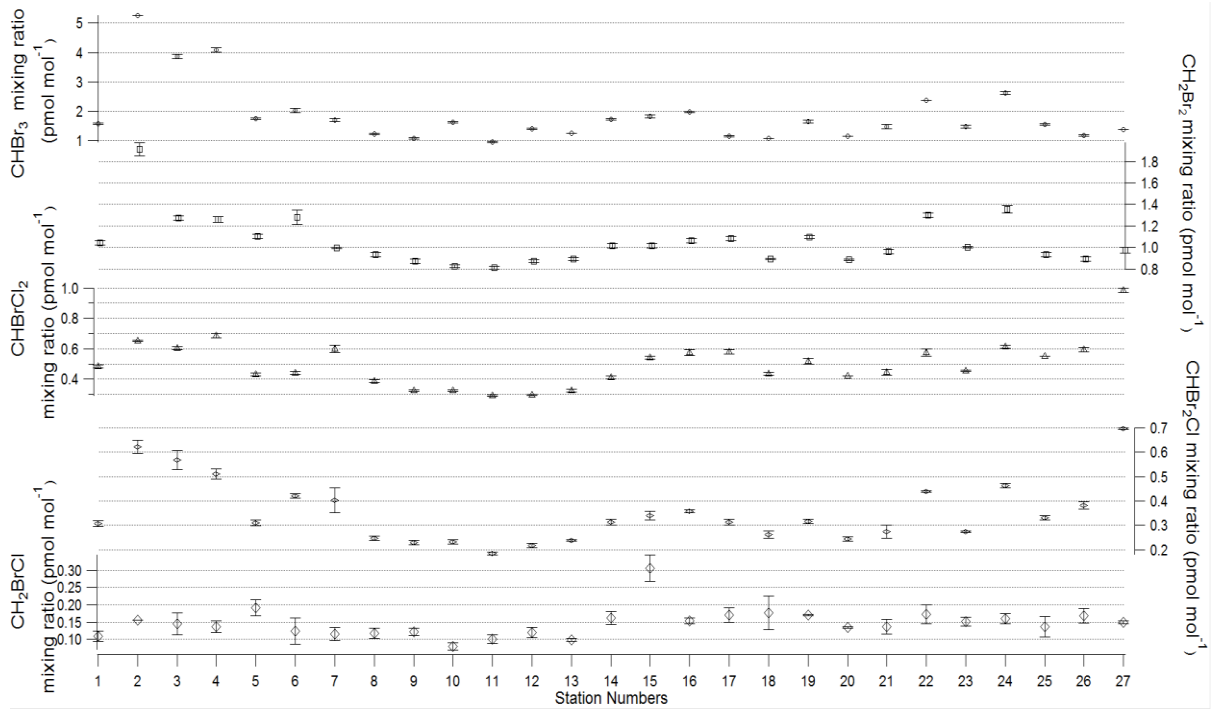


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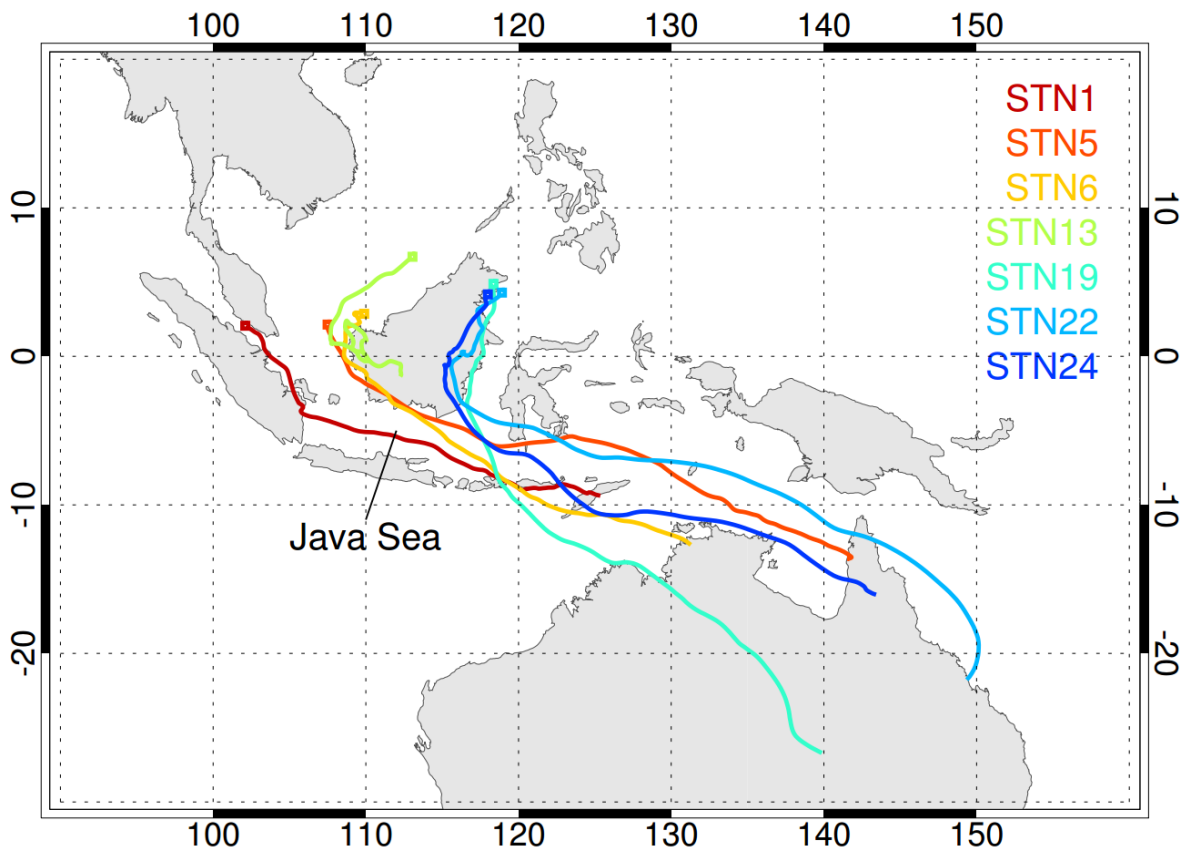
710 **Figure 1:** Sampling locations overlaid with SeaWiFS chl-a during PESC-09 (Labels:
 711 diamond = 1st leg; square = 2nd leg; circle = 3rd leg and triangle = 4th leg).



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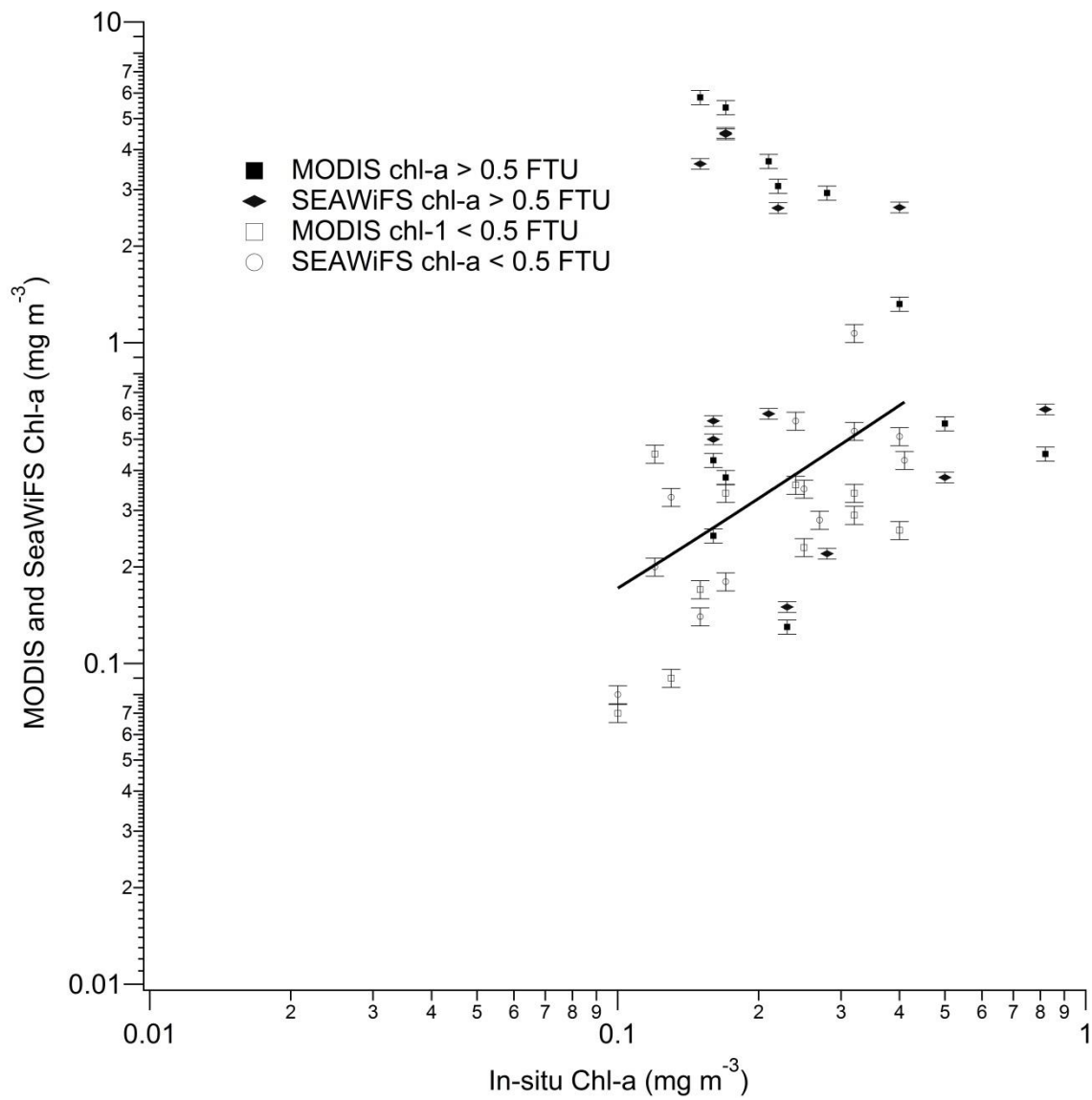
713 **Figure 2:** Bromocarbon mixing ratios for each station during PESC-09.

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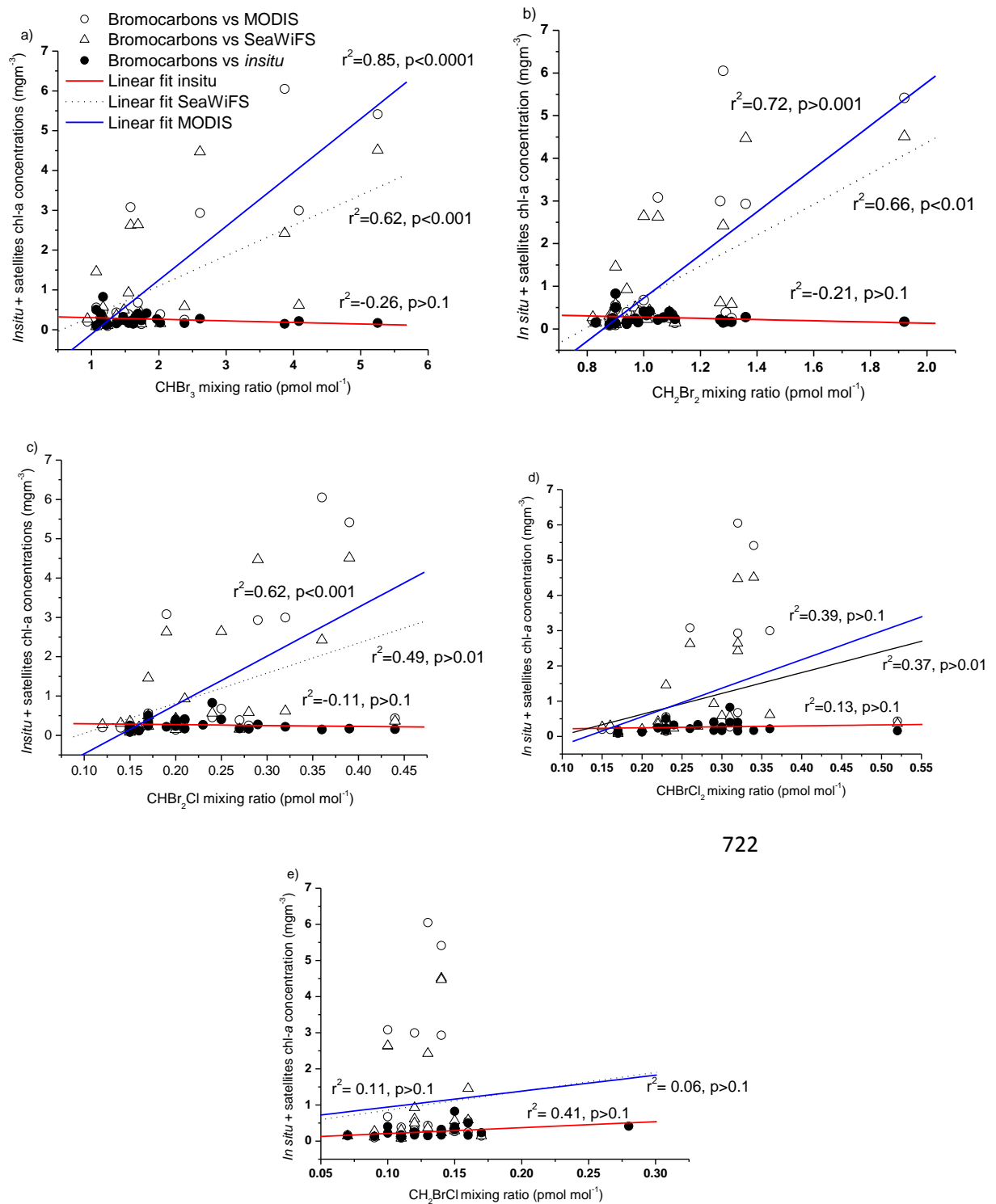
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716 **Figure 3:** 10 days air distribution backward trajectories calculated from the NOAA
717 HYSPLIT model for selected stations.



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719 **Figure 4:** Chl-*a* concentration from the satellite data plotted against *in-situ* chl-*a*. The solid
 720 symbols represent samples where turbidity was >0.5 FTU, and open symbols for turbidities
 721 <0.5 FTU. The line is a linear fit to the lower turbidity samples.



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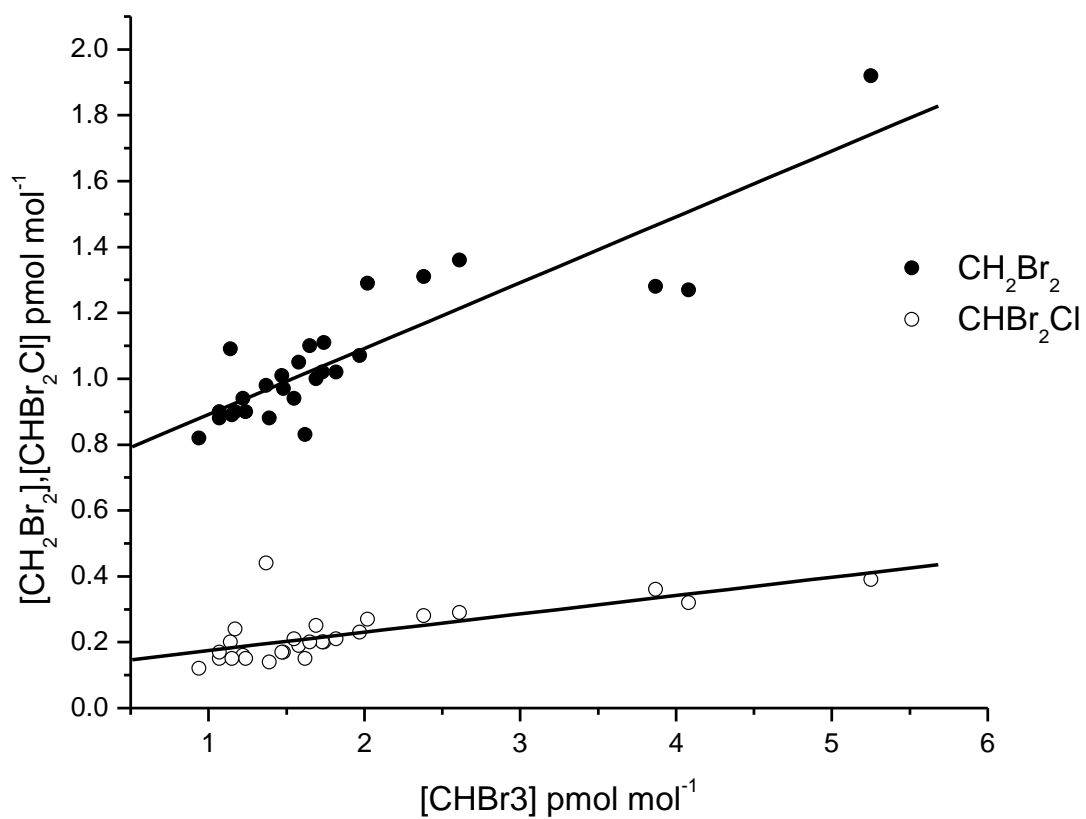
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730 **Figure 5:** Monthly June-July 2009 *in situ* and satellite chl-a concentration as a function of
 731 VLS bromocarbons mixing ratios a) CHBr_3 , b) CH_2Br_2 c) CHBr_2Cl d) CHBrCl_2 and e)
 732 CH_2BrCl .

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736 **Figure 6:** Plot for correlations of CH_2Br_2 and $CHBr_2Cl$ versus $CHBr_3$ concentrations.

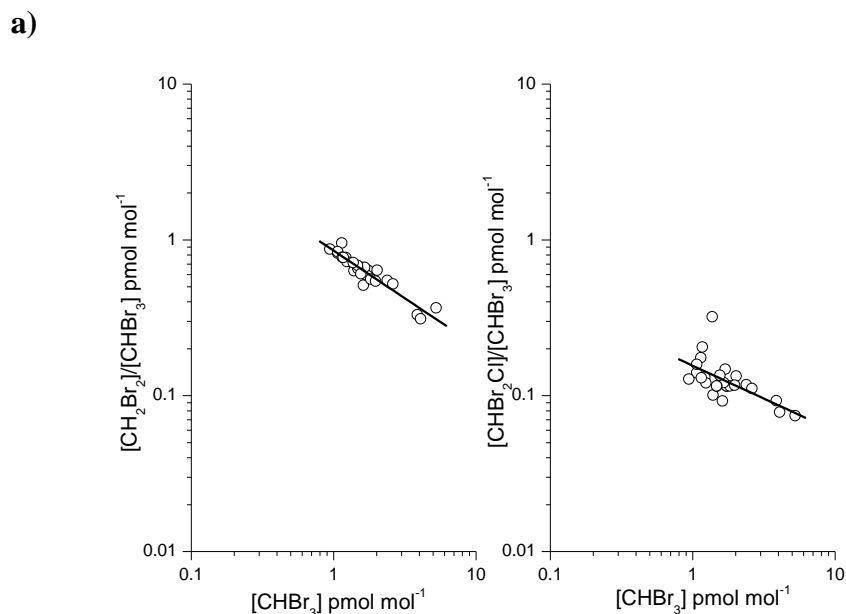
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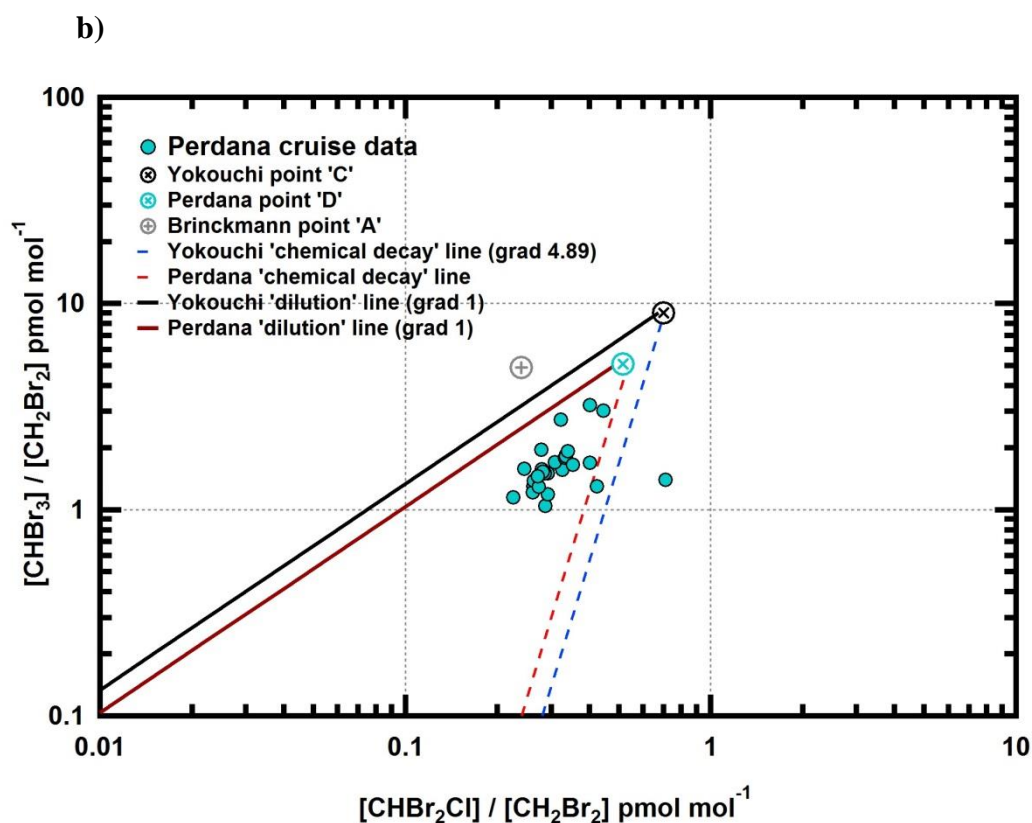
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745 **Figure 7a) Log-log plot $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ and $\text{CHBr}_2\text{Cl}/\text{CHBr}_3$ against CHBr_3 and 7b)**
 746 **Log-log plots of $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ against $\text{CHBr}_2\text{Cl}/\text{CH}_2\text{Br}_2$ for all stations during Perdana**
 747 **Cruise, following Yokouchi et al. (2005) and Brinckmann et al., (2011). The solid line is the**
 748 **dilution line 1:1 and the solid dash line is the chemical decay line which estimated from the**
 749 **lifetime of the 3 species in the atmosphere. In this case, we have followed the example of**
 750 **Yokouchi et al. (2005) by using the lifetimes of 26 days (CHBr_3), 69 days (CHBr_2Cl) and 120**
 751 **days (CH_2Br_2). Thus the decay line has a slope of 4.89. The black point at the top of the data**

752 set is the point C in Yokouchi et al. (2005) and grey point is the point A in Brinckmann et al.,
753 (2011) log-log plots where $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ to be around 9 and $\text{CHBr}_2\text{Cl}/\text{CH}_2\text{Br}_2$ to be around
754 0.7 from Yokouchi et al. (2005) and around 5 for $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ and 0.2 for
755 $\text{CHBr}_2\text{Cl}/\text{CH}_2\text{Br}_2$ from Brinckmann et al. (2011).

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

Area	Author	No. of samples	Bromocarbon's Mixing ratios					<i>Chl-a</i> (mgm ⁻³) (std)	Turbidity (FTU)
			CHBr₃ Mean (std) <i>range</i>	CHBr₂Cl Mean (std) <i>range</i>	CH₂Br₂ Mean (std) <i>range</i>	CHBrCl₂ Mean (std) <i>range</i>	CH₂BrCl Mean (std) <i>range</i>		
Strait of Malacca									
coastal	This study	4	3.69 (1.54) <i>1.85-5.25</i>	0.32(0.09) <i>0.19-0.39</i>	1.38(0.37) <i>1.05-1.92</i>	0.12 (0.02) <i>0.19-0.39</i>	0.12 (0.04) <i>0.1-0.14</i>	0.19(0.3)	3.33(1.22)
South China Sea									
Open ocean	This study	6	1.51 (0.4) <i>1.07-2.02</i>	0.21(0.05) <i>0.15-0.27</i>	1.01(0.19) <i>0.88-1.29</i>	0.22 (0.07) <i>0.17-0.32</i>	0.10 (0.01) <i>0.09-0.11</i>	0.17 (0.09)	0.19 (0.07)
coastal	This study	5	0.90(0.32) <i>0.82-1.02</i>	0.15(0.08) <i>0.12-0.2</i>	0.90(0.09) <i>0.82-1.02</i>	0.18(0.03) <i>0.15-0.22</i>	0.10(0.03) <i>0.07-0.15</i>	0.22(0.12)	0.15(0.07)
Sulu-Sulawesi seas									
coastal	This study	12	1.60(0.5) <i>1.07-2.61</i>	0.23(0.08) <i>0.15-0.44</i>	1.04(0.16) <i>0.89-1.36</i>	0.3(0.08) <i>0.22-0.52</i>	0.15(0.04) <i>0.12-0.28</i>	0.32(0.2)	1.54(0.92)
Previous studies in tropical regions									
South east Asia 100-105°E	Youkouchi et al., 1995		1.2 (n.m) <i>0.3-7.1</i>		0.77(n.m) <i>0.38-1.42</i>				
Western Pacific 43°N, 150°E & 4°N, 113°E	Quack & Suess., 1999		1.2(n.m) <i>0.38-10.67</i>	0.2(n.m) <i>0.07-1.34</i>		0.28(n.m) <i>0.08-2.96</i>			
San Cristobal Island (Loberia)	Youkouchi et al., 2005		14.2 (10.1) <i>4.2-43.6</i>	1.5(1.0) <i>0.5-4.1</i>	3.2(1.5) <i>1.8-7.6</i>				
Christmas Island (Topono)	Youkouchi et al., 2005		23.8 (10.7) <i>16.3-31.4</i>	2.0 (0.7) <i>1.5-2.4</i>	3.0 (1.0) <i>2.3-3.7</i>				
Java Island	Youkouchi et al., 2005		0.9 (0.4) <i>0.4-1.6</i>	0.2 (0.2) <i>0.1-0.6</i>	0.9 (0.2) <i>0.6-1.5</i>				
Pacific Equator	Youkouchi et al., 2005		1.9(0.9) <i>0.8-3.5</i>	0.3(0.1) <i>0.1-0.6</i>	1.3(0.5) <i>0.2-1.9</i>				