Long term halocarbon observations from a coastal and an inland site in Sabah, Malaysian Borneo

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Abstract

Short lived halocarbons are believed to have important sources in the tropics where rapid vertical transport could provide a significant source to the stratosphere. In this study, quasi-continuous measurements of short-lived halocarbons are reported for two tropical sites in Sabah (Malaysian Borneo), one coastal and one inland (rainforest). We present the observations for C_2Cl_4, $CHBr_3$, $CH_2Br_2^*$ (actually ~80% CH_2Br_2 and ~20% $CHBrCl_2$) and CH_3I from November 2008 to January

2010 made using our µDirac gas chromatographs with electron capture detection (GC-ECD). We focus on the first 15 months of observations, showing over one annual cycle for each compound and therefore adding significantly to the few limited-duration observational studies that have been conducted thus far in southeast Asia. The main feature in the C_2Cl_4 behaviour at both sites is its annual cycle with the winter months being influenced by northerly flow with higher concentrations, typical of the northern hemisphere, with the summer months influenced by southerly flow and lower concentrations representative of the southern hemisphere. No such clear annual cycle is seen for $CHBr_3$, $CH_2Br_2^*$ or CH_3I. The baseline values for $CHBr_3$ and $CH_2Br_2^*$ are similar at the coastal (overall median: $CHBr_3$ 1.7 ppt; $CH_2Br_2^*$ 1.4 ppt) and inland sites ($CHBr_3$ 1.6 ppt, $CH_2Br_2^*$ 1.1 ppt), but periods with elevated values are seen at the coast (overall 95th percentile: $CHBr_3$ 4.4 ppt; $CH_2Br_2^*$ 1.9 ppt) presumably resulting from the stronger influence of coastal emissions. Overall median bromine values from $[CHBr_3] + [CH_2Br_2^*]$ are 8.0 ppt at the coast and 6.8 ppt inland. The median values reported here are largely consistent with other limited tropical data and imply that southeast Asia generally is not, as has been suggested, a hot-spot for emissions of these compounds. These baseline values are consistent with the most recent emissions found for southeast Asia using the p-TOMCAT model. CH_3I, which is only observed at the coastal site, is the shortest-lived compound measured in this study and the observed atmospheric variations reflect this, with high variability throughout the study period.

1 Introduction

Reactions involving halogen compounds play an important role in the chemistry of both the stratosphere (e.g. Molina and Rowland, 1974; Yung et al., 1980) and the troposphere (e.g. Read et al., 2008). The sources of halogens are many and varied with important anthropogenic and natural components for many compounds (Montzka and Reimann, 2011). Total atmospheric bromine concentrations are generally dominated by the halons (compounds of only anthropogenic origin widely used for fire control) and CH_3Br (used in agriculture, but with many sources). Their atmospheric concentrations are well known and their lifetimes long enough to know with reasonable accuracy how much of these gases reaches the stratosphere. It was thus puzzling to find that they could only account for 70-80% of the bromine observed in the stratosphere (Wamsley et al., 1998; Dorf et al., 2006) though there remains uncertainty as to whether the discrepancy is that large (Kreycy et al., 2013).

Since there are no other known long-lived sources, the finger of suspicion points to the shorter-lived $CHBr_3$ and CH_2Br_2 which are observed in high concentration in the marine boundary layer and are naturally produced in the surface ocean (e.g. Yokouchi et al., 2005; Butler et al., 2007; Zhou et al., 2008; O'Brien et al., 2009). For these compounds to be the source of the missing 20-30% of the stratospheric bromine budget, they (or their breakdown products) have to be rapidly transported up to the stratosphere. The only credible place for this to occur is at low latitudes where upward transport can be very rapid in the intense tropical convection. This possibility has been investigated in a number of measurement (Schauffler et al., 1999; Laube et al., 2008; Park et al., 2010; Brinckmann et al., 2012) and modelling (Levine et al., 2007, 2008; Aschmann et al., 2009; Hosking et al., 2010; Hossaini et al., 2010, 2012 & 2013) studies and overall it seems likely that the short-lived bromocarbons are responsible for the apparent deficit.

One of the limitations on these studies is the scarcity of high quality measurements in the regions of most importance, i.e. in the highly convective areas. The majority of reported tropical boundary layer measurements have been made using whole air samplers or short-term deployments of GC systems (Yokouchi et al., 2005; O'Brien et al., 2009; Pyle et al., 2011), or ship-borne measurements made during research cruises (Butler et al., 2007; Carpenter et al., 2009; Quack et al., 2004, 2007; Yokouchi et al., 1997; Nadzir et al., 2013 (submitted); Brinckmann et al., 2012). No long-term and continuous measurements in the tropics have been reported to date.

Accordingly, we have set up a small network of instruments to make continuous measurements at a number of sites in the West Pacific / southeast Asian region. This region was chosen as it is where convection is strongest, especially during NH winter (e.g. Newell and Gould-Stewart, 1981; Gettelman et al., 2002; Fueglistaler et al., 2009). In addition, an early model study suggested high $CHBr_3$ emissions and atmospheric concentrations here, due to the many islands and therefore large length of coastlines found in this region (Warwick et al, 2006), although this estimate has since been revised downward (Pyle et al., 2011). The first two instruments were installed in 2008 in the State of Sabah in Malaysian Borneo, one at a coastal site and one inland (Figure 1). Early measurements were reported in Pyle et al. (2011). Here we report measurements from the subsequent years focussing on the period from late 2008 to early 2010. In addition to $CHBr_3$ and CH_2Br_2*, we report our observations of C_2Cl_4, a manufactured compound which we use to identify air with anthropogenic influence, and CH_3I, a compound produced naturally in the ocean which has a short atmospheric lifetime (7 days, Montzka and Reimann, 2011).

In Section 2 we describe the instruments used in this study, their calibration and the measurement quality reported here. Section 3 contains a discussion of the measurement sites including their physical characteristics, while in Section 4 we describe the modelling tools (NAME, p-TOMCAT) used in the interpretation of the data. The measurements for C_2Cl_4, $CHBr_3$, $CH_2Br_2^*$ and CH_3I are presented in Section 5, with particular emphasis on their variability, and with air mass history maps to aid in interpretation. We also consider the implications of the measurements, including an analysis of the total organic bromine in short-lived bromocarbons at each site. Finally, Section 6 summarises our findings and ongoing/future work.

2 Methodology

2.1 Instrument

The instruments used for these observations were the original µDirac gas chromatographs built by us for use on balloons, with electron capture detection (GC-ECD), in a modified configuration appropriate for extended ground-based deployment as described in Pyle et al. (2011). The instrument is described in detail in Gostlow et al. (2010). Briefly, each sample is pre-concentrated using a dual-bed adsorbent trap (1 mg Carboxen-1016 60/80 mesh followed by 1 mg Carboxen-569 20/45 mesh). The trap is then heated and the gaseous constituents are separated on a 10 m long, 0.18 mm i.d. capillary column (Restek MXT 502.2) prior to measurement in the ECD. As the instruments are designed to run unattended, the control software runs chromatograms according to a pre-determined sequence of samples bracketed by calibration and blank chromatograms. The sequence includes frequent calibrations using the same volume as the samples (20 ml) for correction of instrument sensitivity drift and precision determination. The sequence also runs calibrations at a range of different volumes so that instrument response curves are generated for each target compound to allow for non-linearity. The response curves are fit using a third order polynomial. Chromatograms and system data are stored on a host computer for later analysis using in-house software to determine peak heights for the target compounds which are then converted into mixing ratios by comparison with the calibration standards. Mixing ratios are reported as dry air mole fraction in ppt.

Measurement performance is monitored for each target compound during the analysis of the chromatograms, and the typical performance for the measurement period reported here is summarised in Table 1. For C_2Cl_4 the typical measurement precision (1 s.d.) is 2.5 % and 4.0 % at Bukit Atur and Tawau respectively. The typical measurement precision of $CHBr_3$ is 6.0 % and 7.5 % at Bukit Atur and Tawau respectively and those for $CH_2Br_2^*$ are 5.0 % and 6.5 %. Sample concentrations for C_2Cl_4, $CHBr_3$ and $CH_2Br_2^*$ are always above the limit of detection at both sites. CH_3I is only measured at Tawau (the µDirac at Bukit Atur did not achieve satisfactory chromatographic separation for reliable quantification) and the typical precision is 11 %. The CH_3I peak is small in the sample chromatograms so particular care is taken in assessing its signal to noise ratio (SNR). The SNR varies over time depending on the instrument condition and environment, and is calculated separately for each analysis period (typically 1-2 weeks) for which concentrations are calculated. Between January and June 2009, the estimated detection limit (defined using a SNR of 10) decreases from 0.9 ppt to 0.3 ppt as a result of reduced noise in the chromatograms and for the rest of 2009 it is below 0.2 ppt.

The chromatographic set-up uses a 10 m column for these measurements and this provides a good separation for C_2Cl_4 and $CHBr_3$. However, the CH_2Br_2 peak co-elutes with that of $CHBrCl_2$ with a 10 m column and so we report a combined value called $CH_2Br_2^*$ which we estimate to be 10-30 % higher than the CH_2Br_2 value alone (O’Brien et al., 2009). This co-elution problem is further discussed in section 5.3 of this paper and has been previously assessed in Gostlow et al. (2010). In a recently improved version of the instrument where a 20 m long column is used, these two compounds are partly separated and so individual values can be derived by peak fitting using two Gaussian fits. These new measurements of CH_2Br_2 and $CHBrCl_2$ using a 20 m column in similar tropical locations shows the ratio (10-30 %) to be still valid, as in O’Brien et al. (2009).

The instrument based at the coastal site developed a problem with desorption efficiency caused by incomplete thermal desorption of the target molecules from the adsorbent. This affected the quantification of the $CH_2Br_2^*$ peak by carry over from one chromatogram to the next. However, we are still able to use calibration chromatograms for CH_2Br_2 as these are preceded by a blank chromatogram. About one in every ten sample chromatograms is also usable for the $CH_2Br_2^*$ peak as these are also preceded by a blank. As a result of this problem $CH_2Br_2^*$ is only reported for about 1 in every 10 samples at Tawau. The C_2Cl_4 and $CHBr_3$ peaks are not affected by this problem at Tawau as these molecules are always completely retained on the weaker Carboxen-1016 at the front of the dual adsorbent bed.

2.2 Calibration

Samples are calibrated by running frequent chromatograms from cylinders of clean natural air, previously filled at Niwot Ridge (Colorado, USA), at an elevation of 3.5 km above sea level. The cylinder air is subsequently enriched with known concentrations of the target compounds. The cylinders (one for each instrument) are supplied by the Earth System Research Laboratory (ESRL) within the National Oceanic and Atmospheric Administration (NOAA) so that the reported mixing ratios are linked directly to the NOAA halocarbon calibration scales. Figure 2 summarises the period of data coverage for this study together with a time-line of the calibration cylinders in use at the two sites. The calibration gas in use at Tawau for the entire period of this study is in a high quality, humidified stainless steel cylinder (Essex Cryogenics Inc., cylinder SX-3542). The composition of this cylinder for the four compounds of interest is reasonably stable (Table 2a) and we plan to send this cylinder back to NOAA for subsequent analysis. The calibration gas in use at Bukit Atur from November 2008 to May 2009 was decanted into a 36 l stainless steel electropolished flask from a dried NOAA Aculife cylinder (AAL-70424) in October 2008. Comparisons of this decanted cylinder with the Aculife cylinder at either end of this period reveal a significant change for CH_2Br_2 and $CHBr_3$ and a smaller one in C_2Cl_4 (Table 2b). The agreement with the Aculife standard is much better in the later comparison which was performed in Sabah under the same conditions as the atmospheric measurements. We do not know why the first comparison should have been poor (it was done in Cambridge just prior to shipping) though we suspect it is related to temporary adsorption on the canister walls. Given the closer agreement between the baseline measurements of C_2Cl_4, $CHBr_3$ and $CH_2Br_2^*$ at Tawau and Bukit Atur (Section 5.1) using the values derived in the second comparison (last column of Table 2b), we choose to use this for the final analysis, rather than the values from the October 2008 check (or an average of the two checks). From May 2009 the NOAA Aculife cylinder (AAL-70424) used for the decanting is used directly at Bukit Atur. This cylinder appears to be more stable than the decanted cylinder though not as stable as the SX-3542 cylinder in use at Tawau (Table 2c). For the analysis of our Bukit Atur data from May 2009 to January 2010 we use the values from the check against the University of East Anglia (UEA) made in April 2009 using their NOAA SX cylinder, as this is closest in time to the period of the measurements. We also have more confidence in the comparison made at UEA (April 2009) under stable laboratory conditions using their GC-MS than in an incomplete comparison made at Bukit Atur (November 2012) over 3 years later. During June and July 2008 our measurements at Bukit Atur, analysed using the same NOAA (SX-3542) standard (later used at Tawau), compared well with GC-MS measurements made by UEA (Gostlow et al., 2010; Pyle et al., 2011).

In addition, we took part in an inter-comparison of measurements by several laboratories using a round robin NOAA calibration standard (Jones et al., 2011). This showed our laboratory calibration scale to be within the instrumental error (10-20%, 2 sigma) of this new NOAA standard. In July 2008 we ran our two instruments side-by-side at Bukit Atur, measuring C_2Cl_4, $CHBr_3$ and $CH_2Br_2^*$ in ambient air, using the same calibration gas on both GC-ECDs. For this 4 day period we found that the observations of C_2Cl_4, $CHBr_3$ and $CH_2Br_2^*$ from the two instruments were within 6 %, 1 % and 15 % of each other respectively.

3 Field deployment

We have been making halocarbon observations in Sabah (Malaysian Borneo) since April 2008. Initially, the instruments were deployed in the Danum Valley as part of the NERC funded OP3 project (Oxidant and Particle Photochemical Processes above a southeast Asian tropical rainforest), Hewitt et al. (2010). Two µDirac GCs were used in OP3: one was based at the Global Atmospheric Watch (GAW) station at Bukit Atur (Gostlow et al., 2010) and the other made ‘mobile’ measurements at several rainforest locations in Danum Valley and during a 4 day visit to the coast at Kunak (Pyle et al., 2011). At the end of the OP3 campaign the µDirac GC at the Bukit Atur GAW station was left running and the second ‘mobile’ instrument was moved to a coastal site near Tawau where it remained for the period of this study. The instrument at Bukit Atur is visited at ~2 weeks intervals (and on request) by staff from the Malaysian Meterological Department (MMD) who manage the site. The Tawau instrument was visited at ~1 month intervals and on request by one of our collaborators from Global Satria Sdn. Bhd. (an aquaculture company). Neither instrument was connected to the internet so these visits were essential for data recovery and monitoring of instrument performance. Periodic service visits (every 9-12 months) were made to both sites by Cambridge University staff. As a result of this low intensity monitoring, the performance of the instruments varies over time depending on the condition of the instrument and its environment. Each site is now described in the following sub-sections.

3.1 Danum Valley rainforest site: the Bukit Atur GAW station

The Danum Valley conservation area covers 438 km^2 and is one of the largest, most important and best-protected expanses of pristine lowland dipterocarp rainforest remaining in southeast Asia. The GAW station located on Bukit Atur (4.980°N, 117.844°E, elevation 426 m) has been in operation since 2004 and is reasonably remote being ~50 linear km away from the nearest town of Lahad Datu (Figure 1). The station is equipped with a range of monitoring instruments and an automatic weather station located on a 5 metre roof-top platform. The 100 metre tower, which adjoins the laboratory, has air-intakes and platforms for sampling equipment at various levels and is the tallest instrumented structure on Borneo island. The on-going measurement programme at the Bukit Atur GAW station includes surface ozone, greenhouse gases (flask sampling), carbon dioxide (using a Loflo Mk2 analyser), precipitation chemistry, aerosol (load, chemical and physical properties), reactive gases (filterpack sampling), persistent organic pollutants, solar radiation and meteorological parameters. The site is operated by the Malaysian Meteorological Department (MMD) and staff visit weekly from their nearest office at Tawau airport. The station itself is located on a hill-top ~200 m above the valley floor and the inlet for the μDirac instrument is attached 12 m up the tower, several metres above the roof of the site building. The instrument is placed in an air-conditioned room in the main GAW building. The topography in the area consists of a series of hills ~400 m above sea level with valley floors down to ~200 m above sea level. One of the largest mountains in the area is Mount Danum at 1,093 m above sea level. The rainforest extends to all areas including mountain tops. Primary unlogged rainforest in the conservation area is surrounded by areas of secondary rainforest (which have been logged in recent years). In terms of site meteorology, a clear diurnal cycle in rainfall is observed at the nearby Danum Valley Field Centre (DVFC) with an afternoon peak around 15:00 hrs local time resulting from diurnal development of convective cells following the midday peak in temperature (Hewitt at al., 2010). Boundary layer stability also varies diurnally from highly stable at night (often leading to dense fog at night) to highly unstable during the day due to the onset of strong convection coupled with low wind speeds (Pearson et al., 2010).

3.2 Tawau coastal site: Kampung Batu Payong

The Tawau coastal site is located in the peaceful village of Kampung Batu Payong (4.223°N, 117.997°E, elevation 15 m) and is ~10 km from Tawau centre and ~85 km south of the Bukit Atur rainforest station (Figure 1). Between July 2008 and October 2011 the μDirac instrument here was located in an air-conditioned room at a fish hatchery site maintained by the Global Satria company. There are no seaweed beds in the immediate vicinity of the site. The activity at the site does not involve the use of any seaweeds (which are known to emit bromocarbons) and we do not find any evidence of emissions from the hatchery activities. The air inlet is located ~5 m above ground level at the site (about roof-top height) 40 m away from the shoreline. There is an unobstructed view to the sea extending to more than 180° of horizon to the south and the site is situated at the foot of a small group of hills extending to the north, reaching an elevation of 350 m. A low cost weather station at the site gives an indication of wind speed and direction, temperature and humidity. This reveals a typical diurnal variation in wind due to land/sea breezes expected for coastal sites, though this does not obviously influence the observations reported here.

4 Models

Two modeling tools are used in this paper to assist in the interpretation of the observations. They are now described in turn in sub-Sections 4.1 and 4.2

4.1 NAME

The Numerical Atmospheric dispersion Modelling Environment (NAME) is a Lagrangian particle dispersion model developed by the UK Met Office (e.g. Jones et al., 2007), which has been extensively used for analysis of long-term halocarbon data sets (e.g. Manning et al., 2003; Simmonds et al., 2006; Derwent et al., 2007). Abstract particles are moved through the model atmosphere by a combination of 0.5625° longitude by 0.375° latitude mean wind fields calculated by the UK Met Office Unified Model (Davies et al., 2005), and a random walk turbulence scheme. NAME can be run backwards in time, to see where the air measured at a particular site may have originated, and forwards to see where air from a particular emission source might go. Each of these capabilities have previously been used to investigate relationships between sources, transport and measurements of pollutants (e.g. Redington and Derwent, 2002; Witham and Manning, 2007).

Here, NAME is run backwards in time to reveal the origin of air arriving at Bukit Atur and Tawau. For each 3 hour period thousands of inert particles (carrying an arbitrary mass) are released and travel backwards in time for 12 days. At each 15 min time-step the location of each particle is recorded. Then, at the end of the run this information is used to create an 'air history map'. Here, we only record near surface particles (lowest 100 m of the model) which indicate where air may have been exposed to surface emissions. Monthly mean air histories are then calculated. The air history maps made for Tawau are almost identical to those from Bukit Atur so are not shown here.

4.2 p-TOMCAT

The global chemistry transport model (CTM), p-TOMCAT, is used to analyse the causes of seasonal bromoform variability at Bukit Atur. The basic formulation of p-TOMCAT is described in Cook et al. (2007) and Hamilton et al. (2008). Tracer transport is based on 6-hourly meteorological fields, including winds and temperatures, derived from European Centre for Medium-Range Weather Forecasts operational analysis for the years 2008, 2009 and 2010. Here we use a high resolution (0.5° x 0.5°) version with bromoform tracers ‘coloured’ according to the region of emission and simple OH oxidation chemistry, described previously in Pyle et al. (2011) and Warwick et al. (2006). The degradation of bromoform is determined using 3-D fields of precalculated hourly OH values taken from a previous p-TOMCAT integration and photolysis frequencies from an integration of the Cambridge 2-D model using cross section data summarised by Sander et al. (2003). For further details see Pyle et al. (2011). Here we compare time series of bromoform from the model output with the measurements.

5 Results and Discussion

In this section we present the measurements of C_2Cl_4, $CHBr_3$ and $CH_2Br_2^*$ from both sites and CH_3I from Tawau only. We first show that C_2Cl_4 can be used as a good tracer of air mass, differentiating clearly between air masses with anthropogenic and unpolluted origins. This provides a valuable background for the analysis of the three, primarily biogenic, short-lived compounds, $CHBr_3$, $CH_2Br_2^*$ and CH_3I. In this section we also assess the total organic Br coming from $CHBr_3$ and $CH_2Br_2^*$ combined. We discuss the implications of these observations, in particular for the regional emissions of $CHBr_3$ and $CH_2Br_2^*$.

5.1 Perchloroethene

Perchloroethene (C_2Cl_4) is an excellent anthropogenic tracer with few (if any) known natural sources. Its main anthropogenic sources are the textile industry, dry-cleaning applications and in vapour degreasing of metals (Montzka and Reimann, 2011). It currently has a northern hemisphere background concentration of 2-5 ppt with a pronounced seasonal variation, likely due to variation in the concentration of its major sink, the OH radical. In the southern hemisphere the background concentration is lower (0.5-1 ppt), though still with a pronounced seasonal variation (see http://agage.eas.gatech.edu/data.htm; Simmonds et al., 2006). C_2Cl_4 has an estimated lifetime of ~90 days (see Table 1-4 in Montzka and Reimann, 2011), making it a good tracer for studying long range transport.

At Bukit Atur and Tawau the C_2Cl_4 dry air mole fractions ranged typically from 0.3-0.8 ppt in May-August 2009 to 1.0-3.7 ppt from November 2008 to March 2009 (Figure 3a). ‘Above baseline’ spikes are observed occasionally at Tawau, but for most of the time the data at Bukit Atur and Tawau track each other on monthly and daily timescales. As the two sites are 85 km apart and as both C_2Cl_4 time series track each other closely, it seems there is little local contribution from Sabah to the background mixing ratio.

For the 4 month period between December 2008 and March 2009 there is a systematic difference in the C_2Cl_4 observations at the two sites, with the observations at Bukit Atur on average 48 % higher than those at Tawau. It is surprising to find this large systematic difference given that the observations of C_2Cl_4 were within 6 % of each other when the GCs ran side-by-side at the same site and with the same calibration gas at Bukit Atur in July 2008 (Section 2 last paragraph). The differences are probably due to a relative drift in the composition of the calibration gases used at each site. Any drift in composition is likely to be larger for the decanted calibration gas which was used at Bukit Atur between November 2008 and May 2009 and therefore we have more confidence in the time series from Tawau (see Section 2.2). The C_2Cl_4 observations reported at Bukit Atur between December and March are likely to be an upper estimate of the actual mixing ratios at that time.

Although there is a greater frequency of high (local pollution) spikes at Tawau these do not impact significantly on the underlying background which is similar to that at Bukit Atur. The seasonal trend at both sites is clear from box and whisker plots (Figure 4a & d) and the tabulated monthly mean, median and modal values (Table 3a) which show low levels and low variability in the northern hemisphere summer months in contrast with higher levels in winter. To further explore these seasonal differences and site-to-site similarities, for selected months we use probability distributions from the C_2Cl_4 observations, using a size interval of 0.1 ppt (Figure 5a & e). In January/February 2009 there is a broad distribution of mixing ratios at both sites ranging from 0.85 to 3.75 ppt, tailing towards higher mixing ratios. The Tawau coastal median value in January/February 2009 (seen in Figure 5a) is lower (1.30 ppt) than inland at Bukit Atur (1.91 ppt), though recall that the C_2Cl_4 observations at Bukit Atur are likely an upper estimate. In June/July 2009 the distribution at each site has a much narrower range (0.25 to 1.65 ppt) and the median values are similar, though the coastal median (0.45 ppt) is still lower than inland (0.63 ppt). In January/February 2009 the Bukit Atur instrument ran on the decanted calibration air from the NOAA Aculife cylinder AAL-70424, whereas in June/July 2009 the calibration came directly from the Aculife cylinder.

The seasonal changes in C_2Cl_4 are linked to changes in the prevailing monsoon flow, and the inter-hemispheric gradient typically observed for gases with predominantly northern hemisphere anthropogenic sources. Air history maps generated using NAME are used here to illustrate the seasonal changes in transport. From the months of November through to February the air mass history is influenced strongly by air coming from the north and east (Figure 6a, January 2009). The large urban centres in and around China in this region are expected to contribute to the background level of C_2Cl_4 arriving at Sabah. From March to May 2009 the air mass origin tends to be influenced more by oceanic air from the West Pacific though with still some trajectories passing the vicinity of China (Figure 6b, March 2009). During June, July, August and September 2009 the air mass history indicates that Sabah is influenced strongly from the region to the southeast, characterised by southern hemisphere air originating from the Indonesian islands and Northern Australia (Figure 6c, June 2009). As there are no major sources of C_2Cl_4 across this region and the air masses are not influenced by emission from for example Jakarta, we find (as expected) background mixing ratios to be low. October sees a transition between background air influenced by the southern hemisphere and northern hemisphere air influenced by China and other large urban centres. It is thus an example of a transition period between the two monsoon regimes (Figure 6d, October 2009).

5.2 Bromoform

Bromoform ($CHBr_3$) is an excellent tracer of marine air and is an important source of organic bromine to the atmosphere (Carpenter and Liss, 2000). An open ocean, phytoplankton source has been identified (Tokarczyk and Moore, 1994), and macroalgae found in coastal areas are also well known as major sources of bromoform (Moore and Tokarczyk, 1993). Emission fluxes in coastal regions are thought to be higher than in the open ocean (Quack and Wallace, 2003; Yokouchi et al., 2005; Butler et al., 2007) though the relative contribution from coasts and from the open ocean to the total global emission remains uncertain. Recent estimates of the global emissions of $CHBr_3$ are in the range 430-1400 Gg Br/yr (Liang et al., 2010; Pyle et al., 2011; Ordonez et al., 2012 and Table 1-8 in Montzka and Reimann, 2011) though much lower estimates of 120 and 200 Gg Br/yr are given by Ziska et al. (2013). Although bromoform emissions are dominated by natural sources there are minor anthropogenic contributions from by-products of drinking water chlorination in the presence of bromide ions, salt water swimming pools and power plant cooling water (Worton et al. 2006). In the atmosphere, $CHBr_3$ has a lifetime of 24 days (from Table 1-4 in Montzka and Reimann, 2011) which is shorter in the tropics (15-21 days), as discussed in Warwick et al. (2006). The significant loss mechanisms include reaction by photolysis and reaction with OH (Hossaini et al., 2010; Montzka and Reimann, 2011).

The background $CHBr_3$ concentration at both Bukit Atur and Tawau is broadly in the range 0.5 to 3 ppt. In contrast to the time series of C_2Cl_4, there is no unambiguous seasonal variation in the background $CHBr_3$ concentration (Figure 3b). During the periods when we report $CHBr_3$ mixing ratios from both sites, the background concentrations are sometimes the same within experimental error (e.g. Figure 5b for January/February 2009), and in some months the coastal background is higher than inland (e.g. Figure 5f for June/July 2009). These probability distributions also indicate that we do not observe strong seasonality in the background mixing ratio at Tawau. In contrast, there is a suggestion of a seasonal cycle, with a northern hemisphere winter peak, in the data collected inland at Bukit Atur (e.g. Figure 4b). To emphasise this point, the median mixing ratios for the two sites were similar in January/February 2009 (1.67 ppt at Tawau and 2.04 ppt at Bukit Atur), whereas for June/July 2009 the median value for Tawau (1.68 ppt) was higher than at Bukit Atur (0.95 ppt). Clearly, measurements over many years are needed to ascertain whether the somewhat different behaviour we have observed at the two sites in Borneo is a persistent feature. See Table 3b for the statistical summaries of all the relevant periods.

A major difference between the two sites is that there are frequent periods (spikes) at Tawau when very high levels (> 10 ppt) of bromoform are observed, whereas at Bukit Atur such episodes are rare, and the highest concentration is just 5.5 ppt. This difference in variability is shown clearly in the box and whisker plots for Bukit Atur and Tawau (Figure 4b & e) where $CHBr_3$ observations > 10 ppt at Tawau are seen in 12 of the 15 reported months.

Various factors determine the concentrations we observe at these two sites. The sources of $CHBr_3$ are certainly heterogeneous in space, and so the mere fact that the boundary layer is influenced by different regions in different seasons (Figure 6) leads to a varying influence of recent emissions and hence varying observed concentrations. This heterogeneity occurs due to both natural spatial variations in the populations of algae in coastal and open ocean areas, and due to the presence of commercial aquaculture in the region, whose influence on bromoform emissions needs to be assessed. For example, northeast Sabah and the archipelagos between Sabah and the Philippines are major seaweed farming areas whose output has grown quickly over the last 20 years (Phang, 2006; Perez, 2011). At present it appears that entirely natural emissions of bromoform in the region are significantly larger than those linked to aquaculture (Leedham et al., 2013) but continued rapid growth in the cultivation of many species with commercial potential (Goh and Lee, 2010; Tan et al., 2013) could change this situation (Phang et al., 2010). Further, the strength of individual sources is likely to vary over time. In the case of seaweeds, it seems likely that their halocarbon emissions will depend on environmental factors such as temperature, rainfall, wind, sunlight and if applicable, the phase of the cropping cycle (Seh-Lin Keng et al., 2013, Leedham et al., 2013 and references therein). Given this complexity, without extensive biological field surveys it is difficult to explain much of the variability in detail.

However, we are able to examine how well the CTM p-TOMCAT is able to simulate the long-term statistical properties of observed bromoform mixing ratios. The model configuration is described in Section 4.2, and the bromoform emissions are those developed by Pyle et al. (2011) as an update to Warwick et al. (2006). These emissions provide the best match with our earlier observations collected at Bukit Atur during OP3 (Pyle et al., 2011). The observed time series for $CHBr_3$ is consistent with the p-TOMCAT model output using the revised emission estimate as shown for Tawau in Figure 7a. The model is unable to capture the very high values seen in the observations, which is to be expected given the model resolution and the uniform distribution of emissions around the coastlines in the model. The model does a reasonable job of reproducing the background observed concentration throughout 2009 at Tawau. The bromoform observations and model output for the four months from December 2008 to March 2009 are compared as a probability distribution in Figure 7b. The observations show only a slightly broader distribution (inter-quartile range 0.84 ppt) than the model output (inter-quartile range 0.58 ppt) and the median value for the observations of 1.73 ppt is just slightly higher than that for the model output (1.65 ppt).

5.3 Dibromomethane

It is thought that the marine sources of dibromomethane (CH_2Br_2) are similar to those of $CHBr_3$, as shown by the strong correlations observed between their atmospheric concentrations (Yokouchi et al., 2005; Carpenter et al., 2009). Emission fluxes are probably higher in coastal regions than over the open ocean (Ziska et al., 2013), but the relative effect on coastal atmospheric measurements is less marked than for $CHBr_3$ due to a longer lifetime for CH_2Br_2 of ~120 days (Table 1-4 in Montzka and Reimann, 2011). The CH_2Br_2 lifetime is expected to be slightly lower than 120 days in the tropics due to the higher abundance of the OH radical. Open ocean sources are also more important globally than coastal sources. Recent estimates of the global CH_2Br_2 emissions are 50-70 Gg Br/yr (Liang et al., 2010; Ordonez et al., 2012).

The mixing ratios of $CH_2Br_2^*$ measured at Bukit Atur and Tawau are shown in Figure 3c. The observed baseline values of between 1 and 2 ppt for CH_2Br_2* at the two sites are similar, as reflected in the median values in Table 3. Previous work suggests that 10-30% of the CH_2Br_2* signal may in fact be CH_2BrCl_2. During June and July 2009 Nadzir et al. (2013) collected air samples on a ship cruise around the coast of the Sulu-Sulawesi seas close to Tawau and the average CH_2Br_2 mixing ratio was 1.04 ppt compared to 0.3 ppt for $CHBrCl_2$. The authors also found that the two compounds tracked each other closely through the entire cruise. In another study, Sala et al. (2014) report average boundary layer mixing ratios of CH_2Br_2 and $CHBrCl_2$ of 1.19 and 0.34 ppt respectively, from an aircraft campaign in the Western Pacific region during November/December 2011. Both $CHBrCl_2$ and CH_2Br_2 are known to have a common macroalgal source as found by Seh-Lin Keng et al. (2013) and Leedham et al. (2013) in studies of tropical seaweeds from the Malaysian coast. These studies also found that production rates of CH_2Br_2 were generally (though not always) much higher than for $CHBrCl_2$. In the atmosphere $CHBrCl_2$ has a lifetime of 78 days compared to 123 days for CH_2Br_2 (Montzka and Reimann, 2011). Thus we would not expect to see any significant difference in the measured $CHBrCl_2$:CH_2Br_2 ratio between Tawau and Bukit Atur due to differential processing, given the short air mass transit time between the sites of typically 1 day. The variability of $CH_2Br_2^*$ at Tawau is much less than for $CHBr_3$. What may be an important factor here in variability differences between the two sites, is the extent to which boundary layer air at Bukit Atur has been diluted with free tropospheric air with a lower ratio of $CHBr_2Cl$ to CH_2Br_2, given that the site is 426 m above sea level. Statistically, the observations at Bukit Atur and Tawau are similar to each other as shown by the box and whisker plots, although the two months at Tawau with distinctly low median values (March/April 2009) are not reflected in the Bukit Atur observations (Figure 4c & f). There is a definite hint of some seasonality in the $CH_2Br_2^*$ measurements (Figure 5c & g), though multi-year data are required to determine whether there is a seasonal cycle. Median values in January/February 2009 are almost the same at both sites (1.20 and 1.28 ppt at Bukit Atur and Tawau respectively), though in June/July 2009 the median value at Tawau (1.33 ppt) is distinctly higher than at Bukit Atur (1.00 ppt).

We find that in all reported months at Bukit Atur there is always a positive correlation between the observations of $CH_2Br_2^*$ and $CHBr_3$, suggesting a common source (Table 3c). Nadzir et al. (2013) also found a strong positive correlation between $CHBr_3$ and CH_2Br_2 in whole air flask samples taken during a 2009 cruise in the South China and Sulu-Sulawesi Seas (close to the Tawau site) and Strait of Malacca. The strength of the correlation at Bukit Atur and Tawau is highly variable between months. The strongest correlation at Bukit Atur is found in November 2008 with an R^2 value of 0.86. At Tawau the correlation between $CH_2Br_2^*$ and $CHBr_3$ is generally much weaker than at Bukit Atur, though still positive, with the exception of June 2009. Only March and September 2009 show strong positive correlations at Tawau. As we are only able to report a $CH_2Br_2^*$ measurement in about 1 in every 10 samples at Tawau there are less data available for the correlation of $CH_2Br_2^*$ and $CHBr_3$.

5.4 Methyl iodide

Methyl iodide (CH_3I) is ubiquitous in the marine boundary layer, with typically reported concentrations of 0.1–5 ppt (e.g., Lovelock et al., 1973; Rasmussen et al., 1982; Yokouchi et al., 2001, 2008, 2011, 2012). There are several known oceanic sources of CH_3I including phytoplankton (Moore and Tokarczyrk, 1993; Manley and dela Cuesta, 1997), macroalgae (Manley and Dastoor, 1988; Schall et al., 1994; Giese et al. 1999), methylation of iodine by bacteria (Amachi et al., 2001), picoplankton (Smythe-Wright et al., 2006; Brownell et al., 2010), photochemical reactions (Moore and Zafiriou, 1994) and as a by-product of the ozonolysis of dissolved organic matter (Martino et al., 2009). Methyl iodide has an atmospheric lifetime of 7 days (Table 1-4 in Montzka and Reimann, 2011) and has the shortest lifetime of the compounds reported here.

The most extensive, continuous measurements of CH_3I reported to date in the tropics or sub-tropics were made hourly at Hateruma Island (24.1°N, 123.8°E) from August 2008 to January 2010 (Yokouchi et al., 2011). At Hateruma Island, no significant seasonal variation was observed, in contrast to Cape Ochiishi (43.2°N, 145.5°E) where a clear maximum was observed in late summer/autumn coincident with increased variability. No diurnal variation in CH_3I was observed at either location. These high resolution measurements are complemented by the longer, semi-monthly measurements made from the late 1990s to 2011 at 5 remote sites, Alert (82.5°N, 62.5°W), Cape Ochiishi, Happo Ridge (36.7°N, 137.8°E), Hateruma Island and Cape Grim (40.4°S, 144.6°E) as well as regular ship transects of the Pacific (Yokouchi et al., 2012). Summer maxima were seen at all the four sites apart from Alert where a wintertime maximum (attributed to transport) was seen. The discrepancy between the continuous and semi-monthly measurements at Hateruma Island presumably results from low frequency sampling of the highly variable mixing ratio in the late summer. No significant seasonal cycle is seen in the baseline of the higher resolution CH_3I time series. Observations of CH_3I in the tropical boundary layer have otherwise been limited to measurements of whole air samples made at specific sites or on research cruises (see summaries in Table 1 in Yokouchi et al. (2008) and Table 2 in Saiz-Lopez et al. (2012)).

Our CH_3I record for Borneo (Tawau only) is therefore a unique source of information in the tropics. The measurements for 2009 are shown in Figures 3d, 4g and 5d & h. The CH_3I peak is small and hard to separate (using our current column configuration) from the larger peaks that elute at a similar time. The µDirac at Bukit Atur did not achieve satisfactory chromatographic separation for reliable CH_3I quantification and these data are not reported here.

The CH_3I mixing ratios at Tawau (~8400 in total) vary from below 0.1 up to 11 ppt, with the large majority of points towards the lower end of the range. July sees the lowest monthly mean of 0.34

ppt and the highest monthly mean of 2.50 ppt is in September. The highest values and the greatest variability are observed in September and October. Back-trajectories indicate that air containing high amounts of CH_3I had previously passed over large biomass burning events in southern Borneo (as observed by MODIS). Emissions of CH_3I in biomass burning have been reported previously (Andreae et al., 1996; Mead et al., 2008c). However while biomass burning emissions may be significant locally at some times of year, it is not the case globally (Bell et al., 2002; Butler et al., 2007). Interestingly some of the lowest observed values (< 0.1 ppt) of CH_3I occur when the air has previously been in the terrestrial boundary layer, indicating that the tropical rainforests were not normally a source of CH_3I. The seasonal cycle in the baseline (i.e. if the high values seen in the late summer/early autumn are excluded) at Tawau is weak, similar to that seen at Hateruma Island. A longer record is needed to identify whether one exists.

5.5 Total bromine

Here we present and discuss our observations of bromine defined as $[CHBr_3] + [CH_2Br_2^*]$ as an approximate measure of total organic bromine from the two sites. For a two week period of the OP3 campaign (5-12 July 2008) we ran our Bukit Atur instrument alongside a GC-MS system from UEA which measured $CHBr_3$, CH_2Br_2, $CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl (the five main naturally occurring bromine source gases). The GC-MS observations showed that $CHBr_3$ and CH_2Br_2 accounted for 93.5 % of the total Br coming from these five bromine source gases (Pyle et al., 2011a). Total bromine as $[CHBr_3] + [CH_2Br_2^*]$ from our measurements at Tawau over the period November 2008 to January 2010 is shown as a time series in Figure 8a. The black line through the data is the running average total bromine (40 point, 50 pass) to highlight average variability. Bromine from these two compounds (accounting for >90 % of the total organic Br) averages 9.7 ppt over the period of observations and ranges from 3.7 ppt (June 2009) to 189.5 ppt (December 2008). The probability distribution function for total observed bromine as $[CHBr_3] + [CH_2Br_2^*]$ at Bukit Atur is compared with that for Tawau in Figure 8b. The distributions are similar (median values of 6.79 and 7.97 ppt at Bukit Atur and Tawau respectively) and Bukit Atur has a narrower inter-quartile range than Tawau (2.06 ppt compared to 2.80 ppt). The extended tail of very high total bromine values (>20 ppt) is evident at Tawau and completely absent from the Bukit Atur observations.

The fact that the observations of bromine from $[CHBr_3] + [CH_2Br_2^*]$ are so similar at both sites (with the exception of the very high coastal values) shows that an inland site can be used effectively to make regional observations suited to model comparison. In fact, as the model we used here was unable to capture the large variability in the observations, presumably due to insufficient information on the spatial and temporal inhomogeneity of the emissions seen at the coast and to model resolution, we suggest that, for evaluating models, an inland site is preferable to a coastal site. We also calculate total modelled bromine coming from [$CHBr_3$] + [CH_2Br_2] in p-TOMCAT at Tawau and find for the period of our observations a total bromine median value of 6.56 ppt, somewhat lower than the median value of 7.97 ppt from the measurements.

Our data provide a longer-term context for other reports from short campaign-type observations. There are month-to-month variations in total Br in our data that would be missed by shorter deployments. Overall, our mean value of 9.7 ppt from [$CHBr_3$] + [$CH_2Br_2^*$] seems quite consistent with other work in the region. There have been somewhat conflicting reports of the fraction of Br in $CHBr_3$ and CH_2Br_2 compared to the minor very short-lived substances (VSLS). Montzka and Reimann (2011) suggest a boundary layer median value of 8.4 ppt Br from VSLS, with 83 % from $CHBr_3$ (1.6 ppt × 3) and CH_2Br_2 (1.1 ppt × 2). Based on data obtained in July 2008 from the OP3 campaign, Pyle et al. (2011a) report 7 ppt (5-10 ppt) Br from VSLS, with over 90 % of this present as $CHBr_3$, CH_2Br_2 or $CHBrCl_2$. Nadzir et al. (2013) report a mean of 8.9 ppt Br from all VSLS (range 5.2 to 21.4 ppt in individual samples), with ~90% from $CHBr_3$ and CH_2Br_2 during the Prime Expedition Scientific Cruise during June and July 2009.

6 Summary

Until recently, few measurements of short-lived halogenated compounds had been made in southeast Asia. These compounds have significant atmospheric importance, and previous studies have speculated that southeast Asia represents an unusually strong source of the naturally occurring species (e.g. $CHBr_3$). Here we present more than one year of observations (November 2008 to January 2010) of key short-lived compounds from a coastal (Tawau) and an inland (Bukit Atur) site in this region, which together provide valuable data to the atmospheric science community. The data have been placed on the HalOcAt database for community access (https://halocat.geomar.de/). The data allow seasonal cycles, emissions and the role of local and long range transport to be studied.

By combining the observations with air mass history information generated by NAME we explain the strong seasonal cycle seen in the anthropogenic tracer (C_2Cl_4). From December to February, northerly air masses lead to higher and more variable mixing ratios, ranging from 0.8 to 3.7 ppt. In contrast, from May to August the observed air masses originate from regions to the south (typical mixing ratio 0.5 ppt). The overall median values for C_2Cl_4 are 1.33 ppt and 0.99 ppt at Bukit Atur and Tawau respectively.

The naturally occurring brominated tracers $CHBr_3$ and $CH_2Br_2^*$ do not show unambiguous seasonal variation, though there is a slight hint of a seasonal cycle in $CH_2Br_2^*$. Both compounds nevertheless show strong variability over shorter timescales. At the coast, the $CHBr_3$ observations occasionally peak at over 100 ppt compared with the overall median level of 1.7 ppt. At Bukit Atur, the overall inland median level for $CHBr_3$ is 1.6 ppt and the occasional peaks are much lower than at the coast with maximum observations of just over 5 ppt. Coastal $CH_2Br_2^*$ mixing ratios occasionally rise to over 7 times the median level of 1.4 ppt, whereas inland the maximum level observed is a little over 2 ppt. The strong coastal variability of both these compounds is likely related to the strongly heterogeneous nature of their marine sources, which are believed to be a combination of coastal macroalgae and both coastal and oceanic microalgae. Accordingly, the measurements from coastal Tawau are more variable than at Bukit Atur, being made closer to these sources.

The observations of $CHBr_3$ and $CH_2Br_2^*$ also provide a valuable longer term estimate of the contribution to total Br in the boundary layer from the main naturally occurring short-lived brominated compounds. At the coast we observe an overall median value of Br from $CHBr_3$ and $CH_2Br_2^*$ of 8.0 ppt and inland the overall median value is 6.8 ppt. These values are reasonably consistent with other recent estimates of this quantity based on much shorter measurement periods. Our data provide evidence that southeast Asia may not in fact be a region of enhanced brominated VSLS emissions into the boundary layer in relation to other tropical locations where similar measurements have been made.

Our coastal observations of CH_3I show high variability as expected for a short lived tracer with values from less than 0.1 ppt to over 11 ppt. The overall median value is 0.6 ppt. The highest values are observed in September and October 2009 and are attributed to the influence of biomass burning in southern Borneo that year. In other times of the year, air that passed over land showed some of the lowest values observed, indicating that the tropical rain forests in Borneo are not a source of CH_3I.

To date, modelling work has focussed on understanding our $CHBr_3$ data. The $CHBr_3$ observations presented here were recently used by Ashfold et al. (2014), along with NAME trajectories and an inversion method, to estimate regional scale $CHBr_3$ emissions. When extrapolated across the global tropics, the magnitude of their estimated emissions was somewhat lower than most other recent estimates, which have tended to assume strong emissions in southeast Asia. This is consistent with the finding here, that observed $CHBr_3$ mixing ratios in Borneo (and indeed $CH_2Br_2^*$ mixing ratios and total Br estimates) are in fact similar to those measured in other parts of the world. Our measurements also provide a means of testing the ability of global models like p-TOMCAT to reproduce boundary layer time series of short-lived compounds in tropical regions. Although p-TOMCAT was unable to reproduce the same magnitude of variability seen in the Borneo $CHBr_3$ observations, it was able to capture background concentrations using the bromoform emission distribution described in Pyle et al., (2011). This emission distribution is an updated version of the distribution described in Warwick et al., (2006), containing substantial reductions in southeast Asian emissions relative to the original scenario.

We continue to make halocarbon measurements in Sabah and have upgraded to the newer version of μDirac with a 20 m long column and better resolution of species including CH_2Br_2. In addition, we have recently begun measuring the same group of compounds using upgraded versions of the instruments used here at three other sites in the southeast Asia region: at Bachok on the Malaysian peninsula, Kelantan state; at Gunn Point near Darwin, Australia; a coastal site near Taipei, Taiwan. These sites significantly extend the geographic coverage of our measurements.

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Table 1: µDirac target compounds and measurement performance at Bukit Atur and Tawau. Atmospheric lifetimes are taken from Table 1-4 in Montzka and Reimann (2011); the lifetime value for $CH_2Br_2^*$ is actually that for CH_2Br_2; estimated accuracies are ±1 standard deviation; typical measurement precisions are ±1 standard deviation of 6 calibration chromatograms made in a single day; limit of detection is based on a signal to noise ratio of 10:1; n/a means no data available.

Compound name	Formula	Atmospheric lifetime	Estimated accuracy (%)	Typical precision (%)		Limit of detection (ppt)	
				Bukit Atur	Tawau	Bukit Atur	Tawau
tetrachloroethene	C_2Cl_4	90 days	5-10	2.5	4.0	0.04	0.02
bromoform	$CHBr_3$	24 days	5-10	6.0	7.5	0.19	0.18
dibromomethane*	$CH_2Br_2^*$	123 days	5-10	5.0	6.5	0.14	0.14
methyliodide	CH_3I	7 days	10	n/a	11.0	n/a	0.50

Table 2(a-c): Calibration mixing ratios of C_2Cl_4, $CHBr_3$, CH_2Br_2 and CH_3I used for quantifying our data from Bukit Atur and Tawau. Calibration data for (a) the high quality NOAA SX-3542 cylinder based at Tawau; (b) data for the cylinder containing decanted NOAA cal gas (from AAL-70424) based at Bukit Atur from Nov-2008 to May-2009; (c) data for the NOAA AAL-70424 Aculife standard based at Bukit Atur from May-2009 to Jan-2010; n/a means no data available.

Table 2a: SX-3542 used at Tawau (November 2008 to January 2010)

Compound name	Formula	NOAA analysis (Nov-2005) (ppt)	UEA check during OP3 (Apr-2008) (ppt)
tetrachloroethene	C_2Cl_4	2.01	n/a
bromoform	$CHBr_3$	9.00	8.10
dibromomethane	CH_2Br_2	4.80	4.80
methyliodide	CH_3I	3.40	3.30

Table 2b: decanted AAL-70424 used at Bukit Atur (Nov 2008 to May 2009)

Compound name	Formula	check using AAL-70424 (Oct-2008) (ppt)	check using AAL-70424 (May-2009) (ppt)
tetrachloroethene	C_2Cl_4	1.98	2.47
bromoform	$CHBr_3$	2.12	3.31
dibromomethane	CH_2Br_2	2.41	4.48
methyliodide	CH_3I	n/a	n/a

Table 2c: AAL-70424 used at Bukit Atur (May 2009 to January 2010)

Compound name	Formula	NOAA analysis (Nov-2005) (ppt)	UEA check (Apr-2009) (ppt)	check using SX-3542 (Nov-2012) (ppt)
tetrachloroethene	C_2Cl_4	2.22	2.33	1.94
bromoform	$CHBr_3$	7.50	4.66	7.30
dibromomethane	CH_2Br_2	4.30	4.06	4.75
methyliodide	CH_3I	3.20	n/a	n/a

Table 3(a-d): Statistical summary of our observations at Bukit Atur and Tawau: monthly and overall mean, mode and median values for the mixing ratios of (a) C_2Cl_4, (b) $CHBr_3$, (c) CH_2Br_2 and (d) CH_3I. Table 3c also shows the R^2 value for the correlation between $CH_2Br_2^*$ and $CHBr_3$ for each month, the four strongest correlations are shown in bold, all correlations give a positive slope except June 2009 at Tawau (shown in italics). The total sample number varies between months and between sites due to differences in chromatogram cycle times and periods of instrument downtime. Modal values are based on a bin width of 0.1 ppt. For $CH_2Br_2^*$ at Tawau the sample counts are particularly low as we are only able to use about 1 in 10 sample chromatograms for reliable quantification. The overall C_2Cl_4 distribution at both sites is distinctly bi-modal, the secondary mode is shown in parentheses. n/a means no data available

Table 3a: Statistical summary for C_2Cl_4 at Bukit Atur and Tawau

Month	Sample total (n)		Mean (ppt)		Mode (ppt)		Median (ppt)	
	Bukit Atur	Tawau	Bukit Atur	Tawau	Bukit Atur	Tawau	Bukit Atur	Tawau
Nov-2008	416	544	1.00	0.85	0.85	0.75	0.99	0.76
Dec-2008	1748	1766	1.77	1.30	1.55	1.25	1.68	1.20
Jan-2009	1746	1910	2.38	1.61	1.85	1.35	2.28	1.49
Feb-2009	1572	1702	1.72	1.16	1.45	1.05	1.69	1.09
Mar-2009	1759	1896	1.65	1.01	1.65	0.95	1.63	1.00
Apr-2009	1216	604	1.01	0.81	0.85	0.75	0.92	0.80
May-2009	1142	443	0.71	0.55	0.65	0.55	0.69	0.54
Jun-2009	1314	867	0.63	0.44	0.65	0.45	0.62	0.44
Jul-2009	1273	735	0.66	0.48	0.65	0.45	0.65	0.47
Aug-2009	1117	725	0.61	0.74	0.55	0.55	0.58	0.74
Sep-2009	n/a	678	n/a	0.70	n/a	0.65	n/a	0.64
Oct-2009	n/a	1382	n/a	0.70	n/a	0.55	n/a	0.62
Nov-2009	n/a	1296	n/a	1.22	n/a	1.25	n/a	1.22
Dec-2009	n/a	628	n/a	2.57	n/a	2.55	n/a	2.63
Jan-2010	n/a	273	n/a	2.31	n/a	2.25	n/a	2.25
Overall	13303	15449	1.33	1.10	0.65 (1.65)	1.05 (0.55)	1.33	0.99

Table 3b: Statistical summary for $CHBr_3$ at Bukit Atur and Tawau

Month	Sample total (n)		Mean (ppt)		Mode (ppt)		Median (ppt)	
	Bukit Atur	Tawau	Bukit Atur	Tawau	Bukit Atur	Tawau	Bukit Atur	Tawau
Nov-2008	415	544	1.69	5.87	1.25	1.65	1.41	2.63
Dec-2008	1640	1754	1.98	2.89	1.65	1.65	1.85	1.73
Jan-2009	1640	1889	2.39	1.70	1.85	1.65	2.31	1.66
Feb-2009	1526	1676	1.85	2.01	1.35	1.65	1.78	1.68
Mar-2009	1701	1886	1.69	1.72	1.65	1.35	1.66	1.46
Apr-2009	1118	604	1.81	2.38	1.15	1.65	1.57	1.68
May-2009	1020	437	1.67	1.49	1.55	1.25	1.52	1.40
Jun-2009	1247	701	0.93	1.97	0.85	1.15	0.89	1.62
Jul-2009	1305	729	1.11	2.38	0.85	1.65	1.02	1.71
Aug-2009	1119	285	1.35	2.18	1.15	2.45	1.25	2.25
Sep-2009	n/a	679	n/a	3.31	n/a	2.85	n/a	3.21
Oct-2009	n/a	1279	n/a	1.99	n/a	1.15	n/a	1.80
Nov-2009	n/a	1227	n/a	2.29	n/a	1.45	n/a	1.64
Dec-2009	n/a	580	n/a	2.48	n/a	2.05	n/a	2.21
Jan-2010	n/a	201	n/a	2.98	n/a	2.15	n/a	2.33
Overall	12731	14471	1.68	2.32	1.35	1.65	1.57	1.73

Table 3c: Statistical summary for $CH_2Br_2^*$ at Bukit Atur and Tawau

Month	Sample total (n)		Mean (ppt)		Mode (ppt)		Median (ppt)		$CHBr_3$ v $CH_2Br_2^*$ R^2	
	Bukit Atur	Tawau	Bukit Atur	Tawau	Bukit Atur	Tawau	Bukit Atur	Tawau	Bukit Atur	Tawau
Nov-2008	423	36	1.18	1.23	1.05	1.05	1.13	1.14	**0.86**	0.03
Dec-2008	1793	165	1.06	1.51	1.05	1.35	1.05	1.50	0.53	0.02
Jan-2009	1759	181	1.31	1.35	1.35	1.35	1.31	1.32	0.30	0.41
Feb-2009	1580	153	1.08	1.28	0.95	1.15	1.06	1.21	0.47	0.02
Mar-2009	1760	184	1.01	0.93	1.05	0.85	1.01	0.88	0.34	**0.88**
Apr-2009	1208	58	0.92	0.95	0.85	0.95	0.89	0.91	0.50	0.14
May-2009	1571	41	0.95	1.31	0.75	1.25	0.92	1.30	0.43	0.53
Jun-2009	1562	77	0.92	1.32	0.85	1.15	0.90	1.27	0.31	*<0.01*
Jul-2009	1555	70	1.12	1.37	1.05	1.35	1.10	1.37	0.59	0.03
Aug-2009	1134	64	1.20	1.79	1.15	1.75	1.18	1.79	**0.76**	0.01
Sep-2009	n/a	26	n/a	1.59	n/a	1.55	n/a	1.57	n/a	**0.64**
Oct-2009	n/a	115	n/a	1.81	n/a	1.55	n/a	1.60	n/a	<0.01
Nov-2009	n/a	90	n/a	1.56	n/a	1.25	n/a	1.45	n/a	0.01
Dec-2009	n/a	42	n/a	1.49	n/a	1.35	n/a	1.49	n/a	0.07
Jan-2010	n/a	22	n/a	1.72	n/a	1.85	n/a	1.74	n/a	0.15
Overall	14345	1324	1.07	1.37	1.05	1.35	1.05	1.35	0.26	0.01

Table 3d: Statistical summary for CH_3I at Tawau only

Month	Sample total (n)	Mean (ppt)	Mode (ppt)	Median (ppt)
Jan-2009	933	0.46	0.25	0.38
Feb-2009	1259	0.58	0.55	0.56
Mar-2009	1459	0.55	0.45	0.51
Apr-2009	396	0.49	0.45	0.46
May-2009	234	0.68	0.55	0.64
Jun-2009	486	0.54	0.55	0.54
Jul-2009	537	0.34	0.25	0.30
Aug-2009	338	0.85	0.65	0.72
Sep-2009	488	2.50	0.95	1.69
Oct-2009	935	1.17	0.75	0.96
Nov-2009	925	0.86	0.55	0.63
Dec-2009	383	0.94	0.85	0.91
Overall	8372	0.78	0.55	0.58

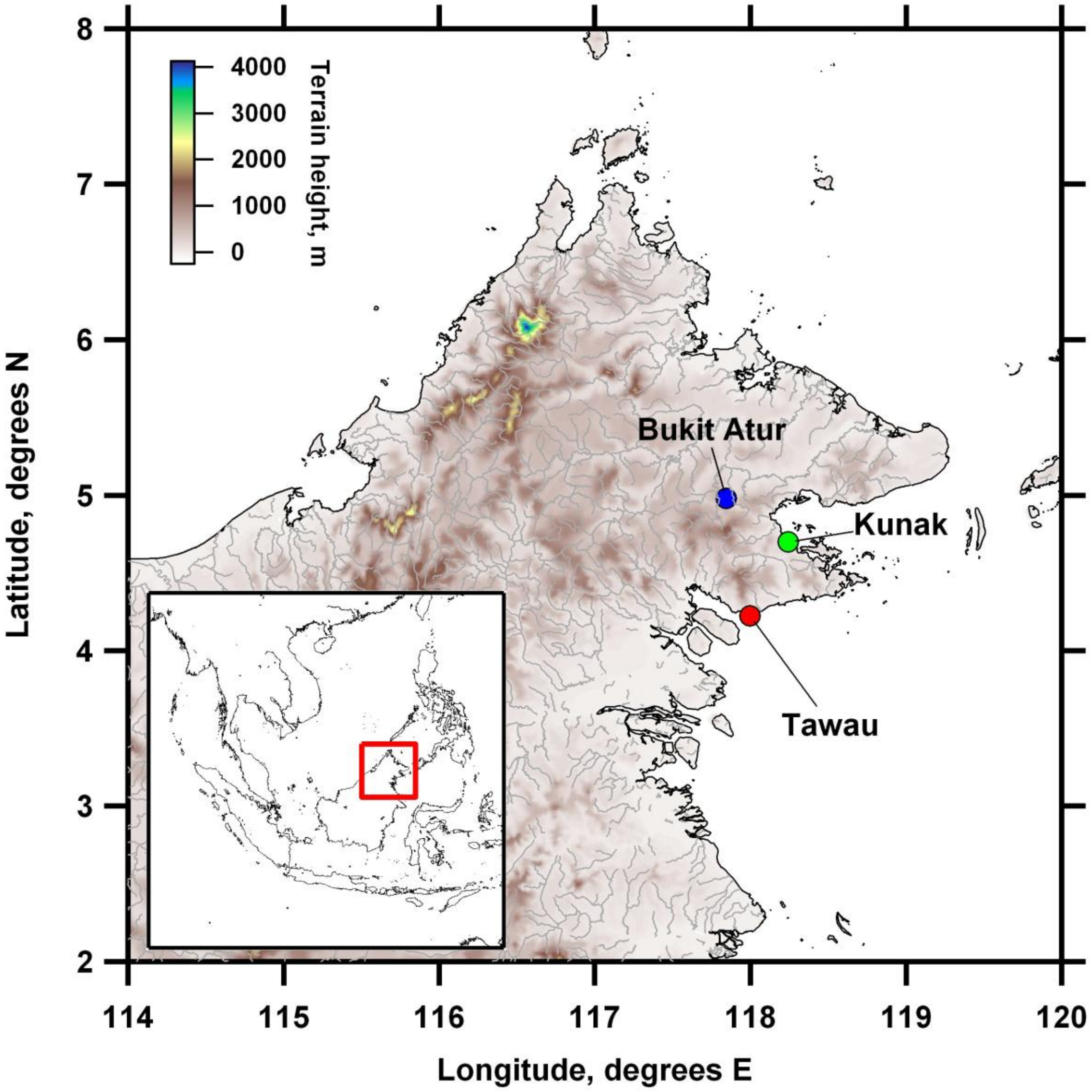

Figure 1: Site location map for Sabah. The inland rainforest site on Bukit Atur is shown by the blue circle, the coastal site near Tawau is a red circle and the coastal site at Kunak (green circle) is also shown as featured in Pyle et al. (2011). The Tawau site is ~85 km to the south of Bukit Atur. The inset (lower left corner of main panel) shows the southeast Asia region with a red square to show coverage of the main map.

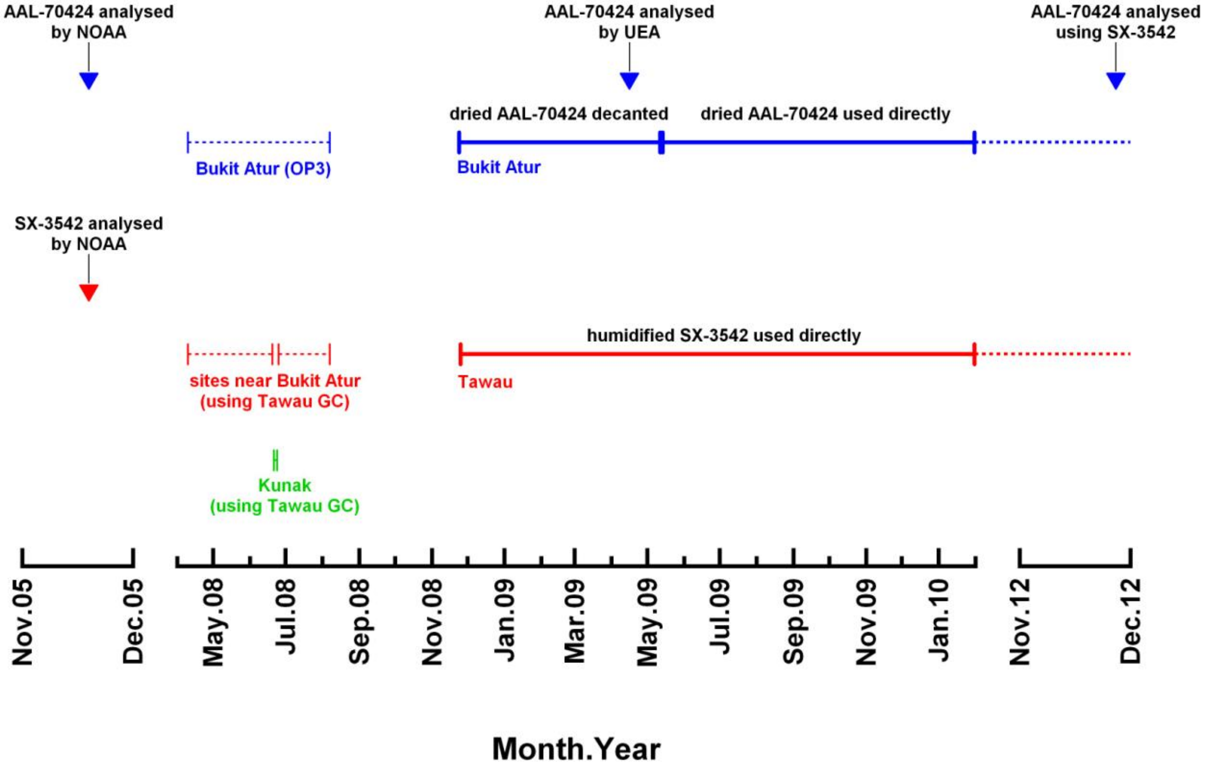

Figure 2: Timeline plot showing calibration comparisons and data coverage for the two sites. The solid blue line shows the data coverage for Bukit Atur and is divided into two periods where different calibration cylinders were used (decanted AAL-70424 from November 2008 to May 2009 and AAL-70424 used directly from May 2009 onwards). The solid red line shows the data coverage for the Tawau site where a high quality calibration cylinder (SX-3542) was used constantly. The arrows show times of the initial calibration by NOAA and the various times of comparisons made for the Bukit Atur site. Other measurement periods not used in this study are shown as dotted lines, including the deployment to Kunak (during the OP3 campaign) shown in green.

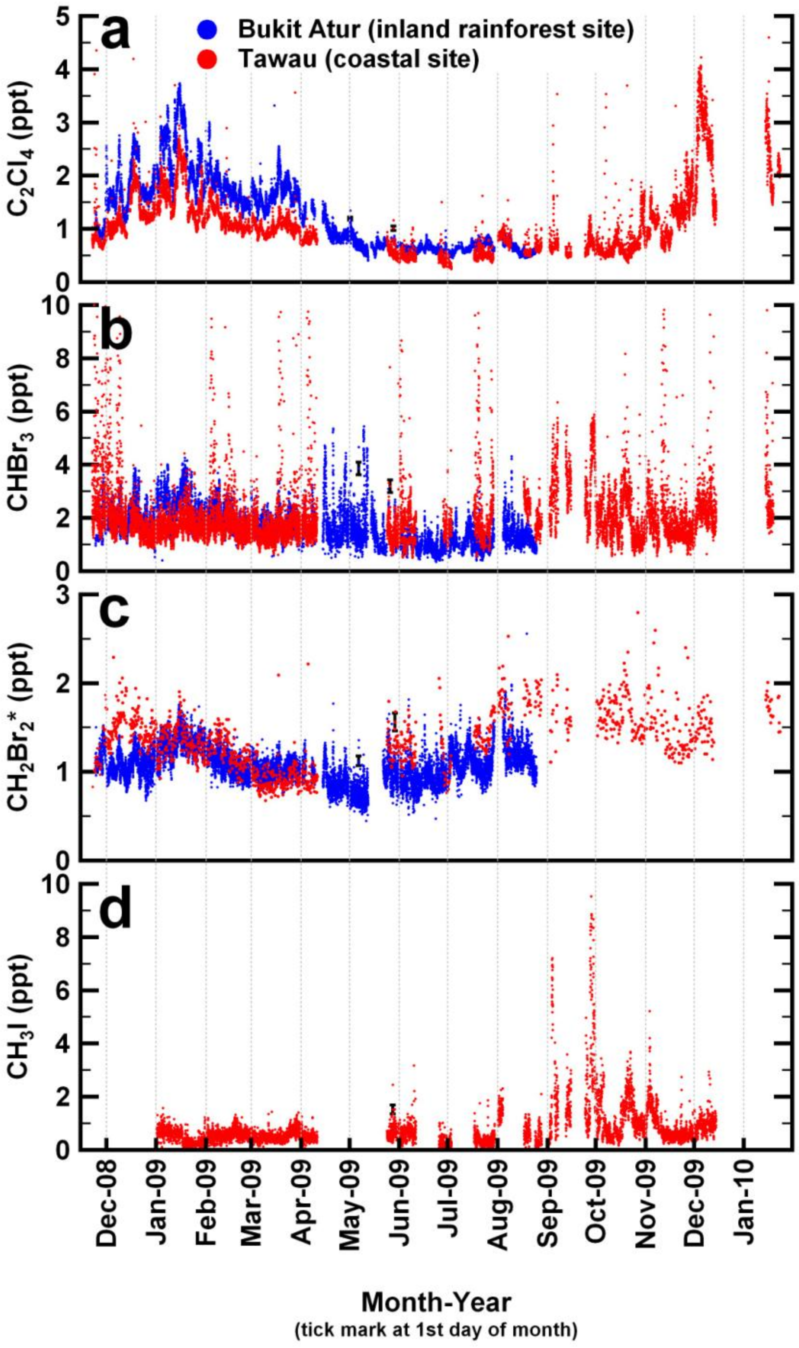

Figure 3(a-d): Time series of the four short-lived compounds (a) C_2Cl_4, (b) $CHBr_3$, (c) $CH_2Br_2^*$ and (d) CH_3I at Bukit Atur (blue) and Tawau (red) made between November 2008 and January 2010. High values beyond the scale of the y-axis are not shown, but are included in the box and whisker plots in Figure 4. A guide to measurement precision (±1 s.d.) is shown by the vertical error bars visible in each panel (May 2009) which show the typical precision for each compound, at each site, for the full period of data coverage. Gaps in the data are due to a combination of power outages and instrument breakdown

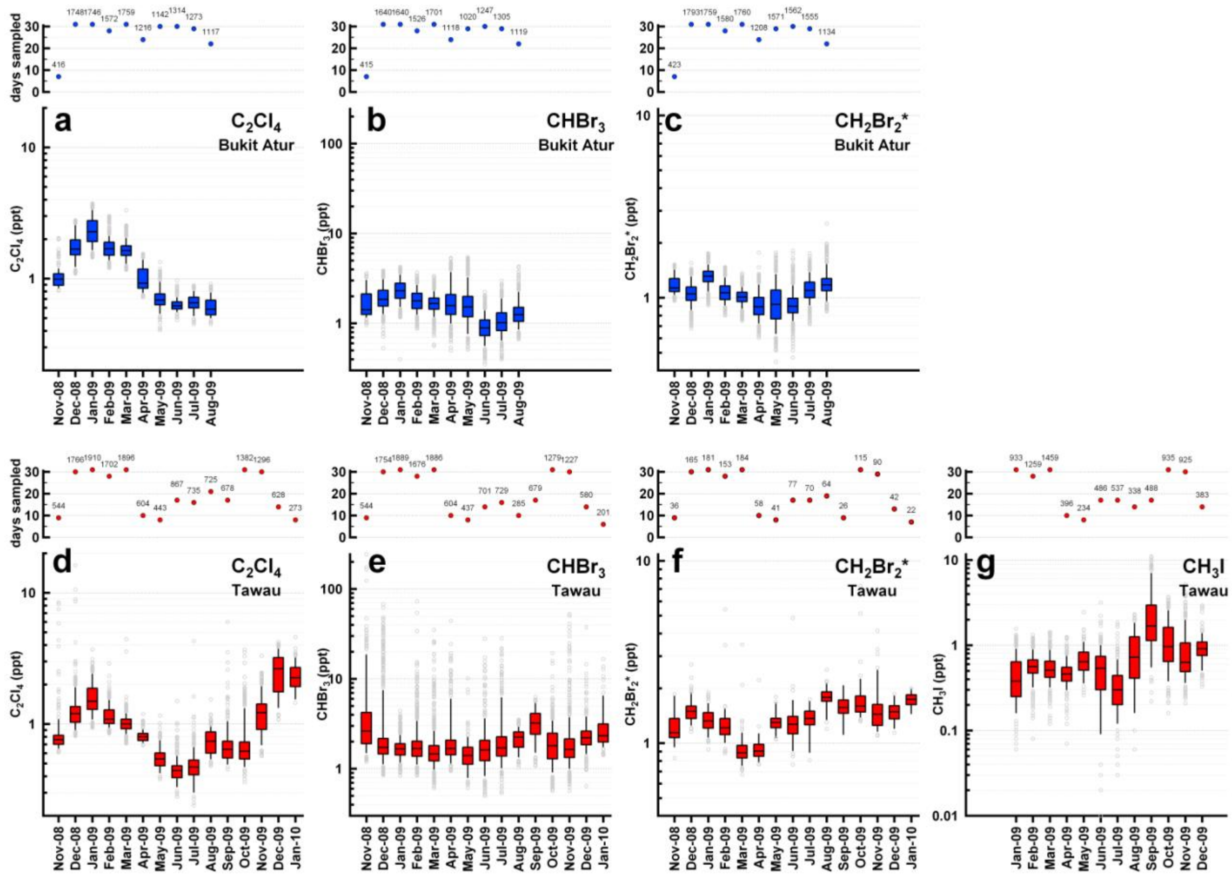

Figure 4(a-g): Box and whisker plots for the halocarbon observations at Bukit Atur for (a) C_2Cl_4, (b) $CHBr_3$, (c) $CH_2Br_2^*$ and at Tawau for (d) C_2Cl_4, (e) $CHBr_3$, (f) $CH_2Br_2^*$ and (g) CH_3I. In each panel, the coloured boxes show the data falling between the 25th and 75th percentiles, with the median value shown as a black horizontal line inside each box. The vertical black lines above and below each box indicate the 95th and 5th percentiles respectively. Outliers (values beyond the 95th and 5th percentiles are shown as grey open circles. The mixing ratio (y-axis) scale is logarithmic in order to show the extreme high values, such as for $CHBr_3$ at Tawau (e). The filled circles in the smaller panel above each box and whisker plot show the number of days sampled each month and labels indicate the number of samples used to generate each box and whisker. The total sample count is different at each site due mainly to different periods of instrument down time and differences in the sampling frequency at each site.

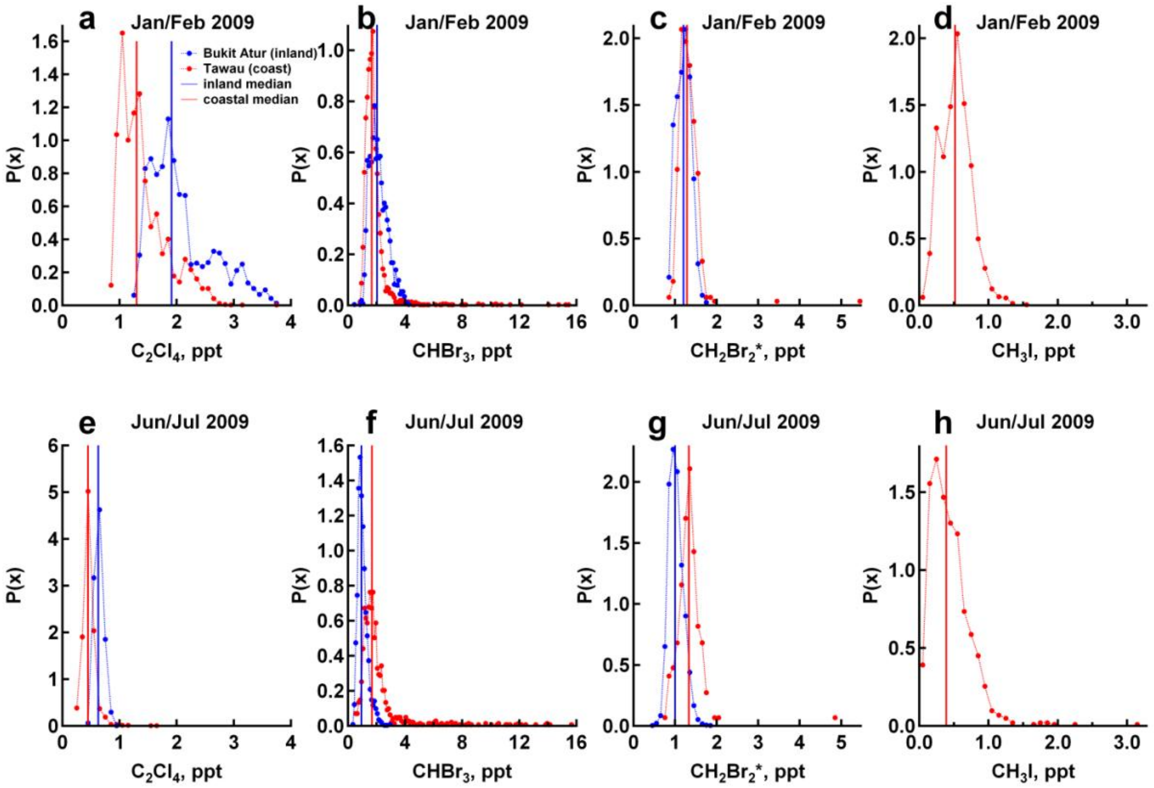

Figure 5(a-h): Probability distributions and median values at each site for January/February 2009 (merged) for (a) C_2Cl_4, (b) $CHBr_3$, (c) $CH_2Br_2^*$, (d) CH_3I (Tawau only) and June/July 2009 (merged) for (e) C_2Cl_4, (f) $CHBr_3$, (g) $CH_2Br_2^*$ and (h) CH_3I (Tawau only). Bukit Atur distributions are shown as blue circles with dotted blue lines and Tawau as red circles with dotted red lines. Median values for inland Bukit Atur are shown by solid vertical blue bars and for coastal Tawau by solid vertical red bars. The bin width for each probability distribution is 0.1 ppt and the area under each curve is equal to 1 (probability of 1). High values beyond the scale of x-axis are not shown, for instance the high tail is not wholly visible for $CHBr_3$ at Tawau (b & f), though all data are included in the box and whisker plots (Figure 4).

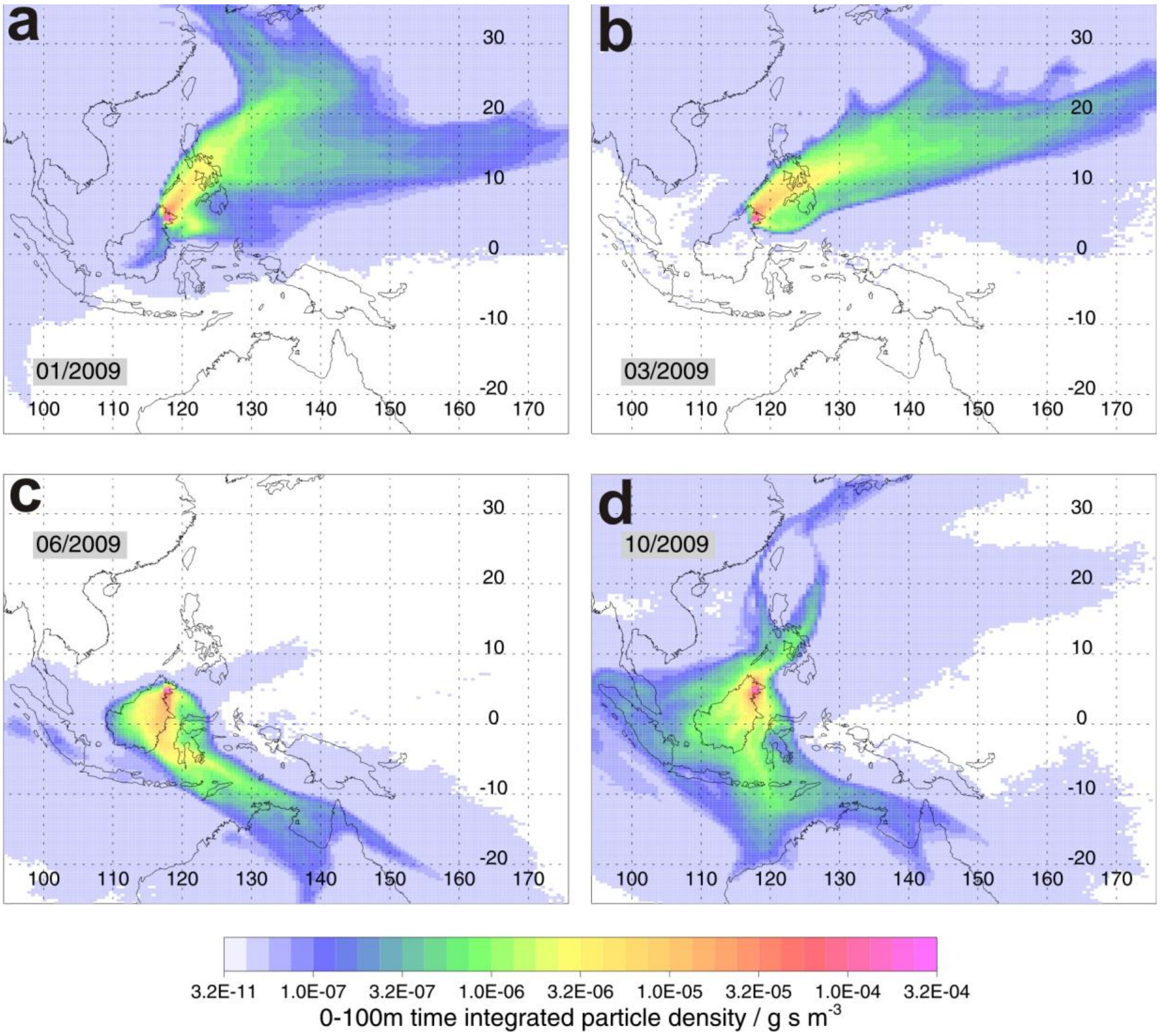

Figure 6(a-d): Air history maps for 2009 for Bukit Atur for selected months: (a) January; (b) March; (c) June; (d) October. Maps for all months were produced but not shown. Each map is compiled from 11000 particles released on an hourly basis by the NAME dispersion model using UK Met Office analysed wind fields at ~50 km horizontal resolution. They show the particle density in the lowest 100 m averaged over the preceding 12 days. From November to February the air mass origin is mainly from the northern hemisphere, often passing close to China (a). Between March and May the air mass origin gradually changes towards West Pacific equatorial latitudes, away from large urban regions (b). From June to September the air mass history is influenced from the region to the southeast, characterised by southern hemisphere air, with sparse anthropogenic emissions (c). October sees a transition back to northern hemisphere air masses (d).

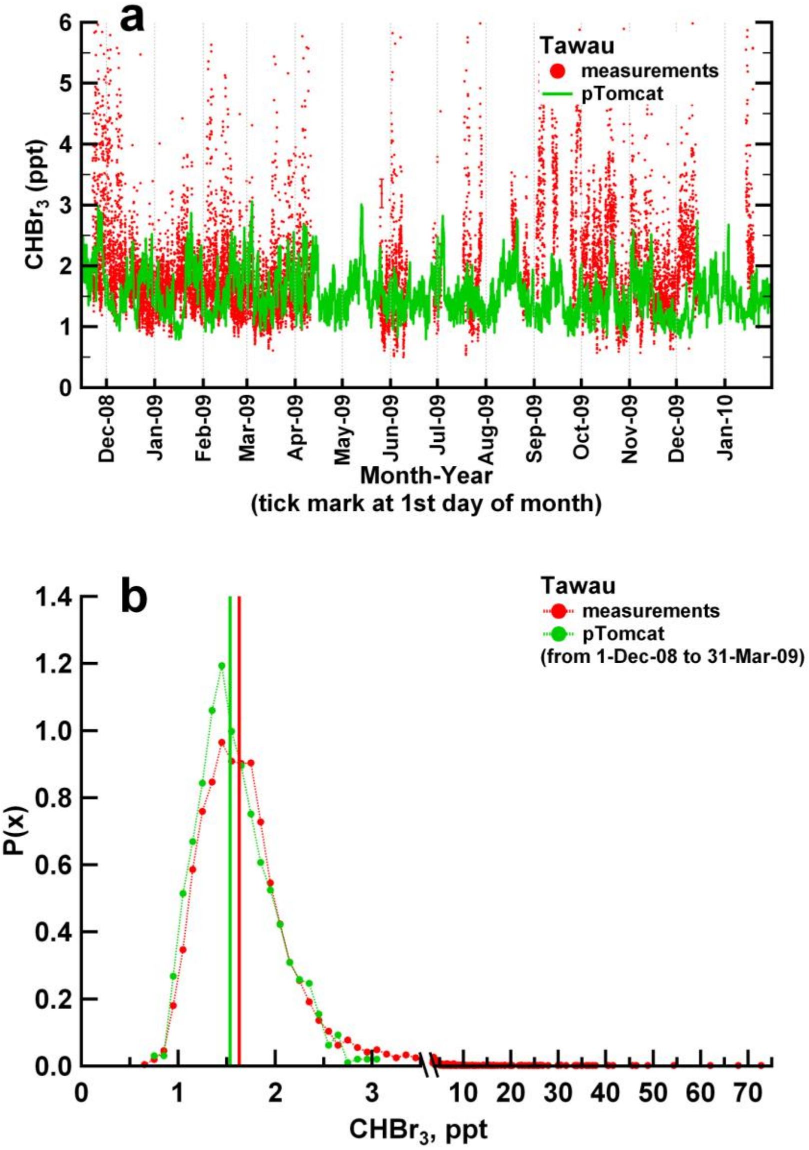

Figure 7(a & b): Time series (a) of observed (red dots) and p-TOMCAT modelled (green line) CHBr$_3$ at Tawau and probability distributions (b) for observed (red circles with red dotted line) and modelled CHBr$_3$ (green circles with green dotted line) for December 2008 to March 2009. The black vertical error bar in (panel a during May 2009) shows the typical CHBr$_3$ measurement precision (±1 s.d.) for the whole observational period. Median CHBr$_3$ mixing ratios are indicated (b) by the red solid line for the observations and by the green solid line for the model. The model compares well overall with the observations though there are periods when the model underestimates the observations (e.g. October 2009). The model does not capture the full variability of the observations which is expected given the model resolution and the uniform distribution of coastal emissions in the model, this is illustrated by absence of the high tail in the modelled CHBr$_3$ (b).

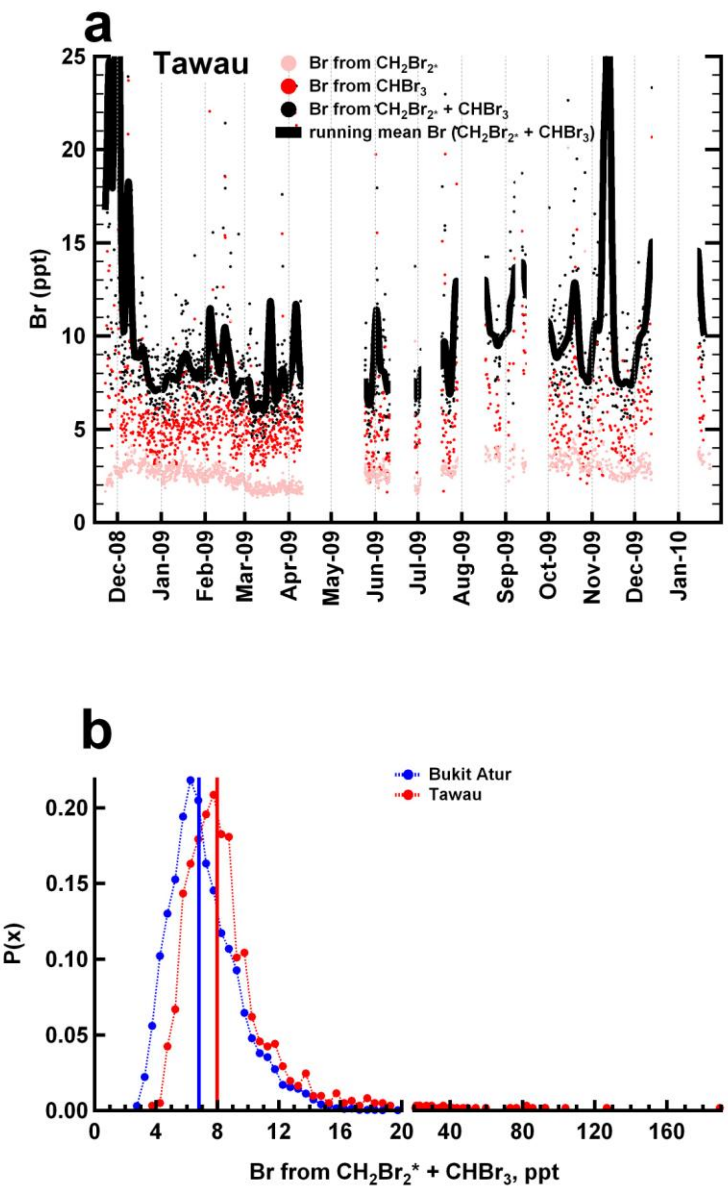

Figure 8(a & b): Estimated total Br (a) from observed $CHBr_3$ and $CH_2Br_2^*$ as a time series at Tawau and (b) as probability distribution functions at Bukit Atur and Tawau. Bromine from $CH_2Br_2^*$ is shown by the light red dots (panel a) and from $CHBr_3$ by the dark red dots, whilst Br summed from $CHBr_3$ and $CH_2Br_2^*$ is shown by the black dots and the heavily smoothed black line. The probability distributions for Bukit Atur (blue circles with blue dotted line) and Tawau (red circles with red dotted line) for the 10 month period from November 2008 to August 2009 are similar (panel b). The total Br median values shown as blue (Bukit Atur) and red (Tawau) vertical lines agree with each other to within 1.2 ppt. Occasionally very high total Br observed at Tawau is clearly seen (right of the x-axis break), events higher than 20 ppt were never observed at Bukit Atur.