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Bromoform in the tropical boundary layer of the Maritime Continent during OP3: the contrast between coast and rainforest

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Abstract

We report measurements of bromoform made by gas chromatography during the OP3 campaign in 2008. Measurements were made simultaneously for a few days at the World Meteorological Organization (WMO) Global Atmospheric Watch (GAW) site in the Danum Valley, a rainforest location in Sabah, Borneo, and at a nearby coastal site at Kunak. Background values at Kunak were higher than those measured in the rainforest (2–5 ppt compared with 1 ppt) and excursions away from the background were very much higher, reaching 10s of ppt. Measurements of C_2Cl_4, an industrial tracer, showed no significant difference in background at the two sites. The data are consistent with a strong, local coastal source of bromoform in eastern Sabah. Modelling using two different models can reproduce many of the observed features. The bromoform data are consistent with a lower global source (190 Gg Br yr^{-1}) than indicated by our recent measurements on Cape Verde (O'Brien et al., 2009) and point to the difficulty for short-lived species of extrapolating local measurements to a global source.

1 Introduction and background

Two major field campaigns of the multi-national OP3 (Oxidant and particle photochemical processes above a south-east Asian tropical rainforest) project took place during 2008 in Sabah, Malaysia, on the island of Borneo. The OP3 project aims were wide-ranging, focussed on the better understanding of the interactions between natural forests, atmospheric composition and the Earth's climate system. A wide range of measurements explored biogenic emissions and their contribution to the oxidizing capacity of the troposphere. For example, measurements of isoprene fluxes from the forest and from palm oil plantations were an important component of OP3 and first results describing the potential implications of land use change for atmospheric isoprene concentrations and for oxidising capacity have been presented by Hewitt et al. (2009). The detailed objectives of OP3, and some preliminary results, are described by Hewitt et al. (2010).

An important sub-focus of OP3 was the investigation of the role of halogen species. Several groups made measurements of halocarbons (see Table 1 in Hewitt et al., 2010) and there was also a supporting modelling effort. There are a number of pressing reasons to study halocarbons in the tropics. Firstly, recent measurements at the Cape Verde Observatory have indicated that halogen species play an important role in controlling tropical oxidizing capacity (Read et al., 2008). The source of the halogen radicals is not well understood so further measurements of potential source gases are required; measurements of both radical and source gases were an OP3 objective. Secondly, there is some evidence that the rainforest might be a direct source of some halocarbons. A number of studies have looked at possible biogenic sources of halocarbons (principally CH_3Cl, but including other chloro- and bromocarbons), with the sources including plants, leaf litter, wood-rotting fungi and insects (Harper, 1985; Hoekstra et al., 1998; Yokouchi et al., 2002; Gebhardt et al., 2008; Mead et al., 2008; Saito et al., 2008). Thirdly, there is increasing interest in the role of natural, short-lived halogen species, which could potentially be lifted rapidly to the low stratosphere in deep convection where they could play a role in stratospheric ozone destruction (see, for example, Law, Sturges et al., 2007). The Maritime Continent is likely the most important tropical location for this rapid transport (see, e.g., Levine et al., 2008), and characterising the background concentrations of these short-lived compounds, and their variability, in that region is an important research objective.

Halocarbons have both natural and anthropogenic sources. The anthropogenic sources are largely well understood and production is controlled under the Montreal Protocol and its amendments (see, e.g., WMO, 2007). Many of the shorter-lived compounds are believed to be emitted naturally and the tropical oceans represent a major source. For example, bromoform ($CHBr_3$) is the major natural contributor of organic bromine to the atmosphere (Penkett et al., 1985; Carpenter and Liss, 2000; Quack and Wallace, 2003); it is predominantly oceanic in origin, with tropical macroalgae constituting an important source (Gschwend et al., 1985). An open ocean source, related to phytoplankton, has also been identified (Tokarczyk and Moore, 1994).

The short-lived biogenic halocarbons have been measured in very variable concentrations in a number of different locations, emphasizing the importance of localized emissions of these compounds, which show both temporal and spatial variability. For example, $CHBr_3$, with a tropical lifetime with respect to photolysis and reaction with hydroxyl (OH) radicals of two to three weeks (Warwick et al., 2006), exhibits large spatial variability. Class and Ballschmiter (1988), Quack et al. (2004) and Carpenter et al. (2007) report mixing ratios of $CHBr_3$ over the eastern tropical Atlantic Ocean, ranging from a minimum of about 0.2 ppt to maxima around 25 ppt. O'Brien et al. (2009) deployed a version of the gas chromatograph used in this study at the Cape Verde Observatory in June 2007. During a measurement period of about 10 days they reported mixing ratios of bromoform with a background of about 4 ppt but with episodes of much higher mixing ratios to greater than 40 ppt. Shallow coastal areas seem to be particularly important for emissions of oceanic halocarbons. Yokouchi et al. (2005) observed a maximum of 40 ppt of $CHBr_3$ at the coasts of San Cristobal and Christmas Islands in the tropical Pacific Ocean. Highest measured concentrations of polybromomethanes coincided with the onshore sea breeze, across the coastal zone. A number of studies show $CHBr_3$ and CH_2Br_2 to be well correlated in coastal locations, suggesting a common source for these compounds (for example see Quack et al., 2007; Yokouchi et al., 2005; O'Brien et al., 2009).

Measurements of short-lived species inevitably display large variability. It is clear that more measurements of the short-lived halocarbons, including bromoform, are required to allow better understanding of their sources and to characterise variability. These were among the OP3 objectives. In this paper we focus on a comparison between rainforest and coastal measurements of two halocarbons by gas chromatography to investigate differences between coast and rainforest. We report data taken during June 2008 when for a few days two of the Cambridge μ-Dirac instruments, as previously deployed in Cape Verde, made simultaneous measurements in Borneo from the GAW site at Bukit Atur (4.98° N, 117.85° E) and at Kunak (4.70° N, 118.24° E), a coastal site about 50 km from Bukit Atur which overlooks the largest bay in Eastern Sabah. The μ-Dirac gas chromatograph with electron capture detector (GC-ECD) (Gostlow et al., 2010; O'Brien et al., 2009) can measure a range of halocarbons. Here two identical instruments were deployed. We focus on measurements of the predominantly biogenic species, bromoform. Our aim is to explore differences between the bromoform measurements at the two sites, to investigate whether they are consistent with current emission scenarios and to see to what extent large scale numerical modelling tools can be used in the interpretation of these local measurements. For purposes of comparison, measurements of an anthropogenic species, C_2Cl_4, are also presented here.

The next section introduces the tools used in this study. First we present a brief description of μ-Dirac and then we outline p-TOMCAT and NAME, two different models used here. Section 3 presents the data while Sect. 4 aims to interpret the data using the models. An outlook for future work is presented in Sect. 5.

2 Experimental tools

2.1 The μ-Dirac gas chromatograph

μ-Dirac is an inexpensive, purpose-built gas chromatograph, which has been designed to make long-term in-situ measurements of a small number of halocarbons (Gostlow et al., 2010; O'Brien et al., 2009). Its relatively low cost and ease of operation mean that multiple instruments can be deployed straightforwardly at a number of surface sites, thereby providing a valuable constraint on variability and emission estimates. μ-Dirac was originally designed for flights on long duration balloons and so is lightweight and able to operate autonomously. It is well suited for long periods of unattended operation. Earlier versions have been deployed on balloons, at ground-based sites and on aircraft (Robinson et al., 2000, 2005; Ross et al., 2004). μ-Dirac has a modular design with an adsorbent-containing micro-trap, which removes the halocarbons from the air. A fixed volume of 20 scc is collected for each atmospheric sample, with a sampling time of approximately 1.5 min. The micro-trap is then flash heated and the desorbed halocarbons are passed through a chromatographic column with temperature and flow programming capability. After temporal separation in the column the flow passes through the ECD, which is extremely sensitive to halocarbons. The absolute calibration for most of the reported gases (including both the gases discussed here) is determined by reference to a NOAA-ESRL calibration standard (certified in December 2005), with an on-board standard gas bottle being filled directly with air from the NOAA-ESRL standard. Mixing ratios are reported as dry air mole fraction in ppt.

Two instruments were taken to Borneo for OP3. Various modes of operation, and locations, were trialled. One instrument was always housed in an air-conditioned laboratory at the GAW site at Bukit Atur in the Danum Valley and collected data via a tube at 10 m on the tower. The second instrument sometimes made measurements side-by-side with the first instrument, including measurements at various heights up the 100 m GAW tower. It was sometimes deployed elsewhere, including overnight on the forest floor in an attempt to detect local rainforest sources and, for the case discussed here, at a fish-farm building a few metres from the shore of the large bay at Kunak. In either case, the run cycle was roughly 14 min, with a blank sample and a calibration standard being sampled on average after ten atmospheric samples (i.e. every 2 to 3 h). The instrument was cooled internally with Peltier coolers. The species that are measured include: CFC-11, CFC-113, CH_3CCl_3, CCl_4, CH_3I, C_2HCl_3, $CHCl_2Br/CH_2Br_2$, C_2Cl_4, and $CHBr_3$. In this paper we report measurements of $CHBr_3$ and C_2Cl_4, natural and anthropogenic species respectively, for a short period during June 2008. We now have data for many species from two sites in Sabah covering two years and a paper describing these data is in preparation. Measurement characteristics have been presented in detail in Table 1 of O'Brien et al. (2009) and in Gostlow et al. (2010) so we do not repeat that here. Suffice to say that for $CHBr_3$ and C_2Cl_4 the overall uncertainties are ±8% and ±4% respectively (1σ values).

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2.2 The models

We have used two different models, p-TOMCAT and NAME, to analyse the halocarbon data we collected during OP3. The basic formulation of the global chemistry and transport model p-TOMCAT is described in Law et al. (2000) and Savage et al. (2004). Here we base the model on the version of p-TOMCAT described by Warwick et al. (2006) which includes emission of the following bromocarbons: CH_3Br, $CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBr_2Cl$ and $CHBrCl_2$. Their degradation is calculated using pre-calculated time-varying 3-D fields of OH (from a previous p-TOMCAT integration) and photolysis frequencies.

The Numerical Atmospheric dispersion Modelling Environment (NAME) is a Lagrangian particle dispersion model developed by the UK Met Office (see, e.g. Ryall and Maryon, 1998), 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 mean wind fields calculated by the UK Met Office's numerical weather prediction model, the 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; Webster et al., 2006; Witham and Manning, 2007). Both modes of operation are deployed here.

3 The data

We report data collected during June and July 2008 in the second phase of OP3. The two instruments were operated side-by-side at the GAW site on 16/17 June and one instrument was then transported the 53 km to Kunak, at the coast. Kunak is a small town with some industry, including a palm oil processing plant. We observed the bay at Kunak to be rich in macroalgae. After four days of operation (21–24 June) the instrument was then returned to the GAW site in the Danum Valley and further side-by-side measurements were performed.

Figures 1 and 2 show our measurements of $CHBr_3$ and C_2Cl_4. For both species, the two instruments made consistently similar measurements during side-by-side operation at Bukit Atur both before and after the Kunak deployment. It seems clear that any differences between Danum and Kunak should represent real atmospheric differences and not a change in instrument characteristics during the Kunak deployment.

There are several prominent features in the bromoform data. First, the background values at Kunak of 2–5 ppt are considerably higher than those measured inland at the GAW site (∼1 ppt) and more consistent with our Cape Verde measurements of May and June 2007 (O'Brien et al., 2009). Bromoform has a tropical lifetime of about 2 weeks, so such a large gradient across 50 km might seem surprising at first sight. In Sect. 4 we use the models to explore this question. Second, there are several occasions when extremely high mixing ratios, up to nearly 60 ppt, were measured. These were all cases with onshore winds and most likely represent the measurement of very local emissions. Third, there seems to be a diurnal signal in the Kunak data with bromoform peaking in the late afternoon, although with only three days of data the significance of the variability is unclear. At Danum there is a much smaller diurnal variation and here the peak occurs around midnight. Analysis of this feature is still ongoing and will not be discussed here.

C_2Cl_4 is a predominantly industrial compound used as a metal degreasing solvent and for dry cleaning. Unlike for $CHBr_3$, the baseline measurements of C_2Cl_4 at Kunak are comparable with the measurements at Danum Valley of 0.7–0.8 ppt. Like bromoform there are large excursions above the baseline up to 2 ppt; however, these do not correlate with the bromoform peaks, suggesting that their origin is real and different to that of bromoform. It seems likely that they represent the influence of an industrial source, either locally at Kunak or from further down the coast towards Tawau (see

Sect. 4).

4 Modelling and data interpretation

In this section we will use two different numerical models to explore features of the bromoform data. Can the models explain the differences seen in the Danum Valley and Kunak measurements? These include the different background levels of bromoform measured at the two sites as well as the strong peaks in both bromoform and C_2Cl_4 measured at Kunak. We also ask here whether the measurements of bromoform are consistent with our current understanding of emissions. The NAME model was run at a higher effective resolution than p-TOMCAT in this study. We use NAME primarily to explore differences between the two sites and p-TOMCAT to assess the implications of the measurements for our understanding of emissions.

The NAME model was first run backwards in time to determine the dominant direction of flow to the measurement sites in Sabah. Figure 3 shows, for air parcels arriving at Kunak on 23 June, the footprint (time integrated particle density) in the lowest 100 m of the model atmosphere at any location during the previous 10 days. Warm colours show the highest fractions and indicate where the measured air parcel has been most sensitive to surface emissions. The meteorological situation during the Kunak deployment was stable and the pattern shown in Fig. 3 barely changes during the measurement period. The large scale flow is south-easterly with the air arriving at Kunak coming from the direction of northern Australia, across the Timor and east Java Seas before turning more southerly along the east coast of Borneo. These are potentially rich emission regions for halocarbons, with both the warm ocean and coastal areas possibly providing significant biological sources (as suggested, for example, by the ocean colour data available from http://daac.gsfc.nasa.gov/giovanni/). In particular, with flow along the Borneo coast air parcels might have been expected to have picked up high concentrations of those bromocarbons emitted by macroalgae.

The flow shown in Fig. 3 offers a plausible explanation as to why high background concentrations of bromoform were measured at Kunak but cannot explain why the Kunak measurements are higher than those at Danum Valley. To explore this question, NAME was run forward in time. As running a dispersion model forwards in time with millions of particles is computationally expensive we chose to release particles only from those coastal regions that we know are likely to have influenced the measurement sites. From backwards calculations we know these to be the eastern coastal strip of Borneo, the coasts of Sulawesi and east Timor and the northernmost coastal strip of Australia, close to Darwin. The mass on each particle has a specified e-folding lifetime of 15 days and is removed completely when the mass drops below 10% of the starting value. So, this experiment mimics the distribution of a coastally-emitted tracer, like bromoform (although bromoform also has an open ocean source). The emitting coastal boxes have dimensions $0.1^\circ \times 0.1^\circ$. Time series of the tracer distributions from this experiment for Kunak and Danum are shown in Fig. 4. Results are for the lowest 100 m of squares of size 0.2° centred on the two locations. With our grid, Kunak directly experiences coastal emissions while Danum does not. Higher resolution would likely degrade the statistics (fewer parcels per box) while a lower resolution would not allow us to distinguish between Danum and Kunak. Note that the resolution of the meteorological forcing fields is only $0.5625^\circ \times 0.375^\circ$ (although our experience is that low resolution winds on a high resolution grid can produce realistic structure).

The results in Fig. 4 show some similarities to Fig. 1. First, the concentrations at Danum are usually less than at Kunak, sometimes by a factor of two or more. (The modelled difference increases if a coarser grid is used.) Secondly, the model for Kunak shows more high concentration excursions, as observed, and has a slightly higher variability than Danum, presumably the influence of emissions local to Kunak. Indeed, we have carried out further NAME experiments to explore the differences in more detail. Thus, when the emissions are labelled by the coastal emission region (with eight different tracers, approximately equally spaced in latitude along the east of Borneo from about 7° N to about 4° S) it is clear that the largest differences between Kunak and Danum arise from coastal emissions around and just to the south of Kunak. These local emissions can have a large, and variable, impact at Kunak but, with the prevailing wind direction during this period, are advected northwards and do not affect Danum significantly. Danum is more influenced by coastal emissions from further south. Notice that in the experiment presented in Fig. 4, a modelled diurnal variation is found at both Kunak and Danum.

The NAME model sometimes predicts similar (or even higher) concentrations at Danum than at Kunak. During our four days of measurements we never saw this feature but a much longer time series of data which we have collected since OP3, with measurements at Danum and Tawau, a coastal site just a little to the south of Kunak, does sometimes show this. It appears that the higher measurements at Kunak in late June 2008 are in part a result of the particular meteorological situation then.

The above has shown that calculations with NAME are consistent with a number of the observed features, in particular, a gradient between Kunak and Danum Valley and the stronger peaks at the coastal site. We now use p-TOMCAT to address the question of emission strengths. Figure 5 shows June surface bromoform mixing ratios around the island of Borneo calculated in a high resolution (approximately 60 km horizontal) p-TOMCAT integration. Emissions of bromoform are specified both over the open ocean and along the coasts, as in Scenario 5 from Warwick et al. (2006). However in order to capture our Borneo observations, these bromoform emissions need to be substantially reduced. For the model scenario presented in Fig. 5, the open ocean emissions have been reduced by a factor of two and the coastal emissions by a factor of six, relative to Scenario 5 from Warwick et al. (2006), giving a global emission of 190 Gg Br yr^{-1}. With this emission reduction, the model is able to capture well the background mixing ratios at the inland measurement site at Danum. The model also captures a concentration gradient between the coast and inland, consistent qualitatively with the differences in bromoform measured at our two sites. Similar to the NAME calculations, the gradient varies with the meteorological situation and sometimes we find no gradient or even a reverse gradient. At the horizontal resolution of about 60 km, the model is, however, still unable to reproduce the large daytime peaks observed at Kunak and does not capture the magnitude of the differences between Danum and Kunak. The modelled "background" at Kunak is somewhat lower than observed, consistent with the coastal emissions at this resolution being spread over too large an area.

5 Conclusions and further prospects

As part of the OP3 project, halocarbon measurements were made in 2008 at two sites in Sabah, Borneo, by gas chromatography using the μ-Dirac instrument. In this second field deployment of μ-Dirac the measurements confirmed the potential of the instrument for long-term observations at a range of sites for studies of halocarbon trends and for the determination of emissions. Observations with two identical instruments at Bukit Atur, Danum Valley, produced identical measurements of two different halocarbons, bromoform and C_2Cl_4. When one instrument was then deployed at a nearby coastal site, higher concentrations of both species were measured. The bromoform background at the coast was higher than inland and the variability was also greater, with occasional peaks of many 10 s ppt. The background of C_2Cl_4 was the same at both sites but, again, the coastal measurements showed occasional very high values. In each case, the explanation appears to lie with coastal sources. In the case of bromoform, these are likely to be related to macroalgae; for C_2Cl_4 industrial emissions from the populated coastal strip are the probable explanation.

Two different numerical models were used to aid data interpretation. The Lagrangian air parcel dispersion model, NAME, confirms that the air parcels during this period had crossed potentially rich oceanic and, especially, coastal regions prior to measurement in Sabah. Both models show that, despite a lifetime of about two weeks, substantial gradients between the coast and inland can be expected for bromoform, with the coastal measurement variability being dominated by local emissions. For the very short period of measurements undertaken, the coastal background was always higher than that measured inland. The modelling suggests that this need not always be the case, a result confirmed by a longer measurement series not reported here. The chemical transport model, p-TOMCAT is able to reproduce the magnitude of the bromoform measurements but only if the emission strengths used by Warwick et al. (2006) are reduced. Here we used global bromoform emissions of 190 Gg Br yr^{-1}, considerably lower than those reported earlier based on our short period of measurements at the Cape Verde observatory in 2007 (O'Brien et al., 2009). The difference serves to emphasise the difficulty with using local measurements of short-lived halocarbons to attempt to infer global emissions. In a further analysis, we scaled the NAME calculations to an effective emission rate of 1.2 Gg Br yr^{-1} from the upwind coastlines (approximately the coastlines within the dark blue shading in Fig. 3) and obtained good agreement with the magnitude of the Danum observations. The contribution to the global emissions in p-TOMCAT (which also agrees well with the observations) from the same geographical region corresponds to 2.6 Gg Br yr^{-1} (p-TOMCAT includes both coastal and open ocean sources). Recall that the local emissions dominate the short-term behaviour at Kunak with the further-field emissions making a smaller contribution. Given this difference, these emissions are in reasonable agreement.

Any model derivation of emissions needs to recognise model uncertainty. In particular, neither model has the resolution to capture very small scale features of transport, for example, the local sea breeze. Treatment of the boundary layer, especially in areas of complex topography like the Danum Valley (see, e.g., Pearson et al., 2010; Pike et al., 2009), will also introduce uncertainty into our analysis. These calculations are at a higher effective spatial resolution than many previous chemical transport studies; nevertheless, one focus of future work needs to be the drive towards even higher resolution.

Source estimates based on short local data records must be subject to considerable uncertainty. We are addressing this issue by extending the deployment of μ-Dirac instruments in time and space. We now have nearly two annual cycles of measurements from two sites in Borneo (Bukit Atur, as reported here, and a new coastal site at Tawau, 85 km from Bukit Atur). These measurements will continue and will soon be complemented by the further installation of μ-Dirac at several new measurement sites in South East Asia.

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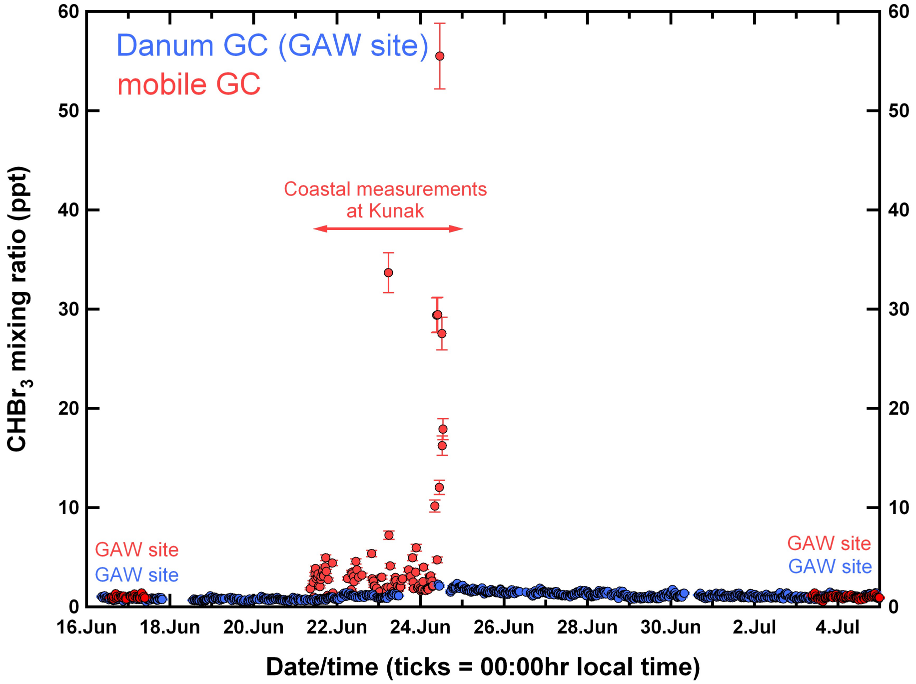

Fig. 1. Concentration of $CHBr_3$ (ppt) measured at Danum Valley and Kunak by the μ-Dirac GC. Blue symbols indicate measurements with the instrument deployed throughout at Danum valley. Red symbols are concentrations measured by the instrument which was deployed at Kunak between 21 and 25 June, but otherwise was at Danum Valley.

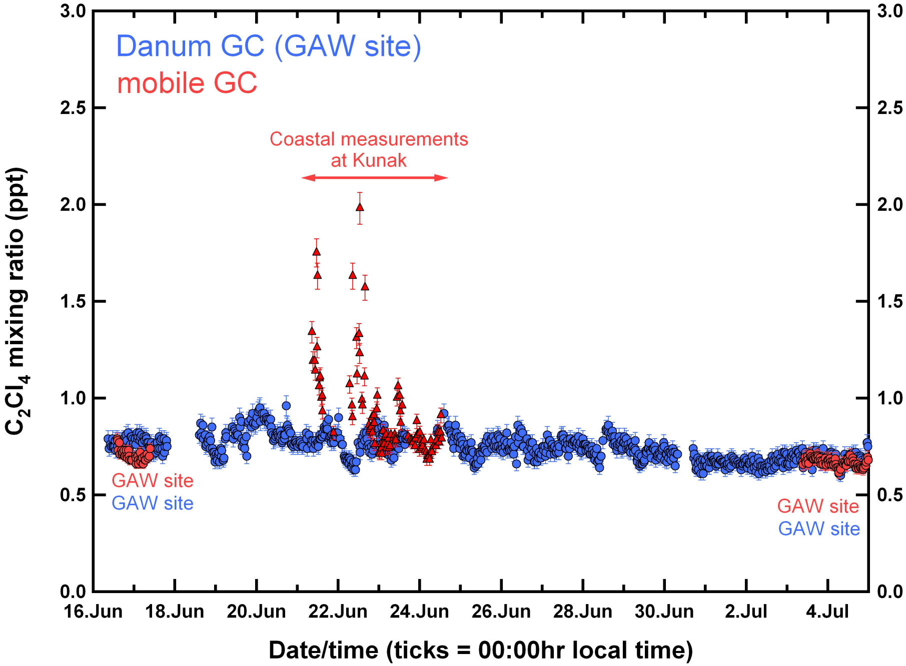

Fig. 2. Time series of measured concentrations of C_2Cl_4. The colour scheme means the same as in Fig. 1.

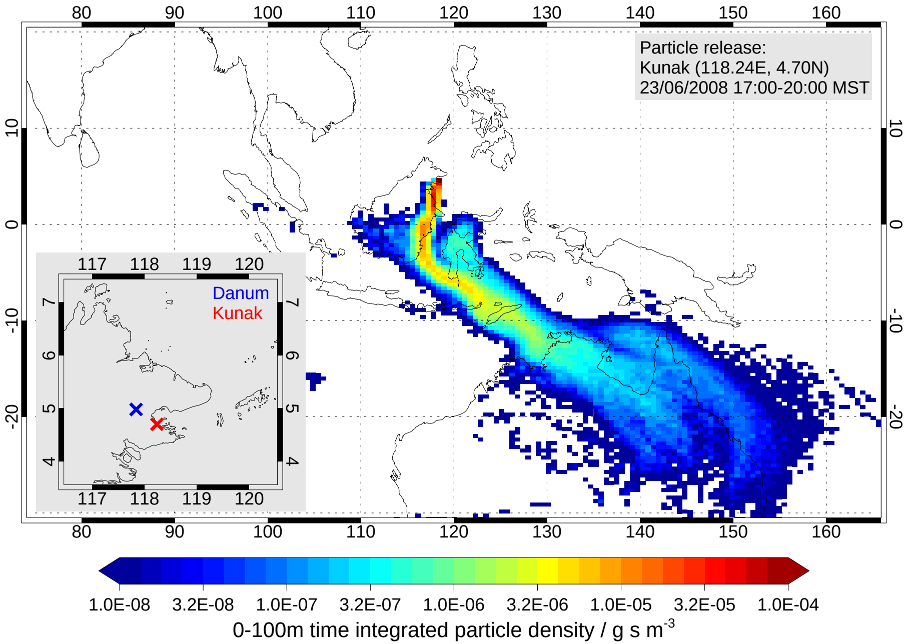

Fig. 3. NAME air history map for Kunak on 23rd June 2008. Thousands of inert particles, which represent a contribution to the measured air parcel, were released from Kunak and carried an arbitrary mass backwards in time for 10 days. At each 15 min time-step the location of each particle within the lowest 100 m of the model atmosphere was recorded. This information, when collected together, indicates where the air parcel measured at the release time may have experienced surface emissions. Warmer colours indicate a greater contribution. Inset: location of Danum and Kunak measurement sites.

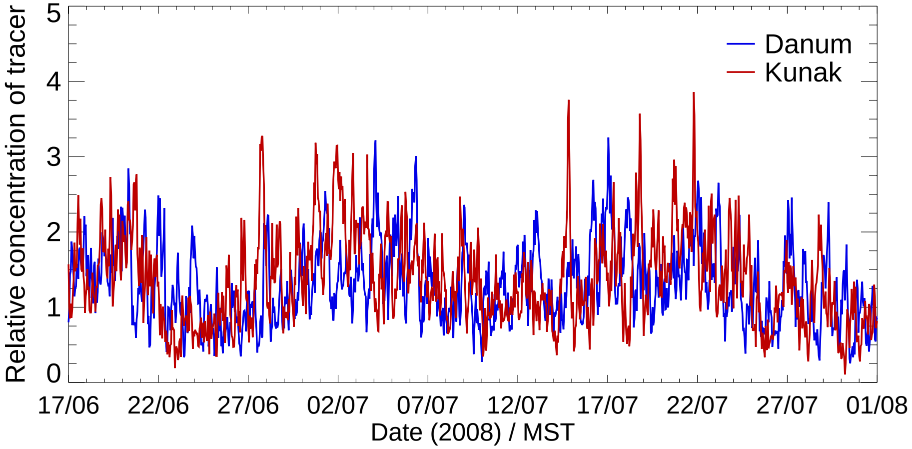

Fig. 4. Variation with time of NAME coastal tracer at Danum and Kunak (results are for the lowest 100 m of squares of size 0.2° centred on the two locations). The modelled tracer concentration at Danum has been scaled; the mean tracer concentration is equivalent to the mean measured bromoform mixing ratio at Danum (1.31 ppt). The modelled tracer concentration at Kunak is treated with the same scaling factor.

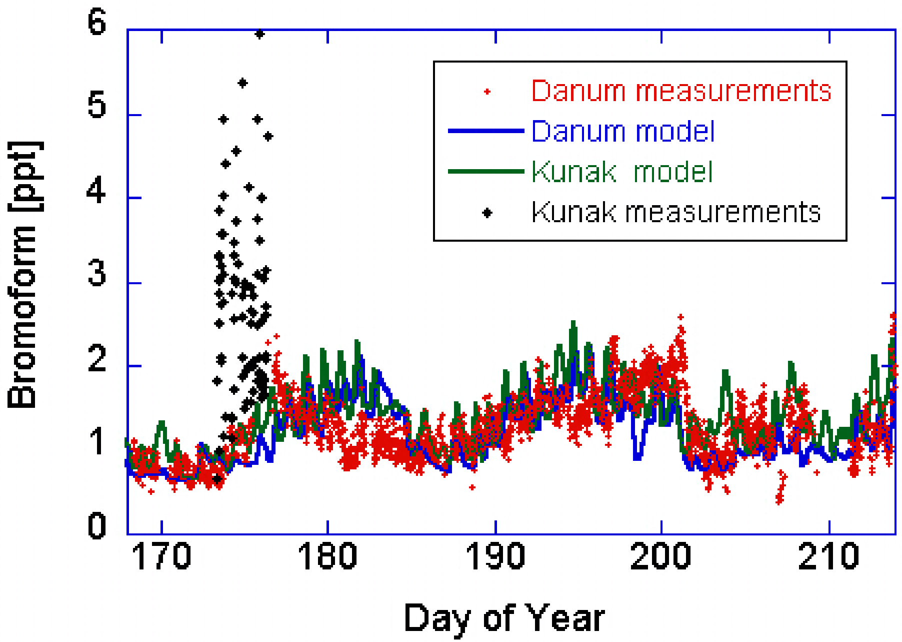

Fig. 5. A comparision of observed and modelled surface bromoform mixing ratios for Danum Valley and Kunak. Modelled mixing ratios are calculated using p-TOMCAT and a coastal and open ocean bromoform emission scenario following Scenario 5 Warwick et al. (2006), scaled down to 190 Gg Br yr^{-1}.