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# Halogenated organic species over the tropical rainforest

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## Abstract

Airborne measurements of the halogenated trace gases methyl chloride, methyl bromide and chloroform were conducted over the Atlantic Ocean and 1000 km of pristine tropical rainforest in Suriname and French Guyana (3–6° N, 51–59° W) in October 2005. In the boundary layer (0–1.4 km), maritime air masses initially low in forest hydrocarbons, advected over the forest by southeasterly trade winds, were measured at various distances from the coast. Since the organohalogens presented here have relatively long atmospheric lifetimes (0.4–1.0 years) in comparison to the transport times (1–2 days), emissions will accumulate in air traversing the rainforest. The distributions of methyl chloride, methyl bromide and chloroform were analyzed as a function of forest contact time and the respective relationship used to determine fluxes from the rainforest during the long dry season.

Emission fluxes have been calculated for methyl chloride and chloroform as  $9.4 (\pm 4.0 \ 2\sigma)$  and  $0.34 (\pm 0.14 \ 2\sigma) \mu\text{g m}^{-2} \text{h}^{-1}$ , respectively. No significant flux from the rainforest was observed for methyl bromide within the limits of these measurements. The flux of methyl chloride was in general agreement with the flux measured over the same region in March 1998 during the LBA Claire project using a different analytical system. This confirms that the rainforest is a strong source for methyl chloride and suggests that this emission is relatively uniform throughout the year. In contrast the chloroform flux derived here is a factor of three less than previous measurements made in March 1998 suggesting a pronounced ecosystem variation. The differences in chloroform fluxes could not be attributed to either temperature or rainfall changes. The global extrapolation of the derived fluxes led to  $1.5 (\pm 0.6 \ 2\sigma) \text{Tg yr}^{-1}$  for methyl chloride, which is in the range of the missing source postulated by previous model studies and  $55 (\pm 22 \ 2\sigma) \text{Gg yr}^{-1}$  for chloroform.

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## 1 Introduction

Halogenated organic compounds have been shown to be important to the chemistry of both the troposphere and the stratosphere (WMO, 2007a). Since these compounds have relatively long atmospheric lifetimes they can effectively transport halogen atoms from surface sources to the stratosphere, and thereby significantly contribute to stratospheric ozone loss (WMO, 2003; Levine et al., 2007). Because the anthropogenic contribution to the organohalogen budget is now restricted by the Montreal Protocol, the ambient concentrations of many such halogenated compounds are stabilizing or declining (WMO, 2003). Therefore the relative influence of naturally produced halocarbons is becoming more important for the budget of ozone depleting substances. Methyl chloride ( $\text{CH}_3\text{Cl}$ ) and methyl bromide ( $\text{CH}_3\text{Br}$ ) are both in part naturally emitted and the most abundant chlorine and bromine containing gases in the troposphere respectively. Currently  $\text{CH}_3\text{Cl}$  contributes up to 16% to the tropospheric organic chlorine and  $\text{CH}_3\text{Br}$  up to about 50% to the organic bromine (WMO, 2003). It is estimated that the contribution of natural  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  to the equivalent effective stratospheric chlorine will rise to more than 50% (currently 23%) until 2050 (WMO, 2007a). Despite its small total contribution to the stratospheric ozone loss chloroform ( $\text{CHCl}_3$ ) is an important natural source of tropospheric chlorine. Therefore it is important to determine the global budgets of these compounds.

The global average concentration of  $\text{CH}_3\text{Cl}$  is approximately  $550 \pm 30 \text{ pmol mol}^{-1}$  with higher mixing ratios observed at low latitudes (Thompson et al., 2004). Small downward trends have been reported recently from the AGAGE measuring sites (Simmonds et al., 2004). According to the emission data provided by WMO (2007b) and references therein, the sources and sinks of  $\text{CH}_3\text{Cl}$  are as shown in Table 1. Earlier global budget estimates indicated that biomass burning was the main source (WMO, 1999), however, after Keene et al. (1999) and Butler (2000) highlighted an imbalance in the budget of this species, a new dominant source of methyl chloride from tropical vegetation was discovered by Yokouchi et al. (2002) and subsequently verified by airborne field mea-

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surements of Scheeren et al. (2003). Although the sources of methyl chloride appear to balance the sinks large uncertainties remain regarding the nature of the tropical source since few measurements are available from this region.

Although much less abundant than the chloride, methyl bromide concentrations are of great interest, because it has a 25 times higher ozone depletion potential than methyl chloride (WMO, 2007a). Due to emission restrictions related to the Montreal Protocol the global average concentration is decreasing from peak values of  $9.2 \text{ pmol mol}^{-1}$  in 1999 to currently about  $7.9 \text{ pmol mol}^{-1}$  (WMO, 2007b). A summary of the present understanding of sources and sinks of methyl bromide is given in Table 1. A discrepancy of  $45 \text{ Gg yr}^{-1}$  remains as a “missing source” which may be located in the thus far poorly characterized tropical regions. Conversely, it is also conceivable that the atmospheric lifetime of methyl bromide has been underestimated, which would help to explain the imbalance between sources and sinks (Reeves, 2003).

The budget of  $\text{CHCl}_3$  is reasonably balanced within the uncertainties and was recently summarized by McCulloch (2003) (see Table 1 for summary). The global distribution of  $\text{CHCl}_3$  is strongly biased between the two hemispheres with 1.7 times higher mixing ratios found in the Northern Hemisphere (Khalil and Rasmussen, 1999a). Antarctic firn air measurements (Trudinger et al., 2004) show a steady increase from  $4 \text{ pmol mol}^{-1}$  around 1940 to peak values of  $6.5 \text{ pmol mol}^{-1}$  in 1990. After the use of  $\text{CHCl}_3$  in pulp and paper production was reduced, global observations show a downward trend. Global average mixing ratios of  $18.5 \text{ pmol mol}^{-1}$  between 1985 and 1995 (Khalil and Rasmussen, 1999a) decreased to average background levels of  $8.9 (\pm 0.1) \text{ pmol mol}^{-1}$  in the years 1994–1998 (O’Doherty et al., 2001). However, a recent model study suggests that a higher anthropogenic contribution (41–50% of the global sources) before 1990, and 25–29% in 2001 would explain the global observations better (Worton et al., 2006).

To gain a better understanding of the global distribution of the missing sources of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  several model studies have been conducted. Lee-Taylor et al. (2001) found that the observed mixing ratios of  $\text{CH}_3\text{Cl}$  can be reproduced by addition of a

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tropical terrestrial source of 2330–2430 Gg yr<sup>-1</sup> and reduced Southeast Asian biomass burning emissions. The inverse model study of Yoshida et al. (2006) suggests an seasonally invariant missing source of 2900 Gg yr<sup>-1</sup> located in the tropics (30° N–30° S) to explain the observed distribution.

Furthermore Lee-Taylor et al. (1998) find that the annual observations of CH<sub>3</sub>Br are best represented if a terrestrial source of 89–104 Gg yr<sup>-1</sup> is assumed located 50 to 71% in the Southern Hemisphere. A later 3-D global chemical transport model run performed by Warwick et al. (2006) used increased biomass burning emissions (+20 Gg yr<sup>-1</sup>) and an additional tropical (40° N–40° S) vegetation source of 45.6 Gg yr<sup>-1</sup> CH<sub>3</sub>Br to reproduce the annual observations.

Tropical rainforest regions are important to investigate for organohalogens, not only because few measurements have been made so far but also their proximity to the ITCZ (Inter Tropical Convergence Zone) means that any emission there will have a strong chance of being transported into the stratosphere by the regionally prevalent deep convection. We present large-scale airborne measurements of the organohalogen species methyl chloride, methyl bromide and chloroform over the rainforest of Suriname and French Guyana during the dry season (October) 2005. The vertical and horizontal distributions of these species are analyzed and fluxes from the rainforest are determined. The influence of biomass burning and entrained air on the derived fluxes is discussed and an extrapolation to the global scale made based on the new data.

## 2 Sampling and analysis

### 2.1 Sample collection

In total 99 pressurised air samples were collected during 10 flights between 0–11 km over the tropical rainforest (see Fig. 1) using an automated air sampling system developed and built at the Max Planck Institute for Chemistry, Mainz. The system consisted of a module containing 18 0.8 L electropolished stainless steel canisters and was in-

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stalled within an adapted wingpod on a Lear jet aircraft (Learjet 35A D-CGFD operated by GFD, Hohn, Germany and Enviscope GmbH, Frankfurt, Germany). The entire sampling system was constructed from 1/4" (=0.635 cm) o.d. stainless steel tubing and connectors (Swagelok, Solon OH, USA). The in- and outlet valves of the canisters were actuated by electric valves (Clippard-24V, Fluitronics, Düsseldorf, Germany). An aircraft metal bellows pump (Senior Aerospace, Herfordshire, UK) was used to draw ambient air through the inlet, flush all tubing throughout the flight and, when the fill valve was activated, to pressurise the canister to at least 3 bar (3000 hPa). Canisters were filled sequentially at 10-min intervals, and depending on the ambient atmospheric pressure, filling took from less than 25 s at 500 m to around 60 s at 8.5 km. Prior to flight, the canister module was evacuated to 10<sup>-4</sup> hPa and directly after landing the filled module was transferred to the laboratory for immediate (<48 h) analysis by GC-MS. Three identical modules were built, allowing flights to be performed in quick succession. Pressure, temperature and valve status were controlled and logged by a computer within the wingpod.

## 2.2 Instrumental set up

The instrumentation used for the canister analysis consisted of a gas chromatograph – mass spectrometer system (GC/MS 6890/5973, Agilent Technologies, Palo Alto CA, USA), modified from the commercial version for analysis of low-level ambient air samples (Gros et al., 2003). The sample was introduced into the sampling inlet, dried by flushing through a magnesium perchlorate filled tube heated to 100°C, prefocussed by a cryo-concentrator unit (1/16" ss line filled with glass beads, cooled to -70°C) and afterwards flushed into the GC. The separating column was a 60 m\*0.248 mm\*1 µm DB-5 capillary column (J&W Scientific, Agilent Technologies, Palo Alto CA, USA). The chromatography parameters were optimised to enable good separation of circa 35 identified compounds; a complete run took about 20 min. The mass spectrometer was operated in Single Ion Mode (SIM) to achieve maximum sensitivity. Post flight, the filled canister module was attached to the GC-MS system and the analysis proceeded semi auto-

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5 matically within 48 h. The detection limit was defined as three times the standard deviation of the noise (for the specific ion at its specific retention time). It was found to be 0.14 pmol mol<sup>-1</sup> for chloroform, 0.51 pmol mol<sup>-1</sup> for methyl bromide and 1.9 pmol mol<sup>-1</sup> for methyl chloride. The overall uncertainty was calculated based on the peak integration accuracy, the accuracy of the calibration standard (5%) and its precision (1–5%) and resulted in 7% for CH<sub>3</sub>Cl, 8% for CHCl<sub>3</sub> and 11% for CH<sub>3</sub>Br.

### 2.3 Calibration

10 Calibrations were performed against a whole air working standard, prepared by filling an aluminium cylinder with ambient suburban air using a three-stage oil-free piston compressor (RIX industries, Benicia CA, USA) modified after Mak and Brenninkmeijer (1994). This cylinder was calibrated relative to a NIST primary standard at the National Centre for Atmospheric Research (NCAR, Boulder CO, USA). The working standard was analysed every five measurements. The average response factor of these analyses was used to calibrate the samples measured in between. At least one  
15 blank (using the same analytical procedure but without collecting an air sample) was performed at the start of each measurement sequence, and showed a generally clean baseline. Linearity of the system was confirmed in the range of measured concentrations.

## 3 Results and discussion

### 20 3.1 Meteorological conditions in Suriname

The northeast coast of South America is an excellent location to study the effects of the tropical rainforest on atmospheric trace gas composition. Meteorological conditions in this region are controlled by the very steady trade winds and the annual migration of the Inter-Tropical Convergence Zone (ITCZ). The data presented here were collected

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from the 6th to the 13th of October 2005 within the Guyanas Atmosphere-Biosphere exchange and Radicals Intensive Experiment with the Learjet (GABRIEL) project. During this time of the year – the long dry season – the ITCZ was located a few degrees north of the Guyanas at approximately 10–15° N (see Fig. 1). Thus, although geographically in the Northern Hemisphere, Suriname (3–6° N, 51–59° W) was atmospherically speaking located in the Southern Hemisphere. The location and height of all measurements is shown in Fig. 1.

The boundary layer height during the day, which is important in calculating the emission flux, was determined using fluctuations in the static air temperature (corresponding to the temperature inversions) measured from the aircraft when ascending. The temperature was recorded by the Enviscope analogue data acquisition system. The derived boundary layer grew from around 600 m around 09:30 local time (UTC-3 h) to 1200 m at 12:30 stabilizing around 1400 m in the afternoon (G. Eerdeken, personal communication). Because most of our measurements took place during midday or early afternoon, we considered an average boundary layer height of 1400±100 m.

During the campaign the meteorological conditions were generally stable with only occasional short thunderstorms. The prevailing wind direction in the boundary layer was easterly (95°), with average wind speeds of 5.8 m s<sup>-1</sup>, which is typical of the trade winds. Closer to the surface the wind weakened and veered to a more northeasterly direction, probably as a result of the increased friction within the boundary layer. Wind speed and direction as a function of altitude are shown in Fig. 2. The data are 100 m binned average values of the 1 Hz data obtained by the aircraft flight management system via ARINC429. From Fig. 3 it can be seen that during the campaign maritime air masses, initially low in forest hydrocarbons, were advected from the Atlantic Ocean and then over approximately 1000 km of pristine rainforest. The 10-day back trajectories of the boundary layer samples are shown in Fig. 3. These indicate that air arriving at the coast of French Guyana and Suriname was transported for the most part within the Southern Hemisphere.

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## 3.2 Vertical distribution

The vertical profiles of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CHCl}_3$  are presented in this section. The measurements span a range from the surface up to 11 km height although measurements were predominately made in the boundary layer. Figure 4 presents the 100 m binned profiles. Generally the profiles can be divided into three different parts: The mixed boundary layer (ML) up to 1400 m, the lower free troposphere below the trade wind inversion (LFT) from 1400 to 3500 m and the free troposphere (FT) above 3500 m.

The  $\text{CH}_3\text{Cl}$  profile shows several distinct features. Clearly the mixing ratios below 3.5 km were higher than those above. In the FT the 100 m average values ranged from 531 to 619  $\text{pmol mol}^{-1}$ ; the one outlier (marked with a circle in Fig. 4) is discussed further below. Within the LFT the mixing ratios seemed to increase approaching the ground to maximum values of 665  $\text{pmol mol}^{-1}$  at 2 km. The ML appears to show pronounced gradients with height; mixing ratios around 641  $\text{pmol mol}^{-1}$  at 1.2 km decreased to around 587  $\text{pmol mol}^{-1}$  at 600 m and increased again to 676  $\text{pmol mol}^{-1}$  near the surface.

The vertical distribution of  $\text{CH}_3\text{Br}$  was quite scattered, the mixing ratios varied between 7.7 and 10.9  $\text{pmol mol}^{-1}$  showing no significant trend with height. In the case of  $\text{CHCl}_3$ , average mixing ratios of 8.8  $\text{pmol mol}^{-1}$  at the surface steadily decreased to values around 7.3  $\text{pmol mol}^{-1}$  at the top of the ML. In the LFT they varied between 6.3 and 7.8  $\text{pmol mol}^{-1}$ . Above 3500 m mixing ratios were slightly higher and more variable than below.

The vertical profiles give a strong indication where the sources of the various compounds are located. The  $\text{CHCl}_3$  profile shows a clear decrease in mixing ratio with increasing height, which suggests the presence of a ground based source. The  $\text{CH}_3\text{Cl}$  vertical profile was more complex, showing two sections with elevated mixing ratios. In this case two different sources can be considered. Firstly, a ground based source similar to chloroform, and secondly a further influence between 2 and 3 km height presumably associated with advection from another source region. The  $\text{CH}_3\text{Br}$  profile was

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too scattered to give relevant information on the height distribution of the sources.

The elevated value at 7.9 km visible in all three components corresponds to a sample taken within air strongly influenced by biomass burning. It coincides with elevated values in the biomass burning tracers carbon monoxide (CO) and acetonitrile (CH<sub>3</sub>CN) (H. Bozem, personal communication).

### 3.3 Influence of biomass burning

As can be seen from the example above the possible influence of biomass burning has to be considered when interpreting the mixing ratios of the investigated compounds. When considering natural fluxes, care must be taken to exclude burning effects from calculated gradients. Burning is known to be a strong source of CH<sub>3</sub>Cl and also a source of CH<sub>3</sub>Br and CHCl<sub>3</sub> (Andreae and Merlet, 2001; Lobert et al., 1999). Since during the period September to November there is widespread burning in the Southern Hemisphere it would not be surprising if some influence of this was detected during this campaign, particularly in CO, CH<sub>3</sub>CN and CH<sub>3</sub>Cl. However, fire maps prepared from GOES-12 satellite images (<http://cimss.ssec.wisc.edu/goes/burn/wfabba.html>) showed no significant burning activity directly in the area where the measurements took place. Furthermore, back trajectories from the measurement locations showed, that the fires occurring south or west of the Guyanas had no impact on the investigated air masses in the boundary layer (see Fig. 3). Generally low levels of CO and acetonitrile in the boundary layer (Stickler et al., 2007; G. Eerdeken, personal communication) also supported the view that the measurements were not significantly influenced by local burning sources.

The ratio  $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO}$  can give information on the sources of both gases, where  $\Delta$  indicates the difference of each mixing ratio from the ambient background. The background mixing ratio was determined as the intercept of a linear fit of the mixing ratio versus time over land (TOL) plot, namely 585 pmol mol<sup>-1</sup> for CH<sub>3</sub>Cl, 95.3 nmol mol<sup>-1</sup> for CO (30 s averaged). The  $\Delta\text{CH}_3\text{Cl}/\Delta\text{CO}$  ratio was  $2.77 (\pm 0.64 2\sigma) \times 10^{-3}$ . In biomass

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burning influenced air previous studies have reported ratios of  $0.95 (\pm 0.01) \times 10^{-3}$  and  $0.496 (\pm 0.035) \times 10^{-3}$  for African fires (Andreae et al., 1996; Rudolph et al., 1995). Other studies have reported  $\text{CH}_3\text{Cl}/\text{CO}$  ratios of  $0.85 (\pm 0.06) \times 10^{-3}$  for South American smouldering fires and,  $0.57 (\pm 0.03) \times 10^{-3}$  for African flaming fires (Blake et al., 1996). Comparing  $\text{CH}_3\text{Cl}$  and CO during this study a ratio of  $2.77 (\pm 0.64 \ 2\sigma) \times 10^{-3}$  was obtained. The ratios measured here lie clearly outside the reported range for biomass burning. Therefore we conclude that the predominant source of the observed  $\text{CH}_3\text{Cl}$  is most likely not biomass burning.

Although no “fresh” burning influenced air was detected, the ML appears to have been influenced by entrainment of such air lying directly above it, advected from a distant burning region. Stickler et al. (2007) examined this possibility, reporting entrainment rates based on CO and formaldehyde data between  $0.01$  and  $0.15 \text{ h}^{-1}$ , where entrainment was defined as fraction of the ML air exchanged with the LFT air per unit time. Scheeren et al. (2003) reported an estimated loss of up to 25% of the surface emissions through entrainment at the top of the mixing layer, depending on the strength of the convective mixing. While large uncertainties remain in the quantification of the entrainment, its presence provides a plausible explanation for the increasing  $\text{CH}_3\text{Cl}$  values between 1000 and 2000 m in this study.

In this case the methyl chloride concentration at 2–3 km was higher than at the top of the boundary layer, and therefore the entrainment will act to increase the perceived mixing ratio versus TOL gradient and consequently the calculated flux. Thus the flux calculated in the following chapter should be seen as an upper limit. Because of its high variability, however, entrainment is not incorporated in the further calculations.

### 3.4 Emission fluxes

As clean marine boundary layer air was advected westwards over the pristine tropical rainforest of French Guyana and Suriname during GABRIEL, mixing occurred between the marine boundary layer air and the forest emissions. Long-lived trace gases emitted

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by the forest can accumulate in the mixed boundary layer air so that mixing ratios of such species will increase westwards and hence be positively correlated with the time the air spent over land. Conversely uptake of gases by the forest will result in a negative correlation. The volume mixing ratios of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CHCl}_3$  samples in the ML (<1400 m) ( $n=35$ ) are shown as a function of time over land (TOL) in Fig. 5.

The mixing ratios in the boundary layer ranged from 546 to 724 (avg 643)  $\text{pmol mol}^{-1}$  for  $\text{CH}_3\text{Cl}$ , 6.6 to 11.2 (avg 8.2)  $\text{pmol mol}^{-1}$  for  $\text{CHCl}_3$  and 7.9 to 9.9 (avg 8.8)  $\text{pmol mol}^{-1}$  for  $\text{CH}_3\text{Br}$ , respectively. These are somewhat higher than the global mean values of  $550 \pm 30 \text{ pmol mol}^{-1}$  for  $\text{CH}_3\text{Cl}$ , although in good general agreement with reported higher concentrations at lower latitudes (WMO, 2007b). For  $\text{CHCl}_3$ , the values reported here are lower than the global average  $18.5 \text{ pmol mol}^{-1}$ , due to higher emissions in the Northern Hemisphere mid-latitudes, however, they agree very well with the average mixing ratio for the SH tropics,  $9.7 \text{ pmol mol}^{-1}$  (Khalil and Rasmussen, 1999b). For  $\text{CH}_3\text{Br}$  the measured range fits the global average  $7.9 \text{ pmol mol}^{-1}$  (Simmonds et al., 2004). The error bars shown in Fig. 5 indicate the total uncertainty of the data points ( $\pm 7\%$  for  $\text{CH}_3\text{Cl}$ ,  $\pm 11\%$  for  $\text{CH}_3\text{Br}$  and  $\pm 8\%$  for  $\text{CHCl}_3$ ).

For  $\text{CH}_3\text{Cl}$  and  $\text{CHCl}_3$  four data points at low TOL appear as outliers to the fit (marked with a black asterisk in Figs. 1 and 5). Interestingly, these samples were taken in somewhat different geographical circumstances than the rest of the dataset. The sample taken at 0 h TOL was deliberately collected at low altitude (200 m a.s.l.) directly above coastal salt marshes as such regions have been suggested to emit  $\text{CH}_3\text{Cl}$  (Rhew et al., 2000) although this view was recently questioned (Wang et al., 2006). The three samples at 5, 7.5 and 9 h TOL were taken in the vicinity of the capital of French Guyana Cayenne directly downwind of Rochambeau airport and therefore probably influenced by anthropogenic emissions. For the aforementioned reasons these points are not included in the flux calculations given below.

To calculate the time the air parcel spent over land we used the following approach. Starting at the sampling position we followed the path of the air parcel along the back

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trajectory in distinct time steps until it reached the coastline. For this procedure we used the trajectories provided by the KNMI (Koninklijk Nederlands Meteorologisch Instituut), which are based on ECMWF meteorological data. We consider that this method will be better than simply extrapolating the instantaneous wind direction and speed.

A linear fit of the mixing ratio versus TOL plot was then used to calculate emission fluxes from the rainforest ecosystem. The slope of the fit gives the increase of the mixing ratio per hour the air mass spent over the jungle. The black line in Fig. 5 indicates the linear regression curve, while the grey shaded area gives the 95% confidence interval of the fit coefficients (equivalent to  $2\sigma$ ). To calculate the fit coefficients and their confidence parameters the total uncertainty of each individual compound was used as weighting parameter. In this case the flux was statistically significant if the given deviation was not bigger than the value of the parameter itself. Two compounds showed a significant correlation with  $TOL-\Delta CH_3Cl/\Delta TOL=3.5\pm 1.5$  ( $2\sigma$ ) and  $\Delta CHCl_3/\Delta TOL=(5.4\pm 2.1)\cdot 10^{-2}$  ( $2\sigma$ ) – and thus appear to be emitted from the forest. For methyl bromide the slope is not significant ( $\Delta CH_3Br/\Delta TOL=(1.3\pm 3.2)\cdot 10^{-2}$  ( $2\sigma$ )) and therefore no emission could be determined within our detection limit.

Using the slope derived from Fig. 5 the flux  $F$  was calculated by following formula:

$$F = (\Delta MR/\Delta TOL) \times H_{ML} \times (p \times M/(R \times T))$$

Where  $F$  is the flux ( $g\ m^{-2}\ h^{-1}$ ),  $\Delta MR/\Delta TOL$  the linear regression slope ( $mol\ mol^{-1}\ h^{-1}$ ),  $H_{ML}$  the mean mixing layer height ( $1400\pm 100\ m$ ),  $p$  the mean air pressure ( $946.31\pm 56.89\ hPa$  ( $2\sigma$ )),  $M$  the molar weight ( $g$ ),  $R$  the gas constant ( $0.08314\ hPa\ m^3\ K^{-1}$ ) and  $T$  the mean air temperature ( $298.56\pm 4.97\ K$  ( $2\sigma$ )).

The result is a flux of  $9.4(\pm 4.0\ 2\sigma)\ \mu g\ CH_3Cl\ m^{-2}\ h^{-1}$  and  $0.34(\pm 0.14\ 2\sigma)\ \mu g\ CHCl_3\ m^{-2}\ h^{-1}$ , respectively.

Using the slope uncertainty of  $\Delta CH_3Br/\Delta TOL$  we determine the lowest detectable methyl bromide flux as  $0.16(2\sigma)\ \mu g\ CH_3Br\ m^{-2}\ h^{-1}$ .

Despite their large size and potential importance to atmospheric chemistry, the Earth's tropical forests are surprisingly poorly characterized for organohalogen species.

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There are only few measurement studies available for comparison and these were mainly performed in Asia (Li et al., 1999; Yokouchi et al., 2002; Yokouchi et al., 2000; Saito and Yokouchi, 2006; Yokouchi et al., 2007), who measured in a tropical glasshouse and on forested islands. Scheeren et al. (2003) measured the two chlorinated compounds in Suriname in March 1998 and Moore et al. (2005) analyzed tropical fungi and soils in Brazil.

Li et al. (1999) observed a very high flux of 41 to 64  $\mu\text{g CH}_3\text{Cl m}^{-2} \text{h}^{-1}$  from a coastal area at Okinawa Island, Japan. Yokouchi et al. (2002) reported an emission flux of 5.4 (3.8–8)  $\mu\text{g CH}_3\text{Cl m}^{-2} \text{h}^{-1}$  from a greenhouse containing vegetation typical of the lowland tropical forest of Southeast Asia and smaller though not quantified fluxes of  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$ . Recently they reported an emission rate of 12–33  $\mu\text{g CH}_3\text{Cl m}^{-2} \text{h}^{-1}$  measured on one of the subtropical Okinawa islands (Yokouchi et al., 2007). The study performed by Scheeren et al. (2003) over Suriname in March 1998 reported fluxes of  $7.6 \pm 1.8 \mu\text{g CH}_3\text{Cl m}^{-2} \text{h}^{-1}$  and  $1.1 \pm 0.08 \mu\text{g CHCl}_3 \text{ m}^{-2} \text{h}^{-1}$ . Moore et al. (2005) reported wood rotting fungi to be a  $\text{CH}_3\text{Cl}$  source and confirmed the soil as a sink, in agreement with previous measurements (Watling and Harper, 1998; Khalil and Rasmussen, 2000). Elevated mixing ratios above the canopy led them to the assumption that there have to be further strong sources in the rainforest beside the fungi.

Comparing the two studies, which took place in Suriname, one in March 1998 and this one in October 2005, it should be noted that they used different analytical techniques. The technique used by Scheeren et al. (2003) (GC-ECD) is less compound specific than the GC-MS system employed here, and in the former campaign longer canister storage times (several months) incurred prior to measurement while in this study the canisters were measured immediately after flight (within 48 h). However, since storage tests on similar canisters (Colomb et al., 2006) have indicated that the investigated halocarbons are stable over 60 days we will assume hereafter that the obtained mixing ratios and fluxes are comparable to our data.

The  $\text{CH}_3\text{Cl}$  fluxes of Scheeren et al. (2003) agree very well with the  $9.4 (\pm 4.0 2\sigma) \mu\text{g CH}_3\text{Cl m}^{-2} \text{h}^{-1}$  derived in this study. Therefore there seems to be little or no

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variation in the  $\text{CH}_3\text{Cl}$  flux between March and October. The fluxes derived by Yokouchi et al. (2002) and Yokouchi et al. (2007) are in the same range, although they were obtained surveying a different kind of tropical species in Southeast Asia, whereas the study of Li et al. (1999) is reporting much higher fluxes than all other studies. Excluding that one, the results presented here are in good agreement with model studies (Lee-Taylor et al., 2001; Yoshida et al., 2004 and Yoshida et al., 2006), which have postulated a large land based, constant source of  $\text{CH}_3\text{Cl}$  all over the tropics.

In the case of  $\text{CHCl}_3$ , the fluxes reported by Scheeren et al. (2003) are approximately three times higher than those measured here. The measurements of Scheeren et al. (2003) were conducted in the short dry season in March and those reported here in the long dry season in October.

Since both studies took place in “dry” seasons there were only small differences in the climatologic parameters. The precipitation and therefore presumably soil moisture were very similar (70.3 mm during March 1998, 65.6 mm in October 2005), whereas the maximum temperature was on average higher by  $1.6^\circ\text{C}$  in October 2005 ( $33.4^\circ\text{C}$ ), while the minimum temperature was similar ( $23.6^\circ\text{C}$  March 1998,  $23.8^\circ\text{C}$  October 2005) (C. Becker, Meteorological Service Suriname, personal communication). Since there are no  $\text{CHCl}_3$  measurements available during the wet season, we are not able to deduce a seasonal emission pattern. However, the results presented here show a strong variation in the  $\text{CHCl}_3$  flux but no or very little change in the  $\text{CH}_3\text{Cl}$  emissions. This leads to the assumption that these compounds are emitted via different formation pathways.

In addition to the anthropogenic, oceanic and biomass burning sources of  $\text{CH}_3\text{Cl}$  and  $\text{CHCl}_3$  several further possible formation pathways have been reported. Isidorov et al. (1985) and Isidorov and Jdanova (2002) showed that  $\text{CH}_3\text{Cl}$  as well as  $\text{CHCl}_3$  is emitted by living leaves and leaf litter of some tree species (e.g. pencil cedar, evergreen cypress northern white cedar, aspen and willow). Other higher plants such as tropical ferns, halophytes and potato tubers show significant emissions of  $\text{CH}_3\text{Cl}$  (Yokouchi et al., 2002; Harper et al., 2003; Rhew et al., 2000; Harper et al., 1999)



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as well as fungi (Watling and Harper, 1998). The metabolic origin of  $\text{CH}_3\text{Cl}$  has been identified as an enzyme catalysed halide methylation reaction, which uses either S-adenosylmethionine (SAM) or methionine as a methyl donor (Harper, 2000; Harper et al., 1999). Hamilton et al. (2003) showed that abiotic chloride methylation by plant pectin was an efficient, environmentally significant process producing methyl chloride. Chloride ions, which are plentiful in the leaf, react with pectin during leaf senescence and an abiotic substitution reaction yields  $\text{CH}_3\text{Cl}$ . This mechanism could account for the methyl chloride release from leaf litter and during biomass burning. Recent results from isotopic studies of  $\text{CH}_3\text{Cl}$  (Keppler et al., 2005) support this abiotic mechanism. Another abiotic process forming monohalogenated alkanes was identified by Keppler et al. (2000). During the oxidation of organic matter by an electron acceptor like Fe (III) in soil, sediments or organic rich waters halide ions are methylated or even build ethyl or propyl halides.

While the aforementioned substitution mechanisms can efficiently produce monohalogenated compounds there are not likely to be the source of the  $\text{CHCl}_3$ , which would require multiple substitution.

Although there is some evidence that chloroform is emitted directly by plants (Isidorov et al., 1985), soil processes are assumed to be the major source in the tropical ecosystem (Laternus et al., 2002; McCulloch, 2003, see Table 1). Several pathways are reported in the literature: Basidiomycetous fungi are able to synthesize  $\text{CHCl}_3$  de novo (Hoekstra et al., 1998a). It can also be formed by chlorination of organic matter catalyzed by extracellular peroxidase-like enzymes (chloroperoxidase CPO) most probably deriving from fungi (Hoekstra et al., 1998b). Another plausible mechanism is the decarboxylation of trichloroacetic acid (Frank et al., 1989; Haselmann et al., 2000a).

Measurements of soils in temperate forest indicate  $\text{CHCl}_3$  emission up to  $340 \text{ ng m}^{-2} \text{ h}^{-1}$  from soils covered with woodchips (Hoekstra et al., 2001). Haselmann et al. (2000b) reports local emissions in a Danish forest from 2.6 to  $160 \text{ ng m}^{-2} \text{ h}^{-1}$ . These rates correspond very well with the flux of  $340 (\pm 140 \ 2\sigma) \text{ ng m}^{-2} \text{ h}^{-1} \text{CHCl}_3$  de-



rived in this study and strengthens the argument that the main fraction of  $\text{CHCl}_3$  in the tropical ecosystem is produced by soil processes. This would support the assumption of Laturnus et al. (2002), who speculated on a similar or even larger input from tropical forest areas as reported from northern temperate forests.

5 The average  $\text{CH}_3\text{Br}$  mixing ratios reported here are slightly elevated compared to global background values (WMO, 2007b), but no significant net emission from the rainforest of  $\text{CH}_3\text{Br}$  could be determined. This is in contrast to greenhouse and small scale experiments (Gan et al., 1998; Yokouchi et al., 2002; Saito and Yokouchi, 2006), which report  $\text{CH}_3\text{Br}$  emission from plants from the brassicaceae family, Asian lowland forest and tropical ferns. A vegetation source providing additional  $45.6 \text{ Gg yr}^{-1}$  in the tropics as postulated by Warwick et al. (2006) would correspond to a local flux of  $0.287 \mu\text{g CH}_3\text{Br m}^{-2} \text{ h}^{-1}$ . An emission of this order of magnitude would have been detected by this study (detection limit for  $\text{CH}_3\text{Br}$ :  $0.160 \mu\text{g m}^{-2} \text{ h}^{-1}$ ). Since soils are known to uptake  $\text{CH}_3\text{Br}$ , one may speculate that the possible release from tropical vegetation is just outweighed by a local soil sink and therefore not visible in a large scale experiment like this one. On the other hand, a recent modelling study in our institute suggests that the atmospheric lifetime of  $\text{CH}_3\text{Br}$  has been underestimated (A. Kerkweg, personal communication), which also closes the imbalance between sources and sinks without the presumed vegetation source.

### 20 3.5 Global emissions

Before extrapolating the observed emission fluxes from the South American rainforest to the global scale several aspects must be noted.

25 Firstly, the fluxes measured here were the net effect of the “rainforest ecosystem” at one time of year. As mentioned previously there are likely several competing sources and sinks (plants, bacteria, fungi, senescencing leaves etc.) within the ecosystem each of which may vary independently in the course of a year.

Secondly, the tropical forest covers a large fraction of the globe and accounts for

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nearly half of the total global forest. The largest areas are found in the Amazon Basin (South America) and the Congo Basin (Africa), as well as large parts of Southeast Asia and Oceania are covered by tropical forest. For these extrapolations, the rainforest from these diverse regions is considered homogenous. This is obviously a simplification and therefore the derived fluxes should be regarded as a rough estimate.

Thirdly, the definition of the forest area is an important issue. Using the widely distributed number of 18.2 million km<sup>2</sup> of tropical forest (FAO, 2001), which refers to all kinds of forest located in the tropics, we obtained fluxes of 1.5 (±0.6 2σ) Tg CH<sub>3</sub>Cl yr<sup>-1</sup> and 55 (±22 2σ) Gg CHCl<sub>3</sub> yr<sup>-1</sup> for methyl chloride and chloroform, respectively. A more conservative estimate using only the area of tropical rainforest (10.8 million km<sup>2</sup>) (FAO, 2001), results in fluxes of 0.9 (±0.4 2σ) Tg CH<sub>3</sub>Cl yr<sup>-1</sup> and 33 (±13 2σ) Gg CHCl<sub>3</sub> yr<sup>-1</sup>.

These numbers are obtained using the flux derived by this study all over the year. Bearing in mind that chloroform emissions seem to be varying and other studies reported higher flux rates, one should regard these flux estimations as lower limit. Taking into account the measurements of Scheeren et al. (2003), which were carried out in the same region by using the average flux of both studies the annual emission of CHCl<sub>3</sub> would be more than doubled. It should be noted that this estimate is particularly uncertain since no measurements have yet been made in the wet season.

Although these extrapolations are inherently uncertain due to the aforementioned assumptions in the calculation (entrainment, seasonal changes in flux), they do represent our current best estimate of the rainforest contribution to the global budgets of these compounds and appear to be quite reasonable. The calculated flux of 1.5 (±0.6 2σ) Tg CH<sub>3</sub>Cl yr<sup>-1</sup> from the tropical forest would account for half the missing source postulated by the models (Lee-Taylor et al., 2001; Yoshida et al., 2006).

To better understand the budgets of these compounds it will be necessary to examine seasonal variations of the various sources and sinks within the rainforest ecosystem. In particular, the driving parameters of the sources and sinks need to be better characterized, e.g. their dependence on ambient temperature and/or soil moisture

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changes. These variations will be particularly important for predicting future changes in the natural halocarbon emissions fluxes, which will become more important as the anthropogenic contribution recedes.

#### 4 Summary and conclusions

This study presents airborne flux measurements of  $\text{CH}_3\text{Cl}$ ,  $\text{CHCl}_3$  and  $\text{CH}_3\text{Br}$  over the tropical rainforest of Suriname. Aircraft measurements of the kind reported here inherently consider the rainforest ecosystem as a whole, and are ideally suited to gauge the net effect over large areas. The fluxes are possibly the result of separate strong sinks and strong sources within the ecosystem, and represent the net flux from the rainforest to the atmosphere in October 2005. For both  $\text{CH}_3\text{Cl}$  and  $\text{CHCl}_3$  a significant correlation between concentration and time the air mass spent over the rainforest was found. The rainforest ecosystem produced  $9.4 (\pm 4.0 \ 2\sigma) \mu\text{g m}^{-2} \text{h}^{-1}$   $\text{CH}_3\text{Cl}$  and  $0.34 (\pm 0.14 \ 2\sigma) \mu\text{g m}^{-2} \text{h}^{-1}$   $\text{CHCl}_3$ .

No significant trend for  $\text{CH}_3\text{Br}$  could be determined from these measurements in disagreement with previous inverse model prediction (Warwick et al., 2006). Our measurements over the Amazon rainforest agree with global observations and vertical gradients between the boundary layer and free troposphere appear to be small or absent. This supports the conclusion that tropical forest does not contribute significantly to the global  $\text{CH}_3\text{Br}$  source.

The  $\text{CH}_3\text{Cl}$  flux is in good agreement with previously measured fluxes by Yokouchi et al. (2002) and Yokouchi et al. (2007), who reported  $5.4 (3.8\text{--}8) \mu\text{g CH}_3\text{Cl m}^{-2} \text{h}^{-1}$  and  $12\text{--}33 \mu\text{g CH}_3\text{Cl m}^{-2} \text{h}^{-1}$  for Asian lowland tropical forest, and Scheeren et al. (2003), who derived  $7.6 (\pm 1.8) \mu\text{g CH}_3\text{Cl m}^{-2} \text{h}^{-1}$  over Suriname. This suggests that the rainforest ecosystem is indeed the continuous source of methyl chloride postulated in model studies. Extrapolating the flux to the global scale resulted in  $1.5 (\pm 0.6 \ 2\sigma) \text{Tg CH}_3\text{Cl yr}^{-1}$  which accounts for more than half of the current missing source.

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Since the soil is known to be a sink for methyl chloride the observed total flux in this study should be considered as lower limit of the possible direct production by plants or plant decay.

Regarding the  $\text{CHCl}_3$  emission we observed a three times weaker flux than that derived by Scheeren et al., 2003. Our lower limit of the global extrapolated flux from the tropical forests is  $55 (\pm 22 \ 2\sigma) \text{ Gg CHCl}_3 \text{ yr}^{-1}$ .

From the different emission patterns we conclude that these two compounds are probably produced via different mechanisms. According to the literature  $\text{CHCl}_3$  is most probably formed by microbial processes in the soil depending on temperature and soil moisture, however, there are no clear meteorological differences between March 1998 and October 2005 to explain the flux differences observed. To obtain a better understanding of the role of the rainforest ecosystem as a possible sink or source of halogenated organic species more studies on the different tropical biomes are necessary. Performing a similar study during the wet season would provide additional information on the humidity dependence of the formation pathways and the seasonal variation of the emissions, which could be incorporated in global models.

Furthermore, a more detailed survey of the possible contributors (plants, soil, leaf litter, fungi etc.) would top of the knowledge about the separate sources and sinks within the tropical rainforest ecosystem.

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**Table 1.** Sources and sinks.

	Source type	Source range /Gg yr <sup>-1</sup>		Sink type	Sink range /Gg yr <sup>-1</sup>		
		min	max		min	max	
CH <sub>3</sub> Cl <sup>a</sup>	Tropical and subtropical plants	820	8200	OH <sup>-</sup> reaction	3800	4100	
	Tropical senescent or dead leaves	30	2500	Loss to stratosphere	100	300	
	Biomass burning	325	1125	Cl reaction	180	550	
	Oceans	380	500	Soils	100	1600	
	Salt marshes	65	440	Loss to polar oceans	93	145	
	Fungi	43	470				
	Wetlands	48	48				
	Rice Paddies	2.4	4.9				
	Fossil fuel burning	5	205				
	Waste incineration	15	75				
	Industrial processes	10	10				
	Subtotal	1743	13578	Subtotal	4273	6695	
	CH <sub>3</sub> Br <sup>b</sup>	Oceans	23	119	OH <sup>-</sup> reaction and photolysis	60	100
		Fumigation	28.2	64.4	Oceans	37	133
Gasoline		0	10	Soils	32	154	
Biomass burning		10	40				
Wetlands		2.3	9.2				
Salt marshes		7	29				
Shrublands		0.5	2				
Rapeseed		4.8	8.4				
Rice paddies		0.5	2.5				
Fungi		0.5	5.2				
Peatlands		0.1	3.3				
Subtotal	77	293	Subtotal	129	387		
CHCl <sub>3</sub> <sup>c</sup>	Open Oceans	270	450	OH <sup>-</sup> reaction	370	830	
	Soil processes	120	320	Soils	not quantified		
	Volcanic and geological sources	9	15				
	Anaerobic fermentation	2	4				
	Pulp and paper manufacture	26	42				
	Water treatment	8	34				
	Other industrial sources	9	13				
	Biomass burning <sup>d</sup>	2	2				
Subtotal	446	880	Subtotal	370	830		

<sup>a</sup>after WMO (2007b) and references therein

<sup>b</sup>after WMO (2003) and references therein

<sup>c</sup>after McCulloch (2003)

<sup>d</sup>(Lobert et al., 1999)

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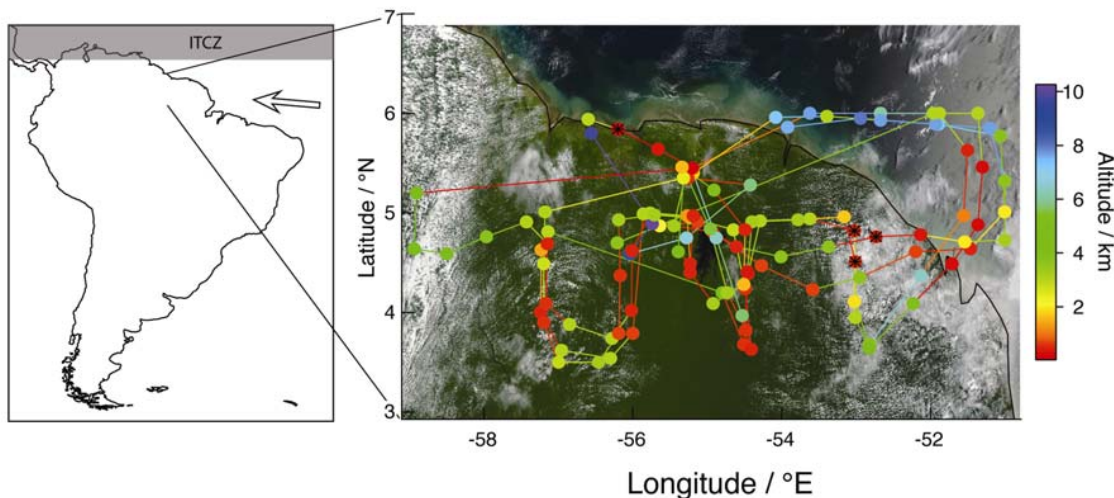
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**Fig. 1.** Sampling area and flight tracks: ITCZ and prevailing wind direction (arrow) are shown on the left. On the right side dots mark the position of the samples, while the color-coding gives the height information, black asterisks mark samples excluded from the calculation (source of satellite picture: Jacques Desclotres, MODIS Rapid Response Team, NASA/GSFC; downloaded September 2007 from: <http://visibleearth.nasa.gov/>).

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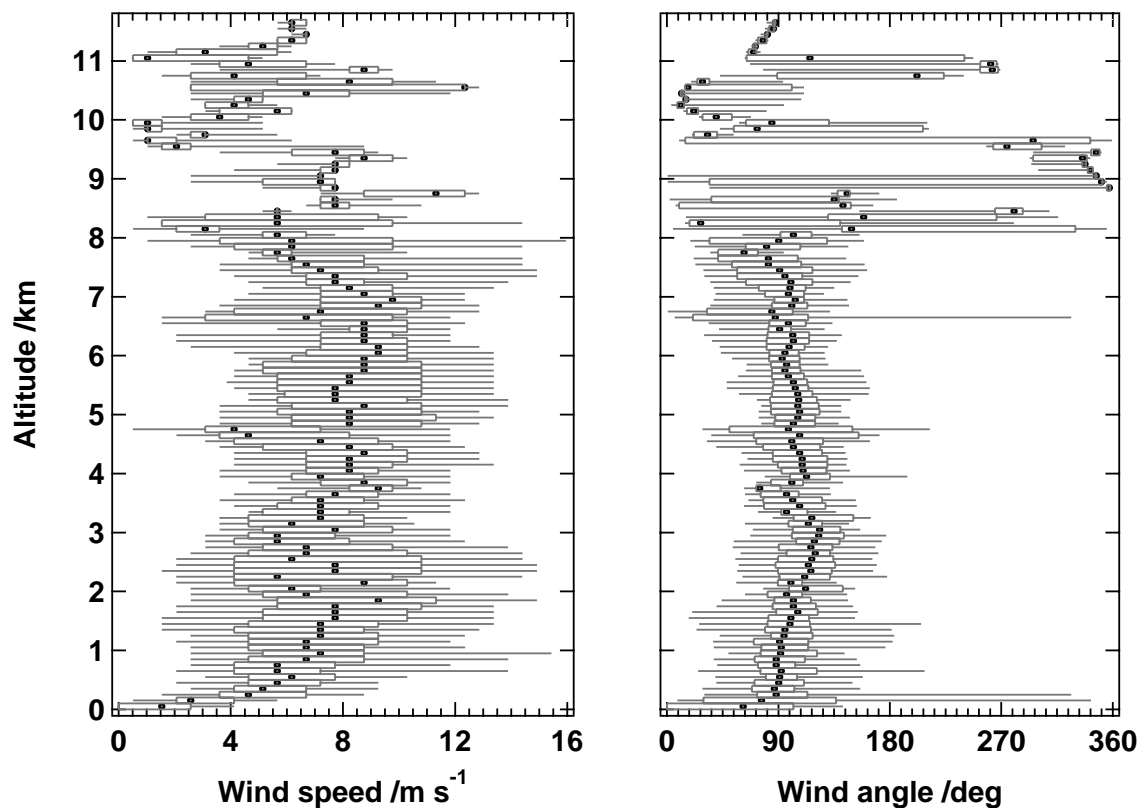
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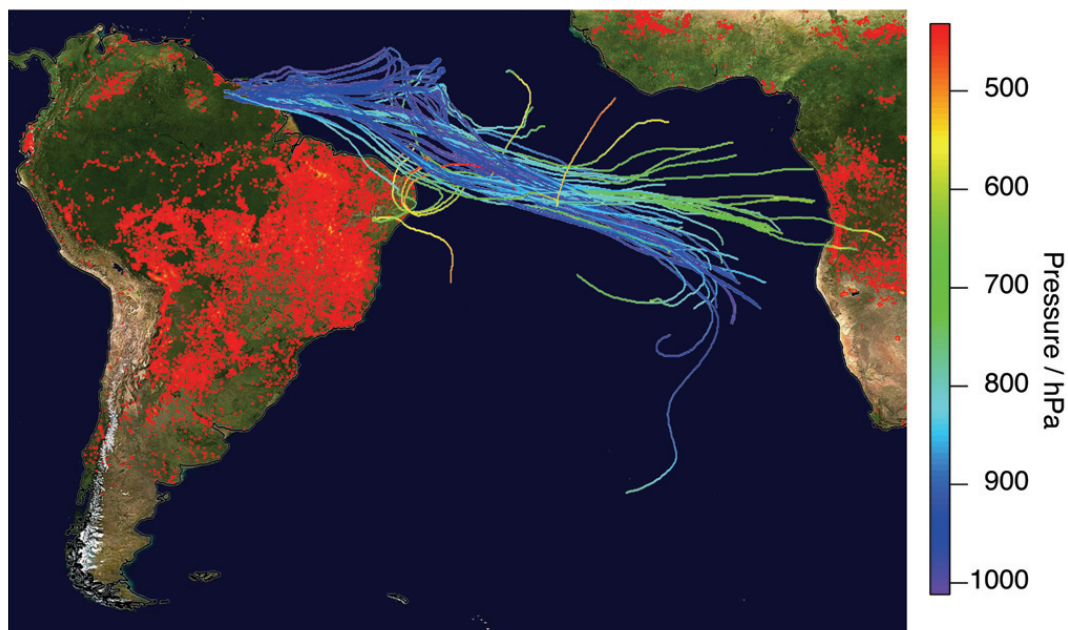
**Fig. 2.** Altitude distribution of wind speed and direction (angle) binned in 100 m intervals (dots: median, boxes: 25/75 percentile, whiskers: 5/95 percentile). A wind angle of 0° is equivalent to northern direction.

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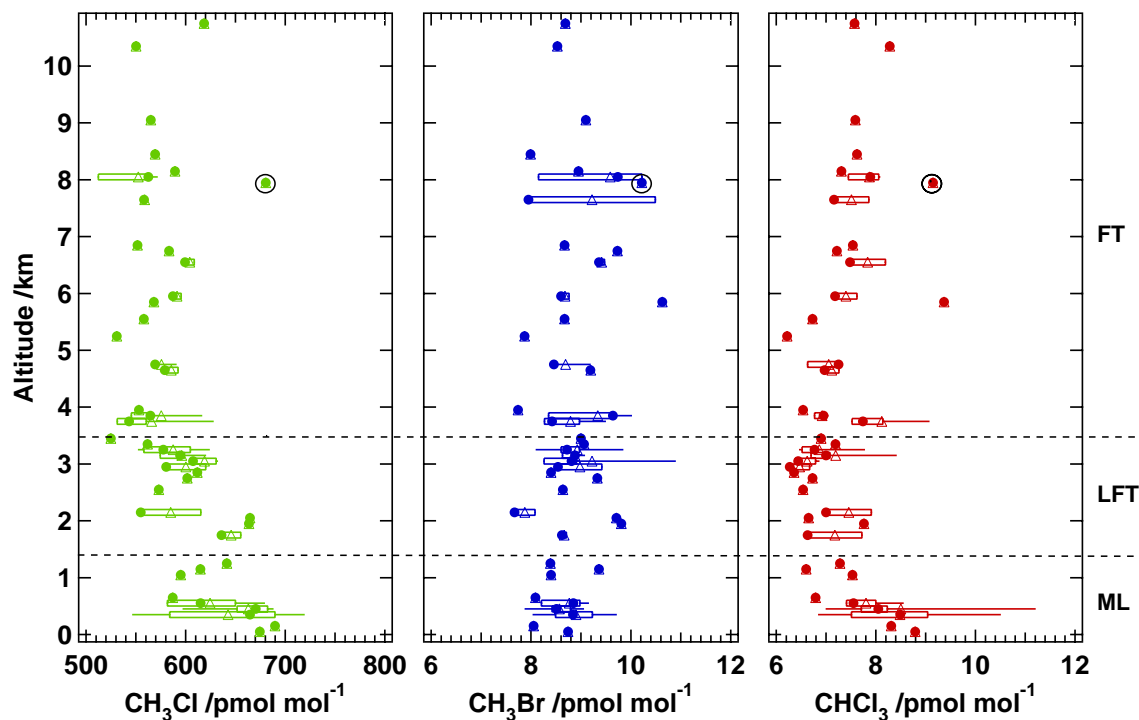


**Fig. 3.** 10-days back trajectories (provided by KNMI) of the canister samples taken within the boundary layer (<1400 m) overlaying a MODIS fire map showing all fires detected in the period from 8 October 2005–18 October 2005 (Source: Fire maps created by Jacques Descloitres, MODIS Rapid Response System at NASA/GSFC; downloaded September 2007 from <http://rapidfire.sci.gsfc.nasa.gov/firemaps/>).

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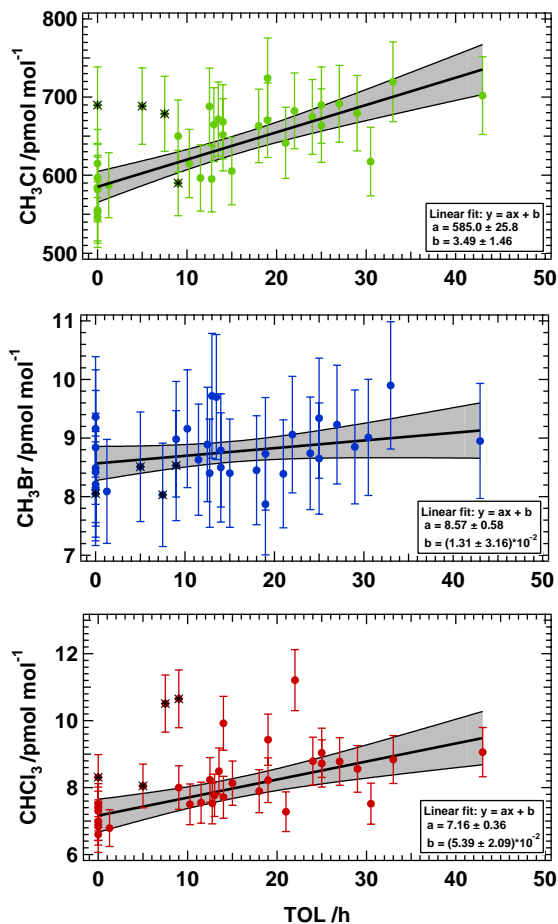


**Fig. 4.** Vertical distribution of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CHCl}_3$  (dots: median, triangles: mean, boxes: 25/75 percentile, whiskers: 5/95 percentile, circles mark a biomass burning event). The horizontal dashed lines mark the divisions referred to in the text as mixed layer (ML), lower free troposphere (LFT) and free troposphere (FT).

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**Fig. 5.** Mixing ratios of CH<sub>3</sub>Cl, CH<sub>3</sub>Br and CHCl<sub>3</sub> vs. TOL. Fit coefficients and 95% confidence intervals are displayed in the box and visualized by the grey shaded area; black asterisks mark samples excluded from the calculation.

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