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Pollution plumes observed during CARIBIC flights in the upper troposphere between South China and the Philippines

S. C. Lai[1], A. K. Baker[1], T. J. Schuck[1], P. van Velthoven[2], D. E. Oram[3], A. Zahn[4], M. Hermann[5], A. Weigelt[5], F. Slemr[1], and C. A. M. Brenninkmeijer[1]

[1]Max Planck Institute for Chemistry, Air Chemistry Division, J.-J.-Becherweg 27, 55128 Mainz, Germany
[2]Royal Netherlands Meteorological Institute (KNMI), P.O. Box 201, 3730 AE, de Bilt, The Netherlands
[3]National Centre for Atmospheric Science, School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK
[4]Institut für Meteorologie und Klimaforschung (IMK), Forschungszentrum Karlsruhe, Weberstr. 5, 76133 Karlsruhe, Germany
[5]Leibniz-Institut für Troposphärenforschung (IFT), Permoserstr. 15, 04318 Leipzig, Germany

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Correspondence to: S. C. Lai (senchao.lai@mpic.de)

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Abstract

A strong pollution episode in the upper troposphere between South China and the Philippines was observed during CARIBIC flights in April 2007. Five pollution plumes were intersected and enhancements in aerosol and trace gas concentrations including CO, CO_2, CH_4, non-methane hydrocarbons (NMHCs) and halocarbons were observed along the flight tracks during four sequential flights. The importance of the contribution of biomass burning was investigated using chemical tracers, emission factor analysis, back-trajectory analysis and satellite images. The Indochinese peninsula was identified as the probable source region of biomass/biofuel burning. However, enhancements in the urban/industrial tracer C_2Cl_4 in the plumes also indicate a substantial contribution from anthropogenic emissions. An estimation of the anthropogenic component of CO shows that biomass/biofuel burning contributed 44–63% to the intersected plumes.

1 Introduction

Over the last few decades, several major research programs have focused on Asian continental outflow, including studies of the regions discussed here. Various pollutants including aerosols, greenhouse gases, non-methane hydrocarbons (NMHCs) and halocarbons have been studied (Blake et al., 1997; Blake et al., 2003; Oshima et al., 2004). Satellite observations are also contributing to investigations in the region (Heald et al., 2004; Singh et al., 2006). However, considering the rapid changes, the vast area concerned, and the fast atmospheric chemistry in the tropics, as well as complex transport processes due to convection, additional observations are highly valuable.

The research project CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrumented Container, phase II) is designed to conduct regular, long-term and detailed observations of the free troposphere and UT/LS regions where passenger aircraft happen to cruise. Use is made of a fully-automated measurement container (1.5 t) onboard an Airbus 340-600 operated by Lufthansa Airlines

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during regular passenger flights to conduct real time trace gas and aerosol measurements and to collect aerosol and air samples on a near monthly basis (Brenninkmeijer et al., 2007) (see also www.caribic-atmospheric.com). Most information is obtained at cruising altitude (9–11 km), while during descent and ascent a limited number of measurements are made. Below flight altitudes of ~500 hPa the air intake is switched off to prevent contamination of the inlet system, tubing and equipment. Statistical analyses have shown that depending on the season and latitude, the CARIBIC aircraft intercepts a range of different air masses, classified as boundary layer air, free troposphere, tropopause, and lower-most stratosphere (Köppe et al., 2009). Therefore, the data give information about air masses from different atmospheric domains.

Since its start in December 2004, CARIBIC (phase II) has covered several major intercontinental routes. A series of Asian flights (Frankfurt-Guangzhou-Manila) began in May 2005 and ended March 2008. The sections of flights over South China to the Philippines cover populated and strongly industrialized regions. It is expected that in addition to anthropogenic emissions, oceanic and biomass burning emissions also influence atmospheric composition in this region. During these flights, many plumes have been identified in the vicinity of Guangzhou and during the flights Guangzhou – Manila by enhanced CO concentrations, but only a fraction of them is well characterized by coincidental whole air samples. The most complete data base for plume characterization is provided by the CARIBIC flights 186–189 (cf. www.caribic-atmospheric.com). In this paper, these four flights have been singled out and the pollution plumes intersected along the flight tracks are characterized. The contribution of regional sources to these plumes is estimated here.

2 Experimental

The measurements took place from 06:00 to 21:00 UTC on 19 April 2007 during four flights: Frankfurt to Guangzhou, Guangzhou to Manila, and the return flights (Fig. 1). The flight sections of interest were the sections of the long-range flights 186 and 189

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(Frankfurt-Guangzhou-Frankfurt) over South China, and the entire regional flights 187 and 188 (Guangzhou-Manila-Guangzhou).

In situ measurements of carbon monoxide (CO; VUV fluorescence, resolution 1 s), ozone (O_3; UV absorption, resolution 4 s), total reactive nitrogen (NO_y; chemiluminescence, resolution 1 s), sub-micrometer aerosols (Condensation Particle Counters, >4 nm (N_4) and >12 nm (N_{12}) diameter, resolution 2 s), acetonitrile (CH_3CN) and acetone (CH_3COCH_3) (Proton Transfer Reaction Mass Spectrometry (PTRMS), resolution 1min) are available (Brenninkmeijer et al., 2007). Due to malfunction of the PTRMS, acetonitrile and acetone data are available only for the long range flights 186 and 189. Whole air samples were collected in glass cylinders over time periods of close to one minute. Eight whole air samples were collected over the region under investigation: W14 from Flight 186; W15–17 from Flight 187; W18–20 from Flight 188 and W21 from Flight 189 (Fig. 1). They were analyzed in laboratories for greenhouse gases, NMHCs, halocarbons and isotopes. Greenhouse gases (CO_2, CH_4, N_2O and SF_6) were analyzed at the Max Planck Institute for Chemistry (MPIC), Germany, by gas chromatography using a flame ionization detector and electron capture detector (GC-FID-ECD) (Schuck et al., 2009). Non-methane hydrocarbons were also analyzed at MPIC using GC-FID (Baker et al., 2009). Halocarbons were analyzed by GC-MS at the University of East Anglia, United Kingdom (Krol et al., 2003; Oram et al., 2009). The stable isotopic composition of CO_2, namely $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$, was measured by isotope ratio mass spectrometry (IRMS) at the Institute for Reference Materials and Measurements (IRMM), Belgium (Assonov et al., 2009).

Flight information including latitude, longitude, pressure, altitude and temperature was routinely recorded from the aircraft system. Except for during ascent and descent, most of the sampling altitudes were above 10 km. The potential vorticity (PV) values and back-trajectories were calculated using data from the European Center for Medium-Range Weather Forecast (ECMWF) and the model of the Royal Netherlands Meteorological Institute (KMMI) (http://www.knmi.nl/~velthove/). Of all observations, 88% was conducted in the troposphere at PV values below 1.5 PVU

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(10^{-6} K kg^{-1} m^2 s^{-1}). All back-trajectories along the flight route were checked for cloud contact during the previous 4 days using a FORTRAN algorithm (Weigelt et al., 2009) overlaying back-trajectories and satellite cloud images from the International Satellite Cloud Climatology Project (ISCCP, http://isccp.giss.nasa.gov/).

3 Intersected plume characterization

The results of in situ measurements and offline analyses of whole air samples are shown in Fig. 2. As shown, five pollution plumes can be identified by distinct enhancements of trace gases and aerosols. The continuous data show that the first plume (Plume 1) was encountered shortly after 06:30 UTC during Flight 186 when the aircraft was over South China. The plume section was intersected at an altitude of 11.4 km and exhibited enhancements in CO (from ~70 ppb to ~150 ppb), aerosol (>12 nm, N_{12} from ~5×10^3 to ~50×10^3 particles/cm^3 STP), O_3 (from ~70 ppb to ~90 ppb), CH_3CN (from ~100 ppt to ~150 ppt) and acetone (from ~350 ppt to ~1800 ppt). The event lasted until 07:00 UTC when the aircraft started to descend. Notably, while descending, aerosol decreased rapidly whilst CO, O_3 and CH_3CN increased further, reaching ~200 ppb, ~250 ppt and ~100 ppb, respectively. No nucleation mode aerosol (4–12 nm, N_{4-12}) enhancement was observed in the plume. The particle concentration N_{4-12} is calculated as the difference N_{12}–N_4 and represents the concentration of particles larger than 4 nm and smaller than 12 nm, which have a very short lifetime (on the order of hours) (Hermann et al., 2003). Unfortunately no whole air sample was collected in this particular plume. As the CARIBIC whole air sampling is designed to obtain representative information, air samples are taken at predetermined intervals over the long distance flights. Prior to reaching this plume, W14 had been collected in the tropopause region at a higher PV level (~2 PVU). Correspondingly lower levels of trace gases were found in Sample W14.

After a ~5 h stopover in Guangzhou, the aircraft departed for Manila (Flight 187) and it encountered another strong plume (Plume 2) during ascent beginning at ~8 km at

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about 12:45 UTC. A strong CO enhancement (from ~120 to ~180 ppb) and a brief N_{12} enhancement (from $\sim 1\times10^3$ to $\sim 10\times10^3$ particles/cm^3 STP) were observed. Sample W15 was collected within this plume and contained the highest mixing ratios of C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10} and C_2Cl_4 of any sample discussed here. A strong decrease in trace gas levels, except for ozone which actually increased, was then observed while the aircraft climbed to a cruising altitude of ~11 km. Carbon monoxide, alkanes and C_2Cl_4, which will be discussed later, were 40% or more lower during this period (Sample W16) than in sample W15. At 13:15 UTC, Plume 3, with enhancements in CO, N_{12} and NO_y was encountered, with peak values of ~150 ppb for CO, $\sim 30\times10^3$ particles/cm^3 STP for N_{12}, and ~1.8 ppb for NO_y. Collection of sample W17 was co-incident with these enhanced values and contained elevated concentrations of CO_2, alkanes and halocarbons. While the aircraft was approaching (Flight 187) and subsequently leaving (Flight 188) Manila, considerably lower levels of CO (~70 ppb) and O_3 (~20 ppb) were observed at an altitude range of 4–8 km. Sample W18 was collected after the aircraft had left Manila for Guangzhou at 16:40 UTC. The lowest mixing ratios of all species were measured in this sample and they were close to the background levels reported during previous campaigns (e.g. Blake et al., 1997). Back-trajectories show that the air had passed over Papua New Guinea five days earlier and traveled along coastal regions of Indonesia and the South China Sea. Hence, clean oceanic air is assumed to have been the main contributor during this period that will be used later as the background air reference.

Plume 4 (observed starting at 16:50 UTC) had enhancements in CO (~130 ppb), N_{12} ($\sim 10\times10^3$ particles/cm^3 STP), O_3 (~75 ppb), and NO_y (~1.2 ppb). Approximately 10 min later sample W19 was collected and the mixing ratio of ethane was similar to W17. In contrast, concentrations of shorter-lived species (inc. propane, i-butane, n-butane) were higher than in Sample W19, showing this plume to have a more recent origin. Nevertheless, an enhancement of O_3 indicates this plume not to have been completely fresh. Sample W20 collected afterwards had similar level of O_3 (~75 ppb) and lower levels of CO (~100 ppb), N_{12} (8×10^3 particles/cm^3 STP) and NMHCs. These

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mixing ratio levels were still slightly enhanced compared to the background levels for the five observed plumes.

The last plume (Plume 5) was observed at an altitude of about 9.6 km over South China during Flight 189 when the aircraft was returning to Frankfurt. The CO concentration in the plume was ~150 ppb, a level similar to that detected in Plume 1 but without concomitant enhancement in aerosol concentrations. Mixing ratios of O_3 collected in the beginning of the plume at 19:58–20:00 UTC whilst the aircraft was ascending were ~50–60 ppb. Only two data points of both acetonitrile and acetone were obtained at 20:16 UTC and 20:34 UTC. The concentrations of acetonitrile were 703.0 ppt and 659.1 ppt and the accompanying acetone concentrations were 2596.9 ppt and 1033.0 ppt, respectively, and were all strong enhanced. Sample W21 was collected in this plume.

To summarize, four whole air samples (W15, W17, W19 and W21) collected in the pollution plumes (Plume 2–5) had elevated mixing ratios of CO_2, CH_4, alkanes (C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}) and certain halocarbons (C_2Cl_4, CH_3Cl) relative to the other samples (W14, W16, W18 and W20).

4 Discussion

As in other studies, increased carbon monoxide was the most evident signal for the intersected plumes. Carbon monoxide in plumes is mainly the product of incomplete combustion of fossil fuel, but also of biofuels, agricultural fires and biomass burning in general (Logan et al., 1981). Significant correlations were found between integrals of continuous CO mixing ratios integrated over the sampling period and the CO_2 mixing ratios measured in the individual air samples ($R^2 = 0.87$), clearly showing that burning is a common source. When air is in contact with the surface, and photosynthesis removes CO_2, a negative correlation between CO and CO_2, or a lack of any correlation, would be expected. This has not been the case and the net CO_2 uptake must have been small compared to production.

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Additional information is provided by the isotopic composition of CO_2 in the air samples. $\delta^{13}C(CO_2)$ ranged from −8.52‰ to −8.31‰. A strong correlation was found between $\delta^{13}C(CO_2)$ and $1/CO_2$ ($R^2 = 0.86$). High CO_2 values always correspond to low $\delta^{13}C(CO_2)$ values because of input of CO_2 from the combustion of fossil fuels and vegetation, both being depleted in ^{13}C. $^{13}C(CO_2)$ generally does not, however, allow for distinction between these two source classes. Photosynthesis produces the opposite effect to combustion and burning as it discriminates against the uptake of ^{13}C. Furthermore, C_2H_6, C_3H_8, n-C_4H_{10} and i-C_4H_{10} are found to be strongly correlated with CO (R^2>0.83). While CO is the main indicator of pollution, NMHCs are usually increased as well. They also act, together with other volatile organic compounds (VOCs), as a precursor for continued CO formation and are often accompanied by increased O_3. As is mentioned, a slight increase in O_3 was observed in the intersected plumes.

Enhancements in N_{12} found in Plumes 1–4 had an order of Plume 1 > Plume 3 > Plume 4 > Plume 2. However, except for a small increase in Plume 1, no increase in N_{4-12} was observed in the other plumes. The large increase in N_{12} (sum of Aitken mode and accumulation mode particles) can be attributed to rapid air transport from lower altitudes and/or formation during plume evolution (Hermann et al., 2003). However, the absence of elevated N_{4-12} concentrations precludes a substantial contribution of fresh in-situ particle formation. The slight increases in O_3 and the absence (or only small increase) of ultrafine particle (N_{4-12}) enhancement in the five plumes suggest that these plumes were photochemically aged. The concomitant strong acetone enhancements observed in Plume 1 and, especially, in Plume 5 over South China also imply secondary acetone formation during the plume aging (Holzinger et al., 2005; Jost et al., 2003).

The general features of the plumes are similar to observations reported for previous campaigns in the western Pacific coast (Blake et al., 2003; Russo et al., 2003). A main conclusion was that Asian continental outflow contained a mixture of fresh and processed emissions from combustion, industrial activities, and biomass burning/biofuel burning (Russo et al., 2003). Air mass back-trajectories during the selected flights

show that the air mainly passed over regions to the southwest of the flight track (Fig 3). The pertinent region in Southeast Asia is the Indochinese Peninsula. The increased emission of anthropogenic compounds and the influence of biomass burning have previously been discussed in the monitoring of Southeast Asian outflow e.g. (Kondo et al., 2004). To obtain a clearer picture and to estimate the contributions from different source types, it is necessary to analyze carefully the variations of other species and the relationship between trace gases.

Firstly, the contribution of biomass burning is taken into account since springtime is the dry season in Southeast Asia during which biomass burning is prolific (Christopher and Kimberly, 1996). Acetonitrile is a unique tracer of biomass burning (Andreae et al., 2001). As is mentioned above, high CH_3CN concentrations were observed in Plumes 1 and 5 over South China. Whilst the aircraft was flying through Plume 1, significant correlation was found between CO and CH_3CN ($R^2 = 0.79$). The CH_3CN increases and strong correlation with CO imply that these plumes contain biomass burning effluents. The similar pattern of acetone increases in Plume 1 and 5 can also be attributed to biomass burning and/or biofuel related sources (as a direct emission or from photochemical formation) (Singh et al., 1994; Jost et al., 2003). Although CH_3CN data are unfortunately not available during the flights 187 and 188, CH_3Cl, another useful biomass burning tracer, was found to be correlated well with CO (R^2>0.72) in all selected samples. These findings suggest that biomass burning was a substantial, or even predominant, contributor to the chemical composition of the observed plumes.

The emission factors (EF) of $\Delta X/\Delta CO_2$ and $\Delta X/\Delta CO$ (Table 1) are now used to show the enhancements of species over their background levels, i.e. $\Delta X/\Delta CO = (X_{plume} - X_{background})/(CO_{plume} - CO_{background})$ (Andreae and Merlet, 2001). Mixing ratios from W18 were used to represent background levels because they are low and the back-trajectories show that the sampled air was not affected by recent pollution. We also note that they are close to the regional background levels reported by others (Blake et al., 1997; Russo et al., 2003).

The $\Delta CO/\Delta CO_2$ ratios of 15.6–29.3 ppb/ppm in our air samples are much lower than

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those cited for fresh tropical forest fire plumes (Andreae and Merlet, 2001; Mauzerall et al., 1998). Moreover they are lower than those determined for strong biomass burning plumes measured in a more southerly region (near Singapore) in 1997 (strong El Niño related fires) with a value of 89 ppb/ppm .(Matsueda and Inoue, 1999). However, our ratios are similar to the value of 13 ppb/ppm found in Southeast Asian outflow during the TRACE-P campaign in February–April, 2001 which represented a mixture of biomass burning and anthropogenic emissions (Russo et al., 2003). Furthermore, $\Delta CH_4/\Delta CO$ ratios varied from 0.3–0.76, which are higher than that for fresh biomass burning plumes and closer to values for plumes impacted by anthropogenic emissions (Andreae and Merlet, 2001; Mauzerall et al., 1998; Muhle et al., 2002). $\Delta O_3/\Delta CO$ ratios were variable (0.4–2.1). In plume samples (i.e. W15, W17 and W19), $\Delta O_3/\Delta CO$ ratios were lower (0.4–0.9) than in non-plume samples (1.7 and 2.1), showing that the plume air was fresher. Nevertheless, $\Delta O_3/\Delta CO$ ratios were still higher than those in non-aged plumes (e.g. $\Delta O_3/\Delta CO \approx 0.1$ after 2 h ageing; Jost et al., 2003), suggesting these plumes were photochemically aged. Conversely, the EFs of alkanes, CH_3Cl and N_2O were all within the range of fresh smoke of biomass burning reported by previous studies. Higher EFs were found for CH_3I and CH_3Br which may be a result of non-biomass-burning sources e.g. oceanic emission in the Pacific Ocean (Chan et al., 2006).

The occurrence of biomass burning and the subsequent transport are further supported by satellite observations. According to the fire map provided by the Moderate Resolution Imaging Spectroradiometer (MODIS) on NASA's Terra satellite, strong fires were observed in the Indochinese Peninsula in April 2007. In particular, many fire points were detected on 18 April 2007 (Fig. 5). Global infrared cloud images from the Space Science and Engineering Center, University of Wisconsin-Madison (SSEC) indicate that strong convection had occurred in the same region on 18 April 2007 (Fig. 5). Cloud contact analysis confirms that probed air parcels had been contacted with the convective clouds (Fig. 4), which gives a clear evidence of an important pathway to uplift pollutants from ground level to the UT. The air parcels were entrained in the general

flow and finally monitored by the CARIBIC aircraft. From the cloud, the air traveled over the aforementioned region 1–2 days before sampling. This is in accordance with the evidence that the intersected plumes were photochemically aged to some degree.

Although the contribution of biomass burning is beyond doubt, the relative contribution is not certain compared to that from other sources. The influence of anthropogenic sources can be further investigated by using the industrial/urban tracer perchloroethylene (C_2Cl_4) which is an entirely man-made compound used as a dry cleaning agent and degreasing solvent in industrial and commercial activities (Wang et al., 1995). During previous campaigns, C_2Cl_4 was suggested as a unique urban/industrial tracer in Asian continental outflow (Blake et al., 1997; Wang et al., 1995). The level of C_2Cl_4 measured during the CARIBIC flights presented here ranged from 0.92 to 2.22 ppt, which is similar to the range observed at altitudes >7 km during TRACE-P (Russo et al., 2003). The significant correlation we find between CO and C_2Cl_4 ($R^2 = 0.88$) shows that the pollution plumes were not only influenced by biomass burning but also by anthropogenic sources. The slope of CO versus C_2Cl_4 during more than 2 years CARIBIC observation in the cruising altitude over this region was 33 ppb/ppt (CO/C_2Cl_4), which is similar to the previous studies investigating on the continental Asian outflows ($CO/C_2Cl_4 \approx 30$ ppb/ppt) (Blake et al., 1997, 2003). Therefore, C_2Cl_4 is used here as a surrogate to estimate the relative contribution of biomass burning relative to anthropogenic emissions. Slope value of 33 ppb/ppt (CO/C_2Cl_4) is assumed to represent the regional correlation between anthropogenic CO and C_2Cl_4. Anthropogenic CO concentration is then estimated using C_2Cl_4 concentration multiplying a factor of 33. The results show that the estimated anthropogenic CO accounted for 37–56% of the observed CO (Table 2). In other words, the contribution of biomass/biofuel burning ranged from 44% to 63%. In the observed pollution plumes, biomass /biofuel burning was the substantial source, contributing slightly more than anthropogenic emission. This finding is lower than the previous estimate (>80%) in highly biomass burning impacted plumes from Southeast Asia in March 2001 during TRACE-P (Woo et al., 2003).

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5 Conclusions

Five distinct plumes were observed in April 2007 during a series of CARIBIC flights over South China to Manila, Philippines. Enhancements in aerosol and a variety of trace gases such as CO, CO_2, CH_4, NMHCs and halocarbons were recorded. Air mass back-trajectories show that the pollution plumes were mainly influenced by the outflow from the Indochinese Peninsula. Signals of CH_3CN during Flight 186 and 189 and the significant correlation between CO and CH_3Cl show that the pollution plumes were strongly impacted by biomass burning. Fire maps of the Indochinese Peninsula, cloud images and back-trajectories together confirm the occurrence of biomass burning, uplift in convection and air transport, implying biomass burning as an importance source of pollutants in the plumes. The plumes were further characterized by the EFs of pyrogenic trace gases, which indicates that the plumes were not only affected by biomass burning but also by anthropogenic emissions. Using C_2Cl_4 as the urban/industrial tracer, an estimate was made of the relative contribution of biomass burning and anthropogenic/urban emissions. Biomass burning accounted for between 42% and 63% of the observed CO enhancement.

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Table 1. Emission ratios during the CARIBIC flights.

Flight	Sample	ΔCO /ΔCO_2	ΔCH_3Cl /ΔCO	ΔC_2H_6 /ΔCO	ΔC_3H_8 /ΔCO	Δi-butane /ΔCO	Δn-butane /ΔCO	ΔO_3 /ΔCO	ΔCH_3Br /ΔCO	ΔCH_3I /ΔCO	ΔCH_4 /ΔCO	ΔN_2O /ΔCO
F187	W15	29.3	0.7	8.5	1.3	0.2	0.2	0.4	0.03	0.0037	0.3	0.0048
F187	W16	17.9	0.4	9.1	1.3	0.2	0.3	1.7	0.02	0.0021	0.6	0.0154
F187	W17	22.6	1.1	5.8	1	0.1	0.2	0.6	0.03	0.004	0.4	0.0075
F188	W18*	72.8 (CO) 383.9 (CO_2)	629.8	351.8	15.8	1.9	3.4	23.1	7.6	0.1	1768.9	320.9
F188	W19	15.6	1.5	6.4	1.6	0.3	0.4	0.9	0.03	0.0037	0.6	0.0115
F188	W20	22.6	N.A.	7.9	1.2	0.1	0.2	2.1	N.A.	N.A.	0.5	0.0122
F189	W21	20.9	0.5	8.8	1.3	0.1	0.2	N.A.	0.01	0.0015	0.8	0.0066

* W18 is used as the reference sample of background for emission ratio calculation;
** The emission factors for W14 are not provided because it was taken in the tropopause region with lower mixing ratios of trace gases;
*** Unit for CO_2 is ppm; Units for CO and CH_4 are ppb and ppt for other species.

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Table 2. Estimation of anthropogenic CO (An-CO) using C_2Cl_4 as a tracer.

Flight	Route	Sample	CO (ppb)	C_2Cl_4(ppt)	An-CO(ppb)	Percentage
187	CAN-MNL	W15	175.1	2.2	73.3	42%
187	CAN-MNL	W16	109.0	1.5	48.9	45%
187	CAN-MNL	W17	147.7	1.6	54.1	37%
188	MNL-CAN	W18	72.8	1.2	40.6	56%
188	MNL-CAN	W19	129.2	1.9	61.8	48%
188	MNL-CAN	W20	99.0	N.A.	N.A.	N.A.
189	CAN-FRA	W21	139.1	1.8	59.8	43%

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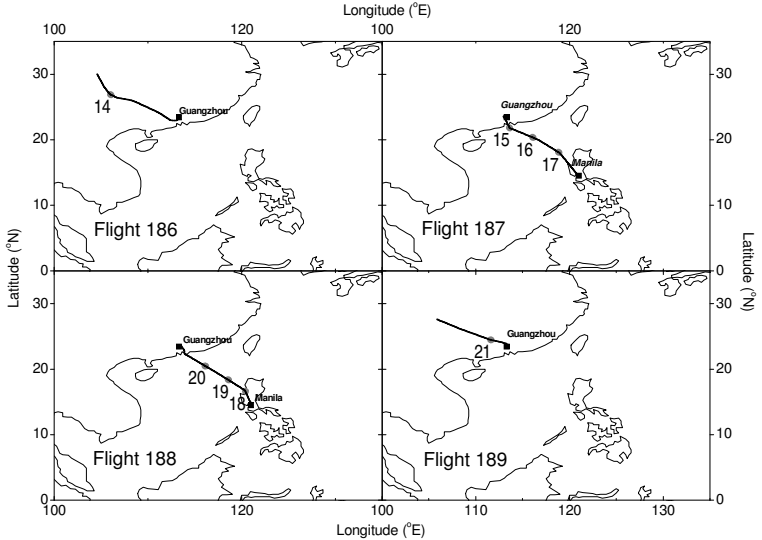

Fig. 1. Flight tracks of selected CARIBIC flights (Flight 186–189) over South China and the Philippines.

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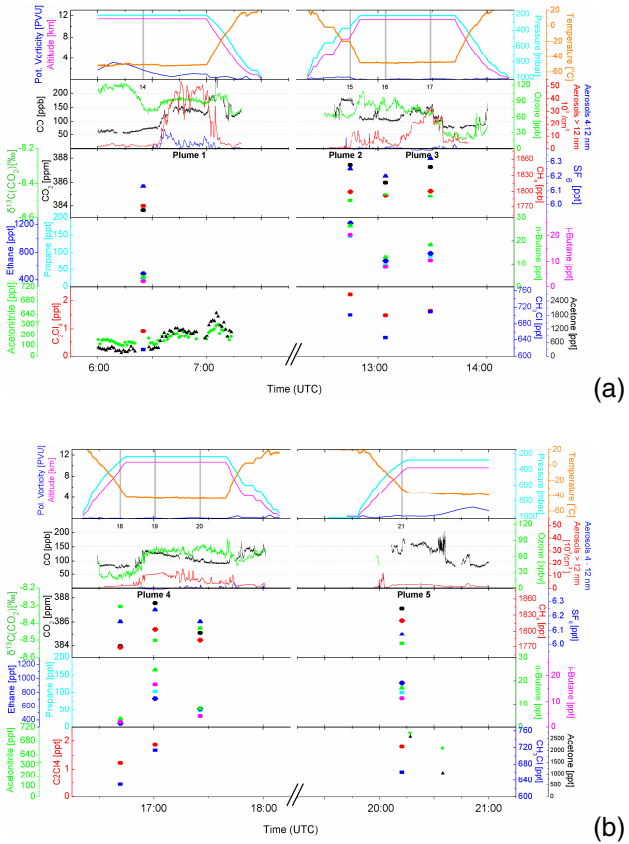

Fig. 2. Data overviews for flights 186–189: **(a)** for Flight 186 and 187; **(b)** for Flight 188 and 189. Panels from top to bottom (i) Flight parameters of altitude, potential vorticity, pressure, temperature and sampling intervals (grey bars); (ii) In situ measurements of CO, O_3, N_{4-12} and N_{12}; (iii) $\delta^{13}C(CO_2)$, CO_2, CH_4 and SF_6; (iv) Ethane, propane, n-butane and i-butane; (v) C_2Cl_4, CH_3Cl, acetonitrile and acetone.

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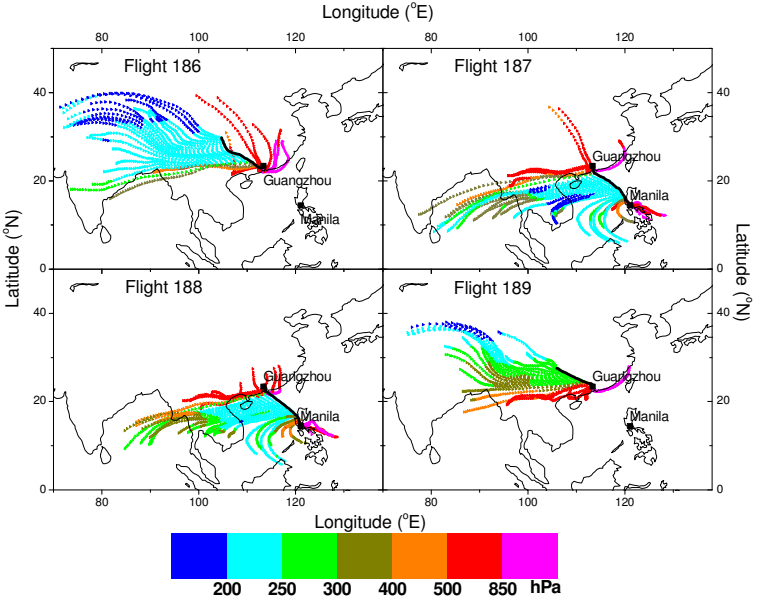

Fig. 3. 2 days back-trajectories of flight 186–189. Colour scale gives altitude in hPa. More back-trajectory information at (www.knmi.nl/samenw/campaign_support/CARIBIC/).

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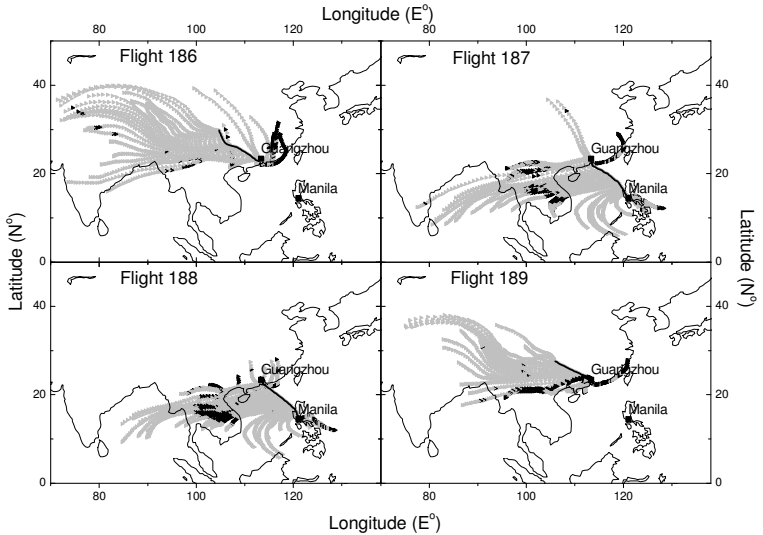

Fig. 4. Cloud contact in the last 48 h of air parcels probed by CARIBIC. Black lines stand for the CARIBIC flight tracks. Back-trajectories in grey and in black denote those without and with cloud contact.

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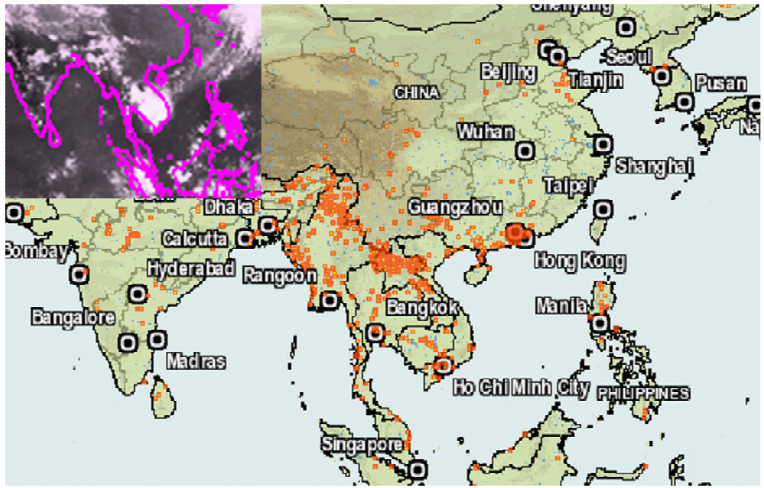

Fig. 5. Fire map and infrared cloud image on 18 April 2007. Fire map is from MODIS (modis.gsfc.nasa.gov) showing the daily fire points; figure inserted in the upper right is the infrared cloud image from SSEC (http://www.ssec.wisc.edu/) at 12:00 UTC.

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