Biomass burning and fossil fuel signatures in the upper troposphere observed during a CARIBIC flight from Namibia to Germany

J. Mühle, C. A. M. Brenninkmeijer, T. S. Rhee, and F. Slemr

Max Planck Institute for Chemistry, Mainz, Germany

D. E. Oram and S. A. Penkett

University of East Anglia, School of Environmental Sciences, Norwich, United Kingdom

A. Zahn

Forschungszentrum Karlsruhe, Institute of Meteorology and Climate Research, Karlsruhe, Germany

[1]   During a CARIBIC flight from Namibia to Germany in July 2000, air influenced by recent convective injection of biomass burning emissions was intersected in the vicinity of the ITCZ at an altitude of 10 km. The observed CO enhancement ratios for non-methane hydrocarbons (NMHCs) and methyl halides are consistent with those reported for fresh biomass burning plumes. Air masses affected by transcontinental transport of natural gas emissions, most probably from the Gulf of Mexico, were encountered over the Mediterranean Sea. These are one of the few observations of deep convection of biomass burning emissions to the upper troposphere and of long range transport of natural gas emissions reported so far. The observations demonstrate the importance of deep convection for the chemistry of the upper troposphere and the potential of commercial aircraft for atmospheric research.   INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. Citation: Mühle, J., C. A. M. Brenninkmeijer, T. S. Rhee, F. Slemr, D. E. Oram, S. A. Penkett, and A. Zahn, Biomass burning and fossil fuel signatures in the upper troposphere observed during a CARIBIC flight from Namibia to Germany, Geophys. Res. Lett., 29(19), 1910, doi:10.1029/2002GL015764, 2002.

1.   Introduction

[2]   Within the project CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrumented Container), an instrumented airfreight container onboard a Boeing 767-ER of LTU International Airways is regularly used for measurements in the upper troposphere (UT) and lower stratosphere (LS) [Brenninkmeijer et al., 1999a]. The container houses analyzers for in-situ measurements of trace gases and aerosol properties and devices for collecting air and aerosol samples for subsequent laboratory analyzes. Compared to research aircraft the container can regularly survey atmospheric composition over large distances at relatively low cost. 44 successful flights have been executed since 1997 mostly along routes from Europe to southeastern Asia and central America. 3 flights went from Europe to southern Africa and back. Here we present a detailed analysis of one of the latter flights from Namibia to Germany which shows the strongest influence by convective processes of all three flights traversing the African continent. The data demonstrate the importance of convective processes for influencing the UT as well as the potential of the CARIBIC platform for atmospheric research.

2.   Experimental

[3]   The CARIBIC container holds automated in-situ analyzers for O_3 (UV absorption, temporal resolution 16 s, accuracy 2.5% or 2 ppbv), CO (gas chromatograph (GC), temporal resolution 130 s, accuracy and precision 3 ppbv), and fine aerosol particles (three counters for particles with diameters >4 nm, >12 nm, and >18 nm, temporal resolution 2 s). Twelve air samples are collected during the flight and subsequently analyzed in the laboratory for CH_4, CO_2, N_2O, SF_6 (uncertainties: 5 ppbv CH_4, 0.5 ppmv CO_2, 1 ppbv N_2O, and 0.03 pptv SF_6), and the isotopic composition of CO ($^{18}O/^{16}O$ vs. Vienna Standard Mean Ocean Water, $^{13}C/^{12}C$ vs. Vienna Pee Dee Belemnite, and $^{14}C/^{12}C$ as molecules per cm^3 STP) at the Max Planck Institute (MPI). The samples are also analyzed for NMHCs at MPI (GC/mass spectrometry (MS), detection limits <12 pptv, precision <10%) and for halocarbons at the University of East Anglia (GC/MS, detection limits ~0.001 pptv, uncertainties $\pm$ (5−10)%). For details see Brenninkmeijer et al. [1999a, 1999b], Hermann et al. [2001], Sturges et al. [2001], Mühle et al. [2002], Zahn et al. [2002].

3.   Results and Discussion

[4]   Figure 1 gives an overview of the flight on 28 July 2000 from Windhoek (22°S, 17°E) to Munich (48°N, 11°E). The flight at ~10 km altitude (Figure 1b) occurred mainly in the mid- to upper troposphere (moderate O_3 mixing ratios of 50−80 ppbv and potential vorticity (PV) values below 2 PVU, see Figures 1c and 1b), with exception of the last part where elevated O_3 and PV values point to air from a stratospheric intrusion. Figures 1d−1f summarizes the trace
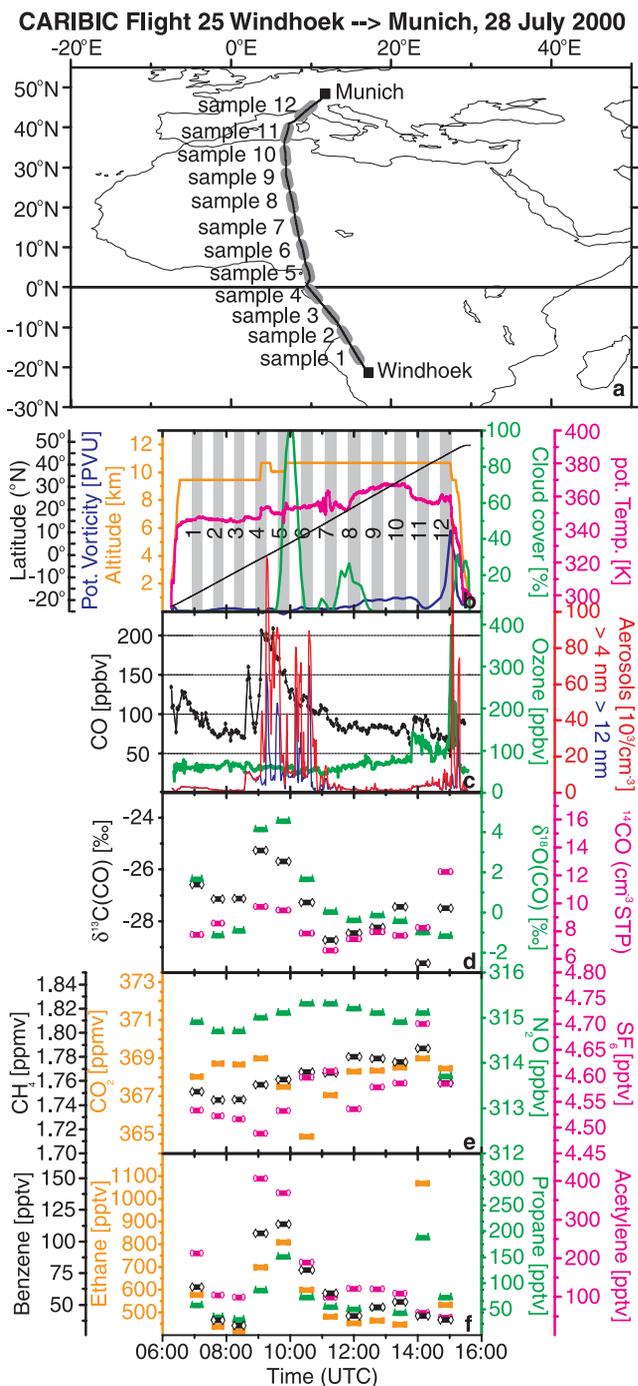
Figure 1. CARIBIC flight from Windhoek to Munich on July 28, 2000: (a) flight track with sampling intervals (~18 min or ~270 km), (b) flight parameters (latitude, altitude), potential vorticity, potential temperature, cloud cover) and sampling intervals (grey bars), (c) in-situ measurements of O_3, CO, and particle number concentrations, (d) isotopic composition of CO, (e) CH_4, CO_2, N_2O, and SF_6, and (f) some NMHCs.

gas composition of the 12 air samples taken at intervals shown in Figures 1a and 1b.

[5] Between 9:00 and 11:00 UTC, i.e., near the equator, the aircraft crossed polluted air masses with up to 200 ppbv

CO (Figure 1c) and ~400 pptv ethyne (Figure 1f). High and strongly fluctuating number concentrations of ultra-fine particles in the range of 4–12 nm (i.e., the difference of the two particle number concentrations shown in Figure 1c) point to recent particle nucleation. This conclusion is based upon the short lifetimes of ultra-fine particles of a few hours to 1 day [*Jaenicke*, 1993]. The nucleation of new particles occurred most likely after old particles being scavenged by clouds within deep convection cells associated with the intertropical convergence zone (ITCZ) followed by oxidation of precursors and cooling of ascending air [*Clarke et al.*, 1999]. Changes in flight altitude and direction (Figures 1b and 1a) indicate that the pilots tried to avoid the most active convection regions. The depleted CO_2 mixing ratios of samples 5–7 confirm the boundary-layer origin of these air masses, due to the strong vegetative CO_2 uptake in the NH summer and the corresponding positive vertical CO_2 gradient in the NH troposphere [*Wofsy et al.*, 1988]. However, CO_2 of sample 4 is not depressed clearly indicating its origin in the southern hemisphere (SH). Indeed, meteorological analyzes based on ECMWF analyzes of the low level equivalent potential temperature and precipitation, vertical wind speed, cloud cover (see Figure 1b), and infrared cloud imagery (http://www.knmi.nl/~velthove/CARIBIC/280700/) show that the ITCZ was located between samples 5 and 6. This is supported by generally lower and less variable SF_6 in samples 1–5 corresponding to the SH when compared to samples 6–12 in the northern hemisphere (NH).

[6] Samples 4–6 show enhanced concentrations of CO, various NMHCs such as ethyne, ethane, propane, butane, benzene, and methyl halides. Together with CO most of these compounds are predominantly emitted in the smoldering phase of burning biomass, with the exception of ethyne and benzene which are comparatively emitted during all phases [*Crutzen and Andreae*, 1990; *Lobert et al.*, 1991]. To quantify this relation of a trace species X to CO enhancement ratios (ERs) are calculated by dividing the excess of X in the plume versus background by the excess of CO, i.e., $\Delta X/\Delta CO = (X_{smoke} - X_{background})/(CO_{smoke} - CO_{background})$ [see e.g., *Andreae and Merlet*, 2001].

[7] To characterize the plume, CO enhancement ratios were calculated for samples 4–6 and compared with published values of fresh and recent biomass burning plumes, see Table 1. The ERs for samples 4 and 5 were calculated using samples 2–3 as representative of the tropical SH background, whilst ERs for sample 6, i.e., north of the ITCZ, were inferred using samples 7–9 as NH background. Mean SH background mixing ratios in Table 1 are comparable to those given by *Mauzerall et al.* [1998] for the tropical South Atlantic, i.e., 462 pptv ethane, 17 pptv propane, 80 pptv ethyne, and 13 pptv benzene. The uncertainties of the ERs in Table 1 are estimated by error propagation of the estimated uncertainty of the individual measurements and the standard deviations of the background mixing ratios. The comparably low and accordingly uncertain enhancements versus background in all samples for CH_3Cl and CH_3Br and in sample 6 for other compounds lead to large uncertainties of these ERs.

[8] Despite the low number of samples almost all ERs fall in the range of previous observations (also listed in Table 1). Exceptions are: (i) the ERs of ethane and propane

Table 1. Comparison of CO Enhancement Ratios of Samples 4–6 With Previous Results Reported for Fresh and Recent Plumes of Biomass Burning

Species	Background[a]		ER ($\Delta X/\Delta CO$)[b]			
	SH (Samples 2, 3)	NH (Samples 7, 8, 9)	Sample 4 (SH)	Sample 5 (SH)	Sample 6 (NH)	Literature[d]
CO	75 ± 1	89 ± 5				
CH_4	1744.3 ± 0.1	$-$[c]	0.159 ± 0.016	0.227 ± 0.035	$-$[c]	$0.07-0.37$
C_2H_6	427 ± 14	465 ± 15	3.4 ± 0.2	5.1 ± 0.3	5.1 ± 1.3	$4-9$
C_3H_8	32 ± 3	52 ± 2	0.68 ± 0.05	1.58 ± 0.08	0.78 ± 0.20	$0.8-3.2$
C_4H_{10}	4.6 ± 1.4	7.9 ± 1.0	0.07 ± 0.03	0.43 ± 0.04	0.1 ± 0.1	$0.1-0.4$
iC_4H_{10}	1.3 ± 0.7	2.9 ± 0.2	0.04 ± 0.01	0.24 ± 0.02	0.09 ± 0.03	$0.04-0.08$
C_2H_2	101 ± 5	113 ± 13	3.9 ± 0.2	3.6 ± 0.3	2.9 ± 0.9	$1-10$
C_6H_6	36 ± 3	45 ± 5	0.9 ± 0.1	1.0 ± 0.1	1.3 ± 0.4	$0.8-1.7$
CH_3Br	10.3 ± 0.3	10.5 ± 0.2	$(6 \pm 5) \cdot 10^{-3}$	$(10 \pm 5) \cdot 10^{-3}$	$(67 \pm 19) \cdot 10^{-3}$	$(5.5-17) \cdot 10^{-3}$
CH_3Cl	584 ± 13	594 ± 18	0.2 ± 0.2	0.3 ± 0.2	0.2 ± 0.8	$0.12-1.1$
CH_3I	0.12 ± 0.02	0.12 ± 0.02	$(6 \pm 1) \cdot 10^{-3}$	$(7 \pm 1) \cdot 10^{-3}$	$(11 \pm 3) \cdot 10^{-3}$	$(1.0-14) \cdot 10^{-3}$

[a] Units are ppbv for CO and CH_4 and pptv for all other compounds.
[b] Units are ppbv/ppbv for $\Delta CH_4/\Delta CO$ and pptv/ppbv for all other ratios.
[c] No background value could be defined for CH_4 in the NH.
[d] *Mauzerall et al.* [1998], *Andreae et al.* [2001] and references therein, *Blake et al.* [1996b], *Ferek et al.* [1998], *Blake et al.* [1997].

for sample 4 are slightly lower, (ii) the ER of isobutane for sample 5 is ∼3 times higher than any value previously reported, (iii) the ER of CH_3Br for sample 6 is ∼5 times higher than the highest value observed before. This latter observation could be explained by emission of CH_3Br by processes other than biomass burning, e.g., from the nearby Atlantic Ocean or other terrestrial sources. Due to the large uncertainty in the ER of CH_3Br and the lack of a specific oceanic tracer the source could not be identified clearly. The absence of O_3 enhancement in the plume (see Figure 1c) further suggests that the transport time of the plume was less than one day [*Mauzerall et al.*, 1998].

[9] Lower alkane ERs in sample 4 compared to sample 5 suggest that sample 4 was dominated by flaming and 5 by smoldering. The ERs for ethyne and benzene are comparable in both samples as they are characteristic for both fire phases. CO_2 mixing ratios are consistent with this. It is mainly emitted by flaming and the vertical CO_2 gradient in the SH is flat (see above) which explains the small CO_2 enhancement over background in sample 4. However, CO_2 in sample 5 is below background, which is expected for convection of smoldering emissions (leading to low emissions of CO_2) late in the day (causing pronounced vegetative uptake of CO_2) in NH summer.

[10] The isotopic composition of CO (Figure 1d) provides further information. $\delta^{18}O(CO)$ values of 4.1‰ and 4.6‰ for samples 4 and 5, respectively, are much higher than typical values for the UT in the SH of $\delta^{18}O(CO) < 0$‰ and thus show the influence of burning of biomass or fossil fuel, which have source signatures of ∼16–18‰ and ∼23.5‰, respectively [*Brenninkmeijer et al.*, 1999b]. The elevated ^{14}CO concentration of samples 4 and 5 excludes fossil fuel combustion and unequivocally indicates biomass burning, as only the burning of recent biomass adds ^{14}C. The $\delta^{13}C(CO)$ values of samples 4 and 5 are, with −25.3 and −25.7‰, respectively, enhanced against background values of ∼−27‰. This is consistent with biomass burning leading to values as high as −10 ‰, whereas the oxidation of CH_4 and NMHC leads to −53 and −32‰, respectively [*Brenninkmeijer et al.*, 1999b; *Kato et al.*, 1999]. Extensive biomass burning activity on July 28, 2000, is further confirmed by satellite data, e.g. the

ATSR World Fire Atlas [*ESA/ESRIN*], the TOMS aerosol index [http://toms.gsfc. nasa.gov/aerosols/aerosols.html], and the onset of a large CO plume in the UT over southern Africa reported by MOPITT [http://www.atmosp.physics. utoronto.ca/MOPITT/home.html]. Similar signatures of biomass burning in the mid- to upper troposphere due to convection have been observed previously [*Pickering et al.*, 1996; *Andreae et al.*, 2001].

[11] Sample 11 taken at ∼40°N with high mixing ratios of alkanes from ethane up to pentane (for ethane and propane see Figure 1f), SF_6 (see Figure 1e), and many anthropogenic halocarbons represents the next unusual air mass encountered. Modest CO (∼90 ppbv), ethyne (∼60 pptv), and $\delta^{18}O(CO)$ values (−1.0‰) preclude combustion processes as the major source of the observed alkanes. The observed pattern of alkanes is also not typical of rural air or oceanic air masses. However, it is similar to natural gas which, apart from methane, consists of several higher alkanes but almost no unsaturated compounds like benzene or ethyne [*Chan and Wang*, 2000], as observed (see Figure 1f). Indeed, 5 day back trajectories for sample 11 originate in the Gulf of Mexico, an area of natural gas exploitation where, according to infrared cloud imagery and the Lightning Imaging Sensor [http://thunder.nsstc.nasa.gov/data/LISbrowse/jul00t.html], some convective activity was taking place. The presence of higher alkanes with a lifetime of a few days and the absence of ultrafine particles with a lifetime of a few hours to 1 day are consistent with the calculated transport duration of ∼5 days. The enhanced O_3 mixing ratios of ∼130 ppbv might be formed photochemically during transport [*Thompson et al.*, 1996; *Jonquières et al.*, 1998] or formed at the emission site and conserved during the transport in the UT. The NO_x required for O_3 formation may have come both from lightning in the convective cells in the source region and along the east coast of the US, as well as from NO_y to NO_x conversion in the UT. All observations taken together suggest that sample 11 was likely to have been influenced by emissions of natural gas originating from Gulf of Mexico. Similar natural gas signatures due to long-range transport from North America were observed by *Blake et al.* [1996a] during airborne measurements near the Azores (∼−22°E, ∼33°N). However, due to the con-

vective activity near the US coast it is likely that sample 11 was influenced by some continental outflow seen at SF_6 and anthropogenic halocarbons.

[12] The last sample (sample 12) is characterized by enhanced PV, low humidity, high O_3 mixing ratios, and drops in N_2O, CH_4, and SF_6 (Figures 1b, 1c, and 1e). These observations and the enhanced ^{14}CO (Figure 1d) produced mainly by cosmic radiation at higher latitudes in the LS and UT demonstrate that the aircraft crossed a stratospheric intrusion while descending to Munich.

4. Conclusions

[13] Fresh outflow from the convection cells near the ITCZ with a trace gas signature typical for biomass burning was found at ~10 km altitude from 10°S to 10°N during a CARIBIC flight from Namibia to Germany. The broad range of species measured using the CARIBIC container enabled a detailed characterization of the plume and an estimation of enhancement ratios for several NMHCs and halocarbons. Over the Mediterranean Sea (at ~40°N) clear signatures of natural gas emissions that most likely occurred ~5 days before in the Gulf of Mexico were observed later in the flight. These are one of the few observations of deep convection of biomass burning exhaust and natural gas emissions to the UT reported so far. The exemplary analysis of this flight demonstrates the importance of deep convection for the UT as well as the potential of the CARIBIC platform for regular sounding of the UT/LS region using a commercial aircraft. To utilize this potential, a new CARIBIC container with extended instrumentation and shorter fill time is being built for an Airbus 340–600 and will be operated in cooperation with Lufthansa for the next 10 years.

References

Andreae, M. O., et al., Transport of biomass burning smoke to the upper troposphere by deep convection in the equatorial region, *Geophys. Res. Lett.*, 28, 951–954, 2001.

Andreae, M. O., and P. Merlet, Emission of trace gases and aerosols from biomass burning [Review], *Global Biogeochem. Cycles*, 15, 955–966, 2001.

Blake, D. R., N. J. Blake, T. W. Smith, O. W. Wingenter, and F. S. Rowland, Nonmethane hydrocarbon and halocarbon distributions during Atlantic Stratocumulus Transition EXperiment Marine Aerosol and Gas Exchange, June 1992, *J. Geophys. Res.*, 101, 4501–4514, 1996a.

Blake, N. J., D. R. Blake, J. E. J. Collins, G. W. Sachse, B. E. Anderson, J. A. Brass, P. J. Riggan, and F. S. Rowland, Biomass burning emissions of atmospheric methyl halide and hydrocarbon gases in the south Atlantic region, in *Biomass Burning and Global Change*, edited by J. S. Levine, pp. 575–594, MIT Press, Cambridge, Mass., 1997.

Blake, N. J., D. R. Blake, B. C. Sive, T. Y. Chen, F. S. Rowland, J. E. Collins, G. W. Sachse, and B. E. Anderson, Biomass burning emissions and vertical distribution of atmospheric methyl halides and other reduced carbon gases in the South Atlantic region, *J. Geophys. Res.*, 101, 24,151–24,164, 1996b.

Brenninkmeijer, C. A. M., et al., CARIBIC-Civil aircraft for global measurement of trace gases and aerosols in the tropopause region, *J. Atmos. Oceanic Technol.*, 16, 1373–1383, 1999a.

Brenninkmeijer, C. A. M., T. Röckmann, M. Bräunlich, P. Jöckel, and P. Bergamaschi, Review of progress in isotope studies of atmospheric carbon monoxide, *Chemosphere—Global Change Science*, 1, 33–52, 1999b.

Chan, S. H., and H. M. Wang, Effect of natural gas composition on autothermal fuel reforming products, *Fuel Process. Technol.*, 64, 221–239, 2000.

Clarke, A. D., F. Eisele, V. N. Kapustin, K. Moore, D. Tanner, L. Mauldin, M. Litchy, B. Lienert, M. A. Carroll, and G. Albercook, Nucleation in the equatorial free troposphere: Favorable environments during PEM-Tropics, *J. Geophys. Res.*, 104, 5735–5744, 1999.

Crutzen, P. J., and M. O. Andreae, Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, 250, 1669–1678, 1990.

ESA/ESRIN, ATSR World Fire Atlas, European Space Agency, via Galileo Galilei, CP 64, 00044 Frascati, Italy.

Ferek, R. J., J. S. Reid, P. V. Hobbs, D. R. Blake, and C. Liousse, Emission factors of hydrocarbons, halocarbons, trace gases and particles from biomass burning in Brazil, *J. Geophys. Res.*, 103, 32,107–32,118, 1998.

Hermann, M., F. Stratmann, M. Wilck, and A. Wiedensohler, Sampling characteristics of an aircraft-borne aerosol inlet system, *J. Atmos. Oceanic Technol.*, 18, 7–19, 2001.

Jaenicke, R., Tropospheric aerosols, in *Aerosol-Cloud-Climate Interactions*, edited by P. V. Hobbs, pp. 1–31, Academic Press, 1993.

Jonquières, I., A. Marenco, A. Maalej, and F. Rohrer, Study of ozone formation and transatlantic transport from biomass burning emissions over West Africa during the airborne tropospheric ozone campaigns TROPOZ I and TROPOZ II, *J. Geophys. Res.*, 103, 19,059–19,073, 1998.

Kato, S., H. Akimoto, T. Röckmann, M. Bräunlich, and C. A. M. Brenninkmeijer, Stable isotopic compositions of carbon monoxide from biomass burning experiments, *Atmos. Environ.*, 33, 4357–4362, 1999.

Lobert, J. M., D. H. Scharffe, W.-M. Hao, T. A. Kuhlbusch, R. Seuwen, P. Warneck, and P. J. Crutzen, Experimental evaluation of biomass burning emissions: Nitrogen and carbon containing compounds, in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*, edited by J. S. Levine, pp. 289–304, MIT Press, Cambridge, Mass., 1991.

Mauzerall, D. L., J. A. Logan, D. J. Jacob, B. E. Anderson, D. R. Blake, J. D. Bradshaw, B. Heikes, G. W. Sachse, H. Singh, and B. Talbot, Photochemistry in biomass burning plumes and implications for tropospheric ozone over the tropical South Atlantic, *J. Geophys. Res*, 103, 8401–8423, 1998.

Mühle, J., A. Zahn, C. A. M. Brenninkmeijer, V. Gros, and P. J. Crutzen, Air mass classification during the INDOEX Ronald Brown cruise using measurements of non-methane hydrocarbons, CH_4, CO_2, CO, ^{14}CO and $\delta^{18}O(CO)$, *J. Geophys. Res.*, 107(D19), 8021, doi:10.1029/2001JD000730, 2002.

Pickering, K. E., et al., Convective transport of biomass burning emissions over Brazil during Trace A, *J. Geophys. Res.*, 101, 23,993–24,012, 1996.

Sturges, W. T., H. P. McIntyre, S. A. Penkett, J. Chappellaz, J. M. Barnola, R. Mulvaney, E. Atlas, and V. Stroud, Methyl bromide, other brominated methanes, and methyl iodide in polar firn air, *J. Geophys. Res.*, 106, 1595–1606, 2001.

Thompson, A. M., K. E. Pickering, D. P. McNamara, M. R. Schoeberl, R. D. Hudson, J. H. Kim, E. V. Browell, V. Kirchhoff, and D. Nganga, Where did tropospheric ozone over Southern Africa and the tropical Atlantic come from in October 1992—Insights from TOMS, GTE TRACE A, and SAFARI 1992, *J. Geophys. Res.*, 101, 24,251–24,278, 1996.

Wofsy, S. C., R. C. Harriss, and W. A. Kaplan, Carbon-dioxide in the atmosphere over the Amazon basin, *J. Geophys. Res.*, 93, 1377–1387, 1988.

Zahn, A., C. A. M. Brenninkmeijer, W. A. H. Asman, P. J. Crutzen, G. Heinrich, H. Fischer, J. W. M. Cuijpers, and P. F. J. van Velthoven, The budgets of O_3 and CO in the upper troposphere: The CARIBIC aircraft results 1997–2001, *J. Geophys. Res.*, 107(D17), 4337, doi:10.1029/2001JD001529, 2002.

J. Mühle, C. A. M. Brenninkmeijer, T. S. Rhee, and F. Slemr, Max Planck Institute for Chemistry, P.O. Box 3060, D-55020 Mainz, Germany.

D. E. Oram and S. A. Penkett, University of East Anglia, School of Environmental Sciences, Norwich NR4 7TJ, United Kingdom.

A. Zahn, Forschungszentrum Karlsruhe, Institute of Meteorology and Climate Research, P.O. Box 3640, D-76021 Karlsruhe, Germany.