Annual Report 2003

for the AFO2000-Project

"Convective Transport of Trace Gases into the Upper Troposphere over Europe: Budget and Impact on Chemistry" (CONTRACE)

FKZ: 07 ATF 19 - 22

by

Deutsches Zentrum für Luft- und Raumfahrt (DLR),
Institut für Physik der Atmosphäre, Oberpfaffenhofen

Max-Planck-Institut für Kernphysik (MPI-K),
Bereich Atmosphärenphysik, Heidelberg

Forschungszentrum Karlsruhe (FZK),
Institut für Meteorologie und Klimaforschung (IMK),
Garmisch-Partenkirchen

Technische Universität München (TUM),
Lehrstuhl für Bioklimatologie und Immissionsforschung,
Freising-Weihenstephan

Project Period: 01.01.2001 – 30.06.2004

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Annual report 2003 by „Gesamtverbund" (DLR, MPI-K, IMK-FZK and TUM)

- CONTRACE-Workshop 30-31 January, 2003 in Oberpfaffenhofen.

The main tasks of the meeting were: (1) to present and discuss results from the CONTRACE-1 field experiment carried out in November 2001; (2) to plan the CONTRACE-2 field phase scheduled for July 2003.

(1) During **CONTRACE-1** a number of events with intercontinental air pollution transport from North America (NA) to Europe were predicted by the forecast models (FLEXPART and MATCH-MPIC, *Lawrence et al.*, 2003) and successfully observed with the chemical instrumentation onboard the Falcon aircraft. These NA pollution plumes reached Europe much more frequently than expected (4 events in three weeks). The airborne CONTRACE measurements are the first one which indicate that NA-plumes even may strongly influence the ozone distribution over Europe in winter (*Huntrieser et al.*, 2003a,b). For the first time large negative and positive ions were observed in these pollution plumes (*Wilhelm et al.*, 2003). Detailed backward modeling studies were performed to trace the pollution plumes back to their source region (*Stohl et al.*, 2003a). In one case the pollution plume travelled extremely fast over the Atlantic (1-2 days) and could even be traced in GOME-NO_2 images (*Stohl et al.*, 2003b).

(2) The **CONTRACE-2** field phase was shifted to July 2003 since the Falcon aircraft was overbooked in summer 2002. As a consequence the project duration was extended to 30 June 2004. Further, as a response to the "Gutachtervotum" it was decided to slightly change the airborne instrument pay load. A rack with aerosol instrumentation was integrated (DLR). It was decided to coordinate the CONTRACE experiment with the EU-project UTOPIHAN (http://dionysos.mpch-mainz.mpg.de/~reus/utopihan/) which has similar objectives as CONTRACE.

- CONTRACE-2 field experiment 2-25 July, 2003 in Oberpfaffenhofen.

Joint flights (Falcon and UTOPIHAN-Learjet) were performed during two weeks. One situation with local convection was investigated in great detail with the two aircraft (Falcon convective outflow and Learjet convective inflow). Further a comparison flight was performed which also included a nearby flight of the chemical observation sites Zugspitze and Hohenpeißenberg. For the planning of the flights the same chemical forecasts were used as for the first campaign (FLEXPART, MATCH-MPIC, and EURAD). However, the events with North American pollution transported to Europe were more rare in summer (two events were observed in three weeks). The events were also more difficult to predict, probably due to embedded convection in the warm conveyor belts that lift the pollution from the boundary layer to the free troposphere. Overall 9 flights were performed. Most of them investigated the convective outflow from frontal or isolated thunderstorms. The flights were carried out over western Europe: in clean regions over the Atlantic and also in very polluted areas close to London, Paris, and the Po valley. The contrast between these outflows will be investigated in great detail next. In two of the flights also pollution plumes transported all the way from Asia were probably identified.

- Cooperation with other groups (within and outside of AFO2000).

Several external partners have joined the CONTRACE-"Verbund": H. Elbern (EURAD, Köln), M. Lawrence & H. Fischer (MPI-C, Mainz), E. Scheel & T. Trickl (IMK-FZK, Garmisch), S. Gilge (DWD-HP), A. Richter (IUP, Bremen) and O. Cooper (NOAA, Boulder).

H. Elbern provided forecasts (EURAD-model) for the flight planning and will use the airborne CONTRACE measurements for 4D-data assimilations (**SATEC4D-AFO2000**). M. Lawrence provided chemical transport model calculations (MATCH-model) for the planning of the flights (**SAPHIRE-AFO2000**). Further CONTRACE-2 was coordinated with the **EU-project UTOPIHAN** (H. Fischer). Joint flights with the Falcon and the UTOPIHAN-Learjet were performed, once passing Zugspitze and Hohenpeißenberg (S. Gilge, E. Scheel). T. Trickl operated the ozone lidar in Garmisch during CONTRACE-2 (**ATMOFAST-AFO2000**). A. Richter provided GOME- and SCIA-NO2-images for CONTRACE-1 and -2 (**NOXTRAM-AFO2000**). O. Cooper provided satellite composites (METEOSAT-GOES).

- Importance of CONTRACE for international programs:

CONTRACE is the first European project that successfully used chemical forecasts to direct an aircraft into pollution plumes transported all the way from the United States to the European continent (*Lawrence et al.*, 2003; *Stohl et al.*, 2003a). These new insights are of great importance for the planning of the future field experiments **INTEX-NENA-ITOP**. In summer 2004 several international field measurements will be performed over the North Atlantic, North America and Europe to quantify the long-range transport of oxidants, their precursor, and aerosols from North America to Europe. In the U.S. the programs are organized by NASA (INTEX) and NOAA (NENA) and includes aircraft measurements with the NASA DC-8 and P3, and the NOAA P3. In Europe the activities are coordinated within the ITOP program and aircraft observations with the DLR and CNRS Falcon, and the new UKMO Bea-146 are planned. Quasi-Lagrangian flights are foreseen to investigate polluted air masses heading east - off the North American coast line - and to identify the same air masses entering Europe few days later. A large set of chemical in situ instrumentation will be installed on the aircraft complemented by airborne lidar observations.

- **CONTRACE publications to intercontinental transport and convective mass flux:**

See reference lists of the individual sub-projects and http://www.pa.op.dlr.de/contrace/ and then click on "Publications".

FKZ: 07 ATF 19

"Convective Transport of Trace Gases into the Upper Troposphere over Europe: Budget and Impact on Chemistry" (CONTRACE)

Annual report 2003 by Deutsches Zentrum für Luft- und Raumfahrt (DLR),

Institut für Physik der Atmosphäre

H. Huntrieser, H. Schlager, R. Busen, J. Heland, and M. Fiebig

- The objective of the CONTRACE-1 field experiment in November 2001 was to investigate aged pollution plumes transported all the way from North America (NA) to Europe and their impact on the trace gas distribution (especially O_3) in the free troposphere over Europe. Four NA pollution events were observed over Europe during the field phase with the Falcon aircraft, which was more than expected. The detailed analyses of these events have now almost been completed (see publication list below).

The DLR group investigated the chemical composition in the NA plumes. Distinct elevated levels of CO, NO_y, and surprisingly also ozone were recorded during the penetrations of these plumes. One of the pollution events (19th November 2001) was investigated in more detail. The event was traced with the FLEXPART model (TUM) for a period of one week from the source region over eastern U.S. to its decay over the Alps. The airborne trace gas measurements from the Falcon were analyzed together with a large variety of surface observations. In the pollution source region over eastern U.S. ozone records from a site in the Appalachian mountains indicated the passage of a pollution plume 4 days prior to the airborne measurements over Europe. Due to a stagnant high pressure weather situation over eastern U.S., favorable conditions for ozone production were established. As an approaching cold front pushed the polluted air mass to the east, elevated ozone was observed at the Appalachian mountain site (~60 nmol mol^{-1}). Airborne measurements from two MOZAIC flights (departures from New York and Washington) also confirmed the presence of an elevated ozone layer up to 2 km altitude. A warm conveyor belt then lifted the pollution plume to the free troposphere where it remained during the transport over the Atlantic. The plume was intersected with the Falcon aircraft over Scandinavia at an altitude between 2 and 4 km. Elevated CO (170), O_3 (53), NO_y (1.1), acetone (4.0), and SO_2 (2.6) mixing ratios (nmol mol^{-1}) were measured. One branch of the plume then descended over the Alpine region where elevated O_3 (54 nmol mol^{-1}) and CO (168 nmol mol^{-1}) was observed at the mountain site Zugspitze (Germany) during two days. At the elevated Alpine site Arosa in Switzerland (climatic spa) the highest daily ozone means of November 2001 were observed during this event. The second branch of the North American pollution plume moved to the northeast and passed the ozone sounding site Sodankylä in Finland on 21st November.

The passage of the NA plume over Europe took almost 3 days. Since the pollution plume descended over the Alpine region these ground sites were most strongly affected by the plume. We compared ozone in the plume to typical background ozone values and in this case found the strongest differences just above the boundary layer. For example at the site Arosa (1840 m) in the Swiss Alps ozone was elevated by 12 nmol mol^{-1} (33 %) during the two days of the plume passage in comparison to the monthly average. The airborne measurements also indicated an ozone enhancement of ~10 nmol mol^{-1} in the pollution plume. These experimental findings are in good agreement with recent model studies carried out by *Li et al.* (Transatlantic transport of pollution and its effects on surface ozone in Europe and North America, J. Geophys. Res., 107, 10.1029/2001JD001422, ACH 4-1 – 4-21, 2002). Especially during "events" of pollution transport from North America the surface ozone concentration over Europe increased significantly by 5-10 nmol mol^{-1} in their model.

- The objective of the CONTRACE-2 field experiment in July 2003 was to investigate the convective outflow from thunderstorms over Europe and its impact on the trace gas distribution (especially NO_x) in the upper troposphere (Fig. 1). Seven flights with this objective were carried out over western Europe: in clean regions over the Atlantic and also in very polluted areas close to London, Paris, and the Po valley. The contrast between these outflows will be investigated in detail next.

a) ***b)***

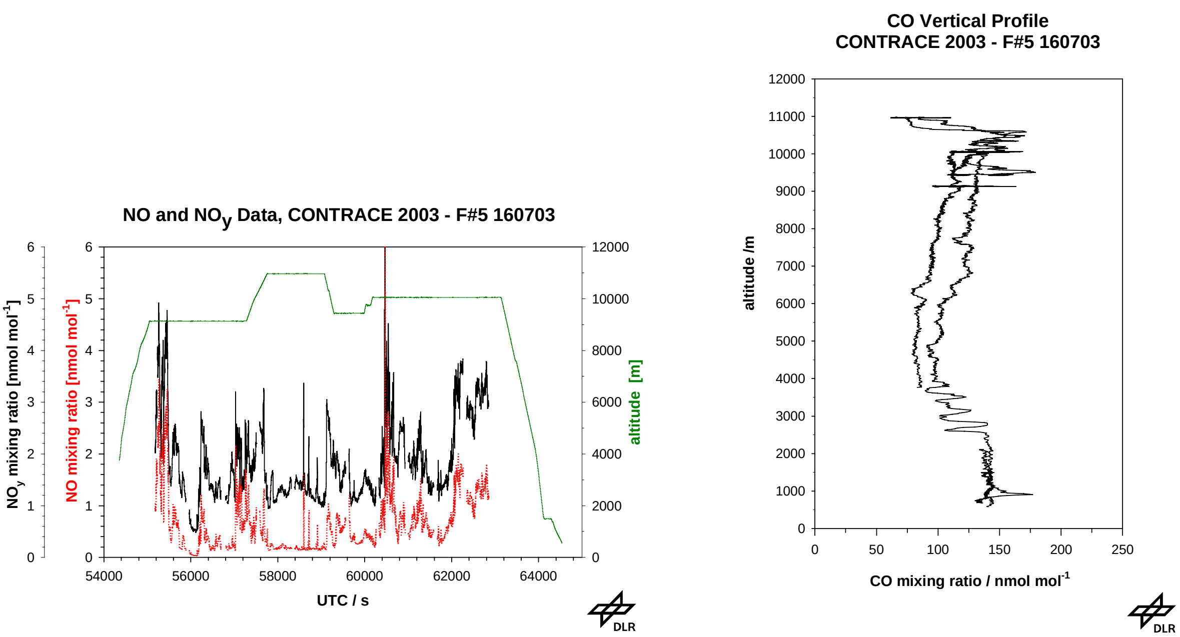

Figure 1: *Time series of NO and NO_y during the flight#5 on 16th July 2003 (a). A frontal zone with embedded convection was penetrated several times which is seen in the elevated NO and NO_y records. The vertical CO profile from the same flight indicates that polluted air from the boundary layer was transported up to the upper troposphere (b).*

Publications 2003

Huntrieser, H., H. Schlager, J. Heland, C. Forster, A. Stohl, M. Lawrence, F. Arnold, H. Aufmhoff, and O. Cooper, Intercontinental transport of pollution from North America to Europe: Airborne trace gas measurements over Central and Northern Europe during CONTRACE, EGS-AGU-EUG Joint Assembly, Nice, France, 7-11 April 2003, *Geophysical Research Abstracts*, Volume 5, 2003a.

Huntrieser, H., et al., Intercontinental transport of pollution from North America to Europe: Airborne trace gas measurements over Central and Northern Europe during CONTRACE: *EXPORT-E2 Final Report, EUROTRAC-2 ISS*, S. Penkett, K. S. Law, U. Platt, A. Volz-Thomas (Eds.), GSF - National Research Center for Environment and Health, Munich, Germany, pp 95-97, 2003b.

Huntrieser, H., and H. Schlager, Air Pollution Export from and Import to Europe: Experimental Evidence, In: *The Handbook of Environmental Chemistry*, Vol. 4 Air Pollution: Intercontinental Transport of Air Pollution (Ed. A. Stohl), Springer Verlag, 2004, *in press*.

Huntrieser, H., et al., Intercontinental air pollution transport from North America to Europe: Experimental evidence from airborne measurements and surface observations, in preparation for *J. Geophys. Res*.,2004.

Lawrence, M. G., P. J. Rasch, R. von Kuhlmann, J. Williams, H. Fischer, M. de Reus, J. Lelieveld, P. J. Crutzen, M. Schultz, P. Stier, H. Huntrieser, J. Heland, A. Stohl, C. Forster, H. Elbern, H. Jakobs, and R. R. Dickerson, Global chemical weather forecasts for field campaign planning: predictions and observations of large-scale features during MINOS, CONTRACE, and INDOEX, *Atmos. Chem. Phys.*, 3, 267-289, 2003.

Stohl, A., C. Forster, S. Eckhardt, H. Huntrieser, J. Heland, H. Schlager, H. Aufmhoff, F. Arnold, and O. Cooper, A backward modeling study of intercontinental pollution transport using aircraft measurements, *J. Geophys. Res.*, 108, 4370, doi: 10.1029/2002JD002862, 2003a.

Stohl, A., H. Huntrieser, A. Richter, S. Beirle, O. Cooper, S. Eckhardt, C. Forster, P. James, N. Spichtinger, M. Wenig, T. Wagner, J. Burrows, and U. Platt, Rapid intercontinental air pollution transport associated with a meteorological bomb, *Atmos. Chem. Phys.*, 3, 969-985, 2003b.

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"Convective Transport of Trace Gases into the Upper Troposphere over Europe: Budget and Impact on Chemistry" (CONTRACE)

Sub-project: Upper tropospheric peroxy radicals

Annual report 2003 by MPI für Kernphysik, Bereich Atmosphärenphysik

F. Arnold, H. Aufmhoff, and M. Speidel

Mass distribution and concentration measurements of atmospheric ions.

Building on the promising results obtained in 2001 the ion measurements were continued and extended during the summer campaign in July 2003. The mass range of the LIOMAS instrument was increased up to 1600 amu. Positive and negative ions were measured simultaneously during all nine flights over the course of the summer campaign. Additionally the altitude range of our measurements was increased from 12 – 5 km during the campaign in 2001 to 12 – 1 km in 2003.

Extensive evaluation of the data obtained during the summer campaign 2003 is not yet completed. Again the focus is set on the investigation of the ion growth mechanism in polluted air masses. Mass distributions show a similar characteristic as those found during the previous campaign in 2001 (Figure 1).
A slightly modified model with respect to the data analysis in 2001 [1] was used to approximate the growth of negative and positive ions by the attachment of condensable gases like H_2SO_4 which should be more abundant in polluted air masses. Figure 2 shows the condensable gas concentration derived from negative gaseous ion mass spectra of flight 1, 09.07.03.
H_2SO_4 formation proceeds via a sequence of reactions whose first and rate-limiting step is the reaction of SO_2 with OH. Once H_2SO_4 has been formed, it may condense onto preexisting aerosol particles as well as it may nucleate. If nucleation occurs, H_2SO_4 forms a cluster starting from a natural gaseous molecular ion together with water molecules. Stability and composition of these clusters were investigated in laboratory experiments, which further identified H_2SO_4 as the major component for ion-induced nucleation due to its strong acidity.
Possible H_2SO_4 concentrations during daytime have been measured to be $< 3\times10^{-6}$ cm^{-3} [*Möhler and Arnold, 1992*]. This relatively low upper tropospheric H_2SO_4 concentration is approved by our newly gained data set (Figure 2).
A kinetically limited nucleation model is described in [1]. The formation of stable cloud condensation nuclei by H_2SO_4 uptake has been investigated in [2].

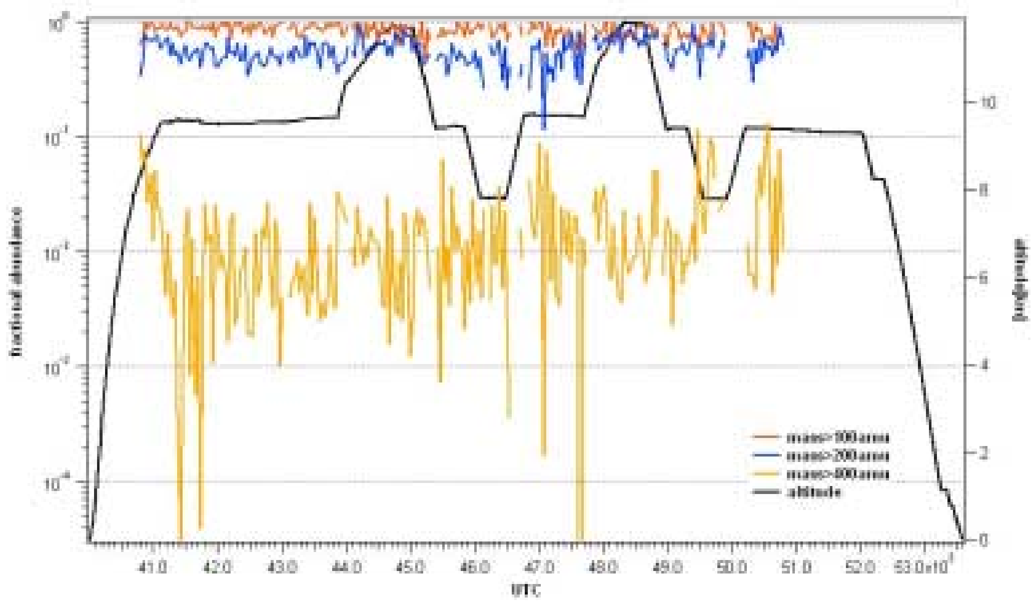

Figure 1: Mass distribution of small, medium and heavy ions (color code) versus UTC together with the altitude profile of flight 1, 09.07.03.

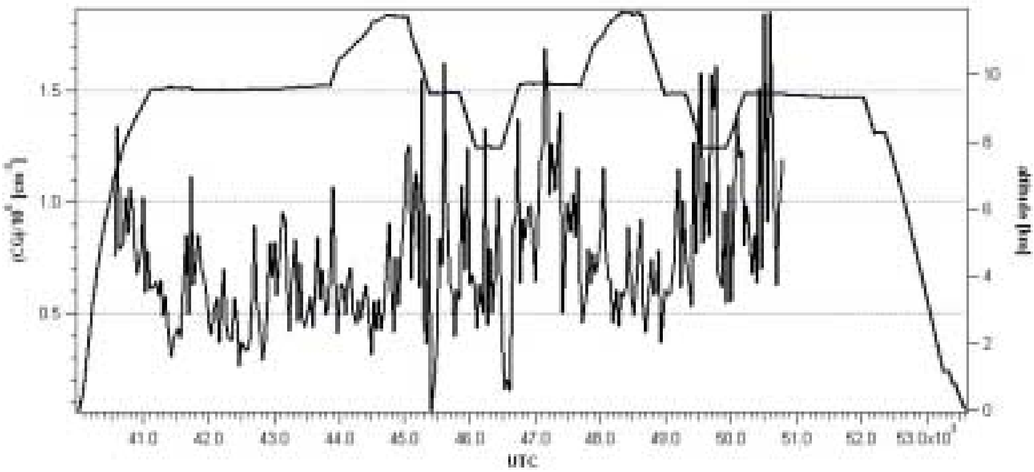

Figure 2: Concentration of condensable gas derived from mass spectra of negative gaseous ions versus time of flight 1, 09.07.03.

[1]. Eichkorn et. al: Cosmic ray-induced aerosol formation: First observational evidence from aircraft-based ion mass spectrometer measurements in the upper troposphere.
GRL, VOL.29,NO.14,10.29/2002GL015044,2002.
[2]. Laaksonen e.al: Upper tropospheric SO_2 conversion into sulfuric acid aerosols and cloud condensation nuclei.
JGR, VOL.105,NO.D1,1459-1469, 2000.

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"Convective Transport of Trace Gases into the Upper Troposphere over Europe: Budget and Impact on Chemistry" (CONTRACE)

Annual report 2003 by IMK-FZK, Garmisch-Partenkirchen

W. Junkermann, B. Rappenglück, and R. Meier

Within 2003 the main activity was the summer campaign in July. For this campaign further preparations and modifications were necessary to guarantee the operation of the instruments also at altitude levels of 39000 ft or appr. 13 km. As in the first campaign an additional instrument, a forward scattering spectrometer probe (FSSP_100) was included to monitor apparent penetration of clouds and their droplet size distribution. To improve the data base for the organic compounds compared to the first campaign more canister samples were taken. Alltogether 76 canisters were sampled and anlyzed during the CONTRACE II campaign on nine flights. All instruments with the exception of the FSSP were running properly during the CONTRACE II campaign. The FSSP failed after the frist flight due to a damaged laser power supply.

Like in the first campaign typically very low mixing ratios were found for CH_2O above the planetary boundary layer. H_2O_2 mixing ratios were elevated also in high elevations and could be used already during the flight as indicator comparable or better than CO to identify aged polluted air masses. Occasionally CH_2O increased above background values under conditions with very high convective vertical transport. Under conditions with less active vertical transport

CH_2O was low, sometimes close to the detection limit of < 100 ppt in all altitudes above the planetary boundary layer. Significant differences to 2001 occurred also in the mixing ratios of the organic compounds reflecting the different emission patterns during summer and winter conditions.

After the final data evaluation towards the end of the year for 2004 now model calculations will be the main activity within CONTRACE.

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"Convective Transport of Trace Gases into the Upper Troposphere over Europe: Budget and Impact on Chemistry" (CONTRACE)

Annual report 2003 by Technische Universität München (TUM), Lehrstuhl für Bioklimatologie und Immissionsforschung

C. Forster

1. Objectives for the reporting period

- Support of the flight planning during the measurement campaign in July 2003
- Model validation using aircraft measurements
- Backward simulations along the flight tracks
- Calculation of tracer age spectra

2. Most important results for the reporting period

During the second CONTRACE measurement campaign in July 2003 TUM provided a set of forecast products for the flight planning on a webpage (http://www.forst.tu-muenchen.de/EXT/LST/METEO/contrace/contrace_fx.html). Meteorological fields (500 hPa geopotential, surface pressure, CAPE, convective precipitation, 500 hPa vertical velocity, convective cloud cover, and equivalent potential temperature) were provided as well as trajectories calculated with the FLEXTRA model and a North American and a European CO tracer calculated with the dispersion model FLEXPART. In contrast to the first measurement campaign in November 2001, this time the forecasts were based on both NCEP GFS (former AVN) and ECMWF wind field data. This allowed a comparison of the different forecasts. The forecasts covered a period of 3 days and were updated every 6 hours during the campaigns, i.e. twice as often as the forecasts of the chemistry transport model MATCH-MPI of the Max-Planck Institute in Mainz, which were also used for the flight planning. Based on the forecasts the aircraft could successfully be guided into polluted air masses. A validation of the TUM forecast products has been performed within the framework of the AFO 2000 project CARLOTTA (Forster et al., 2003).

FLEXPART forward simulations of anthropogenic CO and NO_x tracers were used to analyse the measurement data. The tracers were marked according to their origin (North America, Europe, or Asia), and the tracer age was partitioned into different age classes. During two flights in July 2003 warm conveyor belts (WCBs) were identified as mechanism that can transport pollution from the North American boundary layer to Europe within about 6 days. The model age spectra and the chemical composition of the air mass confirm this time scale. However, the agreement between model results and measurements along the flight track is not as good for these flights as for the flights in November 2001. A possible reason might be that the WCBs at the North American east coast were related to strong convection which was not represented by the model. With the aid of FLEXPART backward simulations along the flight tracks a detailed source analysis of the trace gases measured along the flight tracks was performed. As example figure 1 shows the origin of the pollution measured over Europe during the CONTRACE flight on 9 July 2003. The backward simulations can be regarded as a replacement for conventional back-trajectory calculations (Stohl et al., 2002a).

3. Deviations from the work plan

The second measurement campaign to investigate trace gas transport in convective systems has been deferred to summer 2003 for logistic reasons. Therefore, the high resolution simulations of convective systems and the flash tracer calculations, which were originally planned for 2002, have been deferred to a later time (end of 2003, beginning of 2004) as well. At present a validation of the convective parameterisation in FLEXPART is performed.

4. Publications within the framework of CONTRACE (whole project period)

Eckhardt, S., H. Wernli, P. James, C. Forster, N. Spichtinger, and A. Stohl, A 15-year climatology of warm conveyor belts, J. Climate., accepted for publication, 2003.

Forster, C., O. Cooper, A. Stohl, S. Eckhardt, P. James, E. Dunlea, D. K. Nicks Jr., J. S. Holloway, G. Hübler, D. D. Parrish, T. B. Ryerson, and M. Trainer, Lagrangian transport model forecasts and a transport climatology for the Intercontinental Transport and Chemical Transformation 2002 (ITCT 2k2) measurement campaign, J. Geophys. Res., in press, 2003.

Stohl, A., C. Forster, S. Eckhardt, H. Huntrieser, J. Heland, H. Schlager, H. Aufmhoff, F. Arnold, and O. Cooper, 2003: A backward modeling study of intercontinental pollution transport using aircraft measurements, J. Geophys. Res., 108(D12), 4370, doi:10.1029/2002JD002862, 2003a.

Stohl A., H. Huntrieser, A. Richter, S. Beirle, O. Cooper, S. Eckhardt, C. Forster, P. James, N. Spichtinger, M. Wenig, T. Wagner, J. Burrows, and U. Platt, 2003: Rapid intercontinental air pollution transport associated with a meteorological bomb, Atmos. Chem. Phys., 3, 969-985, 2003b.

Stohl, A., S. Eckhardt, C. Forster, P. James, N. Spichtinger, and P. Seibert, A replacement for simple back trajectory calculations in the interpretation of atmospheric trace substance measurements, Atmos. Env., 36, 4635-4648, 2002a.

Stohl, A., S. Eckhardt, C. Forster, P. James, and N. Spichtinger, On the pathways and timescales of intercontinental air pollution transport. J. Geophys. Res., 107, 4684, doi:10.1029/2001JD001396, 2002b.

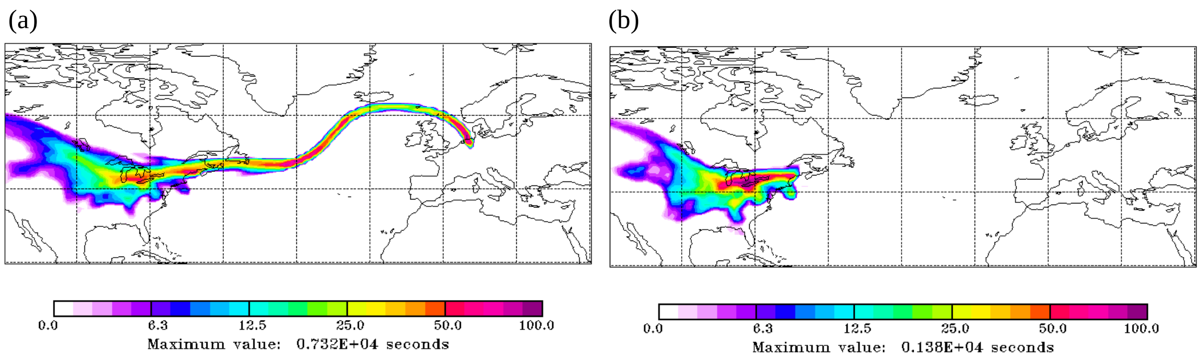

Figure 1: (a) Total column residence times and (b) residence times in the lowest 300 m of the atmosphere of all particles that are started along the flight track between 12:00 UTC and 12:06 UTC on 9 July 2003 and calculated 14 days backward in time. The values are given in percentages of the maximum residence times indicated below each panel.