Summary of CONTRACE-results

from the AFO2000-Project

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

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by

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CONTRACE - Convective Transport of Trace Gases into the Middle and Upper Troposphere over Europe: Budget and Impact on Chemistry

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1. Objectives

The main objective of the CONTRACE project was to investigate the upward transport of polluted airmasses from the boundary layer to the mid (MT) and upper troposphere (UT), and to study their impact on the trace gas budget over Europe. Both the rapid convective transport in thunderstorms as well as the more slow and widespread uplift in warm conveyor belts (WCBs) ahead of cold fronts were studied. The long-range pollution transport from North America to Europe and its impact on European trace gas composition was a major aim. CONTRACE was a joint cooperation between DLR-Oberpfaffenhofen, MPI-K Heidelberg, IMK-IFU Garmisch, and TUM-Freising. The main objectives of the groups were:

- to investigate the importance of frontal systems and long-range advection in transporting polluted airmasses to the MT and UT over Europe, and to study the impact on the ozone budget (DLR);
- to quantify the convective transport and production by lightning of nitrogen oxides in thunderstorms and to compare it to aircraft emissions in the UT (DLR);
- to investigate the ion-induced aerosol formation (MPI-K);
- to investigate the impact of condensable trace gases (mainly acetone and sulphur dioxide) on the aerosol formation (MPI-K);
- to investigate the convective transport of hydrogen peroxide and formaldehyde, and their role as radical precursors in the UT as suggested by Kleinmann [1991] (IMK-IFU);
- to estimate the chemical age of polluted airmasses by using VOC measurements (IMK-IFU);
- to investigate the relative importance of frontal systems and long-range advection for the transport of polluted airmasses by using trajectories (TUM);
- to investigate the origin of polluted airmasses observed in the MT and UT over Europe by using a CO tracer model and backward simulations (TUM).

2. Performance of airborne field campaigns

Two airborne field experiments were performed and coordinated by the DLR in November 2001 and July 2003. Different seasons (summer and winter) were chosen to investigate the impact of convective transport and frontal uplift. The research aircraft *Falcon* was equipped with chemical and particle instrumentation by DLR in Oberpfaffenhofen (CO, CO_2, O_3, NO, NO_y, J_{NO2}, and CN), by IMK-IFU in Garmisch (H_2O_2, CH_2O, JO^1D, VOCs), and by MPI-K in Heidelberg (atmospheric ions, $(CH_3)_2CO$, CH_3OH, and SO_2). The flight planning was supported by new developed chemical tracer forecasts provided by TUM in Freising (Lagrangian particle dispersion model FLEXPART) and MPI-C in Mainz (global chemistry transport model MATCH-MPIC). The transport of two passive tracers representing CO emissions from North America (NA) and Europe (EU) was predicted. Furthermore, forecasts of meteorological fields as well as trajectories were calculated by TUM with the FLEXTRA model.

3. Results from the November 2001 field campaign

The main results from the airborne field campaign carried out in November 2001 were:

- For the first time CO tracer forecasts were used to predict the NA pollution events and to direct a research aircraft very precisely into these polluted layers above Europe [*Lawrence et al.*, 2003; *Stohl et al.*, 2003a; *Forster et al.*, 2004].
- FLEXTRA trajectories and FLEXPART CO and NO_x tracers were used to analyse the airborne measurement. WCBs were identified as a key mechanism that can transport airmasses from NA to EU on a time scale of usually 4-6 days [*Stohl et al.*, 2002b; *Stohl et al.*, 2003a; *Eckhardt et al.*, 2004]. One special episode was observed when pollution was transported in a meteorological bomb from NA to EU within only one day [*Stohl et al.*, 2003b]. It was found that such fast transport episodes can affect the NO_x budget and thus the O_3 chemistry over remote regions.
- FLEXPART backward simulations were introduced as a new method to perform a detailed source analysis of the trace gases measured along the flight tracks [*Stohl et al.*, 2002a; *Stohl et al.*, 2003a]. In one selected case the main contribution to an observed CO maximum over Oslo (**Fig. 3.1**) came from the region in and around the city of New York (**Fig. 3.2 right**). The residence times in the lowest 300m, where anthropogenic emissions mainly are taken up, had their maximum at the East coast of North America (**Fig. 3.2 left**). Multiplying these residence times with the emission strengths given in an emission inventory (here EDGAR 1995 by Olivier and Berdowsky, 2001) gave the detailed source contribution per grid box to the measured CO maximum.
- It succeeded to measure the trace gas composition in several NA pollution plumes over Europe [*Huntrieser and Schlager*, 2004; *Huntrieser et al.*, 2004]. In the most pronounced NA plume (observed in the lower-mid troposphere over Oslo) elevated CO (170), O_3 (53), NOy (1.1), acetone (5.0), and SO_2 (2.6) mixing ratios (nmol mol^{-1}) were measured (**Fig. 3.1**).

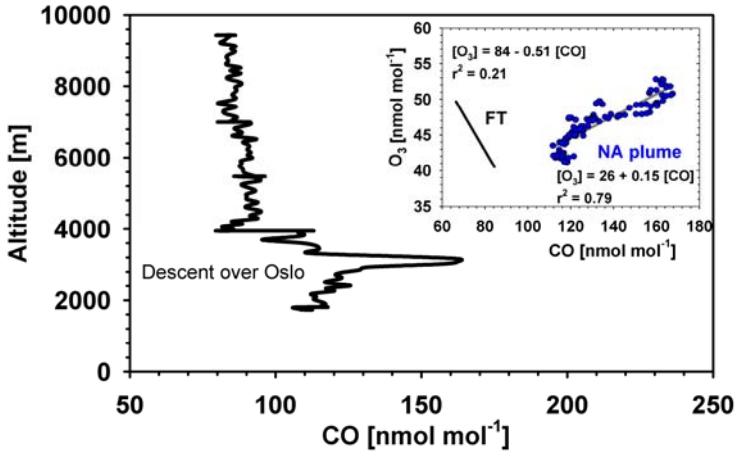

Figure 3.1: Measured vertical CO profile during the *Falcon* descent close to Oslo (Norway) on November 19th, 2001. Superimposed (upper right corner) are O_3-CO correlations in the free troposphere (FT, only regression line) and in the North American (NA) pollution plume. [*Huntrieser et al.*, 2004].

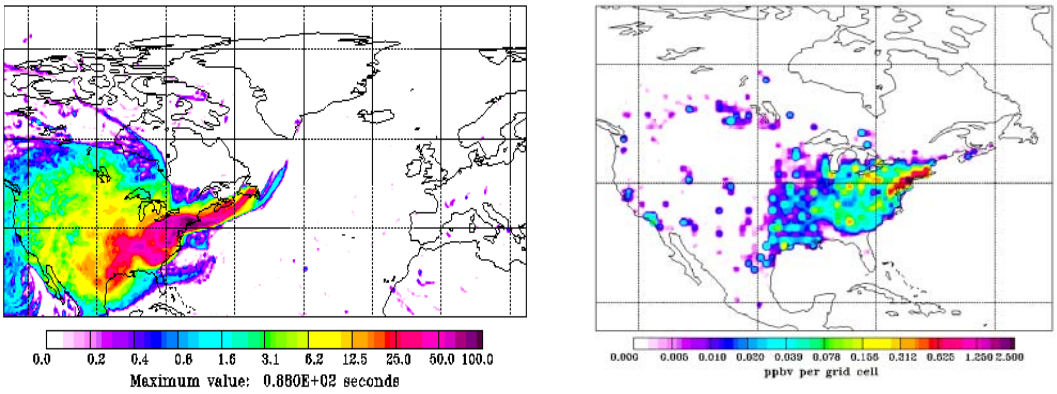

***Figure 3.2*:** Left: Residence times in the lowest 300m of the particles started at 11:53 UTC on 19 November 2001, when a CO maximum was detected over Scandinavia. The times are given in percentages of the maximum residence time given below the panel. Right: Average source contribution per 0.5° grid box to the total CO mixing ratio measured along the flight track on 19 November 2001 at 11:53 UTC. [*Stohl et al.*, 2003a].

- In general, O_3 was elevated by ~10 nmol mol^{-1} in these NA pollution plumes in comparison to the typical background and a positive O_3-CO correlation was observed (**Figs. 3.1, 3.3d**). Observations indicate that the enhanced levels of O_3 were already produced near the source region over the eastern U.S. and not during the transit. Occasionally these polluted NA airmasses even descended to ground level over the Alpine region and affected the air quality considerable [*Huntrieser and Schlager*, 2004; *Huntrieser et al.*, 2004].
- In contrast, O_3 decreased by ~ 20 nmol mol^{-1} in uplifted EU pollution plumes in comparison to the typical background and a negative O_3-CO correlation was observed (**Fig. 3.3d**). Occasionally NA pollution plumes were layered above EU pollution plumes as shown in **Figs. 3.3a-d**. The NOy-CO correlation also showed distinct differences between NA and EU pollution plumes and was used to estimate the time since the emission of the pollutants (as suggested by Stohl et al., 2002). In the uplifted fresh EU pollution the NO_y/CO slope was much steeper than in the aged NA plume [*Huntrieser et al.*, 2004].

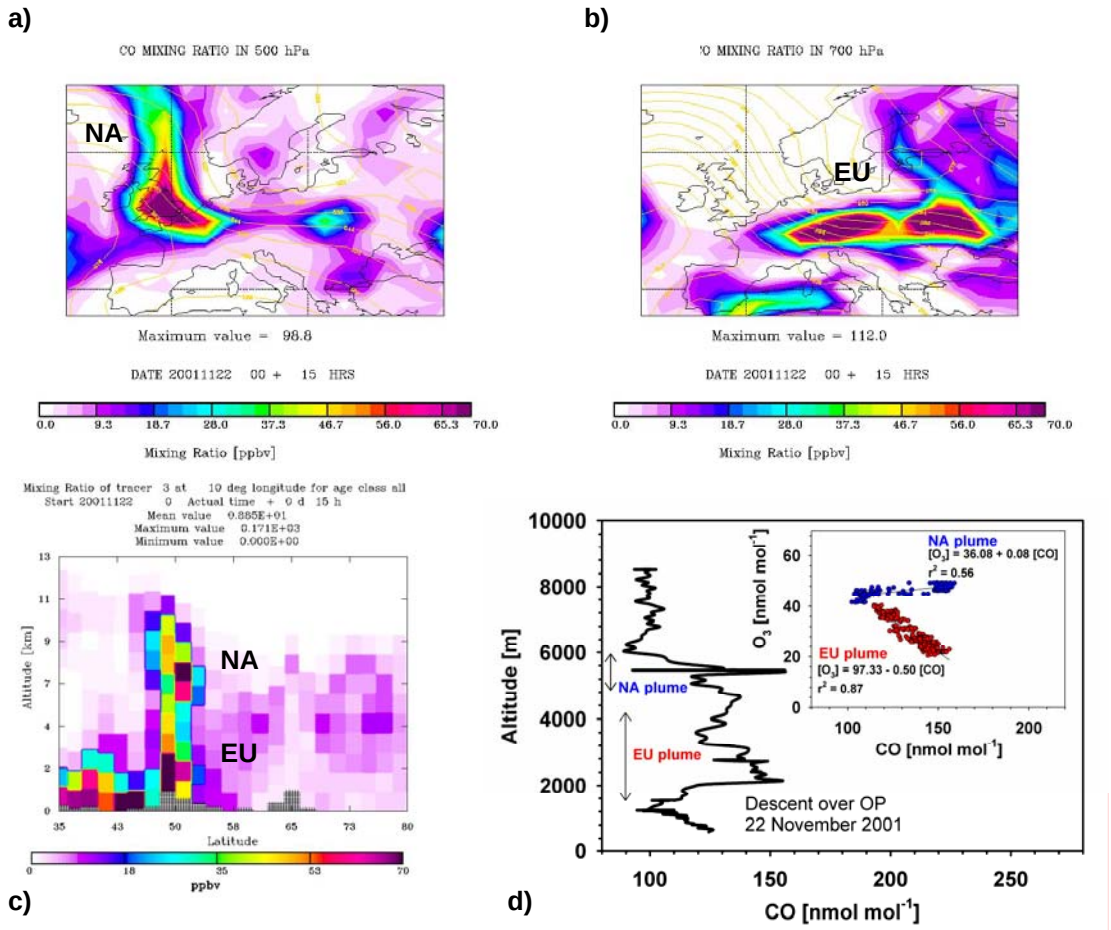

Figure 3.3: FLEXPART 15-hour forecasts of (a) a North American CO tracer at 5000 m a.s.l. and (b) a European CO tracer at 3000 m a.s.l. for 22nd November 2001 at 1500 UTC. Superimposed are isolines of the geopotential height at 500 and 700 hPa, respectively. A North American pollution plume (a) reached Europe and moved rapidly from the west (British Isles) to the east (Poland). European pollution (b) was uplifted over Germany. In (c) the vertical cross section through the FLEXPART European (EU) and North American (NA) CO tracer fields (forecast) for 22nd November 2001, 1500 UTC along 10°E is shown. In (d) the measured vertical CO profile during the descent close to Oberpfaffenhofen (48°N, 11°E) on 22nd November 2001 is presented. Superimposed (upper right corner) are O_3-CO correlations in the European (EU) and the North American (NA) pollution plume. [*Huntrieser et al.*, 2004].

- For the first time large positive and negative ions with mass numbers exceeding 600 could be detected in the UT. These represent fingerprints of ion-induced aerosol formation proceeding via INU (ion-induced nucleation) [*Eichkorn et al.*, 2002]. Furthermore, the large-ion data allow to infer the total concentration of condensable atmospheric trace gases. Laboratory data strongly suggest that the large ions were composed mostly of H_2SO_4 and that INU of H_2SO_4/H_2O took place in the upper tropospheric airmasses intercepted [*Wilhelm*, 2003; *Wilhelm et al.*, 2004]. In relatively unpolluted airmasses INU was more efficient than HONU (homogeneous nucleation).
- In polluted airmasses the condensable trace gases were elevated by up to 5.0 nmol mol^{-1} acetone, 2.5 nmol mol^{-1} methanol, and 3.0 nmol mol^{-1} SO_2. In relatively clean airmasses in the free troposphere SO_2 mole fractions ranged between 0.020 and 0.050 nmol mol^{-1}. It was found that even these low values allow sufficient production of the condensable gas H_2SO_4 and thereby promote formation and growth of aerosol particles in the UT [*Aufmhoff*, 2004].

- In the aged NA pollution plumes the observed formaldehyde mixing ratios were in agreement with model calculations using the RACM2 box model. Formaldehyde is rapidly decomposed by photolysis and never exceeded values of 0.5 ppb in the aged airmasses. Typical for the UT were mixing ratios of about 0.1-0.2 nmol mol^{-1}. H_2O_2 was also found to agree with model calculations for pure gas phase reactions during transport times of more than 5 days.

4. Results from the July 2003 field campaign

The main results from the airborne field campaign carried out in July 2003 were:

- Trace gas measurements were successfully performed in the convective outflow from European thunderstorms. An algorithm was developed to estimate the convective mass flux based on METEOSAT data [*Wimmer*, 2002]. The outflow from an average CONTRACE thunderstorm in the UT contained 1.2 ± 0.4 nmol mol^{-1} NO_x and up to 170 nmol mol^{-1} CO. On average NO_x produced by lightning dominated in the investigated thunderstorm anvils in comparison to the contribution from the boundary layer (60 and 40%, respectively). The results indicate that the annual mean NO_x budget in the UT over Europe is dominated by emissions from aircraft (0.1 TgN yr^{-1}) in comparison to lightning production (0.06 TgN yr^{-1}). However, the overall largest contribution comes from the upward transport of polluted boundary layer air to the UT by convection and fronts (0.3 TgN yr^{-1}).
- One special event was observed where the outflow from a convective frontal system (active over Germany) was advected to the north out over the North Sea and then transported around a low pressure system located over the British Islands. After 5 days of circulation over the ocean the aged EU pollution plume entered Europe again at the French west coast. FLEXPART backward simulations were used to estimate the source region of this aged EU plume and it was found that the strongest industrial center in Germany (Ruhr area) mainly contributed to this pollution plume. CO and H_2O_2 mixing ratios were enhanced in the plume, however, no pronounced change in ozone was observed.
- During thunderstorm flights in the UT formaldehyde mixing ratios were only occasionally elevated (>2 nmol mol^{-1}), which is close to planetary boundary layer values, while peroxide was only enhanced in clearly aged air. In most cases no significant enhancement of both trace gases was found in the UT indicating that washout processes within the convective cells significantly reduce the mixing ratios of these water soluble substances. The role of these trace gases as radical precursors in the UT seems to be minor in convection.

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