

## REGIONAL CLOUD CHEMISTRY

### Case Description

This case is derived from the Chemical transformation and Transport by Clouds (CTC) study that was part of the 2004 ICARTT Intensive [Fehesenfeld, 2006]. The observations were conducted from the National Research Council of Canada Convair 580 as part of. The major relevant instrumentation are listed in Appendix 1. The aircraft was based out of Cleveland, Ohio from July 20, 2004 to August 18, 2004. The main objectives of CTC were:

- to understand the role of cloud chemical processes in the transformation and transport of pollutants, and
- to use the observational dataset to evaluate and identify areas for improvement in the modelling of cloud chemical processing.

This regional case focuses on two flights (study flight #s 16 and 17) conducted on August 10, 2004. The flights were conducted with the time period of 1700 UT to 2400 UT. The aircraft sampled in and below cloud on two north-south lines over Michigan. The first line, sampled during flight 16, was approximately 200 km east of the Chicago area, and the second line, sampled during flight 17, was approximately 200 km east of the first line. Vertical profiles were conducted at each of the north and south points of the first line and at the south point of the second line. Winds were westerly during both flights and a large plume identified by CO, NO<sub>x</sub> and SO<sub>2</sub> was sampled on both winds when the aircraft was downwind of the Chicago area.

The flight tracks for both flights are shown in Figure 1 of the powerpoint file. The emissions map is from NOAA (<http://www.ngdc.noaa.gov/maps/interactivemaps.html>). On flight 16, the aircraft flew from Cleveland to a way point at approximately 42.4 N and 86.1 W where it profiled to 3km-MSL. After completion of the profile, the aircraft flew south to 40.6 N and 86.1W sampling in cloud at 1.2-1.6 km. At that point, it profiled to 3 km again and then returned north along the same line sampling below cloud at 0.7-0.8 km. After reaching the north way point, the aircraft landed in Grand Rapids for re-fuelling. Approximately one hour later the aircraft left Grand Rapids (study flight # 17) and flew to a way point at approximately 42.7 N and 84.0 W approximately 200 km east of the N-S line flown on flight 16. From there, the aircraft flew south sampling below cloud, profiled to 3 km, flew north in cloud that was more broken than on the first line. At the north point, the aircraft turned south again and then about halfway down the line broke off and returned to Cleveland.

Figures 2 and 3 show the surface and 850 hPa analysis for 2400 UT August 10 (00 UT August 11) from the Canadian Meteorological Centre of Environment Canada. The sampling was conducted ahead of the surface cold front. The winds were westerly, and the forecast air trajectories forward from Chicago at the time of the weather briefing prior to flights 16 and 17 are shown in Figure 4. Documentation from the weather briefings of the morning of August 10, prior to the flights, and the evening of August 10, post flights, are in the "briefings" folder.

Figure 5 shows SO<sub>2</sub> along the two lines. These are composites of the transits to the south and back to the north along with the profiles, and thus colours representing different SO<sub>2</sub> levels overlap in places. The two plumes between 41°N and 42°N on each line are connected based on the wind direction.

Figure 6 shows time series from flight 16 of altitude, CO, cloud liquid water content (LWC) and the number concentration of cloud droplets larger than 50 μm (2DC), or precipitation sized particles. The blue lines indicate the aircraft on the north-south line. The CO plume, sampled slightly north of midway on each of the two lines, was downwind of the Chicago region. As indicated by the large droplet number concentrations (2DC) in Figure 3, there was light precipitation towards the north of the flight 16, and no indication of precipitation from the middle of the plume encounter to the south end of the line.

Figure 7 shows the time series of CO, NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> for the below-cloud transect along the line; in the case of flight 16 that is from south to north. CO and NO<sub>2</sub> exhibit similar patterns, whereas the pattern of increased SO<sub>2</sub> is different suggesting some sources of SO<sub>2</sub> distinct from those of CO and NO<sub>x</sub>. Both O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> decrease inside the NO<sub>2</sub> plume.

Figure 8 shows the below-cloud time series for and aerosol particle mass. The particle mass increases well before the increase in CO and NO<sub>2</sub>, and more consistent with the pattern of SO<sub>2</sub>. The total mass from the Aerosol Mass Spectrometer (AMS) is lower than that estimated from the particle size distribution measurements (SPMS and APS) in the plume, but comparable outside of the plume. This difference may be tied into the collection efficiency of the AMS as the in plume composition has a higher fraction of sulphate, and pure ammonium sulphate has a collection efficiency of 20-25% in the AMS. When the counterflow virtual impactor (CVI) intake was used, the AMS and SMPS were switched to sample off the CVI from the straight aerosol intake. Thus, there are no aerosol data after 19:45. The particle size distributions, before and in the plume, are shown in Figure 9. The plume is higher in number concentration for particles >20 nm and the plume particles are larger.

The time series of CO, NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> for the in-cloud line (north to south) are shown in Figure 10. In this case, there is somewhat more correspondence of SO<sub>2</sub> with NO<sub>2</sub> than on the below cloud line. Figures 11 and 12 show the results of the cloudwater sampling along the N-S line. Note that in the plume, the bulk cloudwater indicates a relative increase in sulphate versus nitrate compared with outside the plume. The cloud droplet residual sulphate, as indicated by the AMS measurements that were downstream of the CVI intake, was substantially increased in the plume relative to the residual nitrate as well as higher relative to the increase in bulk cloudwater measurements. This would result if there was substantial evaporation of the residual nitrate, as might result if most of the nitrate entered the cloudwater from the gas phase as HNO<sub>3</sub> and there was insufficient buffering capacity in the cloud droplets. The AMS measurements are included to show the relative composition of the cloud residual particles; the data have not been corrected for collection efficiency.

Figures 13 and 14 show profiles at the north and south points along the N-S line of flight 16. At the north end, the boundary layer was topped about 2000 m. One hour later at the south end it was about 1600 m.

Figures 15-21 inclusive show the observations for flight 17 on the more eastern line. There is very little evidence for precipitation in this case, and the cloud was thinner and more broken than on the western line during flight 16 (1815Z satellite image, Figure 1) that shows more cloud over the western part of the study area.

The below-cloud levels of CO, NO<sub>2</sub> and SO<sub>2</sub> in the plume are all lower than on the western line. O<sub>3</sub> is depleted in the plume, but to a lesser degree. The relative differences between the in- and out-of-plume size distributions are similar to those on the western line. In-cloud, elevated sulphate is associated with the plume in both the bulk cloudwater and residual droplets (Figures 19 and 20). However, across the plume, the SO<sub>2</sub> is much lower and mostly near detection limit. Increases in the SO<sub>2</sub> levels at the beginning and end of the time series in Figure 20 are thought to be from relatively local sources. Only one profile was conducted on the eastern line, at the south end (Figure 21).

#### Some objectives of the case

1) A specific objective of these two flights was to look for changes in the below-cloud aerosol that might have occurred due to cloud processing of the urban plume as it was transported from west to east. Figures 22 and 23 contrast the below-cloud particle number and volume size distributions between flight 16 and flight 17 out of the plume as well as in the plume. On the eastern line (flight 17), the aerosol increased in mass both in and out of the plume. In the plume, the size distribution on the eastern line is slightly but significantly shifted in size with relatively little change in numbers above about 20 nm. With this in mind, it is important to compare how models predict S(IV) oxidation in this situation. Some specific questions for the models are:

- How much sulphate is produced in cloud and in the gas phase?
- Do the NO<sub>2</sub>/SO<sub>2</sub> CO/SO<sub>2</sub> values indicate cloud processing?
- Does HNO<sub>3</sub> scavenging affect S(IV) oxidation?
- What do the models predict for the evolution of the below-cloud aerosol size distributions from 16 to 17, both in and out of the plume?

2) What other chemistry was there that was affected by the cloud, and what is the net effect of cloud on the atmospheric chemistry over the region? Figures 24-25 show concentrations of six carbonyls measured in the bulk cloudwater samples (Figure 24) and in the gas phase as sampled from canisters (Figure 25) from flights 16 and 17. There are differences in the relative values of the different carbonyls between the gas phase and the aqueous phase. Also, among the aqueous phase concentrations the highest levels are in the samples collected in the plume, whereas in the gas phase the plumes samples tend to be among the lower levels. Figure 26 shows the mixing ratios for various carbonyls measured in the aqueous phase and partitioned back to the gas phase. The HCHO in the cloudwater was found to be consistent with the HCHO measured in the gas phase (note there were problems with the gas-phase HCHO on flights 16 and 17), however the larger

carbonyl compounds appear to be enhanced or supersaturated in the the cloudwater [Leithead et al., 2007]. Some specific questions are:

- How do the models predict cloud to affect photolysis rates and how does this impact in-cloud oxidation?
- How do the models scavenge carbonaceous compounds? (oxygenated versus non-oxygenated VOCs?)
- Does  $\text{H}_2\text{SO}_4$  production in aqueous-phase lead to nitrate exclusion in droplet residuals?
- How much of the reduction of  $\text{H}_2\text{O}_2$  in the plume is the result of aqueous-phase oxidation of S(IV) versus changes in gas-phase production? The observations were well downwind of Chicago and the intervening distance was covered with clouds.

3) How well the models predict cloud and plume dispersion? Zhang et al. [2007] have compared cloud liquid water contents simulated from the EC GEM model with observations from the CTC cases and found sometimes reasonable agreement depending on the resolution of the model. Some specific questions are:

- Do the models predict cloud liquid water contents within the limits of the observations?
- Do the models predict cloud amounts and variability across the study region obtained from the aircraft measurements and from satellite observations?
- How much precipitation is predicted and is the precipitation modified by plume? Is the drop in precipitation at the edge of the plume (flight 16) an outcome of the plume or a coincidence of the meteorology?
- Is the modelled dispersion of the Chicago plume across the region consistent with the observations?
- Do the models predict differences in the cloud properties (e.g. microphysics) in the plume versus out of the plume?

### Model simulations: setup and output requirement

#### *Simulation setup*

The final model domain (if nesting) should at least cover the area bounded by 39.5N – 43.5N and 88.5W – 83.5W. This should ensure that the important sources around southern Lake Michigan are included.

The time period for the comparison is 16 – 24 Z, August 10, 2004. Each group can decide on the actual simulation period so long as sufficient model spin-up time is allowed.

Individual groups can use the emission data available to them. The latest U.S. national emission inventory released is for year 2002. However individual groups may adjust their emission input to reflect the changes between 2002 and 2004 particular in consideration for the U.S NO<sub>x</sub> SIP Call.

Meteorological initial and boundary conditions: it is assumed that each group would use its own met model which is driven by its own analysis (e.g., NCEP, ECMWF, CMC, etc).

If necessary, CMC regional analysis over North America on a polar-stereographic 15-km grid can be provided.

Chemical initial and boundary conditions: depending on how the simulation is carried out there are several options. For the groups who will be using a coarse resolution simulation, over a much bigger domain than the area specified above, to drive the fine-resolution simulation for the case study, they can use the IC/BC that they are currently using. The time-independent, climatology-based, IC/BC used for the AURAMS eastern NA domain will be provided, which can be adapted for use by others as an alternative. A set of profiles based on the Convair measurement (CO, O<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, and aerosols) will also be provided, which can be incorporated as BC for the hi-resolution simulation over the study domain as an optional sensitivity run.

*Required output for comparison*

General: provide hourly output fields (specified below) between 16 and 24 Z, August 10, 2004, across two vertical cross-sections along the two flight sampling lines: 86W (Flt 16) and 84W (Flt 17), between 40N and 43N, surface to 4 km. In the following, the fields in *italic* are optional. Also, please provide time series extracted from your model output along the flight tracks (we will supply the time series of aircraft locations). In the following, fields with bold face are desired for the time series.

Meteorology and microphysics: **U, V, W, T, RH, LWC**, 3-D cloud fraction, precipitation water content or flux, *CDNC*.

Chemistry:

Gas (ppb) – **O<sub>3</sub>, CO, SO<sub>2</sub>**, NO, NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, HCHO, NH<sub>3</sub>, OH, and *VOCs (acetaldehyde, acetone, propionaldehyde, butylaldehyde, benzaldehyde, pentanal<sup>1</sup>, and others to be decided)*.

Aerosol (μg m<sup>-3</sup>) – **PM<sub>2.5</sub> mass, sulfate**, nitrate, ammonium, organics, *mass-size distribution*.

Cloud-water chemistry (mole L<sup>-1</sup>) – cloud-water concentrations of SO<sub>4</sub><sup>=</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, *pH*, and *carbonyls (formaldehyde, acetaldehyde, acetone, propionaldehyde, butylaldehyde, benzaldehyde, pentanal, etc.)*

*Diagnostic output – sulfate production due to gas-phase and aqueous-phase oxidations, respectively, at given grids.*

Optional sensitivity runs

1. In-cloud oxidation off;
2. Cloud processing off except for photolysis correction;
3. No cloud.

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<sup>1</sup> Depending on the VOC lumping used in the mechanism, these carbonyl species may or may not be discerned individually from the model output.

## References

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- Zhang, J., W. Gong, W.R. Leitch, and J.W. Strapp, 2007: Evaluation of Modeled Cloud Properties against Aircraft Observations for Air Quality Applications, *J. Geophys. Res.*, 112, D10S16, doi:10.1029/2006JD007596.
- Leithead, A., A.M. Macdonald, S.-M., W. Gong, K.G. Anlauf, D. Toom-Sauntry, K. Hayden, W.R. Leitch, 2007: Leithead Investigation of Carbonyls in Cloudwater during ICARTT, submitted to *J. Geophys. Res.*
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## **APPENDIX 1 – NRCC Convair 580 Instrumentation during ICARTT 2004**

The Convair 580 is a pressurized twin engine turboprop. Details:

- gross weight is 26400 kg
- cabin volume is 70 m<sup>3</sup>
- maximum payload is 2300 kg
- project electrical power is 40 kW
- cruise speed 90-140 m s<sup>-1</sup>
- stall speed 45 m s<sup>-1</sup>
- max speed 160 m s<sup>-1</sup>
- ceiling 23000'
- typical VFR endurance 5.5 hrs
- typical IFR endurance 4.5 hrs
- field length 4100 ft
- deice - boots air

### **Instrumentation**

#### **State Parameters**

- Temperature Rosemount Temperature Sensor (de-iced)
- Temperature Rosemount Temperature Sensor (non-deiced)
- Temperature Reverse Flow Temperature Sensor (NCAR design)
- Dewpoint Cambridge Dewpoint Hygrometer (chilled mirror)
- Static Pressure Static Pressure Ports on fuselage and in 858 probe
- Static Pressure Rosemount 858 ( boom TO, PMS pod CV580)
- Static Pressure Pitot static system on LWC boom
- Aircraft Altitude Bendix radar altimeter (<800 m)
- Aircraft Altitude TRT radar altimeter ( < 7500 m)
- True Airspeed Pitot under wing (CV580) and Rosemount 858
- True Airspeed Rosemount 858 ( boom TO, PMS pod 858)
- True Airspeed Pitot static system on LWC boom
- Humidity LICOR LIC2G2 water vapour/CO2 measurement device
- Humidity Russian chilled mirror and UV hygrometer

#### **Navigational Systems**

- Position IRS (Litton 91), and LORAN
- Position GPS (CV580: Marconi, Northstar, Novotel)
- Attitudes, accelerations, true heading, and ground speeds IRS (Litton 91)
- 3 axis velocities wrt ground IRS (Litton 91)

#### **Winds and Gusts**

- Horizontal Winds, and 3 axis gust velocities IRS (inertial velocities), Rosemount 858 (Pod) and TAS derived

#### **Aerosol Particles**

- Aerodyne Aerosol Mass Spectrometer (AMS)/ SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, Organics; 60 nm to 1 µm aerodynamic diameter
- Particle In Liquid Sampler (PILS) for inorganic ions and a few organic ions
- Scanning Mobility Particle System (SMPS) for particle size distributions from 5-300 nm in geometric diameter

- Aerodynamic Particle Sizer (APS) for aerosol particle size distribution from 0.5-20  $\mu\text{m}$  aerodynamic diameter
- Volume nephelometer for particle light scattering at 3 wavelengths (Sharma, Leitch) inboard
- PSAP
- Particle Measuring Systems (PMS) Passive Cavity Aerosol Spectrometer Probe (PCASP) for aerosol size distributions from 0.14-3  $\mu\text{m}$  geometric diameter - wingpod
- PMS Forward Scattering Spectrometer Probe 300 (FSSP300) for particle size distribution from 0.3-20  $\mu\text{m}$  geometric diameter - wingpod

#### **Trace Gases**

- $\text{SO}_2$  (modified TECO 43C)
- CO (Aerolaser)
- $\text{O}_3$  (Teco 49)
- NMHCs (canisters)
- NO,  $\text{NO}_2$
- $\text{H}_2\text{O}_2$
- Hg0
- $\text{HNO}_3$  (coil sampler and IC)
- HCHO (Aerolaser)

#### **Cloud Chemistry**

- Bulk cloudwater sampling
- AMS and SMPS sampling cloud droplet residuals from a Counter Virtual Impactor (CVI)

#### **Cloud Microphysical Measurements**

- Droplet Liquid Water Content PMS King Probe (long version)
- Droplet Liquid Water Content PMS King Probe (short version)
- Droplet Liquid Water Content Johnson Williams LWC Meter
- Droplet Liquid Water Content Nevzorov LWC probe
- Total water content and phase ratio Nevzorov TWC/LWC probe
- Droplet Spectrum (2-30  $\mu\text{m}$ ) PMS FSSP 100 Probe
- Droplet Spectrum (5-95  $\mu\text{m}$ ) PMS FSSP 100 Probe
- Small cloud particle imaging and spectra (2.3-2000  $\mu\text{m}$ ) SPEC Cloud Particle Imaging Probe (CPI)
- Cloud Particle Spectrum and images(25-800  $\mu\text{m}$ ) PMS 2D-C and PMS 2D2-C mono probes
- Cloud Particle Spectrum and images(25-1600  $\mu\text{m}$ ) PMS 2D-C Grey Probe
- Cloud Particle Spectrum and images(12.5-800  $\mu\text{m}$ ) Droplet Measurement Technologies Cloud Imaging Probe (CIP)
- Precipitation Spectrum and images(200-6400  $\mu\text{m}$ ) PMS 2D-P (mono) Probe
- Large Precipitation Spectrum and images(400  $\mu\text{m}$ -5 cm) SPEC HVPS
- Cloud extinction Nevzorov (direct measurement)

#### **Radiative Measurements**

- Downwelling UV solar radiation Eppley UV radiometers ( 295-385 nm)

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- Upwelling visible solar radiation Kipp and Zonen pyranometer-(305-2800 nm)
- Downwelling visible solar radiation Kipp and Zonen pyranometer (305-2800 nm)
- Upwelling IR radiation Eppley IR radiometers ( 3.5-50 um)
- Downwelling IR radiation Eppley IR radiometer (3.5-50 um)

#### **Video Systems**

- Surface video Side looking video cameras, narrow and wide angle
- Surface video Forward/down looking, and side looking cameras

#### **Data Recording and Display**

- Aircraft Data Systems:
  - IAR VME DAS
  - MSC SEA Model 200 DAS