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CLOUDWATER MEASUREMENTS OF SULFUR, NITROGEN AND ORGANIC SPECIES DURING ICARTT

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1. INTRODUCTION

Clouds play an important role in the processing and transport of atmospheric aerosols and trace gases. These processes, although identified, are generally not well understood and often are not included in the cloud representations of regional air quality models. In particular, there is a lack of field experimental data to investigate the influence of clouds on particle chemistry. During the summer of 2004, in collaboration with the ICARTT (International Consortium for Atmospheric Research on Transport and Transformation) field intensive, measurements were made to study the Chemical transport and Transformation by Cloud (CTC).

The overall approach to address questions of cloud influences on sulfate, nitrate and organics, was first to characterize the chemical and physical properties aerosol particles in and around cloud. Then through the use of a counterflow virtual impactor (CVI), cloud droplets were sampled, evaporated and the resulting residual particles were chemically and physically characterized. This airborne study was held from July 20 to August 18, 2004 using the Canadian NRC Convair 580 aircraft as the observing platform. Observations were made primarily in convective clouds in the vicinity of Lake Erie with the major pollution sources including Windsor/Detroit, Cleveland and Chicago.

2. EXPERIMENTAL

Sulfate, nitrate and total organic mass concentrations in particles (ambient and droplet residuals) were measured with an Aerodyne aerosol mass spectrometer (AMS). More complete particle inorganic chemistry was provided by a Particle-in-Liquid-Sampler (PILS) with in-flight chromatographic systems for anions and cations.

Particle physical characteristics were obtained with a PMS PCASP-100x optical particle counter (OPC), a PMS FSSP-300 OPC, a TSI 3022 condensation particle counter (CPC), a TSI Scanning Particle Mobility System, and a TSI Aerosol Particle Sizer (APS).

Gas-phase NO_x was made with a TECO 42S. HNO_3 was measured with a coil sampler and quantified post-flight by ion chromatography. SO_2 was measured with a TECO 43C. NO_x and SO_2 were sampled through a constant pressure system.

Cloud droplet number concentrations were made using a PMS FSSP 100, and liquid water content was measured with a Nevzorov probe. Cloud droplets were also collected inertially by a CVI (Noone *et al.*, 1988). The droplets were then evaporated and characterized downstream using the CPC, SMPS and the AMS.

Bulk samples of cloudwater were also collected with a slotted rod collector and analyzed post-flight for $SO_4^{=}$, NO_3^-, Cl^-, K^+, Mg^{2+}, NH_4^+, Ca^{2+}, and Na^+ by ion chromatography, for carbonyls by HPLC, and hydrogen peroxide by enzyme fluorescence.

A description of the complete aircraft payload may be found at (http://www.msc-smc.ec.gc.ca/ research/icartt/ /index_e.html).

3. RESULTS AND DISCUSSION

A total of twenty-three project flights were conducted during the sampling period. Sixty cloudwater samples were collected over thirteen flights. Sampled clouds were primarily cumulus and towering cumulus. Median values of $SO_4^{=}$, NO_3^- and NH_4^+ were approximately 18 μg/mL, 19 μg/mL and 4 μg/mL respectively. The average

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mass ratio of NO_3^- to $SO_4^=$ over the entire distribution of cloudwater samples is 1.1 (median 1.0).

Comparison of sulfate and perhaps nitrate in the bulk cloudwater samples to that measured in the cloudwater residuals will allow for a calculation of CVI collection efficiencies.

To better understand the behavior of the CVI and subsequent chemical sampling of the residual particles, we examine here one specific case sampled on August 13, 2004. The clouds of interest are towering cumulus sampled at multiple levels near Toledo, OH. A summary of the flight, altitude, liquid water, and interstitial SO_2 and NO_2 is given in Fig 1. Cloud water samples were collected at four altitudes in the Toledo cloud. Cloud base was at approximately 1.5 km.

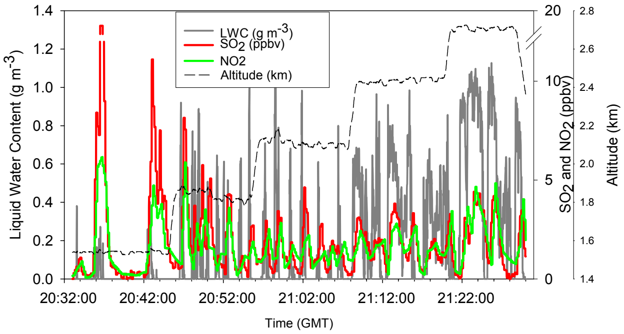

Figure 1: Time series of liquid water content, SO_2, and NO_2 during passes through TCu near Toledo, OH. Also shown is aircraft sampling altitude.

Vertical transport of gaseous species, SO_2 and NO_2 is evident with each pass through cloud. Below cloud base (~ 1 km) SO_2 exceeded 20 ppbv; corresponding NO_2 reached 10 ppbv. Clear air values of gaseous pollutants are decreasing with altitude but the cloud interstitial values remain significant even at 2.7 km. For example, during the cloud pass at ~ 21:23, interstitial SO_2 was ~ 4 ppbv.

Cloud drops were sampled by the CVI throughout this period. The CVI has a cloud sampling cut size which affects the number of drops within a given population that will be sampled. Fig. 2 shows a preliminary comparison of the total number of cloud drops as measured with the FSSP-100 (N_{FSSP}) compared to the number of residual particles counted downstream of the CVI (N_{CVI}) scaled by an estimated CVI sampling enrichment factor (EF). Superimposed on this graph is the drop mean volume diameter (MVD) as calculated from the FSSP number distributions. Comparisons of N_{CVI} and N_{FSSP} appear to be better during the latter half of the cloud sampling period. In fact, the N_{CVI} exceeds the N_{FSSP} at some times. This needs to be investigated further to determine if there is some shattering of larger drops or if the scaling by the EF is inaccurate. The improved agreement between the N_{FSSP} and N_{CVI} is in agreement with the increased MVD of the drops with altitude.

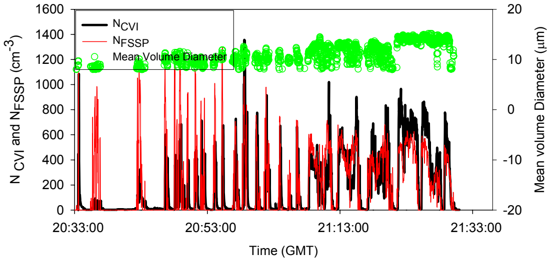

Figure 2: Comparison of number of cloud droplets measured by the FSSP (N_{FSSP}) with number of cloud residual particles scaled by the sampling enrichment factor. Droplet mean volume diameter is also shown as a function of time.

The increases in MVD correspond generally with changes in altitude and are consistent within a particular sampling altitude. Corresponding chemistry of the sampled residuals is shown in Figs. 3-4. Sulfate and nitrate are 30 second averages from the AMS and the mass concentrations are uncorrected for neither time in cloud nor the CVI EF. These factors will be important to determine the total mass of residual SO_4 or residual NO_3 in the cloud drop residuals. In addition, the AMS data needs to be evaluated in terms of its collection efficiency. At higher altitudes in cloud (2.4 and 2.7 km), the cloud residual sulfate correlates well with the interstitial SO_2 (Fig. 3).

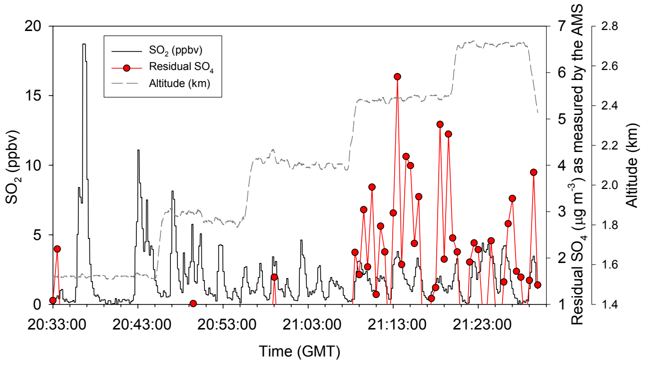

Figure 3: Cloud drop residual SO_4 as measured by the AMS, interstitial SO_2, and altitude.

This is not the case for NO_2 and residual NO_3 (Fig. 4); although some pNO_3 peaks do correspond with higher NO_2 in cloud, overall the cloud residual NO_3 does not show a strong relationship with the interstitial NO_2. Although NO_2 is a precursor gas through the formation and dissolution of HNO_3, the solubility of NO_2 itself is low and its direct relationship to particle residual NO_3 is not expected unless through an intermediate such as HNO_3.

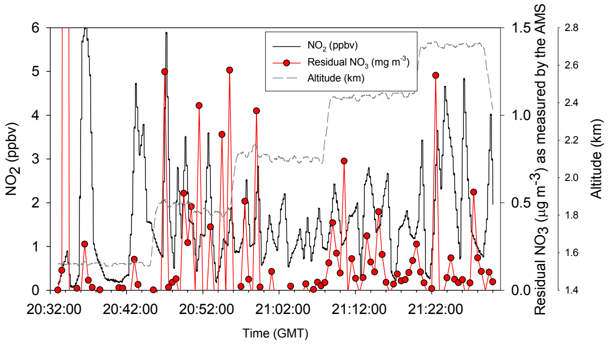

Figure 4: Cloud drop residual NO_3 as measured by the AMS, interstitial NO_2 mixing ratios, and altitude.

Increased residual SO_4 at the higher altitudes may be indicative of in-cloud sulfate production with the increased time in cloud for conversion of the SO_2 precursor to sulfate. Cloudwater samples 1-4 were also collected in this TCu at the following altitudes (CW1 (1.5 to 1.8 km); CW2 (2.1 km), CW3 (2.4 km; and CW4 (2.7km). CW1 and CW2 are higher in pH (6.6 and 5.8) than CW3 and CW4 (pH ~ 4.3 for each sample) which were collected higher in the cloud. Ratios of NO_3^- to $SO_4^=$ in the cloud water are also higher in samples CW1 and CW2, again consistent with the increased residual NO_3 observed by the AMS during the first period and the increased residual SO_4 during the latter period.

This preliminary examination of towering cumulus during summer 2004 will be expanded to include a complete analysis of the cloudwater and cloud drop residual chemistry. Addition of other gaseous measurements including oxidants, will allow for estimation of the in-cloud sulfate production as well as the buffering capacity of the cloudwater and retention of nitrate.

4. REFERENCES

Noone K.J., J.A. Ogren, J Heintzenberg, R.J. Charlson, and D.S. Covert, 1988: Design and calibration of a counterflow virtual impactor for sampling of atmospheric fog and cloud droplets. *Aerosol Sci and Tech*, **8**, 235-244.

7. ACKNOWLEDGEMENTS

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