

CU CIMS HO<sub>2</sub>, HO<sub>2</sub>+RO<sub>2</sub> [Cantrell, Chris (CU-ATOC)] Readme  
SAS/NOMADSS 2013  
Smyrna, TN

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### 1.0 Data Set Overview

The Nitrogen, Oxidants, Mercury and Aerosol Distributions, Sources and Sinks (NOMADSS) project integrates the objectives from three NSF funded projects; SOAS (Southern Oxidant and Aerosol Study), NAAMEX (North American Airborne Mercury Experiment) and TROPHONO (Photolysis of Particulate Nitrate: a Daytime HONO Source and a Re-NO<sub>x</sub>-ification Pathway in the Troposphere). These three projects were not proposed together in advance, but were merged onto the C-130 platform as a means to complete all three projects in the same year and to maximize the scientific value of the combined experiment. Thus the primary objective from each separate project now becomes the primary objective for NOMADSS. These are:

- 1) Quantify biogenic emissions and their interactions with anthropogenic pollutants and to understand the implications for atmospheric chemistry, air quality and climate (primary SOAS goal);
- 2) Constrain emissions of mercury from major source regions in the Eastern United States and quantify the distribution and chemical transformations of speciated mercury in the troposphere (primary NAAMEX goal);
- 3) Investigate the role of particulate nitrate photolysis in the cycling of reactive nitrogen species in the troposphere, focusing on HONO as an intermediate product (primary TROPHONO goal).

Further details, hypotheses and scientific for each objective above described in the original proposals and White Papers at the URLs given below:

SOAS: [http://climate.envsci.rutgers.edu/SOAS/SOAS\\_White\\_Paper\\_final.pdf](http://climate.envsci.rutgers.edu/SOAS/SOAS_White_Paper_final.pdf)

NAAMEX: <http://www.atmos.washington.edu/jaffegroup/modules/NAAMEX/>

TROPHONO:

<http://www.eol.ucar.edu/projects/nomadss/meetings/2012Nov/presentations/TROPHONO.pdf>

NOMADSS took place over the Southeastern U.S. from 30 May -17 July 2013. The NCAR C-130 aircraft will be based out of Smyrna/Rutherford County Airport in Tennessee (36.00° N, 86.52° W-KMQY), which is located approximately 20 km southeast of Nashville, TN. Because of the range of scientific objectives, NOMADSS involved 10 different flight patterns. Flight tracks for NOMADSS covered much of the eastern U.S. This included a north-south stretch from Michigan to Florida, and an east-west

extent from the North Atlantic to western Oklahoma. Detailed flight tracks are given in section 6 of the operations plan document. A ground-based component will use existing sites from the SEARCH network (South Eastern Aerosol Research and Characterization; <http://www.atmospheric-research.com/studies/SEARCH/>). A large ground based experiment will take place at the Centerville, AL SEARCH site (32.90° N, 87.25° W), focused on the SOAS objectives.

## 2.0 Instrument Description

These data were collected using our 4-channel CIMS instrument. An inlet collects ambient air from the free air stream and adds reagents, including O<sub>2</sub> or N<sub>2</sub> diluents, and NO and SO<sub>2</sub> reagent gases. This method, called oxygen dilution modulation (Hornbrook et al., 2011) leads to nearly 100% measurement of HO<sub>2</sub> and RO<sub>2</sub> in the O<sub>2</sub> dilution/low reagent concentration mode, whereas RO<sub>2</sub> is measured with less than 15% efficiency in the N<sub>2</sub> dilution/higher reagent concentration mode. This is because the chemistry converts peroxy radicals to H<sub>2</sub>SO<sub>4</sub> efficiently in the O<sub>2</sub> mode, but RO<sub>2</sub> radicals are converted to RONO in the N<sub>2</sub> mode. The H<sub>2</sub>SO<sub>4</sub> thus produced is ionized by reaction with NO<sub>3</sub><sup>-</sup> ions. The reagent and product ions are detected by mass spectrometry using quadrupole mass filtering and counting by a channel electron multiplier operating in the negative ion mode.

Data are collected once per minute. Signal data for HO<sub>2</sub>+RO<sub>2</sub> are collected during the 0-7 second time interval, and for HO<sub>2</sub> in 30-37 second time interval.

Uncertainty: Approximately 35% (2 sigma) for values well above 2 pptv; estimates are listed for each data point (2 sigma).

## 3.0 Data Collection and Processing

Data are acquired with a custom National Instruments LabView program using a laptop computer and USB-connected data acquisition cards. The program also controls valve position and mass spectrometer mass selection.

These data are reduced using four factors determined in the laboratory and in the field: F<sub>lo</sub> and F<sub>hi</sub> are the radical sensitivities in the HO<sub>2</sub>+RO<sub>2</sub> and HO<sub>2</sub> modes, respectively (units pptv/ion ratio). Alpha<sub>lo</sub> and alpha<sub>hi</sub> are the ratios of RO<sub>2</sub> to HO<sub>2</sub> sensitivity in the HO<sub>2</sub>+RO<sub>2</sub> and HO<sub>2</sub> modes, respectively. HO<sub>2</sub>+RO<sub>2</sub> concentrations are then  $S_{lo} * F_{lo} - (S_{lo} * F_{lo} - S_{hi} * F_{hi}) * (\alpha_{lo} - 1) / (\alpha_{lo} - \alpha_{hi})$ . HO<sub>2</sub> concentrations are  $S_{lo} * F_{lo} - (S_{lo} * F_{lo} - S_{hi} * F_{hi}) * \alpha_{lo} / (\alpha_{lo} - \alpha_{hi})$ . S<sub>lo</sub> is the background corrected ion ratio in the HO<sub>2</sub>+RO<sub>2</sub> mode, and S<sub>hi</sub> is the background corrected ion ratio in the HO<sub>2</sub> mode. The ion ratios are mass 97 signal count rate minus background count rate divided by mass 62 count rate.

Calibration is accomplished by the photolysis of a synthetic water-air mixture with 184.9 nm radiation from a low-pressure mercury lamp. Various slits are used to control the intensity in the photolysis region. The intensity is quantified by N<sub>2</sub>O actinometry with NO/NO<sub>x</sub> chemiluminescence detection.

## 4.0 Data Format

The data files use the ICARTT format which is an ASCII file with detailed header information. Seven pieces of information are included for each time period (1 minute):

- Start Time (seconds since midnight, MST)
- Stop Time (seconds since midnight, MST)
- Middle Time (seconds since midnight, MST)

HO2 mixing ratio (pptv)  
HO2 mixing ratio uncertainty (2 sigma, pptv)  
HO2+RO2 mixing ratio (pptv)  
HO2+RO2 mixing ratio uncertainty (pptv)

Current data revision R0: Preliminary, processed October-November 2013.

Upper Limit of Detection Flag: -77777  
Lower Limit of Detection Flag: -88888  
Missing Data Flag: -99999

### **5.0 Data Remarks**

Missing data for a few early flights (30 May-14 June 2013) and occasional periods elsewhere, which are indicated by the missing data flag.

### **6.0 References**

Hornbrook, R. S., J. H. Crawford, G. D. Edwards, O. Goyea, R. L. Mauldin III, J. S. Olson, and C. A. Cantrell, Measurements of tropospheric HO2 and RO2 by oxygen dilution modulation and chemical ionization mass spectrometry, *Atmos. Meas. Tech.*, 4, 384-442, 2011.