Measurement of OH, H_2SO_4, MSA, DMSO, and $DMSO_2$ on the NASA P-3B Aircraft

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Summary of Research

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Summary Report

This project involves the deployment of a variety of unique aircraft measurements for the PEM-Tropics program. These measurements were all to be accomplished on a near simultaneous basis using a two channel selected ion chemical ionization mass spectrometer instrument. The first year of this project consisted of four components; improve and perform additional testing of the OH, H_2SO_4, and MSA instrument which had only flown on one previous mission (ACE-I); develop and test the vacuum and electronic hardware and software which would allow two independent mass spectrometer systems to be operated from a single instrument (one vacuum/pumping system); construct an aircraft compatible DMSO/$DMSO_2$ ion source and calibration system; and operate the above system on the NASA P-3B during PEM-Tropics. The first two of the components were to be accomplished at NCAR. The third component was to be completed at Georgia Tech and the fourth was to be conducted by researchers from both institutions on the NASA P-3B.

Upgrade and Testing of OH, H_2SO_4, and MSA Instrument

A new electronics lens control box was built for the PEM-Tropics study along with an identical backup in case of a major failure during the mission. The box was capable of providing up to 40 independently regulated high voltage outputs. This is sufficient to control all the lenses and ion source potentials on two different mass spectrometer systems. The aperture through which ions enter the main vacuum chamber is a unique virtual iris design. It controls the amount of sample gas and ions entering the mass analysis regions by differential pumping across a 2 layer aperture. Modifications of this aperture since ACE-I made the measurement sensitivity more altitude independent during the PEM-Tropics study.

Since the P-3B could consistently reach higher altitudes than those achieved by the C-130 during ACE-I, additional tests of the possible effect of low H2O concentrations on the OH measurement were made. These tests were quite extensive, but showed that little to no effect is expected for the conditions encountered on the P-3B. These tests are discussed in more detail in reference 1.

Due to the high cost of $^{34}SO_2$ gas mixtures, the SO_2 used in the measurement of OH is typically made in our laboratory from ^{34}S. This was also accomplished prior to PEM-Tropics. In addition, a wide range of modifications, improvements and reconfigurations had to be completed prior to the present mission. Some of these were necessary because the custom made instrument rack and inlet interface used in ACE on the C-130 would not fit on the P-3B. Others were simply desirable because there are always improvements to be made after something is tried for the first time. Of course, the final tasks in this component were packing, shipment, and installation on the P-3B.

Two Channel Mass Spectrometer System

Several tasks had to be undertaken to allow 2 independent mass spectrometer systems to be operated using a single vacuum system, and computer hardware and software. As mentioned earlier, the electronics to drive all of the lenses in both systems had to be constructed. Also, the electronics to operate 2 detectors were now required, as well as the computer interface to control 2 mass spectrometers and to record data from detecting ambient DMSO. The presence of unlabeled DMSO along with the isotopically labeled DMSO in the calibration sources, however, still precluded any useful measurements of ambient DMSO. After reaching Tahiti where more parts and supplies were available, it was clear that a major overhaul of the calibration system was necessary but extremely risky. Since the instrument could not provide useful data in its then present state, a complete cleaning was undertaken with available supplies. Unfortunately, a new, less volatile set of contaminants were introduced which precluded further measurements.

Measurement Campaign/OH, H_2SO_4, and MSA

Measurements of OH, H_2SO_4 and MSA, were quite successful and supplied a great deal of new insight in several areas including photochemical oxidation, sulfur oxidation, new particle formation, and the uptake and re-evaporation of acids. Highlight of these results will be discussed at the end of this summary.

In addition to successful OH, H_2SO_4, and MSA measurements, the PEM-Tropics mission also showed that a two channel mass spectrometer could be operated on an aircraft. Two different ion sources, measuring at two different pressures that both vary with aircraft altitude were operated in a stable and controllable manner over the full range of environments encountered. While major difficulties were encountered with the individual DMSO/$DMSO_2$ ion source used, the two channel instrument itself operated extremely well, providing: high ion count rates and through-put in both channels; complete, independence of operation between the primary and secondary channels; little loss of sensitivity in the primary channel; little additional weight or size beyond that of the primary channel; no additional computers and only slight more elaborate control hardware. The merging of multiple mass spectrometer channels into a single instrument is an extremely promising technique that offers the ability to dramatically expand measurement capabilities without significantly increasing weight or size.

Data Analysis

The PEM-Tropics flight mission was completed in the first year of this project and our efforts in the beginning of this second year focused on data analysis and calibration checks. Our final data set was turned in by the end of January, as requested with some format corrections shortly thereafter. Once data submission was completed, our effort was shifted to interpretation of our data with respect to the overall P-3B data archive and some initial model calculations. As a result of this recent work, at least 4 papers were published in the initial special issue.

Following this initial round of analysis and publication less obvious but no less important implications were investigated. These have resulted in one Science paper on particle nucleation and a second nucleation paper on the way.

Highlights of Research Results

a. Good agreement was observed between measured and modeled OH concentration. These are discussed in more detail in reference 1.
b. Gas phase sulfuric acid concentration are seen to track OH and SO_2 concentrations in the expected manner particularly at Christmas Island where relatively stable boundary layer conditions prevail. this is discussed in more detail in reference 2.

c. A nucleation event is observed in the tropical boundary layer and discussed in terms of sulfur oxidation products such as sulfuric acid in references 3,4.

d. It is observed that the gas phase production of MSA is not sufficient to explain particle MS in the Tropical Pacific. This result suggests that much of the particle MS probably has a heterogeneous source (see reference 5).

e. While gas phase MSA appears to be incorporated quickly onto particles in the marine boundary layer it is observed primarily in the gas phase in the drier free troposphere. The much higher gas phase concentrations observed in the latter region are thought to arise from evaporation from particles particularly at low ambient water and ammonia concentrations. This process is discussed in more detail in reference 5.

Overall this project was quite successful providing new insight in the areas of photochemistry, sulfur chemistry and particle production and growth.

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