Airborne Measurements of NO, NO_2, and NO_y as Related to NASA's Pacific Exploratory Mission

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Scientific Objectives

The Tropospheric Trace Gas and Airborne Measurements Group's (TTGAMG) efforts on NASA GTE (Global Tropospheric Experiment) PEM (Pacific Exploratory Mission) West A & B field campaign primarily involved the acquisition of NO, NO_2 and NO_y measurements, as well as the subsequent analysis and interpretation of the data base obtained during the PEM West field campaign. These investigations focused on the distribution of trace gases, sources and sinks of ozone, ozone producing precursors with a heavy emphasize on ozone's photochemical state, and the partitioning of the molecules within the NO_y family over the north western Pacific Ocean. The two components of PEM West were focused on observing air masses as they reached the Asian Continent (PEM West A) or as the air mass departed the Asian Continent (PEM West B).

NO_x concentrations play a pivotal role in controlling the photochemical lifetime of ozone in these environments, and understanding the NO_x species partitioning is paramount. The transport of NO_x into the regions, in the form of longer lived NO_y family members, was examined in relation to the comparison of natural occurring sources of NO_x (i.e., lightning and stratosphere/troposphere exchange) to those produced as a result of anthropogenic activity (i.e., biomass burning and aircraft emissions). The TTGAMG's measurements of NO_x and NO_y, in conjunction with other investigators' measurements of PAN (H. B. Singh's group) and HNO_3 (R. W. Talbot's group), have been used to assess the total reactive odd nitrogen levels over the study regions, the partitioning of the reactive odd nitrogen species in their various forms, and the usefulness of the NO_y measurement and its measurement technique.

The TTGAMG's primary PEM West objectives were the characterization of the factors controlling the distribution and fate of reactive odd nitrogen compounds over the western Pacific Ocean and an analysis of the concentration of various trace gases in the troposphere as the air mass aged by both dynamical mixing and photochemical processes in the troposphere.

Summary of Results

From the data the science team collected during the PEM West A field mission, the TTGAMG took the lead role in developing a collaborative paper on the characterization of aged western Pacific air. This paper was presented at the first IGAC meeting in Eilat, Israel and was subsequently published in the JGR special issue on the results of PEM

West A. This paper, in conjunction with a series of papers by Gregory and Talbot, gave a detailed examination of the overall chemical composition of the air observed over the western Pacific Ocean during PEM West A. It also showed the importance of in situ NO_x production by comparing the ratios of long lived hydrocarbons, which were used as relative "atmosphere processing" markers, to both NO_x mixing ratios and anthropogenically produced species.

At the request of the GTE project office, the TTGAMG carried out an analysis of the GA TECH and the Nagoya University's NO and NO_y measurements. After a preliminary report at the second PEM West A workshop, a Blue Ribbon Panel headed by Dr. Crosley was organized. As a result of the Blue Ribbon Panel's critical review of the PEM West A NO and NO_y measurements and their measurement techniques, the TTGAMG made a couple of modifications to their sensor during the upload for PEM West B. A flow diffuser at the front end of the sampling probe, the capability to add zero grade air in flight to the NO_y converters flow stream, and the ability to do HCN, HNO_3, and n-propyl nitrate standard addition calibrations in flight were all added. The diffuser allowed us to maintain a high flow rate through the sampling probe at the upper altitudes without compromising our ability to keep from sampling large aerosols. The zero air additions allowed us to address our NO_y converters so called "offset" or "bias" correction. In the past, zero grade air was used mainly as part of conversion efficiency tests, and only on the ground as part of preflight and postflight. NO values obtained while sampling bottled air in flight were generally at or below the LOD for the instrument and as a result we did not make any adjustments to our reported measurement. The ability to do HCN and n-propyl nitrate calibrations addressed the issue of what is really being converted in the hot converter and on the catalytic surface of the converter. It should be noted that NO_y conversion efficiency tests conducted to date indicate that several "non-reactive" nitrogen compounds having less than a +2 oxidation state are being converted to a measurable NO signal in our system. These compounds include HCN, NH_3, and CH_3CN. In addition, the nitro-alkanes were converted (nitro-ethane, nitro-propane, etc. as does nitro-toluene).

Three papers are being reviewed by JGR covering our involvement in the PEM West B field campaign. The first is an instrument paper that covers modifications to our LIF sensor since it was last reported in the literature. The second covers the topic of NO_y and the data the TTGAMG collected over the last ten years on various NASA GTE field programs. It also addresses the troubles and difficulties in collecting and analyzing data from what one would initially think is a very simple instrument and the definition of what constitutes being a molecule included in the NO_y family. The third revolves around the comparison of the chemical signatures between air mass classes from the PEM West experiments over the western Pacific Ocean. In this paper, we compare the use of chemical signature air mass classification schemes with a back-trajectory method to elucidate some of the similarities and variations between autumn (PEM West A) and winter (PEM West B) data sets. This paper investigates the difference between the seasonal change in atmospheric processing and the effect on the NO_x relationships with the hydrocarbon ratios.

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