PANs Measurements on the C-130 during MIRAGE-Mex

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The MIRAGE-Mex study focuses on the chemical and physical evolution of the outflow from the Mexico City Metropolitan area and its impacts on the downwind region. Specifically, the science objectives of the mission include investigating the extent and persistence of the plume, the photochemistry in the plume including the formation and loss of photooxidants and their impact on downwind regions. To achieve these goals, The C-130 aircraft will probe the outflow as it evolves from the time of emission directly over the city through the region surrounding the city to the larger regional scale several days downwind of the city. The C-130 will carry instruments to measure a comprehensive set of photochemically relevant compounds, aerosol size and number distributions, composition and physical properties, and actinic fluxes. Models will be used to interpret the observations and assess a potential global impact of these emissions.

We plan to contribute to the MIRAGE-Mex campaign an instrument package for the measurement of peroxyacyl nitrates (PANs, i.e., PAN, PPN, PBN, PBzN, APAN, MPAN, MoPAN, and others) on board the C-130 aircraft. We will fly our new PAN-CIGAR chemical ionization mass spectrometer which provides up to 7 PAN species simultaneously with a time resolution of 2 seconds. Data will be available real-time for in-flight planning and preliminary field data will be available within 24 hours of the flight. A prototype of the instrument has been deployed successfully last summer during the ICARTT campaign. Special consideration will be given to the extreme mixing ratio gradients to be expected between fresh outflow and background air.

PANs are important for a number of the specific science objectives listed in the MIRAGE-Mex SOD (specifically nos. 1, 2, 3, and 4). Enormous amounts of PANs are predicted to be formed in the city and have been measured during previous field campaigns in the Mexico City area. These PANs can contribute significantly to sustain the photochemical reactivity of the plume by releasing NO_x through thermal decomposition as is demonstrated in figure 4 of the SOD. PANs will also be an excellent marker for the plume extent and large-scale impact at least at medium to higher altitudes. Since PANs are a significant part of the NO_y family, the measurement of PANs is essential to understand the NO_y budget and the transformation of the different NO_y species.

The relative composition of different PANs in the plume can give us information on the hydrocarbon mix contributing to photochemical oxidant formation, the possible influence of biogenic emissions and the emissions from biomass burning outside the city.

Appendix – PAN species:
PAN = peroxyacetyl nitrate
PPN = peroxypropionyl nitrate
PBN = peroxybutyryl nitrate
PBzN = peroxybenzoyl nitrate
MoPAN = methoxyperoxyacetyl nitrate

APAN = peroxyacryloyl nitrate
MPAN = peroxymethacryloyl nitrate