Whole air sampling from the NASA DC-8 aircraft during INTEX-A

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During INTEX-A the University of California-Irvine (UCI) research group will combine whole air sampling aboard the NASA DC-8 aircraft platform with analysis by gas chromatography (GC) to monitor more than 50 trace gas species, including C_2-C_{10} nonmethane hydrocarbons (NMHCs), selected C_1-C_2 halocarbons, C_1-C_4 alkyl nitrates, and carbonyl sulfide OCS. These species have been identified by the INTEX-A science team as gases as: very important to the success of the experiment (Priority 2 - NMHCs and halocarbons); important (Priority 3 - organic nitrates); and useful (Priority 4 - OCS). The NMHCs are precursors for tropospheric ozone and can directly affect HO radical concentrations. Several of the halocarbon species that we propose to measure impact climate change and stratospheric ozone levels.

Numerous studies, especially as part of previous GTE missions, have demonstrated the power of NMHC and halocarbon measurements to diagnose sources and transport in the atmosphere as well as providing information about photochemical aging. (See Special Issues of *Journal of Geophysical Research* for PEM WEST A, PEM WEST B; TRACEA, PEM TROPICS A, PEM TROPICS B, and TRACE-P). Our proposed measurements will be critical to the correct interpretation of the direct observations of climatically relevant trace gases (e.g., CO_2 and CH_4).

Correlations between a wide range of different species will provide constraints on their sources, which will also help to constrain top-down model estimates of emissions. As stated in the INTEX-A white paper (http://www.espo.nasa.gov/intexna/overview/white_paper.pdf) there is a great need to address the ultimate fate of ozone and aerosols of North American origin. However, describing the near-field evolution of pollutant outflow, is a major challenge for global CTMs, and so for global tropospheric chemistry. Relatively high near-field concentrations lead to active chemistry and superimposition of different influences associated with continental outflow (anthropogenic pollution, natural continental sources, lightning, stratospheric intrusions) and introduce significant complications. The suite of gases we propose to measure will be invaluable for teasing out these different influences.

Experiment Description

We anticipate collecting whole air samples from beyond the laminar boundary layer of the NASA DC-8 into a stainless steel gas-handling manifold employing a two-stage metal bellows pump. Normally we will collect 168 samples per flight. Our sampling frequency will be 4-5 minutes on the horizontal legs and 1-2 minutes on selected vertical ascent/descents. Typical sampling time on horizontal flight legs is 1 minute, corresponding to a sampling distance of roughly 12 km. During standard vertical flight legs, the samples will be collected every 1500-2000 ft.

The filled canisters will be analyzed at UCI within 10 days of collection using two three-GC, five-column, five-detector analytical systems including flame ionization detection (FID), electron capture detection (ECD) and mass spectrometer detection (MSD). For each sample, 1520 ± 1 cm^3 (STP) of air is pre-concentrated in liquid nitrogen, revolatilized, flushed into a helium carrier gas, and the sample flow is quantitatively split into 5 streams, with each stream directed to a different column-detector combination. In previous missions we have found that the split ratios are highly reproducible. During INTEX-A, the 5 column-detector combinations will be DB5ms/MSD; DB1/FID; PLOT-DB1/FID; Restek1701/ECD; and DB5-Restek1701/ECD.

The range of accuracies for the gases we report is 2-20%. The precision of the measurements varies by compound and by mixing ratio. For example, the measurement precision for the NMHCs is 1% or 1.5 pptv (whichever is larger) for the alkanes and alkynes, and 3% or 3 pptv (whichever is larger) for the alkenes. The measurement precision for OCS is 5%CFC-12 at 550 pptv is ±3 pptv, while that for methyl iodide at 0.02 pptv is ±0.01 pptv. The limit of detection (LOD) is 3 pptv for the NMHCs, better than 20 pptv for OCS. Although the LOD is different for each halocarbon, the halocarbons that we report are usually present at mixing ratios above their LOD.