

Analysis of North Atlantic Aircraft Data on Oxygenated Intermediate Species Using an Adapted Regional Chemistry-Transport Model

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Our study is on the interaction of nitrogen oxides with organics as they are exported from their complex sources in Eastern North America. Both urban and specific industrial emissions contribute the nitrogen of the C-H-O-N compounds that affect the global atmosphere, helping determine both ozone and the self-cleaning radical chemistry of the troposphere mediated by the OH radical. Different industrial sources, urban, and natural emissions contribute the organic C. Peroxyacetyl nitrate, CH₃C(=O)OONO₂ is the most interesting compound for which we can measure the outflow to the full depth of the Atlantic troposphere. As we adapt the 3-d chemical model to describe outflow for specific periods with sufficient accuracy, we are analyzing some valuable information in the NARE-97 complete airborne dataset. (NARE: North Atlantic Regional Experiment).

Ames researchers find that there are substantial puzzles in the ratios of PAN/NO₂. Peroxy acetyl nitrate provides one of the major long-distance export pathways for active nitrogen from Eastern North America. It should be closely linked with NO_x (defined as the sum NO + NO₂) by simple thermal association and decomposition reactions, at least when the ambient temperature is substantially above 5° C. Over the course of many hours, the ratio

$$[\text{PAN}]/[\text{CH}_3\text{C(=O)OO}][\text{NO}_2] = k_{\text{dissoc}}/k_{\text{assoc}}$$

should be maintained. The ratios observed below ~4 km (>5° C) in NARE are significantly variable.

This variability may imply significant variation in the concentration of the important smog radical CH₃C(=O)OO, peroxy acetyl, and this may provide important information about variations in the radical activity that go beyond current theory. We report progress in understanding these variations. Observations of such unexplained great radical activity in the upper troposphere (SONEX, the Subsonic (A)ssessment Ozone and NO_x EXperiment. also a 1997 field mission with complimentary information) have never been completely explained. Implications for the reactive radical chemistry of the free troposphere will be outlined.

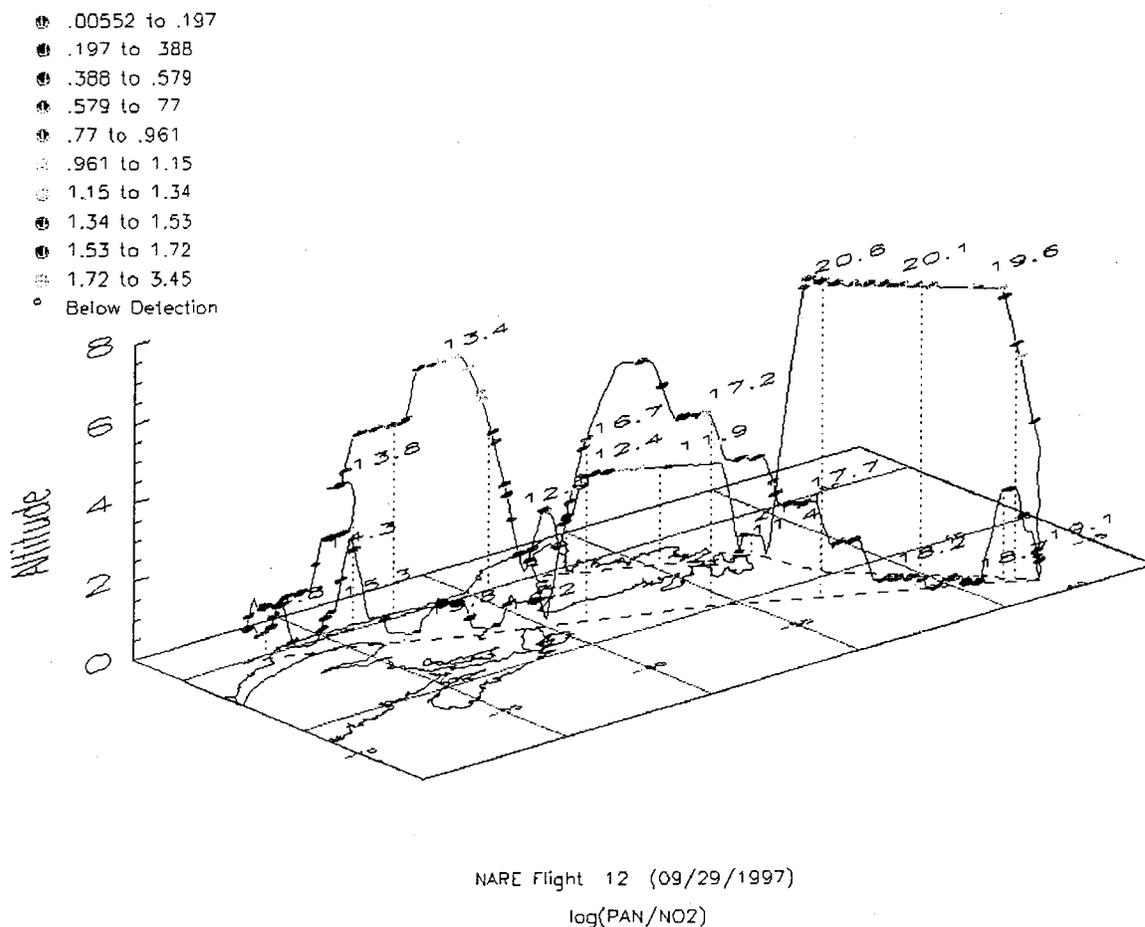


Figure 1. Values of $\log_{10} ([\text{PAN}]/[\text{NO}_2])$ plotted along airplane flight path during NARE-97. Significant mid-altitude variations suggest $\text{CH}_3\text{C}(=\text{O})\text{OO}$ radical variability and are discussed in text.