QUANTITATIVE MEASUREMENTS OF BULK AEROSOL PARTICLE INORGANIC AND ORGANIC COMPOSITION FROM THE NASA DC-8 DURING ARCTAS

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Research Summary

Note, there are no inventions associated with this project.

NASA supported our participation in all phases of the ARCTAS field study. In addition, through a no cost extension, the final year of this funding was used to augment a smaller NASA grant for our participation in SEAC4RS. Both are discussed in more detail below.

1. ARCTAS

The ARCTAS field study comprised three phases. Phase 1 involved NASA DC-8 deployment out of Fairbanks Alaska to investigate Arctic Haze in early spring, Phase 2 was based out of Cold Lake Alberta in summer and focused on characterizing boreal fire plumes and Phase 3 was a smaller campaign, CARB, undertaken to mainly characterize emissions in Southern California. Our role in these aircraft studies was to deploy a Particle-Into-Liquid sampler for measurements of fine particle chemical composition, with a focus on water-soluble organic carbon (WSOC).

Measurements were made during all aspects of this study, final data submitted to the NASA archive and the results were analyzed and published. A significant component of this analysis was the detailed identification of the many plumes intercepted during all phases of the ARCTAS study. A. Hecobian (the PhD student supported on this project) identified approximately 500 individual plumes and provided a detailed time database to the ARCTAS community to assist in plume analysis. This effort was complicated by the fact that many investigators continued to update their data long past the end of the field deployments, requiring repeated ammendments to the database. The work comprised a significant portion of A. Hecobian's PhD thesis and led to a publication with her as first author. Her database and our WSOC data were also critical to a second Georgia Tech paper by the A. Nenes research group. Both papers investigated the characteristics and evolution of the wide range of plumes encountered during ARCTAS and strongly linked to the measured WSOC concentrations of plumes and so discussed in more detail below. The Hecobian paper focused on the chemical properties of the plumes and the Lathem paper focused on the particle CCN properties, as a function of organic composition.

Hecobian, A., et al. (2011), Comparison of chemical characteristics of 495 biomass burning plumes intercepted by the NASA DC-8 aircraft during the ARCTAS/CARB-2008 field campaign, *Atm. Chem. Phys.*, *11*, 13325-13337.

This paper is a summary comparing measurements of gaseous and particulate emissions from a wide range of biomass-burning plumes intercepted by the NASA DC-8 research aircraft during the three phases of the ARCTAS-2008 experiment: ARCTAS-A, based out of Fairbanks, Alaska, (3 April to 19 April 2008); ARCTAS-B based out of Cold Lake, Alberta, Canada (29 June to 13 July 2008); and ARCTAS-CARB, based out of Palmdale, California, (18 June to 24 June 2008). Approximately 500 smoke plumes from biomass burning emissions that varied in age from minutes to days were segregated by fire source region and urban emission influences. The normalized excess mixing ratios (NEMR) of gaseous (carbon dioxide, acetonitrile, hydrogen cyanide, toluene, benzene, methane, oxides of nitrogen and ozone) and fine aerosol particulate components (nitrate, sulfate, ammonium, chloride, organic aerosols and water soluble organic carbon) of these plumes were compared. A detailed statistical analysis of the different plume categories for different gaseous and aerosol species is discussed in the paper.

Briefly, we found through comparisons of NEMR values that fresh biomass burning plumes mixed with urban emissions showed a higher degree of oxidative processing in comparison with fresh biomass burning only plumes. This was evident in higher concentrations of inorganic aerosol components such as sulfate, nitrate and ammonium, but not reflected in the organic components. Lower NOx NEMRs combined with high sulfate, nitrate and ammonium NEMRs in aerosols of plumes subject to long-range transport, when comparing all plume categories, provided evidence of advanced chemical processing of these plumes. An additional key finding was the speed at which the aerosol in these biomass-burning plumes was oxidized. It is anticipated that this analysis of a wide range of biomass burning plumes will provide a data set for comparisons with measurements from future studies.

Lathem, T. L., A. J. Byersdorf, K. L. Thronhill, E. L. Winstead, M. J. Cubison, A. Hecobian, J. L. Jimenez, R. J. Weber, B. E. Anderson, and A. Nenes (2013), Analysis of CCN activity of Arctic aerosol and Canadian biomass burning during summer 2008, *Atm. Chem. Phys.*, *13*, 2735-2756.

DC-8 aircraft characterized the aerosol properties, chemical composition, and cloud condensation nuclei (CCN) concentrations of the summertime Arctic during the 2008 NASA Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) campaign. Air masses characteristic of fresh and aged biomass burning, boreal forest, Arctic background, and anthropogenic industrial pollution were sampled. Observations were spatially extensive (50–85◦ N and 40–130◦ W) and exhibit significant variability in aerosol and CCN concentrations. The chemical composition was dominated by highly oxidized organics (66–94 % by volume), with a water-soluble (WSOC) mass fraction of more than 50 %. The aerosol hygroscopicity parameter, κ , ranged between $\kappa = 0.08–0.32$ for all air mass types. Industrial pollution had the lowest κ

of 0.08 ± 0.01, while the Arctic background had the highest and most variable κ of 0.32 ± 0.21, resulting from a lower and more variable organic fraction. Both fresh and aged (long-range transported) biomass burning air masses exhibited remarkably similar κ (0.18 ± 0.13), consistent with observed rapid chemical and physical aging of smoke emissions in the atmosphere, even in the vicinity of fresh fires. The organic hygroscopicity (κorg) was parameterized by the volume fraction of water-soluble organic matter (εWSOM), with a $\kappa = 0.12$, such that $\kappa org = 0.12 \varepsilon WSOM$. Assuming bulk (size-independent) composition and including the κorg parameterization enabled CCN predictions to within 30 % accuracy for nearly all environments sampled. The only exception was for industrial pollution from Canadian oil sands exploration, where an external mixture and size-dependent composition was required. Aerosol mixing state assumptions (internal vs. external) in all other environments did not significantly affect CCN predictions; however, the external mixing assumption provided the best results, even though the available observations could not determine the true degree of external mixing and therefore may not always be representative of the environments sampled.

2. SEAC4RS

In the final years of the project this grant helped with preparation for the NSF DC3 component of SEAC4RS. Our research objective for this project was to investigate the prevalence, sources, and processes that produce water-soluble brown carbon and to assess its optical importance throughout the troposphere. This involved collaboration with Dr. J. Dibb of the University of New Hampshire, where we developed new methods for measuring particulate water-soluble carbon (WSOC) concentrations and most importantly the light absorption spectra of extracts from UNH filters collected from the DC-8 aircraft. Both modeling and laboratory studies suggest brown carbon may be a product of secondary organic aerosol formation within cloud drops and so a potentially interesting parameter given the mission science objectives.

Preliminary work in preparation for SEAC4RS included testing Teflon filter extractions using both water and methanol as contrasting solvents on the UNH filters and in addition we purchased all supplies for the mission. Preliminary results from brown carbon measurements are exciting. Our data are the first direct measurements of brown carbon throughout the free tropospheric column.

The aircraft measurements show the prevalence of chromophores throughout the free troposphere and, relative to black carbon (BC), show that brown carbon becomes increasingly important with altitude. For example, the estimated pure BC light absorption at 365 nm dropped off fairly rapidly from the near surface measurements, especially above roughly 4 to 5 km above sea level (asl), however, the concentration of brown carbon in water or methanol extract was more uniform with altitude. This resulted in a predicted brown carbon absorption that was also more uniform with altitude compared to BC. The cumulative light absorption relative to total column, for each component, showed that at 365 nm, half the column BC absorption occurred at roughly 4 km asl, while for brown carbon, water or water plus methanol extract, this occurred between 5 and 6 km, indicating less influence of absorption closer to the surface. Thus the fraction of brown carbon absorption relative to total light absorption showed that the brown carbon contribution to light absorption substantially increased relative to total

absorption with increasing altitude. These relative differences in vertical light absorption distributions may be due to a more regional source for brown carbon, possibly from dispersed biomass burning emissions or in-situ heterogeneous (e.g., cloud drop) secondary production. A more widely distributed source, and hence influence for brown carbon throughout the tropospheric column, indicates a greater importance than what would be expected from just surface measurements. These preliminary results suggest the optical importance of brown carbon may be under appreciated, even in remote regions. We anticipate that these results will be published in the near future.