Characterization of Fine Particulate Matter (PM) and secondary PM Precursor Gases in the Mexico City Metropolitan Area

A collaborative project among University of Colorado, Boulder (J.L. Jimenez),
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Final Report

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Summary

The objectives of this funded project were (a) to further analyze the data collected by our group and collaborators in Mexico City during the MCMA-2003 field campaign, with the goal of further our understanding of aerosol sources and processes; and (b) to deploy several advanced instruments, including the newly developed high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and thermal-denuder (TD), during the MILAGRO/MAX-Mex/MCMA-2006 field campaign, and to analyze those data (together with the 2003 data) to provide additional insights on the formation and transformation of aerosols in the Mexico City area. These goals were addressed in collaboration with our project partners, MIT/Molina Center, and Aerodyne Research. Overall this project was very successful, resulting on 22+ journal papers including six “highly cited papers” and three papers that are the most cited in their respective journals (out of several thousand papers) since the year in which they were published. Multiple discoveries, such as the underestimation of SOA in urban areas even for short photochemical ages, the demonstration that urban POA is of similar or higher volatility than urban SOA, and the first analysis of organic aerosol elemental composition in real-time have been recently published. Several dozen presentations at major US and international conferences and seminars also acknowledged this grant.

Key Activities and Results

(a) Analysis of MCMA-2003 field campaign data

The analysis of MCMA-2003 data has been very fruitful, leading to the publication of 10 papers plus an additional paper which is currently under peer-review. Several important results include: (1) the first unequivocal demonstration that anthropogenic VOCs produce much larger amounts of secondary organic aerosols (SOA) in urban areas than predicted with current models [Volkamer et al., *GRL*, 2006]; (2) a thorough description of the aerosol concentration and physical and chemical properties in the MCMA and a comparison with previous campaigns, confirming the dominance of organic species, the local formation of ammonium nitrate, and the regional formation and transport of sulfate [Salcedo et al., *ACP*, 2006]; (3) the characterization of the dynamics, sources, and possible sinks of polycyclic aromatic hydrocarbons (PAHs) in Mexico City, and the first

field intercomparison of three different methods to measure these species [Marr et al., *ACP*, 2006]; (4) the development of a method to quantify PAHs from the AMS and the identification of some very reactive PAHs that may be destroyed by ozone during filter sampling, but that were detected by the AMS [Dzepina et al., *IJMS*, 2006]; (5) the confirmation that the measured inorganic species appear to be in equilibrium with the gas-phase, and the characterization of the expected concentrations of HCl in the Mexico City atmosphere and their influence in aerosol chloride [San Martini et al., *ACP*, 2006]; (6) the characterization of the particle collection efficiency and beam focusing efficiency of the Aerodyne AMS using a Beam Width Probe (BWP) in the field for the first time [Salcedo et al., *ACP*, 2007]; (7) and overview / review of the findings related to fine particles from the MCMA-2003 campaign, and also including some new data on nanoparticle composition [Molina et al., *ACP*, 2007]; (8) an overview of the concentration and composition of non-refractory inorganic and organic aerosols in the Northern Hemisphere including our Mexico City results, showing that organic aerosols (OA) represent a significant fraction of the fine PM mass at all locations, and that oxygenated OA (OOA, an SOA surrogate at most locations), represents the majority of the mass even in urban areas [Zhang et al., *GRL*, 2007]; (9) the demonstration that there is a missing sink for gas-phase glyoxal in Mexico City which correlates with aerosol surface area, which leads to SOA formation accounting for about 15% of the observed SOA [Volkamer et al., *GRL*, 2007]; (10) the first published intercomparison of AMS with PIXE and PESA showing good a comparison for sulfate during most of the campaign, and evaporation losses of OA and ammonium chloride during PIXE analysis [Johnson et al., *ES&T*, 2008]; (11) a reanalysis of the SOA formation case study of Volkamer et al. [2006] using several recently-proposed SOA models, which allow reaching mass closure but still leave many open questions about the sources and processes that lead to the observed SOA formation [Dzepina et al., *ACPD*, 2009] (see Figure 1 below).

Figure 1. Total model SOA and gas-phase SVOC for the base case of Dzepina et al. [ACPD, 2009]. Part (a) shows the contributions of each model to the total model SOA, and (b) shows the contributions to the total model gas-phase.

(b) MILAGRO/MAX-Mex/MCMA-2006 field campaign and data analysis

The Jimenez group participated in the MILAGRO/MAX-Mex/MCMA-2006 field campaign by deploying several advanced instruments at the T0 / IMP Supersite. The main instrument was a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) of which this was only the second ever field deployment (the first one having been also carried out by our group in Riverside, as described in Docherty et al., *ES&T*, 2008). The HR-ToF-AMS was operated in V/W mode alternation for the first time following the development of this mode early in the campaign, and this mode has since become standard for the more than 20 HR-ToF-AMSs around the world. We also deployed a scanning mobility particle sizer (SMPS), a nano-SMPS, a thermal denuder, a particle concentrator, and a TSI DustTrak. The instruments performed very well during most of the campaign, and produced a very rich dataset of aerosol concentration and physical and chemical properties.

Figure 2. Daily source apportionment of OA from (a) PMF-AMS and (b) CMB-OMM with (c, d) the average composition of each, respectively, for the overlapping sampling period from 17–30 March, 2006. Note: CMB-OMM OC results converted to OM (from Aiken et al., *ACPD*, 2009).

Results from the analysis of this dataset have been presented in four publications, one paper in press, and five papers currently under review, with several additional papers in preparation. Some key results include: (1) a thorough characterization of the composition of submicron particles at T0 during MILAGRO, with similar overall results to IMADA-AVER in 1997 and MCMA-2003, and including the first application of PMF to high-resolution AMS OA spectra, which compared well to source apportionment of OA using chemical mass balance of organic molecular markers performed by the Schauer group [Aiken et al., *ACPD*, 2009] (see Figure 2 above); (2) an analysis of the elemental

composition of organic aerosols at T0 which is the first ever characterization of this property with high time resolution and that showed that O/C is lowest during the rush hour period in the morning and highest during the photochemical peak in the afternoon [Aiken et al., *ES&T*, 2008] (see Figure 3 below); (3) a demonstration of the thermal-denuder + AMS (TD-AMS) technique for chemically-resolved aerosol volatility measurements, including comparisons of laboratory and Mexico City data [Huffman et al., *AS&T*, 2008]; (4) a demonstration that OOA and O_x form at similar rates in polluted urban air, making O_x a better tracer than O_3 due to the removal of the NO titration effect, and allowing the use of the ratio of OOA and O_x formation rates as a target for photochemical models [Herndon et al., *GRL*, 2008]; (5) an analysis of the sources and sinks of HNO_3 in Mexico City, showing the importance of the NH_4NO_3 equilibrium, reactive loss of HNO_3 to dust, and dry deposition of HNO_3 in the mass balance of that species [Zheng et al., *ACP*, 2008]; (6) an analysis of the factors controlling light scattering and absorption in Mexico City, which showed very good correlation between AMS mass and submicron scattering, and demonstrated that secondary species account for 70% of the mass and scattering on the late afternoon [Paredes-Miranda et al., *ACP*, 2009]; (7) the first detailed analysis of chemically-resolved volatility of inorganic and organic aerosols in the field, showing that all types of OA are semivolatile and that POA is of similar or higher volatility as OOA/SOA, with the most aged OOA/SOA showing the lowest volatility [Huffman et al., *ACP*, 2009]; (8) an analysis of the volatility of POA from various sources of potential importance during MILAGRO, all of which showed a semivolatile character although with a wide range of variation [Huffman et al., *ES&T*, 2009]; (9) a comparison of the PMF-AMS results with the output of two regional models (WRF-CHEM and CHIMERE) showing that POA is reasonably well-predicted in Mexico City as well as a significant contribution of biogenic SOA to the regional background in Central Mexico [Fast et al., *ACPD*, 2009; Hodzic et al., *ACPD*, 2009].

Figure 3. Diurnal averages of atomic O/C, H/C and N/C and OM/OC sampled at the T0 ground site in Mexico City during MILAGRO.

Publications Acknowledging this Grant

We have published the 14 peer-reviewed papers on our research in this project, while one paperwebwebelements is “in press” and 7 more are undergoing peer-review. The results of this project have been received with very high interest by the scientific community: these papers have already been cited 353 times (from ISI Web of Science). Six (6) of these papers are classified as “Highly Cited Papers” (Top 1% in citations in their journals) by ISI. Finally, 3 of them are the most cited paper in *Geophysical Research Letters* since 2006 (of 5085 papers), the most cited paper in *Geophysical Research Letters* since 2007 (of 3382 papers), and the most cited paper in *Environmental Science and Technology* since 2008 (of 2099 papers).

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