Carbonaceous Aerosol Processing in the Mexico City Metropolitan Area

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INTRODUCTION

The Mexico City Metropolitan Area (MCMA) is a mega-city environment with significant air pollution. Emissions of primary particles and secondary particle precursors are high. Chemical and physical transformations alter the particles as they are transported out of the city basin and into the surrounding region. The fate and role of primary carbonaceous aerosols in the aerosol loadings of Mexico City Metropolitan Area are explored and discussed through multiple fixed site measurements made during the MILAGRO campaign in 2006.

The spatial and temporal variations of the ambient aerosol in the MCMA were characterized during the MILAGRO campaign in the spring of 2006 using a mobile laboratory equipped with gas and particulate measurement instrumentation [Herndon *et al.*, 2005]. The laboratory was operated at various fixed site locations in and around the metropolitan area. Size-resolved (mobility and vacuum aerodynamic) and chemistry-resolved particulate mass was measured with a time-of-flight aerosol mass spectrometer (TOF-AMS), scanning mobility particle sizers (SMPS), multi-angle aerosol photometer (MAAP) and various other particle instruments. Selected trace gas species were also measured using a proton transfer reaction mass spectrometer and tunable quantum cascade laser systems.

RESULTS AND DISCUSSION

The aerosol in MCMA is predominantly (~55%) organic in composition with lesser amounts of inorganic ammoniated nitrate and sulfate salts, black carbon and small amounts of particulate chloride and crustal material [Salcedo *et al.*, 2005]. The organic component was composed of mixed hydrocarbon-based and oxygenated organic compounds. The hydrocarbon-based organic particles are highly correlated with primary traffic emissions, and the oxygenated organics are likely dominated by secondary organic aerosol generated through photochemical processes. The composition of the organic particle matter was dependent upon the time of day and the location of the measurements within MCMA, especially with respect to local traffic sources and meteorological transport.

Most urban sites were influenced by a strong diurnal particulate mass trend indicative of primary organic emissions from traffic during early morning and subsequent accumulation of oxygenated organics and ammonium nitrate particles starting in the mid-morning (~9 AM) and continuing throughout the day. Morning traffic-related primary organic emissions were strongest near center city and less intense at other urban sites further from the center.

Simultaneous measurements by the TOF-AMS and SMPS instruments yielded the particle mass, volume, density, composition, dynamic shape factor, and fractal dimension [Slowik et al., 2004]. Two types of ambient particles were observed: (1) fractal-like (i.e. nonspherical) particles containing significant hydrocarbon-based organic, polycyclic aromatic hydrocarbons [Marr *et al.*, 2005] and black carbon; (2) near-spherical particles characteristic of regional-scale transport. During the early morning, the ambient fractal particles were similar in morphology and composition to diesel-generated particles. However, as the morning progressed, the ambient fractal particles became larger and nearly spherical due to gas-to-particle condensation.

The coatings on the fractal particles contained organic and inorganic compounds and are shown to be likely products of atmospheric photochemistry. The rate of photochemistry increased throughout the morning, as evidenced by ozone and particulate nitrate formation due to the increase in incident solar radiation. The fractal particles were no longer evident after late morning due to morphological changes implying that primary soot emissions in a polluted urban environment are processed rapidly via photochemically driven gas-to-particle condensation.

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