Microscopy and Microprobe Studies of Individual Atmospheric Particles Collected During MILAGRO 2006

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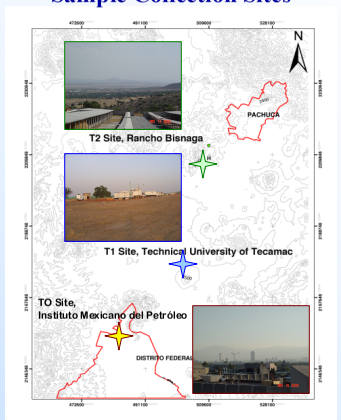
ABSTRACT

Complementary capabilities of several analytical microscopy and microprobe techniques are being utilized to provide comprehensive chemical and morphological analysis of aerosol samples collected during the 2006 MILAGRO study. The analysis is currently focused to target the following areas: (a) internal structure and mixing characteristics of soot and sulfur containing particles, (b) the phenomenon of emissions of heavy metals and soot from overnight industrial activities at T0, (c) identification of major particulate emissions sources at three sites through composition and morphological analysis, (d) evidence of aerosol processing (chemical reaction or physical mixing) from T0 to T1 to T2, (e) hygroscopic properties of mixed urban aerosol and susceptibility to wet-removal by washout/rainout.

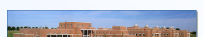
Sample Collection Sites



• Particles were collected from three sites to investigate the spatial and temporal variability of chemical and physical properties. Samples were collected at "T0" (Instituto Méxicano de Petróleo, IMP) in an industrial area within the city, as well as "T1" (Universidad Autónoma de Tecamac) and "T2" (Rancho la Biznaga) located ~25 km and ~50 km northeast of T0, respectively. These sites were chosen to study generation of pollution inside the city and subsequent transport towards the city boundaries.

Field Sampling Devices

Laboratory Analysis



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• **CCSEM/EDX** – computer controlled microscopy and X-ray analysis of a statistically significant number of particles.

• **TOF-SIMS** – depth profiling of ensembles of individual particles providing molecular speciation of their contents.

• **TEM/EDX, EELS, SAED** – high resolution microscopy of individual particles.

• **FTIR Microscopy** – monitoring of hygroscopic properties of ensembles of individual particles.

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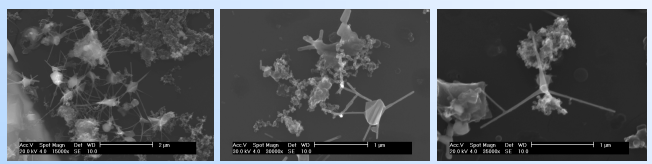
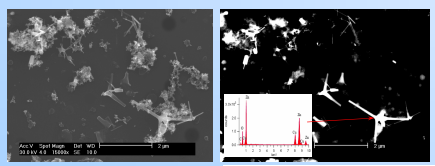
• **STXM/NEXAFS** - chemical bonding information on different elements for individual particles.

PARTICULATES FROM OVERNIGHT INDUSTRIAL ACTIVITIES AT T0

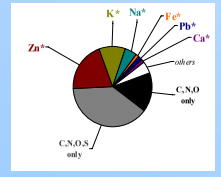
• Overnight industrial emissions are important sources of metals originating from northern sections of the city. Several early morning (~ 1am) samples were studied, which corresponded with peak values in various metals including Zn and Pb measured by PIXE. SEM images show fine needle-like Zn particles mixed with soot. Occasional small Pb containing particles were also distinguishable using BSE mode imaging and X-ray analysis.
• CCSEM/EDX analysis indicate a profound presence of mixed soot/metal containing particles
• PIXE data indicates their night time origin and provides an estimate of the levels of their emissions.



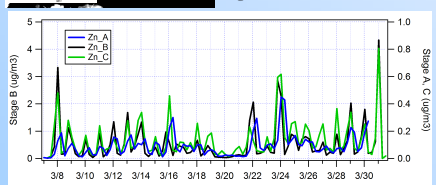
↑ *SEM images of ZnO particles mixed with soot*



← *BSE image highlights high Z inclusions in soot*



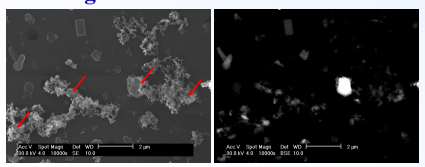
↑ *CCSEM/EDX obtained particle type classification*



↑ *Total Zn concentrations in aerosol measured by PIXE*

INTERNAL STRUCTURES AND MIXING CHARACTERISTICS OF SOOT AND SULFUR CONTAINING PARTICLES COLLECTED AT T0 SITE

Morning Rush Hour Emissions



• Aerosol samples collected during morning rush hours are dominated by soot particles. Ca, K, P, S, Zn, Na and combination of these species are very common soot inclusion (red arrows).

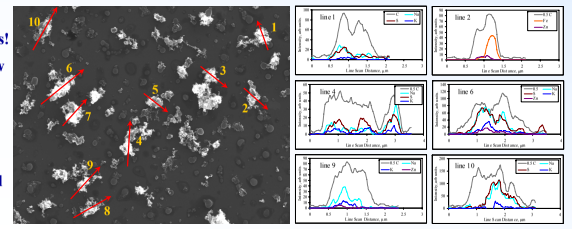
← *BSE image highlights inclusions in soot*

↓ *X-ray line scans of soot particles* ↓

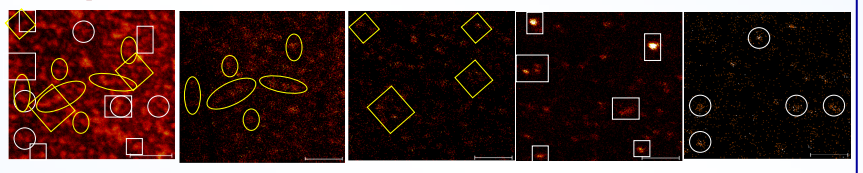
• Different inorganic inclusions are typically located inside of soot particles!

- X-ray line scans of soot particles show that characteristic signals originating from inclusions are narrower than the corresponding carbon signal for all probed particles.

- TOF-SIMS ion mapping reveals metal ion signals only after destructive sputtering of soot particles.



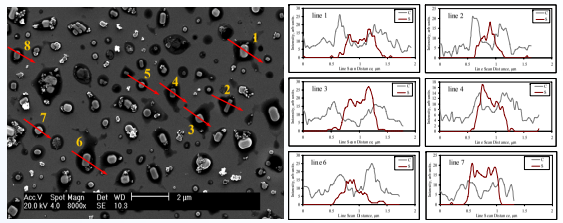
C_2^- Sn^+ Zn^+ Fe^+ Pb^+



↑ *TOF-SIMS ion maps of soot particles with metal inclusions* ↑

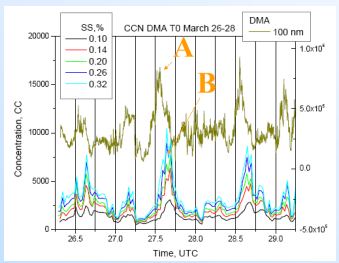
Typical Afternoon Samples

• Aerosol samples collected in the afternoon are dominated by S-containing particles (bright core particles in the SEM image) which are evidently coated by organic compounds (dark hallows). X-ray line scans indicate their carbon content versus S-containing material of bright cores.

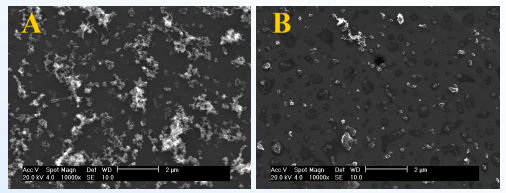


↑ *X-ray line scans of typical afternoon particles* ↑

CHEMICAL CHARACTERIZATIN OF CCN ACTIVE PARTICLES (data from T0 site)

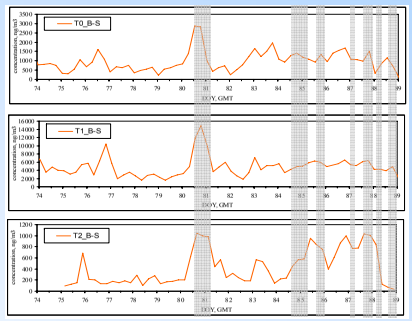


↑ *Fragment of particle concentration (dark green) and CCN concentration (colored lines) records measured at* T0 *site*



Research efforts are focused on samples A and B to study differences on a temporal scale. Companion data from a cloud condensation nuclei (CCN) counter located at T0 suggested that sample B particles are more hydrophilic than those of A. While particles in sample A were collected during a maximum in total particle count at morning rush-hour traffic, sample B particles were collected during a peak in number of active CCN occurring several hours later. Possible explanations for the offset include chemical reaction (e.g. OH or O_3 oxidation) or physical processing (e.g. mixing with soluble inorganic salts) of the same type of particles, or emission of different types of particles altogether.

T0 → T1 → T2 AEROSOL PROCESSING

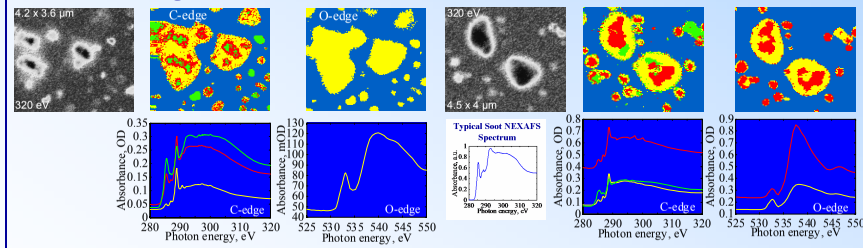


PIXE records of sulfur from three sites have been used to confirm T0→T1→T2 transport of air masses and indicate specific time stamps of the samples for focused microscopy and microprobe analyses. Grey shadowed area on the plots indicate forecasted (B. de Foy) T0→T1→T2 transport trajectories. There is striking evidence of the same air plum captured on DOY 80-81. Comparisons of samples collected on those days in relation to transport from T0 to T1 and to T2 are currently in progress.

← *PIXE (stage B) records of Sulfur from T0, T1, and T2 sites*

Evolution of Carbonaceous Particles from T0 to T1 – Mixing Characteristics

T0 - Morning T1 - Afternoon

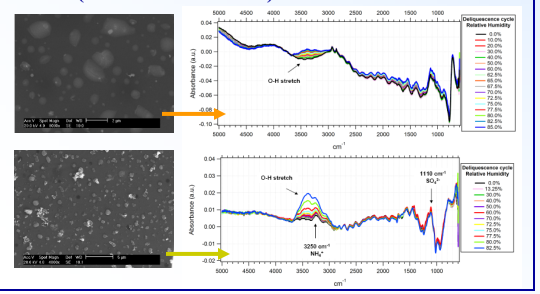


Principle component analysis (PCA) shows these aerosol particles contain a soot-like core which correspond to the green regions (see typical soot NEXAFS spectrum). This core is surrounded by a more oxidized carbonaceous material (red and yellow regions). Functional groups assignments are as follows: 285.5 eV aromatic-C, 286.7 eV aliphatic-C or ketonic carbonyl, 288.8 eV carboxyl carbonyl, 290.5 eV carbonyl.

PCA shows that the green regions display higher aromatic-C content. The red and yellow regions display similar NEXAFS spectra to one another. However, the inner red regions contain potassium and are more oxidized. These aerosol particles collected at T1 are considerably more oxidized than those collected at T0 and do not display NEXAFS spectra of 'typical' soot.

PROBING HYGROSCOPIC PROPERTIES OF FIELD COLLECTED PARTICLES (data from T0 site)

Current efforts are exploring the method of micro FTIR spectroscopy to study hydration properties of field collected particles. In these experiments, substrates with particles of interest are placed in a cell and then FTIR spectra are recorded as a function of relative humidity. From the FTIR spectra we determine the phase (solid or liquid) and estimate the amount of water associated with the particles. Typically, an ensemble of hundreds of sub-micron particles are monitored in a given experiment. Results from two such experiments are illustrated here.



Acknowledgements:

The authors acknowledge support provided by the Atmospheric Science Program of the Department of Energy's Office of Biological and Environmental Research.

The authors appreciate the cooperation of: Dr. D. J. Gaspar, who provided important guidance and access to the TOF-SIMS instrument; T. Tylisczcak for STXM 11.0.2 assistance, expertise with NEXAFS & standards; A.L.D. Kilcoyne for STXM 5.3.2 assistance.

Sample analyses were performed in the W.R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory and at the Advanced Light Source supported by the Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy at Lawrence Berkeley National Laboratory.

K.S. Johnson, R. Gonzalez and R.J. Hopkins acknowledge participation and support of 2006 Summer Research Institute in Interfacial and Condensed Chemical Physics organized by PNNL

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