

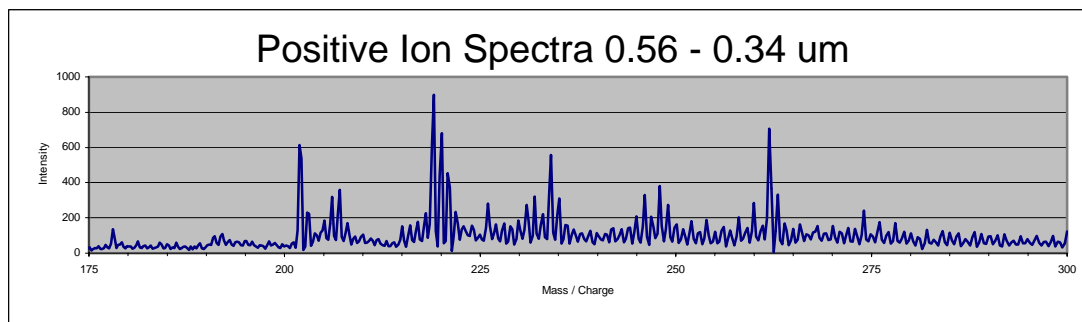
Direct Measurement of Speciated Size-Resolved Organic Aerosols at MLO, Spring 2000

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The Interagency Monitoring of Protected Visual Environments (IMPROVE) program has been continuously sampling aerosols at Mauna Loa Observatory (MLO) since 1988. The sampler uses a 3-4 day average night only (MALO2) and continuous average (MALO1) protocol. At MLO organic matter (OM) is inferred from mass closure, namely that the sum of all species should equal the mass of elements weighed on the filters. There is uncertainty associated with the precise chemical state of the sulfates and lack of data on nitrates [Perry et al, *J. Geophys. Res.*, 104, 18,521-18,533, 1999]. Organic matter in spring at MLO is much higher in the nighttime downslope winds (MALO2) than in the average (MALO1) or upslope winds. The nighttime concentrations of OM are much higher than at the Hawaii Volcanoes visitor center or Haleakala on Maui. The elevated values persist from February-July and are roughly equal to sulfates in mass and roughly one-half of the fine (<2.5 micron) soil transported to MLO during this period. However, the composition, size, and sources of the organic particles from Asia are unknown. To address these questions, two 8-stage rotating drum samplers were installed at MLO in late March 2000 that ran continuously through May 18, 2000. The samples were collected in eight size modes: Inlet to 5, 5 to 2.5, 2.5 to 1.15, 1.15 to 0.75, 0.75 to 0.56, 0.56 to 0.34, 0.34 to 0.24, 0.24 to 0.07 μm diameter, onto greased Mylar substrates. Time-resolved samples on aluminum substrates have been archived from the same period using the sampler. The time-integrated samples were analyzed by synchrotron-XRF and by laser desorption time-of-flight mass spectrometry (LDI-TOF/MS; figure). It has been found that the intensity of the emissions are low, and there are characteristic mass peaks near mass/charge 100 and 150 that act as blank identifiers. The earlier assumptions that sulfates were much greater than nitrates are proved to be correct. The peak of sulfates is in the region of 0.56 to 0.34 μm .



Positive ion spectra of stage 6 (8-DRUM sampler) from MLO Spring 2000 using LDI-TOF/MS.

The most striking aspect of the analyses is in the complexity of the organic species that far exceeds those seen in either ambient (wood smoke dominated) or source enriched (diesel) tests done to date. The figure shows the positive ion spectrum that is normally dominated by Polycyclic Aromatic Hydrocarbon's (PAH). While pyrene (near mass/charge 200) and derived compounds are evident, there appears to be mass present at almost every mass/charge value up to and above 300. While a great deal needs to be done to understand this result, it is in qualitative agreement with earlier GC/MS tests done at clean western sites showing that organic matter in these areas look little like the presumed sources. The inference is that during transport to MLO, organic gasses have converted to particles, and organic particles have been oxidized and polymerized into new compounds in the intense UV and ozone rich environment of the lower free troposphere. We will test this hypothesis during the Aerosol Characterization Experiment (ACE)-Asia, Spring 2001.