

Discrete Measurements of PM_{2.5} Mass and Composition in the Southeastern U.S.: Regional and Seasonal Trends between 1999 and Today.

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Summary

A three-channel Particle Composition Monitor (PCM) was used to measure PM_{2.5} mass and composition as well as denuder-derived vapor-phase NH₃, HNO₃, HONO, SO₂, and light organic acids (LOA, i.e. acetic, formic and oxalic) over integrating periods of 12 and 24 hours since June 1999. Sampling sites included urban/metropolitan, suburban, and rural regions in Tennessee, Georgia and Texas. Seasonal averages of the gas and particle phase species and aerosol acidity for summer'99, fall'99, winter'99/'00, summer'00, summer'01, and fall/winter'01/'02 and selected daily measurements are presented.

The measurement principle of our PCM is based on successive separation of particles larger than 2.5 microns aerodynamic diameter, followed by the separation of gaseous species from the particles prior to PM_{2.5} collection on Teflon membrane and quartz fiber filters backed by specifically impregnated adsorbing filters. The sampler operates three channels each controlled at a nominal flow rate of 16.7 lpm. PM_{2.5} separation is achieved by standard, Teflon coated cyclone heads, and reactive gases are separated by means of appropriately coated denuders, i.e. sodium carbonate for removal of acidic gases in one, and phosphorous or citric acid for alkaline gases in an other channel. Mass is determined gravimetrically on the Teflon filters of both channels, after which the filters are extracted in water and analyzed via IC. The routinely detected anions are chloride, nitrate, sulfate, and LOA (formate, acetate, and oxalate), and the cations sodium and ammonium. In a few special cases and sites, fluoride, potassium, and calcium were also detected and quantified. The denuders are extracted and the extracts are analyzed by IC to determine gas phase concentrations of NH₃, HCl, HONO, HNO₃, SO₂, and LOA.

The third channel serves the measurement of particulate organic and elemental carbon (OC/EC) from quartz filter samples downstream of an XAD coated annular denuder [*Gundel et al.* 1998, *Lane et al.* 2000], similar to the one used in the VAPS. The XAD coated annular denuder removes gas phase organic species (either volatile or semi-volatile organic species) to minimize positive artifacts on the quartz fiber filter. The quartz front filter is followed by an XAD impregnated quartz fiber filter [*Baumann et al.* 2002] used to estimate the fraction of semi-volatile organic compounds (SVOC) volatilized from the particles collected on the front filter. Results from *Lewtas et al.* [2001] indicate negligible collection of VOC on quartz-fiber filters placed downstream of an XAD denuder. The front quartz-fiber filter is analyzed for OC and EC by thermal optical transmittance (TOT) following the NIOSH protocol. The XAD coated quartz backup filter undergoes a modified analysis that is significantly different than conventional TOT analysis. In this case, O₂ is not introduced into the system and EC is not measured, since EC is efficiently collected on the quartz front filter. The maximum oven temperature for this analysis is 176°C in pure He atmosphere.

At certain sites, semi-continuous PM_{2.5} mass and ion measurements were made in addition to and much higher resolved than the discrete filter measurements, using a Tapered Element Oscillating Microbalance (TEOM) and Particle In Liquid Solution (PILS) method. The TEOM mass concentrations agreed with the gravimetric filter mass well within 5 %, which is attributed

to i) the active humidity control employed with the TEOM, and ii) the fact that all Teflon sample filters were dehydrated in a desiccator located in a temperature- (21°C) and humidity- (40%) controlled clean room prior to weighing. The samples remained in the desiccator for at least 3 days, in most cases longer.

In all cases, sulfate and OC are the main contributors to overall PM_{2.5} mass. A clear seasonal pattern of PM_{2.5} mass, maximum ozone concentrations, and some acidic gases has been identified, with absolute values being highest during summer and dropping during fall and winter. The underlying parameters causing ozone and PM_{2.5} formation (stagnant periods associated with high temperatures, relative humidities, and UV radiation) varied between the different summers, correlating with the observed pollutant concentrations. A seasonal pattern is observed for particulate sulfate and mass, whereas OC concentrations show relatively little seasonal variation. This correlation between sulfate and fine aerosol mass can be seen also on much smaller time-scales from the TEOM and the PILS data, following impacts of certain plumes. A regional pattern can be observed, with metropolitan/urban PM_{2.5} and gas concentrations being higher than suburban/rural concentrations. Concentration differences at suburban and rural sites point to effects of different boundary layer mixing heights. Acidity calculations based on the H₂SO₄/HNO₃/NH₃ system show an acidic aerosol in summer and more alkaline conditions during fall and winter.

For the urban site, almost complete closure in the mass balance is achieved when SVOC, collected on the XAD coated quartz backup filter are included. Investigating the application of different factors to account for Other Organic Elements (OOE) associated with OC and semi-volatile OC (here 0.6 and 0.4, respectively), considering different physical properties of carbon species collected on denuded quartz front versus XAD coated quartz backup filters leads to the conclusion that photochemically well-aged and well-mixed air masses contain particulate organic compounds with more highly oxygenated and less volatile functional groups, whereas under more stagnant conditions, particle phase organics might be less oxygenated and therefore more volatile.

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