

**“HIGHLY TIME--RESOLVED ORGANIC  
COMPOUNDS CONCENTRATIONS OF  
PRIMARY AND SECONDARY ORIGIN DURING THE BALTIMORE  
PM2.5-SUPERSITE STUDY”**

by

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**Abstract**

Most of the knowledge about the nature of ambient organic compounds associated with airborne fine particulate matter is obtained from integrated particle sampling over 24 hours and sometimes even longer. Although much has been learned about the average organic composition of airborne carbonaceous aerosol, little is known about diurnal concentration changes due to the interplay of meteorology with emissions from local sources and pollutant transport from distant source regions. Likewise, the impact of atmospheric chemistry on the composition of organic aerosol matter is mainly unknown or limited to smog chamber experiments.

Here, a specially designed sampling system was deployed during the 2002-2003 Baltimore PM-Supersite Study to collect PM<sub>2.5</sub> on filters and PUFs with a 3-hourly resolution for three weeks during summer and another three weeks during winter. From the sample sets, a total of four weeks for summer and winter were subjected to chemical analysis. Over 100 individual compounds including homologues series of n-alkanes, n-alkanoic acids, n-alkenoic acids, n-alkylcyclohexanes, hopanes, PAHs, oxy-PAHs, levoglucosan, resin acids, syringyl-moieties, aromatic and aliphatic dicarboxylic acids, secondary biogenic compounds, sterols, tris(2,4-ditert-butyl-phenyl)phosphate and others were quantified.

For primary organics, typically, no repeatable diurnal concentration patterns on a day to day basis are observed as one would expect if major local sources such as vehicular traffic would be isolated from nearby or more distant source regions. In contrast, averaging daily 3-hourly ambient concentrations reveal ambient diurnal patterns that relate to diurnal emission patterns of major source classes. With the increased time resolution, short-term release of pollutants from a temporary source can also be detected. For example, for a two day period, even carbon numbered higher molecular weight n-alkanes, indicators for plastic waste burning, have been measured at substantially elevated concentrations together with the locally prevailing meteorology, allowing pinpointing possible source regions. Another surprise is the substantial depletion of unsaturated fatty acids during the summer and the pronounced diurnal variations in ambient concentration between daytime and nighttime during winter. Key biogenically derived secondary organic compounds have been detected as well, and their ambient concentration levels increase during the night when the relative humidity levels increase and chemical formation is favored.