

A Quantitative Protocol for Highly Polar Organic Compounds in PM_{2.5} from the New York City Airshed

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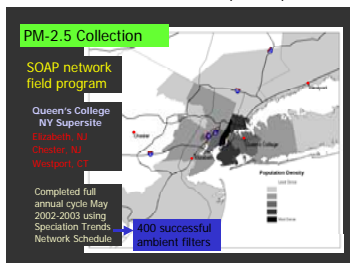
Introduction

Highly polar organic compounds (HPOC) are not well studied in U.S. urban airsheds. HPOC are thought to consist mainly of secondary organic aerosol (SOA). This study investigates the atmospheric abundance of HPOC markers in the New York City (NYC) metropolitan area. The contribution of SOAs to PM_{2.5} and OC mass in this highly populated urban area is of interest because of its seasonally variable and potentially high mass contribution to the total allowable mass of fine particulate matter (PM). The composition and ambient mass of HPOC to PM_{2.5} and OC mass are important factors needed for controlling the total mass of suspended fine particulate matter (PM). In addition, the anthropogenic and biogenic sources of secondary fine particles in the NYC area are not well known. SOA fine PM mass and composition also are valuable information for source apportionment models such as the EPA CMB 8.2.

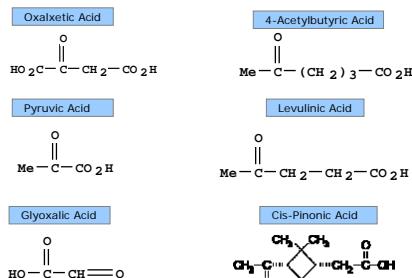
A key science question concerning fine PM mass in urban airsheds is how much of the carbonaceous PM_{2.5} is primary versus secondary? To address this question, a group of highly polar, low molecular-weight organic acids were monitored. The acids are not found in the chemical profiles of primary urban PM_{2.5} emissions sources such as motor vehicle exhaust and commercial cooking. A compound indicative of biogenic SOA, cis-pinonic acid, also was screened to assess this potential source of HPOC in PM_{2.5} in the metropolitan NYC airshed.

Fine PM_{2.5} Collection

Fine PM samples were collected as part of the *Speciation of Organic Compounds for Source Apportionment* (SOAP) network. Samples were collected at 4 receptor sites from May 2002 to May 2003. Samples were obtained from two urban sites, (Queens, NY and U.S. EPA Super site, Elizabeth, NJ), an upwind (Chester, NJ) and downwind site (Westport, CT) and operated on the STN sampling schedule (1 in 3 day). Ten seasonal composites were generated for each site with 6 to 10 filters per composite.



Highly Polar Organic Compounds Studied



Compound Name	Molecular Weight	Formula	CAS Number	pKa
Oxalixetic Acid	132	C ₂ H ₂ O ₄	328-42-7	1.25
4-Acetylbutyric Acid	130.14	C ₆ H ₁₀ O ₃	3128-06-1	4.63
Pyruvic Acid	88.06	C ₃ H ₄ O ₃	127-17-3	2.65
Levulinic Acid	116	C ₅ H ₈ O ₃	123-76-2	4.78
Glyoxalic Acid	74	C ₂ H ₂ O ₃	563-96-2	2.61
cis-Pinonic Acid	184.23	C ₁₀ H ₁₆ O ₃	61828-55-9	4.72

Method Development

HPOC standards were selected originally because each contained a carbonyl group and possibly could be detected as 2,4DNPH derivatives by liquid chromatography (LC) with UV-Vis detection. An Agilent LC1200 instrument was used, equipped with binary pumps, a diode array detector and a Phenomenex C8 Monolithic column. The binary mobile phase consisted of matched HPLC grade water [90%]; tetrahydrofuran [10%] (Bottle A) and methanol [90%]; tetrahydrofuran [10%] (Bottle B). Although these ketoacids did form 2,4DNPH derivatives, these were relatively weak chromophores. Consequently, the ability to detect and reliably measure atmospheric levels of the ketoacids was in question.

As an alternative approach, the HPOC standard suite was converted to trimethylsilyl (TMS) ethers for measurement by Gas Chromatography/Mass Spectrometry (GCMS). The samples were derivatized with N,O-bis(trimethylsilyl)trifluoroacetamide with trimethyl-chlorosilane (BSTFA-TMS) using hexane and pyridine as the solvents. The chemicals were added under a stream of N₂ gas. The samples were baked at 60 °C for 30-40 minutes to complete the reaction. BSTFA with 1% TMS was purchased through Supelco. The standards and ambient samples as TMS derivatives were analyzed with a Shimadzu QP2010 GCMS.



Agilent LC UV/Vis Ion Trap MS



Shimadzu GCMS

Ambient concentrations of HPOC were characterized in seasonal composites from the SOAP 2002-2003 fine PM network using GCMS analysis, because of superior quantitation and instrument stability.

Ambient Samples Analysis

The method adopted for HPOC was BSTFA followed by GCMS analysis. This method was more robust and a smaller volume of sample could be used which was consistent with the small volume of sample obtained from ambient filters. Finally with a HPLC the only compound verification is the retention time where as the GCMS has both a retention time and a mass spectra.

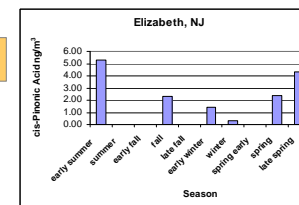
Ambient fine particle samples were extracted with acetone and methylene chloride (1:1) using soxhlet extraction. The acid standards were obtained from Sigma Aldrich. The organic acid standards were run to determine compound retention times and to obtain and confirm spectra as the BSTFA necessary compound specific data. These were combined into a single standard solution that was run as 5-level calibration standards

Results & Discussion

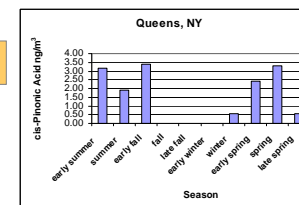
Analysis of the SOAP 2002-2003 fine PM ambient samples solvent-soluble fraction indicated the target HPOC were not consistently present either spatially or seasonally in the NYC airshed. The most abundant HPOC marker, cis-pinonic acid, was found at all SOAP sites. Ambient concentrations were slightly higher at Chester, NJ (background site) and Westport, CT (downwind site) during summer. The highest cis-pinonic acid concentration was 8 ng/m³ at Chester, NJ. Levulinic acid was detected in early summer for Chester, NJ and Elizabeth, NJ. No other ketoacid was found at any other site in the early summer. Pyruvic acid only was found in Queens, NY during summer. Based on this survey of these HPOC target compounds, most are not detected in the metropolitan NYC area. However, the occurrence of measurable levels of a model biogenic SOA such as cis-pinonic acid suggests contributions of other oxidized biogenic compounds likely are present in this urban airshed. The magnitude of the biogenic SOA contribution to fine PM mass in the NYC airshed remains an important topic for future study.

SOAP 2002-2003 Polar PM Marker Profiles

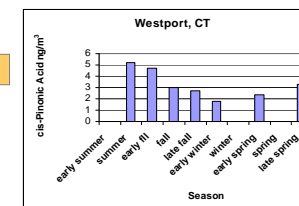
Traffic dominated NJ Turnpike



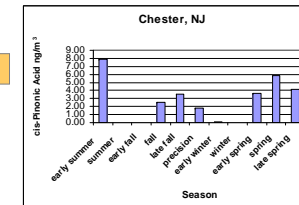
Densely populated urban



Downwind residential



Upwind, background



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