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Speciation and Atmospheric Abundance of Organic Compounds in PM2.5 from the New York City Area. I. Sampling Network, Sampler Evaluation, Molecular Level Blank Evaluation

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This study demonstrates an approach for evaluating a molecular level sampling and analysis protocol for organic marker compounds at the high picogram m^{-3} (ppt) to low nanogram m^{-3} (ppb) mass concentrations in urban and background receptor sites. The Speciation of Organics for Apportionment of $PM_{2.5}$ in the New York City Area (SOAP) project was conducted from May 2002 to May 2003 at four sites in New York City, New Jersey, and Connecticut. Its chief objectives were to expand the chemical characterization of organic compounds and to estimate the source contributions of carbonaceous fine particles at urban and background monitoring sites. Two major challenges were faced in order to successfully implement the SOAP sampling network. First, collection of adequate fine PM mass was necessary for successful quantitation of organic marker compounds. Second, sufficiently low blank levels were required for each marker compound for accurate identification and quantitation needed for source-receptor modeling. Initial field tests of representative samplers designed for sampling PM chemical species indicated insufficient sample mass collection, unless analytical sensitivity for organic markers could be greatly improved. Adequate PM mass was collected using a Tisch TE-1202 sampler that operated at a much higher flow rate (113 lpm). Preliminary field tests also revealed unacceptably high travel blank levels for *n*-alkanes and carboxylic acids. The mass of organic marker compounds observed on travel blank filters was reduced significantly by shipping filters in sealed filter holders. Further evaluation of the Tisch TE-1202 sampler also demonstrated the sampler was free of organic components and impactor grease upstream of the filter. These features also reduced the contribution of carbonaceous species to system blanks and therefore, to the total mass collected. As a result, blank levels for hopanes, PAHs, and dicarboxylic acids were below limits of detection (LOD), and *n*-alkanes (C25 to C32), *n*-alkanoic acids (C12, C14, C16, and C18), and phthalic acid exhibited acceptable low levels in all SOAP blanks ranging from 1 to 10 times the limit of detection for each compound class. Overall, adequate sample mass and sufficiently low blank levels were achieved successfully with the SOAP fine particle collection protocol.

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INTRODUCTION

More than 32 million people in four major urban areas along the Northeast Corridor of the United States live in counties that are in nonattainment of the new National Ambient Air Quality Standards for fine particulate matter ($PM_{2.5}$) (USEPA 2005). Altogether, the metropolitan areas of New York, Philadelphia, Baltimore, and Washington, D.C., account for more than one third of those living in $PM_{2.5}$ nonattainment areas, with most in the New York City metropolitan area (USEPA 2005). Carbonaceous PM is a major if not the largest contributor to $PM_{2.5}$ mass in many U.S. cities, including New York City (USEPA 2004). Since 1980, several field studies have measured and identified extractable organic matter associated with PM in the New York City metropolitan area as part of short-term intensive campaigns (Daisey et al. 1980, 1982, 1984; Lioy et al. 1983; Harkov et al. 1984; Offenberg et al. 2003; Cass, 1998; Fine et al. 2002). These studies focused on specific chemical groups such as PAH compounds and organic acids, or specific source components such as wood smoke markers. The results provided early insights on the composition and sources of organic particulate matter in New York City and the Northeastern United States based on these target groups. The Speciation of Organics for Apportionment of $PM_{2.5}$ in the New York City Area (SOAP) project was initiated for the purposes of expanding the chemical characterization and estimating organic source contributions for urban and background $PM_{2.5}$.

Molecular organic markers in particulate organic matter are useful indicators of $PM_{2.5}$ sources that can be used for source apportionment to help develop control strategies (Simoneit et al. 1980; Currie et al. 1982; Simoneit and Mazurek, 1982; Mazurek, 2002; Mazurek and Simoneit, 1984; Simoneit 1984, 1985, 1986, 1989; Mazurek et al. 1989, 1991, 1997; Hildemann et al. 1991; Rogge et al. 1993; Brown et al. 2002; Cabada et al. 2002; Chen et al. 2002; Fraser et al. 2002, 2003; Chow et al. 2004, 2007; Lee et al. 2002, 2004; Zheng et al. 2002, 2006, 2007; Schauer et al. 1996; Manchester-Neesvig et al. 2003; Sheesley et al. 2004; Yue and Fraser, 2004a,b; de Gouw et al. 2005; Gorin et al. 2006; Herkes et al. 2006; Herner et al. 2006; Ondov et al. 2006a,b; Pekney et al. 2006; Rinehard et al. 2006; Robinson et al. 2006a–c; Subramanian et al. 2006a,b; Ward et al. 2006; Brook et al. 2007; Kleeman et al. 2007). We have refined a method for analysis of molecular markers in fine particulate matter (Li et al. 2005, 2006), and reported earlier the detailed organic chemical composition of particulate matter in Philadelphia (Li et al. 2006; Sihabut et al. 2005; Ray and McDow, 2005). Organic matter emitted from sources such as motor vehicle exhaust, biomass burning, and cooking typically accounts for a considerable fraction of urban fine particles. The organic fraction contains numerous compound classes and individual molecules that can be used as markers which link to sources and/or atmospheric transformation processes. Gas chromatography/mass spectrometry (GCMS) methods were developed by Mazurek et al. (1987, 1989) for analysis of molecular markers associated with urban sources. This protocol has been applied successfully in several U.S. airsheds for source apportionment (e.g., Schauer et al. 1996; Schauer and Cass, 2000; Zheng et al. 2002, 2006, 2007; Fraser et al. 2002, 2003; Manchester-Neesvig et al. 2003; Yue and Fraser, 2004a,b). In this article we describe research results centered on the evaluation and implementation of sampling and analysis procedures for a three state regional $PM_{2.5}$ sampling network. The purpose of the SOAP experiment was to collect fine particulate organic matter to evaluate the molecular markers present and relate this information to emission sources. SOAP results will assist NY, NJ, and CT with the development of air quality management plans aimed at reducing emissions from sources of carbonaceous fine particles. The results we report in this paper focus on a two-year effort that evaluated existing standard operating protocols for Speciation Trends Network (STN) chemical species and modified these protocols for the molecular level sampling and analytical requirements of the SOAP network.

Although the primary purpose of the SOAP project was to support source apportionment specifically in the New York City metropolitan area, the approach and challenges described here can be more broadly applied to other PM sampling networks focusing on source apportionment, epidemiological, and atmospheric chemical studies requiring molecular level organic composition information. For example, existing sampling networks such as STN or the Interagency Montitoring of Protected Visual Environments (IMPROVE) routinely operate multiple sampling channels that can be modified for sampling organic components. Also, archived filters from these networks have great potential for use in understanding sources of exposure and health impacts of species or sources. In the SOAP study, samplers already in use by the STN network were considered carefully and the feasibility of using these samplers was evaluated. Key challenges included collection of sufficient mass reduction of blank levels for accurate quantitation of marker compounds and total organic carbon (OC) aerosol mass, and acceptable sample handling and storage procedures. The evaluation of these sampling challenges and approaches to addressing and validating acceptable alternative procedures are presented.

EXPERIMENTAL

Sampling Network

The SOAP sites were located at existing air quality monitoring sites operated by NY, NJ, and CT (Figure 1). Sites were selected to correspond to existing speciation network sites of the Air Quality System (AQS) $PM_{2.5}$ and the Speciation Trends Network so that simultaneous mass and total organic and elemental carbon concentrations were available. The four sites included the principal U.S. EPA supersite in New York City in Queens, NY; an urban site in Elizabeth, NJ that generally is upwind of the supersite; a suburban site in Westport, CT that usually is downwind of the supersite and is within 1 km of the Long Island Sound; and a regional background site in Chester, NJ. The Queens College site is in an urban area with typical urban traffic patterns. Mobile sources also are likely to contribute a large

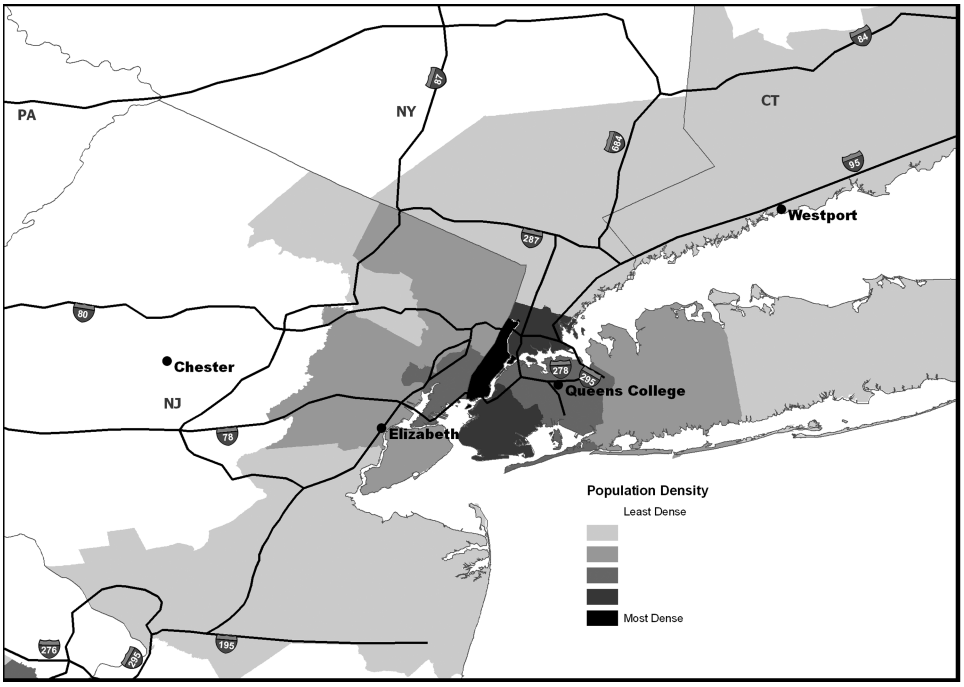

FIG. 1. Map of the SOAP sampling network showing Queens College (Flushing, NY), Elizabeth, NJ, Westport, CT, and Chester, NJ sites.

portion of the fine particulate matter at the Queens site because two busy interstate highways are within 1 km of the site: the Long Island Expressway (I-495) and the Van Wyck Expressway (I-678). Interstate 95 and La Guardia airport also are near the Queens site. Elizabeth, NJ is an urban industrial site adjacent to Toll Plaza 13 of the New Jersey Turnpike. Approximately 220,000 vehicles per day traverse the Turnpike section which is within 500 m of the Elizabeth site (Ozbay, 2006). Three major industrial facilities are located within 1.25 km of the site, and frequently there is heavy air traffic above the site with aircraft en route to Newark Liberty Airport approximately 0.8 km away.

TABLE 1
Target measurements at SOAP 2002–2003 network sites

	Queens [a]	Elizabeth	Chester	Westport
PM-2.5	X	X	X	X
Speciation	R&P	SASS	SASS	R&P
PM-10		X		
O_3	X		X	X
SO_2	X	X	X	X
NOx	X	X	X	X
CO	X	X		
VOCs	X	X	X	
Carbonyls	X	X		
PAH's		X	X	
Meteorological Data	X			X

[a]Queens is an EPA Supersite.

The Elizabeth, NJ site is within 0.5 km of Port Elizabeth which is part of the Port of NY/NJ. The port complex is the largest maritime transportation center in the Eastern U.S. Westport, CT is a coastal suburban site located in Sherwood Island State Park in Fairfield County, approximately 0.5 km south of I-95. Although the immediate vicinity of the site is sparsely populated, it is surrounded by residential suburban neighborhoods beginning within 1 km of the site. Chester, NJ is a rural, commercial site with moderate traffic from local New Jersey Routes 513 (372 meters north) and 24 (221 meters west). Other potential industrial $PM_{2.5}$ sources are at least 5 km away.

Sampling began May 2, 2002 and continued through May of 2003. Samples were collected with a Tisch TE-1202 sampler for 24 hours, from midnight to midnight every third day, following a sampling schedule that was identical to that used by the Speciation Trends Network. Seasonal sample composites were obtained by combining five to ten 24-hour samples at least once per season at each site. Collection dates are listed for composite samples in Supplementary Table 1 and for blanks in Supplementary Table 2. Generally, the number and dates of samples included in a composite were based on the number of samples collected successfully at all four sites in a given season. Westport was excluded from the first two composites because of early sampling problems at that site. Over 700 successful filters were obtained; however, selection of individual samples for composites was based mainly on completeness of the data. In several instances one or more of the samples either failed to sample for the entire period or were otherwise invalidated. Although completeness exceeded 80% at individual sites,

TABLE 2
Molecular level testing of common analytical and sampling background contaminants

Compound	Formula	Source	Diagnostic Ion
1-Butene, 1-methoxy- (E and 1Z isomers)	$C_5H_{10}O$	Analytical reagent background; solvent	71, 86
Benzaldehyde	C_7H_6O	Analytical reagent background; solvent	106, 105, 77
Phenol	C_6H_6O	Analytical reagent background; solvent	94, 66, 65
1,1′-Bipheny	$C_{12}H_{10}O$	Analytical reagent background; solvent	154, 76, 115
(1,1′-biphenyl)-3-ol	$C_{12}H_{10}O$	Analytical reagent background; solvent	170, 141, 115
Tributyl phosphate	$C_{12}H_{27}O_4P$	Plasticizer contributed from reagents, filter storage media (plastic containers), or sampler components	99, 155, 266
Phthalic acid derivatives	homologous series (4 identified)	Plasticizer contributed from reagents, filter storage media (plastic containers), or sampler components	149
Polysiloxanes	homologous series (8 identified)	Column bleed (OV1, 1701, SE30); lubricating grease; base oil; high vacuum grease; soap additive (thickener); vacuum pump oil; bearings lubricant; lubricating grease additive	89, 105, 73
n-Alkanes*	homologous series (27 identified)	Petroleum products; motor oils; lubricating oils; greases; plant waxes; higher vegetation	85, 99, 113
n-Alkanoic acids	homologous series (27 identified)	Petroleum pyrolysis; combustion; metabolic byproduct; fermentation	74, 87, 99

*Used as SOAP molecular markers.

successful collection at all four sites was required for including a sample in a composite. A travel blank and four field blanks were analyzed from each site. A field blank was collected during each season (spring, summer, fall, and winter) at each site, and one additional field blank was collected at Chester during the collocated sampler comparison for a total of four travel blanks and seventeen field blanks. In addition to collecting $PM_{2.5}$ mass and speciation data, criteria pollutants, meteorological data and other pollutants such as volatile organic compounds (VOCs), carbonyls, and polycyclic aromatic hydrocarbons (PAHs) were collected at some of the network sitesk (Table 1).

Organic Compound Chemical Analysis

The full description of the molecular marker extraction and GCMS analysis procedures is reported by Li et al. (2005, 2006). Perdeuterated *n*-tetracosane ($nC_{24}D_{50}$) was added as the internal standard to all blank filter composites prior to solvent extraction. A uniform mass (10 ng) was added to each filter blank composite. The same mass of $nC_{24}D_{50}$ was added to the entire set of ambient filter composites, thereby allowing direct quantitative comparison of the blank organic compositions with the SOAP ambient samples.

Travel, dynamic and field blank filter composites were extracted by soxhlet extraction in 250 ml mixture of 1:1 methylene chloride: acetone. The extracts were evaporated to 5 ml by using a Kuderna-Danish apparatus and then to 100 μL by high-purity nitrogen gas. The extracts were divided into two portions for further analysis by a Varian Saturn 3800 GC Gas Chromatograph/Ion Trap Mass Spectrometer (GCMS). One aliquot was derivatized by adding freshly prepared diazomethane (CAS number 334-88-3) to convert organic acids and phenolic compounds to their methyl derivatives (Fatty Acid Methyl Ester "FAME" fraction) (Mazurek et al. 1987, 1989). Approximately 1 μl of concentrated extract was injected in splitless mode onto a DB-1701 fused silica capillary column to separate organic mixture components (30 m length, 0.25 μm coating thickness and 0.25 mm internal diameter, Agilent/J&W Scientific, Wilmington, Delaware). The GC temperature program consisted of the following steps: (1) initial isothermal hold for 3 minutes at 50°C; (2) a temperature ramp of 20°C /min up to 150°C; (3) isothermal hold for 3 minutes; (4) temperature ramp of 4°C/min to 280°C; and (5) a final isothermal hold of 17 minutes.

Selective ion monitoring (SIM) was used to test for background levels of common contaminants that have the potential to interfere with organic marker analysis. Common classes of contaminants tested are summarized in Table 2 and are listed individually in Supplementary Table 3. Standard mixtures were prepared for the SOAP ambient molecular markers (Table 3), providing the highest level of compound authentication and quantitation in the organic extract mixtures. The internal standard ($nC_{24}D_{50}$) was added to the standard suites. A single quantitation ion (m/z) was used with two confirming ions (m/z) for the compound measurement. Quantitation was based on linear five-point calibration curves ($R^2 > 0.95$) for each compound (Li et al. 2005) determined before and after sample analysis.

TABLE 3
SOAP molecular markers

Compound	Formula	MW	Quan Ion	Ref Ion 1	Ref Ion 2
n-alkanes					
n-Pentacosane	C25H52	352	71	57	85
n-Hexacosane	C26H54	366	71	57	85
n-Heptacosane	C27H56	380	71	85	57
n-Octacosane	C28H58	394	71	57	85
n-Nonacosane	C29H60	408	71	57	85
n-Triacontane	C30H62	422	71	57	85
n-Hentriacontane	C31H64	436	71	57	85
n-Dotriacontane	C32H66	450	71	57	85
PAHs					
Benzo[b]fluoranthene (Benz[e]acephenanthrylene)	C20H12	252	252	253	251
Benzo[k]fluoranthene	C20H12	252	252	253	251
Benzo[e]pyrene	C20H12	252	252	253	251
Indeno[1,2,3-cd]fluoranthene	C20H12	276	276	277	137
Indeno[1,2,3-cd]pyrene	C22H12	276	276	277	138
Benzo[g,h,i]perylene	C22H12	276	276	138	125
Coronene	C24H12	300	300	150	149
Hopanes					
18alpha(H)22,29,30-Trisnorneohopane	C27H46	370	191		
17alpha(H)-22,29,30-Trisnorhopane					
17alpha(H),21beta(H)-29-Norhopane	C29H50	398	191		
18alpha(H)-29-Norneohopane					
17alpha(H),21beta(H)-Hopane	C30H52	412	191		
22S-17alpha(H),21beta(H)-30-Homohopane	C31H54	426	191		
22R-17alpha(H),21beta(H)-30-Homohopane	C31H54	426	191		
22S-17alpha(H),21beta(H)-30-Bishomohopane	C32H56	440	191		
22R-17alpha(H),21beta(H)-30-Bishomohopane	C32H56	440	191		
n-Akanoic acids					
C9	C10H20O2	172	74	87	99
C10	C11H2202	186	74	43	87
C11	C12H2402	200	74	43	87
C12	C13H26O2	214	74	43	87
C13	C14H28O2	228	74	43	87
C14	C15H30O2	242	74	87	43
C15	C16H32O2	256	74	87	43
C16	C17H34O2	270	74	87	43
C17	C18H36O2	284	74	87	43
C18	C19H38O2	298	74	87	43
C19	C20H40O2	312	74	87	43
C20	C21H42O2	326	74	87	43
C21	C22H4402	340	74	87	43
C22	C23H46O2	354	74	87	43
C23	C24H48O2	368	74	87	43
C24	C25H50O2	382	74	87	43
C25	C26H52O2	396	74	43	87
C26	C27H54O2	410	74	43	87
C27	C28H56O2	424	74	43	87
C28	C29H58O2	438	74	87	43

(Continued on next page)

TABLE 3
SOAP molecular markers (*Continued*)

Compound	Formula	MW	Quan Ion	Ref Ion 1	Ref Ion 2
C29	C30H60O2	452	74	43	87
C30	C31H62O2	466	74	43	87
Dicarboxylic Acids					
Malonic	C5H8O4	132	101	74	57
Succinic	C6H10O4	146	115	55	87
Methyl succinic	C7H12O4	160	129	59	100
Glutaric	C7H12O4	160	100	101	129
Adipic	C8H14O4	174	111	114	55
Suberic	C10H18O4	202	138	69	129
Phthalic	C10H10O4	194	163	133	164
Isophthalic	C10H10O5	194	163	135	193
Azelaic	C11H20O4	216	152	55	83

RESULTS AND DISCUSSION

Speciation Sampler Evaluation

Because STN samplers have been operating routinely throughout the United States for more than seven years, a convenient and efficient approach for collecting organic PM for understanding source contributions to PM ambient levels would first involve little to no modification of these existing collectors. The suitability of the STN speciation samplers for subsequent molecular level analysis of the PM filters was evaluated with a subset of molecular marker compounds in this study. The test markers included the *n*-alkanes, PAHs, hopanes, and *n*-alkanoic and dicarboxylic acids (as methyl esters). The two objectives of this evaluation were (1) to verify that sufficient fine $PM_{2.5}$ mass was collected in a composite sample for each of the target compounds to be analyzed, and (2) to verify that blank levels were sufficiently low for each marker, and thereby avoid sampling bias that could cause interference with accurate identification and measurement.

We first investigated the feasibility of molecular marker analysis generated from composite samples. The ambient samples were collected on 47 mm quartz fiber filters using an extra channel of an approved speciation sampler. Original plans called for the evaluation of four samplers available for speciation sampling: Anderson Reference Ambient Air Sampler (RAAS) Met One Speciation Air Sampling System (SASS), University Research Glassware (URG) Mass Aerosol Speciation Sampler (MASS), and Rupprecht & Patashnick (R&P) Partisol Model 2300 Speciation Sampler. Except for the R&P 2300 Partisol Sampler, each sampler was evaluated for total organic carbon mass in $PM_{2.5}$ samples by Solomon et al. (2000). At the time of implementation, all three states involved in the SOAP study had selected either the Met One SASS or the R&P Partisol 2300 Speciation Sampler for use in the Speciation Trends Network so initial sampler evaluation was limited to these two instruments.

A composite fine PM sample was generated by sampling all channels in parallel with the Met One SASS and the R&P Partisol 2300 instruments. The Met One SASS was operated at a flow rate of 6.7 liters per minute (9.6 m^3 sampled air volume) and the R&P Partisol 2300 sampled at a flow rate of 10.0 liters per minute (14.4 m^3 sampled air volume). The Chester, NJ, site upwind of the NYC metropolitan area was selected as the evaluation site since it consistently had the lowest $PM_{2.5}$, EC and OC masses of all four sites based on evaluation of STN reported data. Consequently, the Chester, NJ, site would provide the greatest challenge for collection of sufficient $PM_{2.5}$ mass and associated organic molecular marker quantitative measurement.

Neither the Met One SASS nor the R&P Partisol 2300 speciation sampler collected sufficient mass for quantitative analysis of all classes of compounds by GCMS. Ample amounts of *n*-alkanes and *n*-alkanoic acids were collected with both samplers. There was no difficulty quantifying alkanes or carboxylic acids from the composite ambient test samples. The *n*-alkanes contained 22 to 28 carbon atoms and each homolog ranged in concentration from about 10 to 50 ng/m^3. However, other key species of high value for source apportionment such as hopanes and PAHs, were not detected because insufficient PM2.5 total mass was collected. In earlier source apportionment studies of particulate organic matter, hopanes were identified as a valuable marker for motor vehicle exhaust (Schauer et al. 1996). Only two hopanes were detected of the eight hopanes reported in relevant motor vehicle source profiles. The two hopane homologs were barely above limits of detection ($\sim$0.01 ng m^{-3}). Detection limits for the marker compounds as groups were determined by GCMS analysis of low concentration standards with concentrations prepared in the range of 0.001 to 0.1 μg/mL. Mass-to-charge (m/z) ions were monitored corresponding to the quantitation ion of the molecular markers (Tables 4 and 5). If the area of the m/z ion was greater than 5 times the area of the baseline noise peak, the compound was judged "detected" by

TABLE 4
Composition of trace level organic background chemicals contributed from extraction solvents in SOAP travel and field blanks

Retention Time[a] (min)	Compound	MW	CAS #	Quantitation ion (m/z)
	SAMPLE: Elizabeth NJ #1 TRAVEL BLANK (derivatized, acid+neutral fraction)			
7.363	Cyclopentasiloxane,decamethyl-	370	541-02-6	73, 267, 355
8.773	Cyclohexasiloxane,dodecamethyl-	444	540-97-6	73, 341, 429
5.915	Cyclotetrasiloxane,octamethyl-	296	556-67-2	73, 281, 282
10.820	Cycloheptasiloxane,tetradecamethyl-	518	107-50-6	73, 147, 281
14.038	Cyclooctasiloxane,hexadecamethyl-	592	556-68-3	73, 221, 355
5.825	2-Pentanone, 4-hydroxy-4-methyl	116	123-42-2	43, 45, 58
5.746	2-Pentanone, 4-hydroxy-	102	4161-60-8	43, 45, 58
6.718	2-Hexanone, 4-hydroxy-5-methyl	130	38836-21-4	41, 43, 87
36.740	Bis-2-ethylhexyl phthalate	390	117-81-7	57, 149, 167
	SAMPLE: Elizabeth NJ #1 TRAVEL BLANK (underivatized, neutral fraction)			
5.645	Propanoic aicd, 2-methyl-	88	79-31-2	41, 43, 73
6.103	Diacetone alcohol	116	123-42-2	43, 59, 101
6.950	2-Hexanone, 4-hydroxy-5-methyl-	130	38836-21-4	41, 43, 87
7.528	Cyclopentasiloxane, decamethyl-	370	514-02-6	73, 263, 355
8.263	2-Butanol, 3-methyl acetate	130	5343-96-4	43, 70, 87
8.990	cyclohexasiloxane,dodecamethyl-	444	540-97-6	73, 341, 429
37.392	Bis-2-ethylhexyl phthalate	390	117-81-7	57, 149, 167

[a]GC/MS retention times based on the following program: Total run time of 60.5 minutes with the following steps: 1) initial isothermal hold for 3 minutes at 50°C; 2) a temperature ramp of 20°C /min up to 150°C; 3) isothermal hold for 3 minutes; 4) temperature ramp of 4°C/min to 280°C; and 5) a final isothermal hold of 17 minutes.

TABLE 5
Comparison of area ratios of molecular marker quantitation ions to m/z to n-$C_{24}D_{50}$ internal standard m/z 82 for tracers present above the instrument detection levels for the Varian Saturn 3800 GCMS

Molecular Marker	All SOAP Blanks Average Area Ratios (n = 17)	All SOAP Blanks STD[a]	All SOAP RSD[b]	All SOAP Ambient Average Ratios (n = 40)	Average Area Ratio All SOAP Ambient/Average Area Ratio All Blanks
n-Alkanes[b]					
nC25	0.00132	0.00096	73	0.05915	45
nC26	0.00106	0.00094	89	0.04065	38
nC27	0.00138	0.00096	69	0.05508	40
nC28	0.00136	0.00083	61	0.02696	20
nC29	0.00162	0.00052	32	0.08041	50
nC30	0.00159	0.00077	49	0.03071	19
nC31	0.00137	0.00054	40	0.05120	37
nC32	0.00092	0.00057	62	0.01108	12
Mono and Diacids as FAME[c]					
C12 FAME	0.01004	0.00762	76	25.30060	6
Phthalic	0.07454	0.11694	157	52.35560	3
C14 FAME	0.01318	0.00700	53	17.70418	7
C16 FAME	0.06717	0.03072	46	15.28006	7
C18 FAME	0.06410	0.03290	51	17.14010	4

[a] Standard Deviation (STD) calculated as the square root of the mean of the squared deviation values.
[b]Relative Standard Deviation (RSD) calculated as coefficient of variation = (STD/Mean)*100
[c]LOD expressed as area ratios to the internal standard n-$C_{24}D_{50}$ were: hopanes, 0.00073; n-alkanes. 0.00025; PAH, 0.00210; diacids, and n-alkanoic acids, 0.00720.

the Varian ion trap GCMS. M/z areas were converted to ambient mass concentrations using compound response factors and the air volume for a typical sample composite. For polycyclic aromatic hydrocarbons, concentrations of all target compounds were consistently below the detection limit ($\sim$0.05 ng m^{-3} for the PAH compounds). Detection limits for *n*-alkanes were 0.01 ng m^{-3}, and were 0.02 ng m^{-3} for diacids and *n*-alkanoic acids (Li et al. 2005). Based on these results from the Met One SASS and R&P 2300 Partisol speciation samplers, we concluded that greater sensitivity was required for these samplers to be used routinely for molecular marker analysis. The Tisch TE-1202 sampler was selected as a candidate sampler for evaluation because its substantially higher flow rate allowed collection of greater $PM_{2.5}$ mass.

The Tisch TE-1202 sampler had a considerably higher flow rate than the other speciation samplers tested. The sampler operated at 113 liters per minute (162.7 m^3 sampled air volume) and was equipped with a 2.5 μm cyclone inlet (Part No. TE-3-900-20). It was designed to sample with a filter and polyurethane foam sorbent in series. For sampling in the SOAP network, just the filter portion of the Tisch collector was used because only the particulate components were of interest. Particles were collected on quartz fiber filters which were processed at 550–600°C, to produce low carbon background levels needed for molecular marker chemical analysis (Mazurek et al. 1987, 1989).

Bulk Carbon Background Evaluation

Besides $PM_{2.5}$ sample mass, a second major objective of this project was to obtain blank levels low enough for quantitative analysis of each marker compound. This goal required identification of all background organic matter and verification that contaminant mass levels were approximately a factor of 10 less than the 300 pg m^{-3} to 10 ng m^{-3} ambient concentrations typical of most molecular markers. Therefore, early in the SOAP network design an initial study was conducted on the existing STN samplers at the four SOAP sites as potential instruments for fine particle organic molecular marker analysis. Using an approved speciation sampler was a desired outcome for two reasons. First, the samplers were already at the sites, and second, state operators were experienced in the standard operating procedures involving the instruments. Inspections were performed of the candidate samplers and interviews were conducted with the site operators at the collocated SOAP and STN sites. During this preliminary step, potential sources were noted of organic contamination stemming from sample collection and handling procedures. Molecular-level GCMS analysis of a combination of travel, dynamic and field blanks were used to isolate the source(s) of carbon contamination to ambient samples. Field blanks were filters placed in the sampler for the same period as a real sample, but for which the sampler was not in operation (i.e., no air flow through the sampler). The dynamic blank test for potential contaminants from the sampler was carried out by placing the filter holder in the sampler, turning the sampler on for 10 minutes, and removing the blank filter. In all other aspects, field and dynamic blanks were treated as samples, and underwent the same shipping and storage procedures. The travel blank was prepared and shipped in the same manner as the samples, but was not removed from the polyethylene bags by the site operators. Only laboratory personnel opened the travel blanks after the blanks were returned from the field. Multiple blanks of each type were collected to correspond to the anticipated number of ambient filters that would eventually be grouped to form a composite.

The quartz microfiber sampling filters usually collect considerable organic carbon mass on passive exposure to ambient air (McDow and Huntzicker 1990). Also, impactor greases and plastic sampler parts can be sources of organic contaminants (Mazurek et al. 1991). Common organic contaminants that may be contributed from commercial sampler components include plastic, rubber, oils, and hydrocarbon and silahydrocarbon greases (Table 4). Artifacts can be single compounds or, more frequently, as homologous series and complex mixtures present in greases and oils. Molecular level analysis of several blanks was performed by GCMS analysis of the filter extracts. Selected ion monitoring (SIM) targeted homologous compound series and individual compounds in the blank samples (Table 4).

Travel blanks from the initial sampler tests with the Met One SASS and R&P Partisol 2300 speciation samplers indicated unacceptably high *n*-alkane levels. The presence of the *n*-alkanes most likely was due to grease or oils contributed by sample storage and handling operations, and unrelated to sampler materials or characteristics. However, because of the small sampling flow rates, a relatively small mass of *n*-alkanes in the travel blanks translated into substantial contributions to apparent ambient concentrations, in excess of 1 ng m^{-3}. Therefore, before proceeding with the Tisch TE-1202 sampler evaluation, an effort was devoted to improving the design of the filter housing cassettes and shipment packaging materials. The filter cassettes would be used to store the unsampled blanks and sampled filters during shipping and storage at the sites. The goal of the design effort was to produce a shipping module that would substantially reduce or eliminate the unacceptable *n*-alkane levels in the travel blanks. The sample filters used for the study were baked at 600°C in a muffle furnace for 4 hours to remove organic contaminants. Immediately after baking out, filters were placed in shipping modules specially designed for this project. A shipping module is shown in Figure 2. It consisted of three parts: (1) the filter holder to be used in the sampler; (2) an aluminum shield that seals off the upstream portion of the filter holder from exposure to airborne contaminants; and (3) a plug that seals off the downstream portion. The shipping module was placed in a resealable polyethylene bag and placed in a commercial, well-insulated cooler (36 quart volume) and chilled to $\leq$4°C using 6 to 8 freeze-packs (Little Shivers, Lifoam Corp.). The coolers were shipped to the state agencies responsible for sampling. Once collected, the site operators were instructed to store the

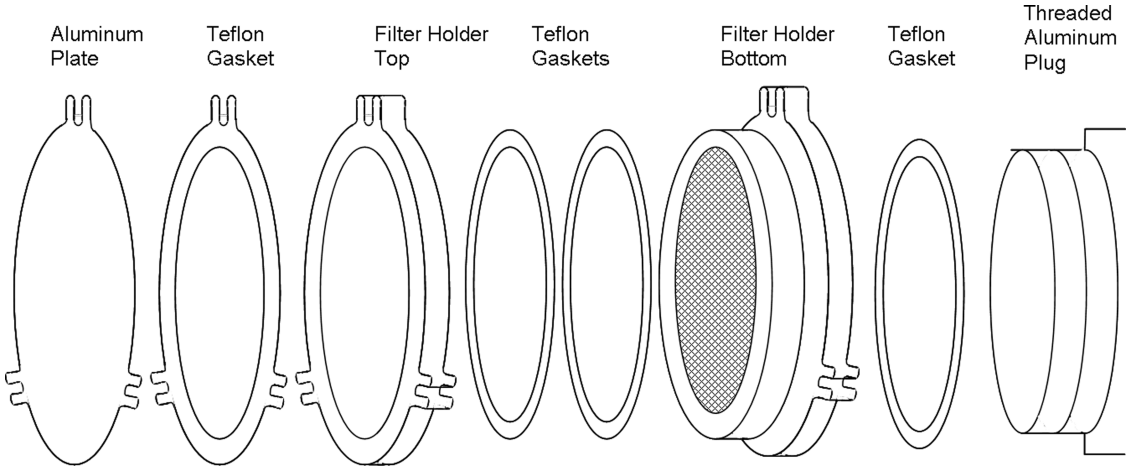

FIG. 2. Shipping Module for Filter Holder.

filter holders in onsite freezers until shipping by overnight express delivery to the laboratory. Upon return to the PI's analytical laboratory, sampled filters were removed from the filter holders and stored frozen at –10 C in prefired glass jars to prevent alteration of the organic compounds prior to the molecular marker analysis process.

The Tisch TE-1202 sampler is well suited for the collection of organic PM. As previously indicated in samplers not specifically designed for this purpose, the impactor greases and plastic and rubber sampler parts can be sources of organic contaminants collected along with the ambient PM (Mazurek et al. 1991). In the Tisch sampler the $PM_{2.5}$ cutpoint is achieved with a cyclone inlet and inlet tubes and filter holders are constructed from anodized aluminum. Therefore, impactor greases and organic polymeric materials such as plastic, rubber or other carbon-containing components are not present upstream of the sample filter.

After developing and incorporating the filter shipping modules, the carbon blank levels associated with the Tisch sampler were evaluated using field, dynamic and travel blanks. The purpose of this study was to investigate the importance of deposition and contamination of the prefired microquartz filters. In an initial field test of the Tisch sampler, the *n*-alkanes were the only compounds detected in any of the blanks, and in all cases, average blank levels were present at concentrations under 300 pg m^{-3}. These blank levels were generally less than about 10% of ambient sample concentrations of 2 to 8 ng/m^3 recently observed in Philadelphia ambient PM10 samples (Li et al. 2006). Field blanks appeared to be greater than the travel blanks, and dynamic blanks indicated no significant contribution from the sampler. Overall, the Tisch TE-1202 sampler was judged to be the only sampler option for the SOAP network because of two factors: 1) larger ambient sample size, and 2) significantly lower background organic carbon levels. New Tisch TE-1202 (2-channel) or TE-1204 (4-channel) samplers were purchased by the states and installed and tested at the 4 sites before beginning operation of the SOAP network for ambient samples.

SOAP Network 2002–2003 Blanks

Blanks consisted of 1 to 4 filters that were scheduled during the SOAP network operation (13 months). Every sixth sampling day corresponding to the STN PM sampling schedule (i.e., every calendar eighteenth day) was designated for field blank collection (Supplementary Table 2). Travel blanks were never opened except by laboratory personnel while in the analytical lab. During operation of the SOAP network, field blanks were collected on non-sampling days designated by the STN annual schedule. Field blanks were exposed from 1–2 days within the Tisch collector to monitor the exposure of ambient filters while the sampler was off (no air flow through sample filters). Since no significant contribution from the Tisch sampler was indicated by the initial field test, dynamic blanks were not collected during the SOAP 2002–2003 field experiment due to scheduling and logistical constraints at the 3 state-operated STN/SOAP sites.

All blanks were treated identically to the ambient filters, including molecular level analysis by GCMS. Composites were generated seasonally to coincide with the seasonal composites of the SOAP ambient samples. Figure 3a–f shows the GCMS plots of the Reconstructed Ion Current (RIC) for the Elizabeth, NJ, travel blank, summer 2002, fall 2002, winter 2002/03, and spring 2003 field blank, and the summer 2002 ambient PM sample composite (July 25, 28, August 12, 15, 18, 21, 24) for comparison. The SOAP travel and field blanks from all 4 sites were virtually the same in composition and abundance to those blank composites shown for the Elizabeth, NJ site.

Table 4 lists the retention time, compound identity, molecular weight (MW), Chemical Abstracts Service (CAS) number, and quantitation ions for peaks present in the Elizabeth, NJ blanks. Contaminant compounds were identified by comparing the peak mass spectral fragmentation pattern with the NIST/EPA/NIH Mass Spectral Database (release 2, 2002). The early peaks <10 min are low MW polar compounds that are trace impurities in the high-purity extraction solvents and reagents. Siloxanes are another subgroup of contaminants eluting before

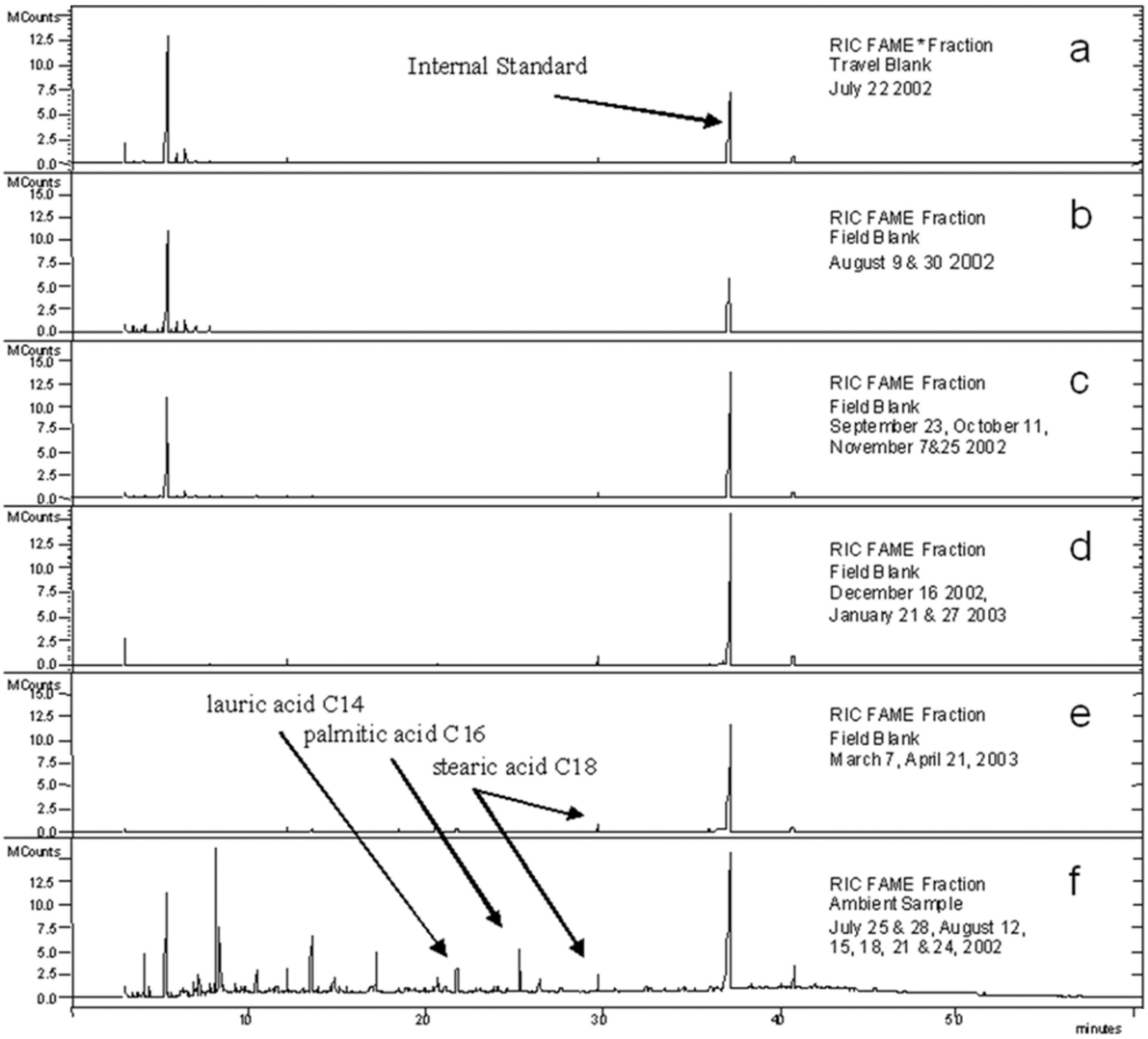

FIG. 3. Comparison of the organic complex mixture (as methyl derivatized fraction, Fatty Acid Methy Esters, FAME) extracted from Elizabeth, NJ, travel and seasonal composite field blanks with a summer ambient sample composite. The reconstructed ion current (RIC) intensity is plotted against elution time.

10 min and likely are from distillation apparatus used in the manufacture of distilled-in-glass grade high-purity solvents. The siloxanes demonstrated m/z 73 ions in the mass spectra and the spectra matched well with the NIST database. The single large peak at 37.39 minutes is 1,2-benzenedicarboxylic acid, mono-2-ethylhexyl ester ("diethylhexyl phthalate," DEHP). DEHP has a base peak of m/z 149 and was present in all SOAP blanks. DEHP is a common plasticizer found in vinyl and plastic products, including chemical packaging materials, plastic tubing and laboratory vinyl gloves. The impurities were present at roughly the same level in all blanks and ambient samples and did not interfere with the identification and measurement of the molecular markers because Selected Ion Monitoring detection (SIM) was used for quantitation. Peaks eluting before 10 min were not generally of interest for the SOAP study. The absence of many unresolved peaks in the blank RIC plots from 30 to 50 minutes demonstrates hydrocarbon lubricating greases and oils were not present. Because most compounds present in the travel and field blanks were semivolatile compounds eluting before 10 min, we believe the organic contaminants were contributed from extraction solvents and chemical reagents, most likely during the solvent extraction and diazomethane addition steps. Very little organic background was contributed to the organic mass during the sample collection, handling and storage stages based on the comparison of the SOAP travel and field blanks (21 total blanks). The absence of higher molecular weight compounds, specifically *n*-alkanes and the polysiloxanes as monitored by GCMS SIM, verify low and acceptable organic carbon background levels during sample collection, transport, and storage.

Additional verification was needed to confirm the suitability of the chemical analysis procedures for molecular marker quantitation using SIM and key m/z ions. All SOAP travel and

field blanks were monitored for the complete suite of markers using the characteristic m/z ions (Table 3). An equivalent mass of the internal standard was added to each blank composite and ambient composite (n-$C_{24}D_{50}$ total added mass = 10 ng), which allowed a mechanism for quantitative comparison of the blank levels to the ambient samples. Area ratios of the marker compound m/z quantitation ion to m/z 82 of n-$C_{24}D_{50}$ were calculated for each ambient sample and blank (Table 5). The average area ratio, standard deviation (STD) and relative standard deviation (RSD) were calculated for each marker compound in all SOAP blanks (n = 20). The average blank area ratio for the marker compound was compared to the ambient sample average area ratio (n = 40) to verify whether the blank concentrations were low enough for accurate quantitation of that compound. Most marker compounds in the SOAP 2002–2003 blanks were below limits of detection. The limit of detection area ratios to n-$C_{24}D_{50}$ were calculated as: hopanes = 0.00073; n-alkanes = 0.00025; PAH = 0.00210; diacids and n-alkanoic acids = 0.00720.

Thirteen out of 39 molecular markers were detected in some blanks when monitored by SIM (Table 5). PAHs and hopanes were not detected in any blank. Low levels of C25 to C32 n-alkanes were detected by GCMS SIM analysis. These alkanes were detected in the Queens and Westport travel blanks and only 1, 2, or 3 homologs were detected in five out of 12 total field blanks. The average areas of the m/z quantitation ion for the marker compounds shown in Table 5 were compared to the average areas of the same ion in the blanks. The average ambient levels for the individual n-alkanes were from 12 to 50 times higher than the average area ratio for that homolog in the blanks. The lowest ambient to blank comparisons were for the n-C30 (19 times) and n-C32 (12 times) alkanes and were approximately 4 to 6 times higher than the average blank levels. The highest ambient to blank comparisons were 45 (n-C25) to 50 (n-C29) times the blank levels.

Blank levels were generally lower than limits of quantitation. Guidelines provided by the ACS Committee on Environmental Measurements establish the limit of quantitation as 10 times the standard deviation just above the limit of detection (LOD) (ACS 1980). These guidelines have been updated by Keith (1991) with the same recommended factor and have also been recognized by the U.S. EPA (USEPA 2003). With the exception of the n-C30 and n-C32 alkanes, the blanks were comfortably below the analytical method limits of quantitation for the n-alkane molecular markers. However, in the worst case blank levels of the n-C30 and n-C32 alkanes were still only about 5–10% of ambient levels for these compounds, and blank subtraction of these compounds is likely to have little effect on ambient concentration.

Mono- and dicarboxylic acids also were screened in the SOAP blanks. The average area ratios of target compounds in all blanks were calculated for each compound using the quantitation ion and m/z 82 of the internal standard (n-$C_{24}D_{50}$) (Table 5). Most compounds were below the detection limits (BDL, ratio of quantitation ion to m/z 82 for n-$C_{24}D_{50}$ = 0.0072 area ratio). Only the C_{12}, C_{14}, C_{16}, C_{18}, monocarboxylic acids and phthalic acid were present in the SOAP blanks above this threshold. The relative standard deviations of the field blanks for these compounds ranged from 46% (C_{16} acid) to 157% (phthalic acid). The high variability of the acids present in the SOAP blanks can be explained by the fact the measurements were conducted with marker concentrations ranging from 1–10 times the LOD level (0.00720 area ratio). Because the presence of the C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, and phthalic acids in the blanks were between only 1 to 10 times limits of detection, blank subtraction is likely to have little impact on ambient sample concentration. Overall, the SOAP 2002–2003 blanks were consistently below or near limits of detection for all target molecular markers.

CONCLUSIONS

Measurement of organic molecular markers in fine PM requires detailed chemical analysis at the bulk and molecular levels. Test ambient filters collected with candidate samplers must be screened for the presence of marker compounds and for adequate mass of each marker compounds for good quantitation. The SOAP 2002–2003 fine PM sampling network demonstrated high quality control levels with the 80% success rate of ambient filters collected and with the organic marker background levels in the field and travel blanks below limits of detection for 26 of 39 target compounds. The markers screened in the SOAP blanks using new Tisch speciation samplers were at very low levels. Over 67% of all molecular markers in the SOAP 2002–2003 blanks, including the compound classes of hopanes, PAHs, dicarboxylic acids, and about half of the monocarboxylic acid markers, were below limits of detection. The other 33% of the markers (C25–C32) were present in mass levels from 1 to 10 times the limit of detection. N-alkanes from 25 to 32 carbons are contained in petroleum based lubricating oils and greases. These compounds were seen initially at unacceptably high levels in test ambient filters collected with STN samplers available at the SOAP monitoring sites. Evaluation and slight modification of the Tisch speciation samplers eliminated the contribution of high background levels of the petroleum-derived n-alkanes. The Tisch samplers also provided $PM_{2.5}$ samples with sufficient mass for good quantitation of the target organic markers given the higher operating flow rates with this sampler.

Limits of detection (LOD) and limits of quantitation (LOQ) were determined for all organic markers using the current U.S. EPA guidelines. Because the background levels of marker compounds were near or below detection limits (BLD), we developed an alternative method of comparing SOAP blank mass levels with the ambient mass levels for each marker. The target n-alkanes were 12 to 50 times greater in mass compared to the average levels determined for 20 SOAP field and travel blanks. N-alkanoic acids and phthalic acid had lower mass ratios of the average ambient samples to average blanks that ranged from 3 to 7.

Incorporating routine evaluation of field and travel blanks provided good knowledge of the background levels of organic

markers. This practice is essential for confirming molecular marker ambient concentrations as well as for bulk carbonaceous fine PM fractions such as elemental (EC) and organic carbon (OC).

Three major outcomes of this effort to establish and validate the SOAP network sample collection procedures are relevant to adapting current monitoring networks and to designing new field studies requiring collection of organic molecular markers. First, greater sensitivity is required for STN samplers to be useful for quantitative marker analysis. Second, shipping filters in sealed containers significantly reduces semivolatile organic contaminants. Third, sampling in the absence of impactor grease or plastic, rubber or polymeric organic carbon sampler components provided sufficiently low travel blanks. This step avoided organic species blank problems that otherwise would have introduced interferences, preventing accurate detection and quantitation of molecular markers. The focus on the molecular level organic constituents benefited OC mass levels in the SOAP field and trip blanks. These results are useful guidelines for designing new sampling or updating current protocols for field measurements of organic marker compounds.

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