



Chemical speciation of organic aerosol during the International Consortium for Atmospheric Research on Transport and Transformation 2004: Results from in situ measurements

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[1] We report the first ever hourly in situ measurements of speciated organic aerosol composition. Measurements were made during July and August 2004 at Chebogue Point, Nova Scotia, using a novel thermal desorption aerosol GC/MS-FID (TAG) instrument as part of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT). Hourly time resolution measurements of organic marker compounds were used to define several different source types contributing to the aerosols observed, including two aged anthropogenic sources from the United States, oxidized biogenic aerosols from Maine and Canada, local biogenic contributions to secondary organic aerosol (SOA), local anthropogenic contributions to hydrocarbon-like organic aerosol (HOA), and a potential marine or dairy source. These TAG-defined sources were used to separate aerosol mass spectrometer (AMS) measurements of total organics, SO_4^{2-} , NO_3^- , and NH_4^+ , along with total aerosol black carbon (BC) into several distinct particle types. Average organic aerosol mass ranged from 33% of the total aerosol mass during anthropogenic U.S. outflow events to 81% of total aerosol mass during biogenic oxidation events arriving from Maine and Canada during 26 July to 15 August 2004.

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1. Introduction

[2] Understanding the origins, transformations, and fate of aerosols present in the Earth's atmosphere is critical to determining the extent to which these particles affect human health and the global radiation balance [*Intergovernmental Panel on Climate Change*, 2001; *Schwartz et al.*, 2001]. The ICARTT 2004 project was aimed at characterizing particle and gas phase pollution exported from North America and its effect on the global troposphere [*Fehsenfeld et al.*, 2006]. Here we use chemically resolved measure-

ments of organic aerosol and related tracers from Chebogue Point, Nova Scotia during ICARTT 2004, to determine the origins of atmospheric aerosols at this site, characterize their chemical properties, and determine the relative importance of their major sources. Hourly measurements of specific marker compounds in the organic portion of atmospheric particles provides a valuable and widely applicable tool for understanding chemical processing and source apportionment of the atmospheric aerosol. By defining and separating particle sources with higher time resolution than is possible with traditional filter collection we can compare with other fast changing meteorological, radiation, gas, and particle measurements, increasing understanding of the contributions that primary and secondary biogenic and anthropogenic sources have on total aerosol concentration and composition.

[3] Over the past few decades, significant progress has been made in measuring organic aerosol chemical composition and defining signatures of specific source categories, using filter collection followed by solvent extraction [*Rogge et al.*, 1993a, 1993b, 1993c; *Schauer and Cass*, 2000] or thermal desorption [*Waterman et al.*, 2000; *Falkovich and Rudich*, 2001] and GC/MS analysis. In this study, we used a new in situ instrument, thermal desorption aerosol GC/MS-FID (TAG), to identify and quantify organic aerosol chem-

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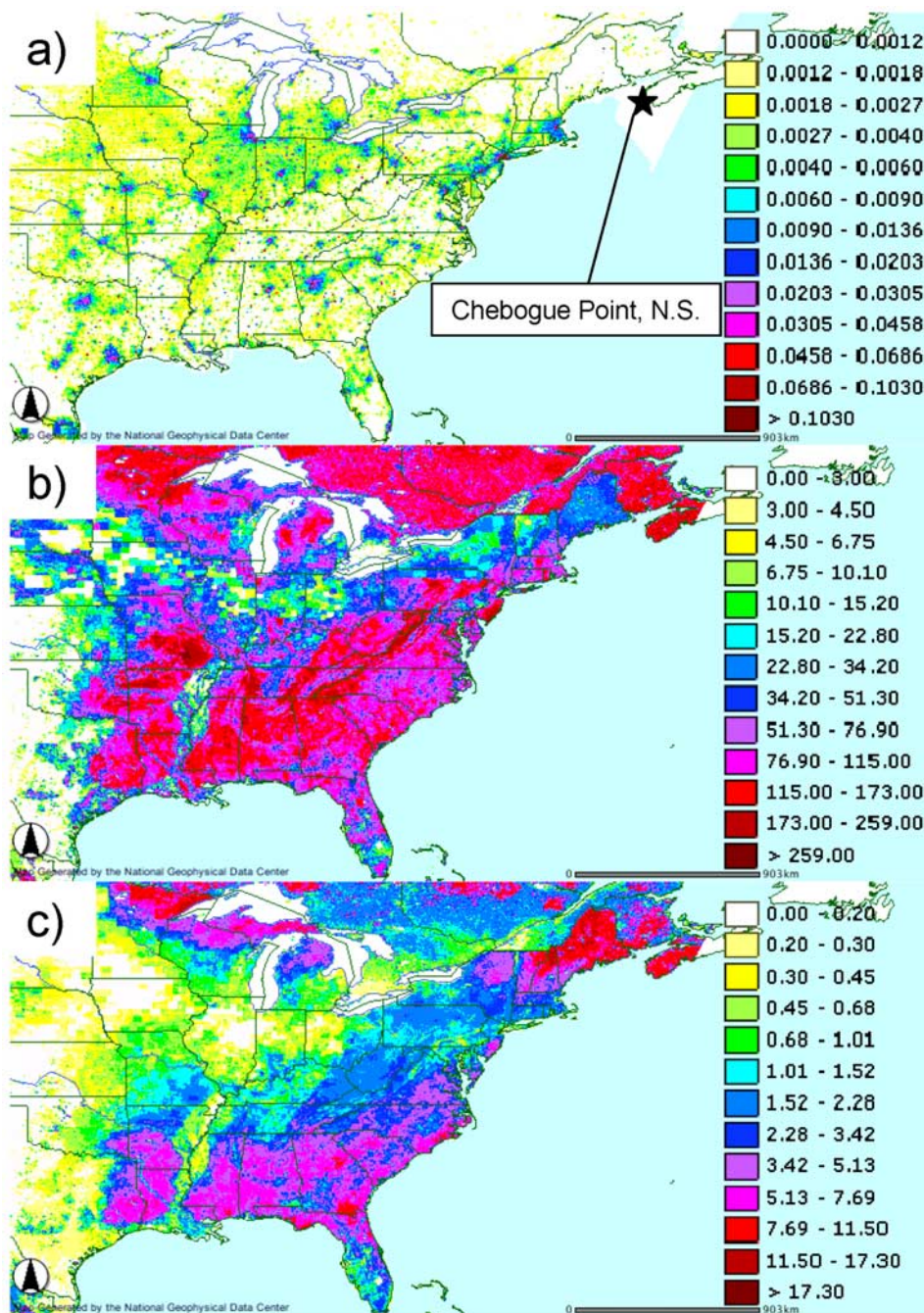


Figure 1. View of the ground-based field site at Chebogue Point, Nova Scotia ($43.75^{\circ}N$, $66.12^{\circ}W$). (a) Anthropogenic $PM_{2.5}$ -PRI emissions in short tons/ozone season day/grid cell, plotted on a 4-km Lambert-Conformal grid. (b) Isoprene BEIS3.11 reference emissions in moles/ km^2 /hr. (c) Terpene BEIS3.11 reference emissions in moles/ km^2 /hr. These emission maps were created using the NOAA-NESDIS/OAR Emission Inventory Mapviewer found at <http://map.ngdc.noaa.gov/website/al/emissions/viewer.htm>. Note that dramatic differences in emissions along borders (e.g., Maine and New Brunswick in Figures 1b and 1c) may be due to differences in inventories as opposed to land use.

ical composition with one hour time resolution [Williams *et al.*, 2006]. With the TAG system, ambient atmospheric $PM_{2.5}$ (particulate matter $<2.5 \mu m$ in diameter) is collected by means of humidification and inertial impaction. The sample is then thermally desorbed, separated by GC, and identified and quantified at the molecular level using electron ionization quadrupole mass spectrometry (MS)

and flame ionization detection (FID). With the exception of periodic manually applied calibration standards, TAG is fully automated, offering around the clock measurements to determine diurnal, weekly, and seasonal patterns in organic aerosol composition. In this paper, we describe the TAG system's calibration and general performance during ICARTT 2004. We then use molecular marker compounds

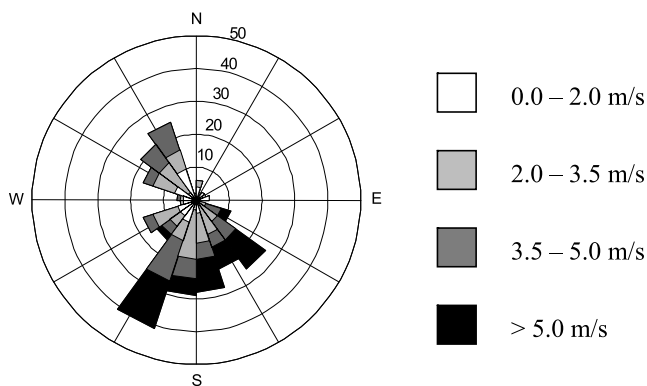


Figure 2. Wind rose plot for 26 July to 15 August 2004 at Chebogue Point field station. Concentric rings represent frequency of observations (0–50).

to define the dominant particle sources. On the basis of these sources, we define several particle types and compare the organic and inorganic speciation for each of them. Finally, we determine the relative contribution each source has toward total organic aerosol loading at the site.

2. Methods

2.1. Field Site

[4] TAG was deployed at the Chebogue Point, Nova Scotia (43.75°N, 66.12°W) ground station during July and August 2004 (Figure 1). The Chebogue Point ground site was composed of four temporary laboratories situated in a remote field on the southwest point of Nova Scotia, approximately 100 m from the coastline. Chebogue Point is located 430 km northeast of Boston, MA, 730 km northeast of New York City, NY, a region high in anthropogenic PM_{2.5} (Figure 1a), 130 km southeast of the New Brunswick/Maine coastline, a region high in biogenic emissions (Figures 1b and 1c), and 9 km south-southwest of Yarmouth, Nova Scotia (approximate population of 8,000).

[5] The field site included a full range of meteorological, radiation, trace gas and aerosol measurements. Instrumentation particularly relevant to this paper included an Aerodyne aerosol mass spectrometer (AMS) that reported concentrations of nonrefractory PM₁ aerosol components (NR-PM₁) [Allan *et al.*, 2004; Jimenez *et al.*, 2003; Jayne *et al.*, 2000], a gas phase pre-concentration GC-MSD-FID [Millet *et al.*, 2006], and a Proton-Transfer Reaction Mass Spectrometer (PTR-MS) [Holzinger *et al.*, 2007]. Other supporting measurements used in this manuscript include: CO measured by nondispersive infrared absorption (TEI, model 48C), CO₂ and H₂O by infrared absorption (Li-Cor Inc., model LI-6262), ozone measured using a UV photometric O₃ analyzer (Dasibi Inc., model 1008-RS), Radon (Rn²²²) gas measured with a dual-flow loop, two-filter radon detector (ANSTO Inc.), black carbon (BC) measured using a MultiAngle Absorption Photometer (Thermo Electron Inc.), photosynthetically active radiation (PAR) measured with a quantum sensor (Li-Cor Inc., model LI-190SZ), wind speed and direction by propeller wind monitor (R.M. Young Co.), and temperature and relative humidity were monitored on an RH&T probe (Campbell Scientific Inc., model HMP45C).

[6] Winds at Chebogue Point shift through time (Figure 2), bringing trace gases and aerosols of varying composition depending on the pollutants origin and time spent in the atmosphere. This variation in time allows TAG to separate sources and transformation processes according to covarying organic marker compounds present in the ambient aerosol and comparing them to previously published source signatures [Rogge *et al.*, 1993a, 1993b, 1993c, 1997a, 1997b, 1998; Schauer *et al.*, 1999; Nolte *et al.*, 1999; Fine *et al.*, 2001; Forstner *et al.*, 1997; Yu *et al.*, 1999; Claeys *et al.*, 2004; Kavouras and Stephanou, 2002].

2.2. Speciated Organic Aerosol Measurements

[7] TAG is described in detail by Williams *et al.* [2006], thus only a summary of its operation and application specific to this experiment follows. Air was sampled through 8 m of 3/8 inch tubing with the inlet mounted on top of a 10 m tower. A particle size cut was made using a PM_{2.5} cyclone (SCC, BGI Inc., Waltham, MA). Aerosol samples were collected by means of humidification and inertial impaction for 29 min at a typical flow rate of 8 L min⁻¹. The 9-nozzle impaction jet characterized by Williams *et al.* [2006] was employed during ICARTT 2004. Sample volume was determined from the measured flow rate through the sampling period, and was typically 0.23 m³. After collection, samples were thermally desorbed and separated by gas chromatography (GC, Agilent 6890) using a relatively nonpolar, general purpose, Rtx-5MS column (30 m, 0.25 mm i.d., 0.25 μm film thickness; Restek Corp.) while ramping the GC oven from 48°C to 300°C at a rate of 8.6°C min⁻¹. Compound identification and quantification was achieved using electron impact ionization and quadrupole mass spectrometry (EI + QMS, Agilent 5973), and simultaneous flame ionization detection (FID) was used for further quantification. Note that the EI + QMS detection system is the same as in the AMS, but the two instruments differ in the way in which the aerosol compounds are introduced into the ionizer: direct introduction without separation using an aerodynamic lens and rapid thermal desorption for the AMS, and particle impaction followed by slow thermal desorption and gas-chromatographic separation for TAG.

[8] Automated TAG sampling was set on a 26 hour cycle throughout the study, including 19 ambient aerosol collections, 5 filtered ambient samples, and 2 zero air samples. The filtered samples were obtained by sending the sample stream through a Teflon membrane filter (Zefluor 2.0 μm, Pall Corp.) prior to humidification. These filtered ambient samples were used to detect any gas phase compounds collected on the walls of the CTD cell. For zero air samples, pure air (AADC0 737, zero air generator, Cleves, OH) was introduced upstream of the humidifier. These samples were used to test for within-system contamination. Contaminants present in zero air samples were subtracted from both filtered and unfiltered ambient air measurements.

[9] Previous laboratory work has shown that GC/MS measurements of particulate organic species can be affected by a thermal decomposition artifact for thermally labile species [e.g., Tobias *et al.*, 2000]. Thus it is possible that some of the species reported here were not those originally present in the aerosol. However, this does not limit their

Table 1. TAG Calibration Results for ICARTT 2004^a

		MS					
Compound	Formula	Average Response, 10 ³ cts/ng	σ , 10 ³ cts/ng	Slope, 10 ³ cts/ng	Intercept, 10 ³ cts	R ²	
Phthalic acid	C ₈ H ₆ O ₄	280.1	26.7	276	17	0.971	
Acenaphthene	C ₁₂ H ₁₀	36.5	2.0	24	42	0.860	
Hexadecane	C ₁₆ H ₃₄	11.5	1.7	7	20	0.661	
Eicosane	C ₂₀ H ₄₂	152.5	13.9	172	119	0.959	
4,4'-dimethoxybenzo-phenone	C ₁₅ H ₁₄ O ₃	598.2	99.2	884	-1016	0.996	
Chrysene	C ₁₈ H ₁₂	1,574.1	247.3	1,887	-116	1.000	
Octacosane	C ₂₈ H ₅₈	563.3	53.1	861	-176	0.997	
Cholestane	C ₂₇ H ₄₈	2,227.4	145.2	2,700	-50	0.994	

		FID					
Compound	Formula	Average Response, 10 ³ cts/ng	σ , 10 ³ cts/ng	Rel. Response, cts/fMC	Slope, 10 ³ cts/ng	Intercept, 10 ³ cts	R ²
Phthalic acid	C ₈ H ₆ O ₄	50.1	3.8	1.04	47	-18	0.985
Acenaphthene	C ₁₂ H ₁₀	5.6	0.7	0.07	3	10	0.684
Hexadecane	C ₁₆ H ₃₄	6.3	0.6	0.09	4	7	0.834
Eicosane	C ₂₀ H ₄₂	56.2	3.4	0.79	51	36	0.956
4,4'-dimethoxy-benzophenone	C ₁₅ H ₁₄ O ₃	41.5	3.6	0.67	45	-13	0.998
Chrysene	C ₁₈ H ₁₂	29.3	2.5	0.37	37	-6	0.998
Octacosane	C ₂₈ H ₅₈	132.3	9.3	1.87	153	-33	0.997
Cholestane	C ₂₇ H ₄₈	258.4	16.7	3.57	338	-6	0.995

^aStandards were quantified by single ion peak integrations on the MS and total scan peak integrations on the FID. MS values are reported in number of counts (cts) per compound mass. FID values are reported similarly, however counts arbitrarily represent a voltage response. FID relative (Rel.) response has been normalized to femtoMole of carbon (fMC) for each compound.

value as tracers of sources, as long as their thermal decomposition is reproducible across time during TAG analysis.

2.3. Instrument Calibration

[10] Liquid standards were applied manually using microliter syringe injection directly into the CTD cell. These external standards were injected and desorbed on a previously desorbed surface intermittently between ambient samples. An average of two standard injections were run per day.

[11] The standard mixture was provided by the Wisconsin Laboratory of Hygiene and contains a range of polar and nonpolar organic compounds. Multipoint calibrations were conducted three separate times throughout the study. These calibrations were used to determine the linearity of compound transfer from the desorption cell through the GC column and into the MS and FID detectors. Also, two reproducibility tests were conducted with repetitive 10 μ L injections of this standard.

2.4. Data Reduction and Analysis

[12] Chromatograms were integrated using HP ChemStation (G1701AA Version A.03.00) software. Mass spectra were identified using the Palisade Complete Mass Spectral Library (600K edition, Palisade Mass Spectrometry, Ithaca, NY) for EI quadrupole mass spectral matching to 495,000 unique compounds using 606,000 available mass spectra. All subsequent data processing and QA/QC was performed using custom-developed code in S-Plus 6.2 (Insightful Corp.). Analysis presented here is restricted to 26 July to 15 August 2004 because of a severe storm on 14 July which led to water entering the sample line and caused an eventual need to replace the GC column. The time period discussed here represents a consistent measure-

ment period for TAG, where only routine maintenance (e.g., support gas cylinder replacement) was performed.

3. Results

3.1. Instrument Calibration

[13] Reproducibility and multipoint calibration results from analysis of the standard mixture on the MS and FID are shown in Table 1. The results shown are from the same ambient measurement period explored in this report, and are expressed as signal per mass (ng) for each individual compound. To compare transfer efficiency between all compounds, a relative response per femtomole carbon has been calculated using the FID signal (Table 1). Cholestane had the highest transfer efficiency (3.57 cts/fMC), and acenaphthene had the lowest transfer efficiency (0.07 cts/fMC) owing to its high volatility and expected loss during the cell purge cycle.

[14] Reproducibility is represented by the standard deviation of the average response from 6 sequential 10 μ L injections of the standard mixture. Relative standard deviations ranged from 0.05 to 0.17 on the MS and from 0.06 to 0.13 on the FID. For a majority of these compounds, reproducibility was better than 10% on both detectors.

[15] Multipoint calibrations were performed by injecting 5 μ L, 10 μ L, and 15 μ L of the standard mixture. All compounds except acenaphthene and hexadecane displayed a very linear response ($R^2 > 0.95$) on both detectors (Table 1). Acenaphthene and hexadecane can exist in the gas phase at surface temperatures and pressures, and thus may be partially desorbed and purged with the solvent. Earlier laboratory experiments using smaller standard injection volumes proved a better method for achieving linear calibrations for even these more volatile compounds [Williams

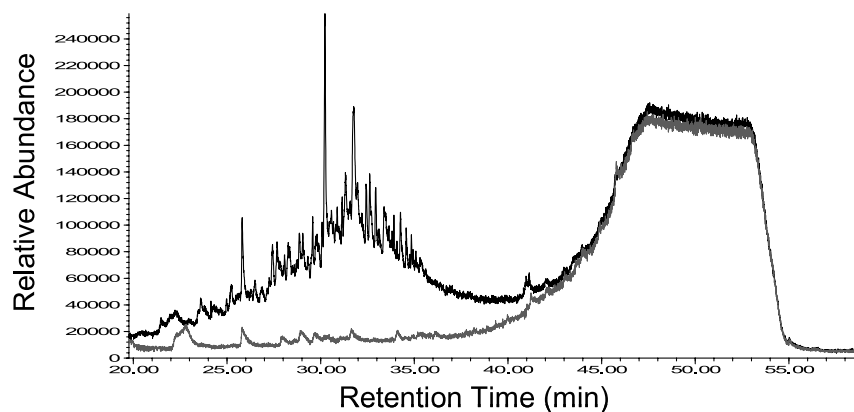


Figure 3. An example chromatogram from a high organic aerosol loading period at Chebogue Point. Displayed here are an ambient atmospheric aerosol sample (black) and a filtered ambient aerosol sample (dark grey, below ambient aerosol levels). The rise in baseline levels occurring after 40 min is typical column bleed observed in all chromatograms.

et al., 2006]. Because of the limited number of standards analyzed at Chebogue Point, we focus on the relative temporal variations (rather than absolute concentrations) of specific marker compounds, how they can be used to differentiate major sources, and what they can teach us about the contributions of each source category to aerosol loading at this site.

3.2. Compound Identification

[16] According to AMS measurements at the site, there was on average a very high level of oxidation throughout the aerosol organics. J. Allan (manuscript in preparation, 2007) reports an average of only 7.4% of the organic mass being associated with hydrocarbon-like organic aerosol (HOA), which is typically associated with primary urban emissions [Zhang *et al.*, 2005a, 2005b]. Since the Chebogue Point ground site is located a great distance from large urban centers, air masses reaching the site from those regions have had two or three days to undergo photo-oxidation in the atmosphere. This results in highly oxygenated organics reaching the site, regardless of whether they are anthropogenic or biogenic in origin [Robinson *et al.*, 2006].

[17] A chromatogram from a high organic mass loading period at Chebogue Point is displayed in Figure 3, along with a chromatogram from a filtered ambient sample acquired 1 hour before the ambient sample. The majority of aerosol mass (both resolved and unresolved) elutes prior to 40 min. (i.e., approximately 240°C in the GC oven). Since particle-phase hydrocarbons generally elute after 40 min., regardless of where ambient sampling occurs, this suggests, along with tentative mass spectral library matches, that the majority of resolved and unresolved aerosol mass at Chebogue Point is oxygenated. Williams *et al.* [2006] elaborate on this point by comparing this Chebogue Point chromatogram to an urban sample collected in Berkeley, CA.

[18] A total of 37 resolved compounds, approximately 70% of which were matched to known compounds in the MS database, were chosen for our analysis on the basis of their chromatographic separation, large relative peak size, and lack of contamination or blank problems throughout the

study. These compounds do not make up the entirety of the organic compounds observed by TAG at Chebogue Point (i.e., TAG measured over 100 resolved compounds), but they represent several different source types and thus cover a useful range of the detected compounds.

[19] A complete list of these 37 integrated compounds is provided in Table 2, including molecular formulas and structures (Figure 4) for those with good matches to the Palisade Complete Mass Spectral Library. An estimate of uncertainty in compound identification is provided in column 4 of Table 2 (“low” uncertainty being an excellent match, and “high” uncertainty being a poorer match). Unknown compounds are labeled as, “unknown.**.m/z”, where ** has been used to track retention time order between compounds, and m/z is the ion used for integration on the MS.

[20] The total aerosol organic matter (OM) is equal to the sum of the compounds that are resolved (R), not resolved (NR), and not eluting (NE) through the gas chromatography column. For the purpose of this analysis, we will state that the resolved fraction was generally less than 15–20% of the total organic aerosol mass as measured by the AMS. A more detailed analysis of TAG total OM (separated between the three components) along with further comparisons to the Aerodyne AMS will be performed in a future report.

3.3. Source Apportionment

[21] Particle source apportionment is performed by separating TAG marker organic compounds into time-covarying groups that represent different sources or transformation processes of aerosols arriving at the study site. TAG compounds are grouped using a statistical approach called factor analysis [Kaplunovsky, 2005], where the variation in marker compound profiles measured at the receptor site can be described by several independent factors. Each factor is associated with a grouping of marker compounds, which can offer insights to the origin of the factor (or source) [Lamanna and Goldstein, 1999; Millet *et al.*, 2004].

[22] Relative abundance timelines were completed for the dominant 37 TAG compounds, after correcting for abundances in the filtered ambient samples. The most significant corrections were made for phthalic acid, and the later

Table 2. Factor Analysis Results for Air Sampled at Chebogue Point, Nova Scotia, 16 July to 25 August 2004^a

Compound	Structure (See Figure 4)	Formula	Uncertainty of ID	Loadings (Values < 0.35 omitted)					
				F1	F2	F3	F4	F5	F6
5, 6-Dihydropyran-2-one, 5-acetoxy-6-(1, 2-epoxypropyl)- unknown.fl.43	1	C ₁₀ H ₁₂ O ₅	high	0.90
7-Oxabicyclo[2.2.1]heptane-2, 3-dicarboxaldehyde, (2-endo, 3-exo) unknown.u1.98	2	C ₈ H ₁₀ O ₃	high	0.88
unknown.cc1.98	0.88
4s, 6s-Dimethyl-7R-acetoxy-3-nonanone (acetyl serricornin)	3	C ₁₃ H ₂₄ O ₃	high	0.87
5-Hexenoic acid, 5-methyl- unknown.ll.156	4	C ₇ H ₁₂ O ₂	mid	0.86
Pelletierine unknown.c1.81	5	C ₈ H ₁₅ NO	mid	0.85
4-Pentenoic acid, 2-acetyl-2, 3-dimethyl-, ethyl ester unknown.bb1.86	6	C ₁₁ H ₁₈ O ₃	high	0.85	...	0.36
2(3H)-Furanone, 3-acetyldihydro- unknown.w1.98	7	C ₆ H ₈ O ₃	mid	0.84
unknown.k1.98	0.82
2H-Pyran-2-one, 4-hydroxy-6-pentyl unknown.il.70	8	C ₁₀ H ₁₄ O ₃	high	0.81
unknown.q1.151	0.81	0.45	...
unknown.aa1.99	0.79	0.42
Hexanoic acid, 9-decen-1-yl ester unknown.sl.141	9	C ₁₆ H ₃₀ O ₂	high	0.76
.delta.-Lauro lactone	10	C ₁₂ H ₂₂ O ₂	low	0.76	0.38
Heptadecane	11	C ₁₇ H ₃₆	low	0.69	...	0.43	0.46
.delta.Undecalactone	12	C ₁₁ H ₂₀ O ₂	low	0.64
Pinonaldehyde	13	C ₁₀ H ₁₆ O ₂	low	0.58	0.53
3, 5-di-tert-butyl-4-hydroxybenzaldehyde	14	C ₁₅ H ₂₂ O ₂	low	0.53	0.68
Phenanthrene	15	C ₁₄ H ₁₀	low	0.52
Phthalic acid	16	C ₈ H ₆ O ₄	low	0.52	0.70
1, 6-Dioxaspiro[4,4]nonane-2, 7-dione	17	C ₇ H ₈ O ₄	low	0.42	0.65	...
2-Hydroxy-3, 5-dimethylcyclopent-2-en-1-one	18	C ₇ H ₁₀ O ₂	mid	0.39	...	0.44	0.35	0.41	...
Pristane	19	C ₁₉ H ₄₀	low	0.41	...	0.64	...
Tricosane	20	C ₂₃ H ₄₈	low	0.74
Methylbis(phenylmethyl)-benzene	21	C ₂₁ H ₂₀	low	0.77	...	0.39	...
Tetracosane	22	C ₂₄ H ₅₀	low	0.44	...	0.52	...
Pentacosane	23	C ₂₅ H ₅₂	low	0.48
Hexacosane	24	C ₂₆ H ₅₄	low	0.39
Heptacosane	25	C ₂₇ H ₅₆	low	0.39	...	0.46	0.37
Ozone		O ₃		...	0.60	-0.40	0.37
Radon		Rn ²²²		0.61	0.40	0.39	...
Carbon monoxide		CO		...	0.47	...	0.53	0.40	...
AMS organics				0.55	0.72
AMS sulfate		SO ₄ ²⁻		...	0.94
AMS nitrate		NO ₃ ⁻		...	0.46	...	0.51
AMS ammonium		NH ₄ ⁺		...	0.96
Importance of factors									
Sum square loadings				16.57	4.60	3.84	3.37	2.73	2.65
Proportion of variation				0.38	0.10	0.09	0.08	0.06	0.06
Cumulative variation				0.38	0.48	0.57	0.65	0.71	0.77

^aFactor analysis was performed in SPLUS 6.2 (MathSoft, Inc.), using varimax rotation and principal factors extraction. The model was limited to six factors because additional factors did not have significant sum square loadings and did not explain a significant portion of the variation. Proportion variation defines the fraction of data explained by each factor. Cumulative variation is the sum of the proportion variation, indicating that these six factors explain 77% of the variance of the observations. Chemical structures of identified compounds are drawn in Figure 4. Uncertainty of compound identification (uncertainty of ID) is separated between three categories (i.e., high, mid, low): high uncertainty for compounds with poorer mass spectral library matches, mid uncertainty for compounds with better matches and fewer other possible structures, and low uncertainty for compounds with very good library matches (many of which are also matched using chemical standards).

retention time hydrocarbons such as phenanthrene and all alkanes. Filtered ambient samples were typically less than 25% of the ambient values during source impact periods for all compounds. For this specific study period, the source apportionment analysis provides the same general results with or without subtracting the filtered ambient samples.

[23] The resulting variation within and between these compounds is driven by, and thus contains information about, the different sources and aerosol transformation processes and meteorological changes affecting the air sampled at the site. Figure 5 compares two different TAG compound timelines over an 11 day period. It is observed

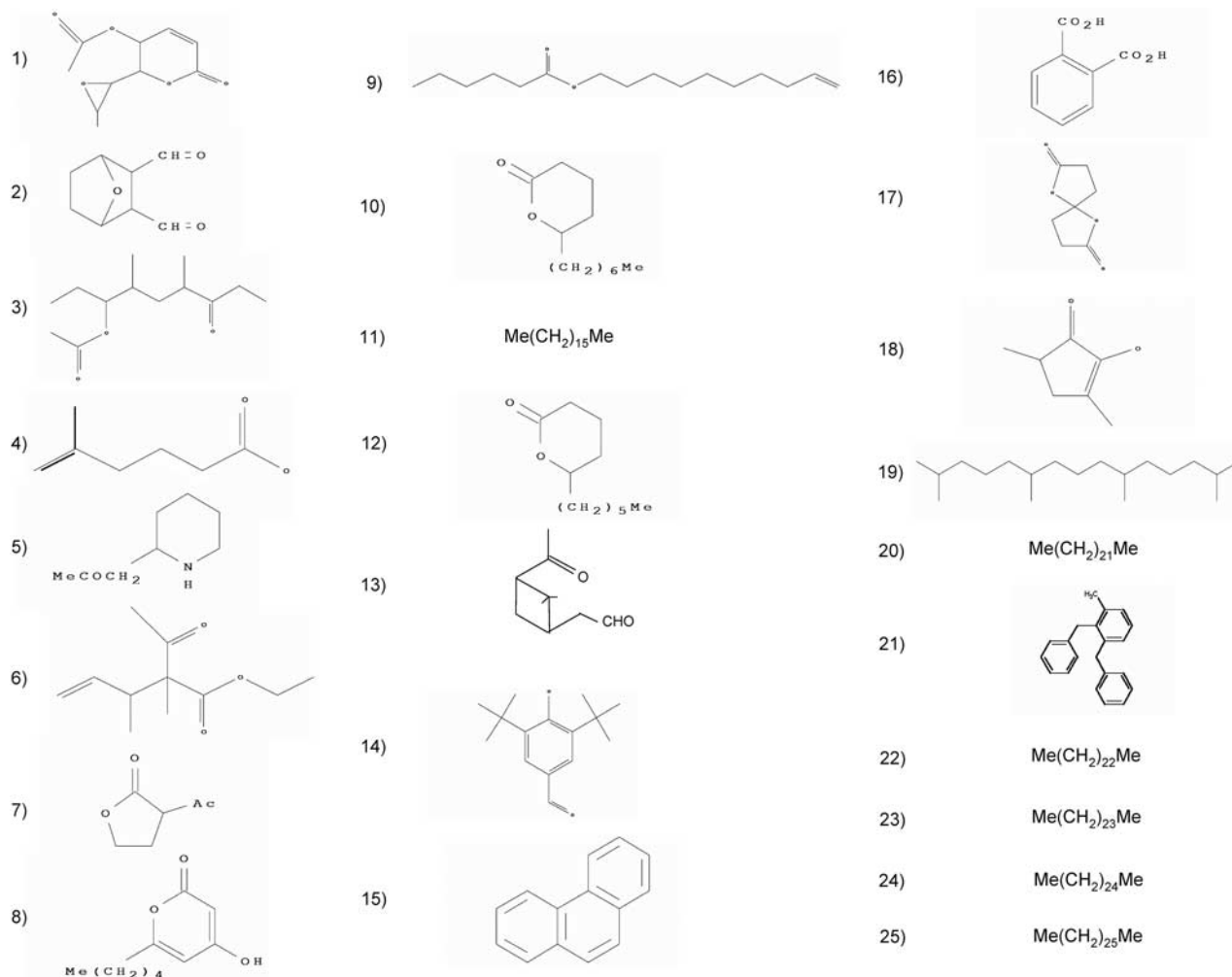


Figure 4. Chemical structures of the identified compounds (Table 2) used for this analysis. The methyl functional group (CH_3) is abbreviated as Me, and the acetyl functional group (COCH_3) is abbreviated as Ac. Most chemical structures are from the Palisade Mass Spectral Browser (Palisade Corporation).

that TAG compound A (identified as 4-pentenoic acid, 2-acetyl-2, 3-dimethyl-, ethyl ester) increases with AMS organics between days 218 and 221, whereas TAG compound B (identified as 1, 6-dioxaspiro[4,4]nonane-2, 7-dione) correlates with AMS SO_4^{2-} and AMS organics between days 224 and 226. This indicates that these two TAG compounds will be associated with two different particle sources.

[24] In order to find covariance within the entire data set a factor analysis using principal components extraction with varimax rotation [Millet *et al.*, 2004, 2006] was performed on the 37 TAG compounds, O_3 , CO, Rn^{222} , and AMS measurements of NR- PM_{10} aerosol organics, total sulfate, total nitrate, and total ammonium mass over the period of 26 July to 15 August 2004 (Table 2). The gases O_3 , CO, and Rn^{222} were included with the particle data to provide additional information, based on variability of these well studied gases, about the air masses associated with each factor. For example, O_3 is a tracer for aged urban pollution transported from the eastern seaboard of the U.S., CO is a combustion tracer, and Rn^{222} , $\tau \sim 4$ days, is a radioactive gas emitted from soils and serves as a tracer for recent

interaction with land. The input parameters fit best to six different factors which can be thought of as signatures of sources or transformation processes. Additional factors individually explained less than 3% of the variance, or less than half of the smallest contributing factor, and therefore were not included in the analysis. The factors explored here are not affected by including or excluding the previously mentioned gas phase species in the analysis.

[25] “Impact periods” are created to identify times when each factor has a major contribution to the composition of aerosols arriving at the site. Here we use two different methods to define impact periods with significant contributions and with dominant contributions. The first approach, defined by Millet *et al.* [2006], creates significant impact periods based on the factor score being >1 standard deviation (σ) above the mean. This method will be referred to as the “ $F > 1\sigma$ ” method. The second approach creates impact periods based on a factor score being $>1\sigma$ above the mean and also greater than the sum of all other factor scores. This method will be referred to as the “dominant factor $>1\sigma$ ” method, and will be used to filter out mixing between multiple sources. The use of this method will determine

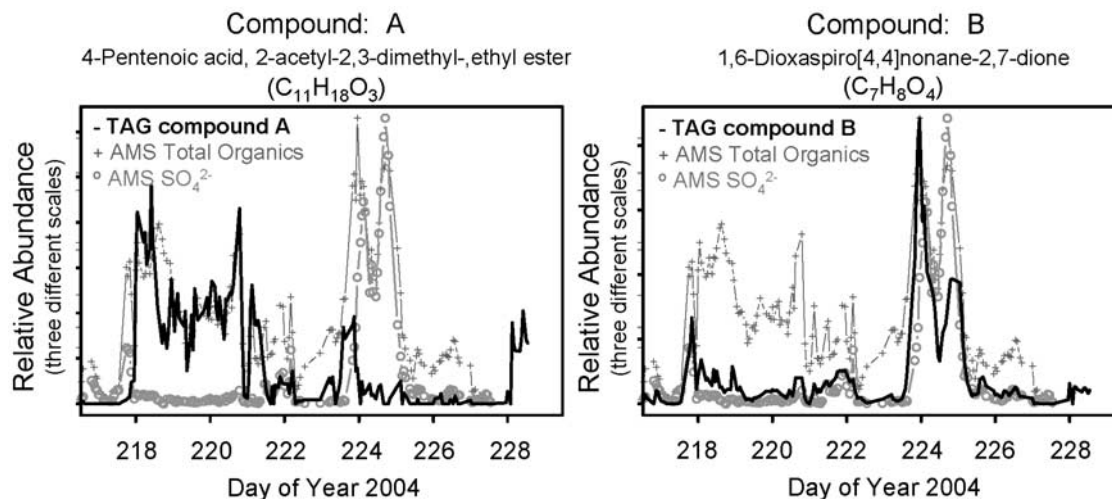
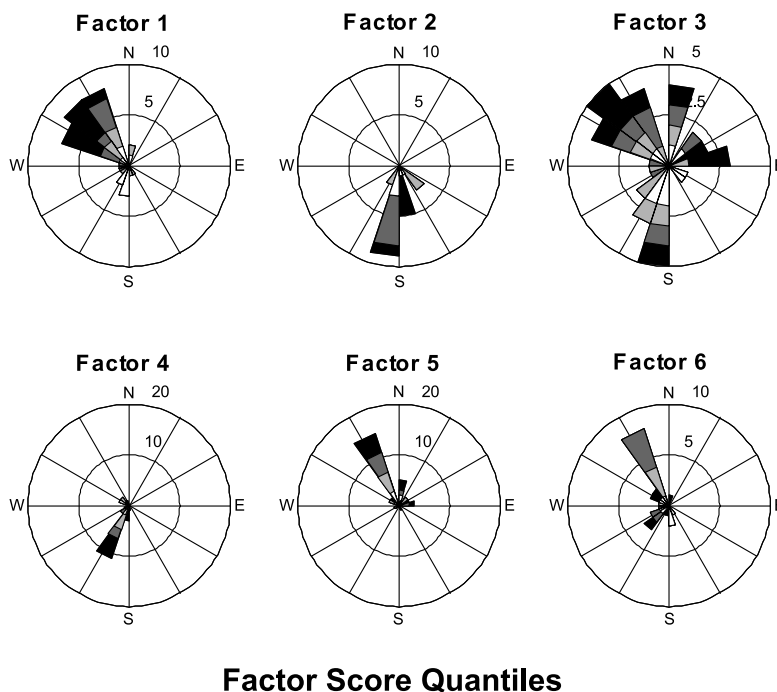


Figure 5. A comparison of an 11 day timeline for two different compounds (solid line) measured by TAG at Chebogue Point, N.S. Included in both timelines are AMS total organics (plus symbol) and AMS SO_4^{2-} (circle symbol), all of which are plotted on different relative scales. It is observed that TAG compound A (4-pentenoic acid, 2-acetyl-2, 3-dimethyl, ethyl ester) increases with AMS organics part of the time (day 218–221), and TAG compound B (1, 6-dioxaspiro[4, 4]nonane-2, 7-dione) correlates with AMS SO_4^{2-} and a later occurring organics event (day 224–226), indicating these two TAG compounds have different sources.

whether sources tend to mix and arrive at the site at the same time, or if there is more frequently a single dominant factor. A more distinct factor will display fewer differences between these two methods. Generally, factors associated with longer-range transport arrive in more distinct events

associated with higher wind speeds (greater mixing with the air aloft), and for these factors good agreement is found between the two impact period definitions. This is probably at least partially due to the homogenization of multiple individual sources into a regional emission signature, rep-



□ 0.00 - 0.25 □ 0.25 - 0.50 □ 0.50 - 0.75 ■ 0.75 - 1.00

Figure 6. Rose plots of the six aerosol factors using $F > 1\sigma$ impact period criteria. Frequency of observations are represented by the length of each wedge and labeled by concentric rings.

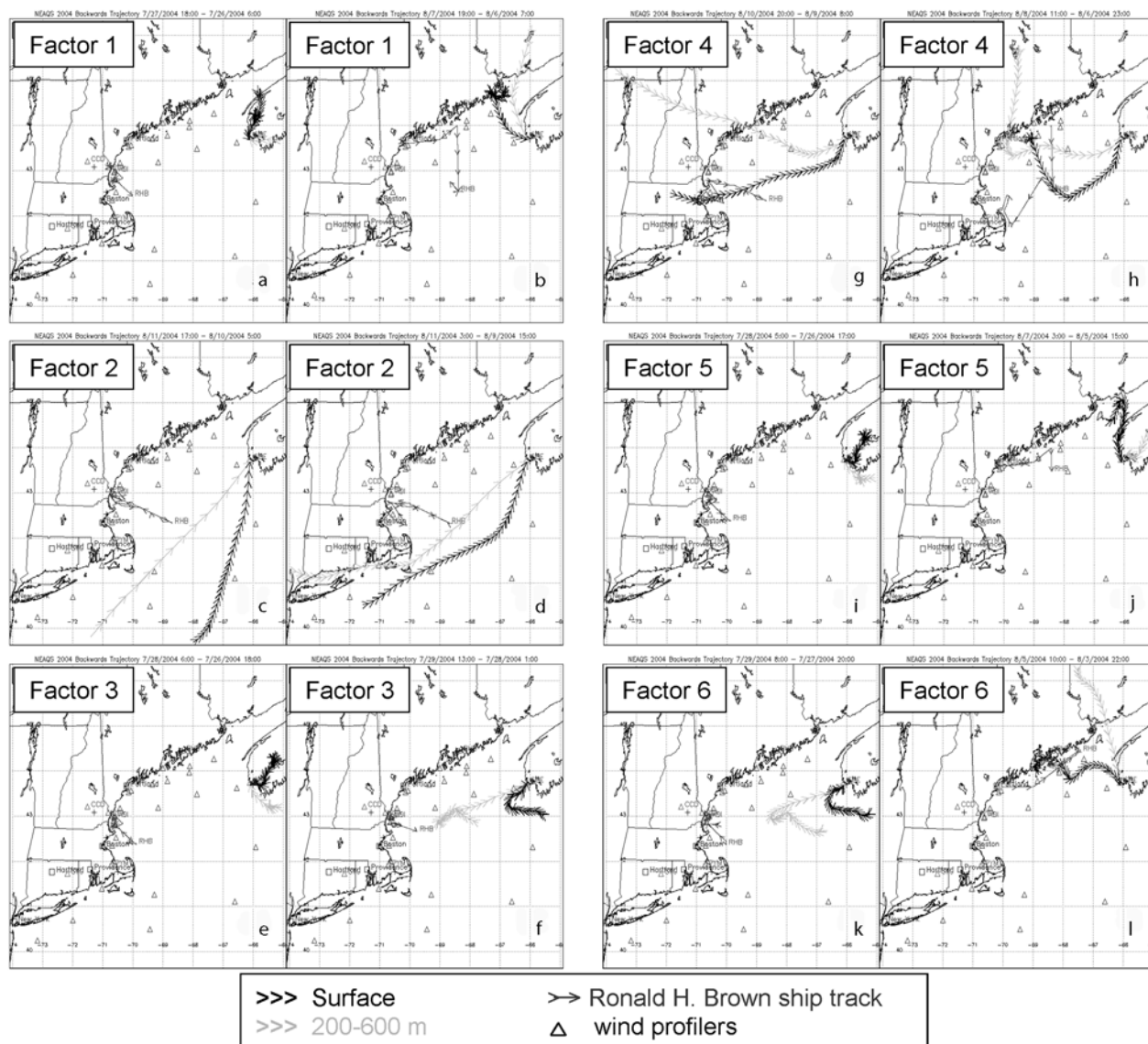


Figure 7. Air mass 36-hour wind profiler back trajectories for each of the six factors. Figures show the surface (dark arrows) and 200–600 m elevation (light grey arrows) back trajectories for air masses arriving to the site during (a) 27 July 2004 factor 1 event at 1800 UT, (b) 7 August 2004 factor 1 event at 1900 UT, (c) 11 August 2004 factor 2 event at 1700 UT, (d) 11 August 2004 factor 2 event at 0300 UT, (e) 28 July 2004 factor 3 event at 0600 UT, (f) 29 July 2004 factor 3 event at 1300 UT, (g) 10 August 2004 factor 4 event at 2000 UT, (h) 8 August 2004 factor 4 event at 1100 UT, (i) 28 July 2004 factor 5 event at 0500 UT, (j) 7 August 2004 factor 5 event at 0300 UT, (k) 29 July 2004 factor 6 event at 0800 UT, and (l) 5 August 2004 factor 6 event at 1000 UT. Events chosen are from the maximum of the two highest scoring episodes for each factor, using $F > 1\sigma$ criteria. Wind profilers used are displayed as triangles, along with the wind profiler on board NOAA's *Ronald H. Brown* ship. The ship track is displayed as a series of arrows.

representative of the urban areas along the east coast of the United States. In contrast, local sources are on average dominant at lower wind speeds, allowing multiple local sources to mix and contribute to the aerosol composition at the site with less homogenization allowing short-term distinct source contributions to be apparent. This results in a greater contrast between the two impact period methods for local influences, since several sources could have a factor score $>1\sigma$ at the same time, potentially eliminating

each of them from being a dominant factor during such episodes.

[26] Factor 1 explains 38% of the variance between all input parameters, and frequently arrives at the site from the northwest (Figure 6). Back trajectories conducted using a new wind profiler trajectory tool described by *White et al.* [2006] suggest that these particles originated from mainland Canada (New Brunswick), Maine, and northwestern Nova Scotia (Figure 7). There is a high Rn^{222} loading into this

Table 3. Impact Periods of TAG Factors During 26 July to 15 August 2004^a

Factor	Source Description	Average Wind Speed, m s ⁻¹	Average Duration, h	Percentage of Total Time, %	Average Aerosol Concentration, μg m ⁻³	Average Organics Concentration, μg m ⁻³	Relative Importance for Organics
F1	isoprene oxidation	3.3	6.7	10.5	7.0	5.7	1.00
F2	U.S. outflow 1	4.7	31.0	6.9	22.1	7.3	0.84
F3	local alkane	1.7	6.5	11.6	4.5	2.8	0.54
F4	U.S. outflow 2	4.0	4.3	7.6	6.3	3.3	0.43
F5	terpene oxidation	2.4	3.6	8.9	4.2	3.1	0.46
F6	marine or dairy	1.5	3.1	6.9	4.4	2.9	0.33

^aAll values calculated using dominant factor >1σ criteria, except average duration and percentage of total time which were calculated using $F > 1σ$ criteria. Aerosol concentrations calculated using sum of all AMS aerosol species reported (i.e., organic carbon, sulfate, nitrate, and ammonium) plus black carbon. Relative importance for organics is calculated as the product of average organics concentration multiplied by the percentage of total time, normalized to factor 1. This value provides a relative scale to compare each factor's contribution to total organic aerosol loading at Chebogue Point.

factor (Table 2), indicating a terrestrial source. According to $F > 1σ$ criterion, this factor contributes to the particle composition at the site 10.5% of the time period analyzed, with an average total PM_{1,0} loading of 7.0 μg m⁻³ as measured by AMS + black carbon (BC) (Table 3). Many TAG marker compounds have a high correlation with this factor. Most of these compounds are oxygenated and contain multiple functional groups including aldehydes, ketones, and acids. This indicates aged particles that have had time to undergo photochemistry in the atmosphere, along with gas phase oxidation products partitioning to the particle phase. As is shown in Table 4, there is a positive correlation (0.69) between this factor and the isoprene oxidation factor described by Millet *et al.* [2006], indicating this aerosol factor is influenced by biogenic oxidation products contributing to secondary organic aerosol formation. There is also high correlation found between these factor 1 compounds and the aged biogenic source described by Holzinger *et al.* [2007].

[27] Factor 2 explains 10% of the variance, and frequently arrives at the site from the south (Figure 6). Back trajectories suggest that these particles originated in the eastern United States (Figure 7). This factor contributes to the particle composition at the site 6.9% of the time period analyzed, with an average PM_{1,0} loading of 22.1 μg m⁻³ (Table 3). Although this factor did not appear as frequently as other factors, it had the longest duration (31 hours) and was responsible for the largest particle concentrations measured at Chebogue Point. This source has a positive correlation with the gas phase U.S. outflow factor described by Millet *et al.* [2006], which contains many anthropogenic compounds. This factor also has a positive correlation with O₃, CO, and BC (Table 4). According to AMS measure-

ments, factor 2 aerosols contain the most oxygenated organics throughout the entire study, and hence it is expected that fewer of these highly oxygenated compounds would elute through TAG's GC column as used in this study (without chemical derivatization). However, within the dominant 37 compound list, there were still enough marker compounds eluting during this time period (e.g., 1, 6-dioxaspiro[4, 4]nonane-2, 7-dione, and 2-hydroxy-3, 5-dimethylcyclopent-2-en-1-one) to define this as a separate source. Although these particles are likely coming from an anthropogenic source, there are no primary organic compounds remaining above TAG's detection limits (i.e., approximately 0.1 ng for large alkanes, or 0.4 ng m⁻³ with the given sample rate).

[28] Factor 3 explains 9% of the variance, and local wind measurements show it arrives at the site from many directions (Figure 6). Back trajectories (Figure 7) and lower than average wind speeds (Table 3), suggest that this is a local source. Differences between the $F > 1σ$ rose plot (Figure 6) and the dominant factor > 1σ rose plot (Figure 8), show that this source mixes with other sources when arriving from the northwest (288°–342° azimuth) and from that direction it is not the dominant factor. The TAG compounds with the highest loading for this factor are large alkanes (i.e., C₂₅, C₂₆, C₂₇) (Table 2). These primary hydrocarbons can have anthropogenic [Simoneit, 1984], biogenic [Eglinton and Hamilton, 1967], and marine origins [Marty and Saliot, 1982]. There is little evidence for a large odd-carbon number preference [Kolattukudy, 1976] in these alkanes. If there was an odd-carbon number preference it would indicate a dominant biogenic source of primary compounds such as plant waxes [Simoneit and Mazurek, 1982; Simoneit, 1984]. However, we do observe a positive correlation

Table 4. Gas Phase Species and Black Carbon Correlations to TAG-Derived Factors 1–6 (Values < 0.2 Not Reported)^a

	U.S. Outflow	Local Anthro.	Local Bio.	OVOC + B.B.	Alkanes	Isoprene Oxn.	O ₃	CO	CO ₂	Rn ²²²	BC
Factor 1	0.29	...	0.69	...	0.29	0.39	0.62	0.30
Factor 2	0.42	0.29	0.61	0.48	0.43
Factor 3	...	0.23	0.56	0.34	0.36	...	0.23
Factor 4	0.27	0.34	0.39	0.57	...	0.42	0.53
Factor 5	...	0.39	0.73	0.26	...	0.35	...	0.41	0.42	0.40	0.25
Factor 6

^aGas phase sources (i.e., U.S. outflow, local anthropogenic (Anthro.), local biogenic (Bio.), OVOC+biomass burning (B.B.), alkanes, and isoprene oxidation (Oxn.)) are those reported by Millet *et al.* [2006]. All values are calculated using $F > 1σ$ criteria. Only measurements between 26 July and 15 August 2004 are incorporated.

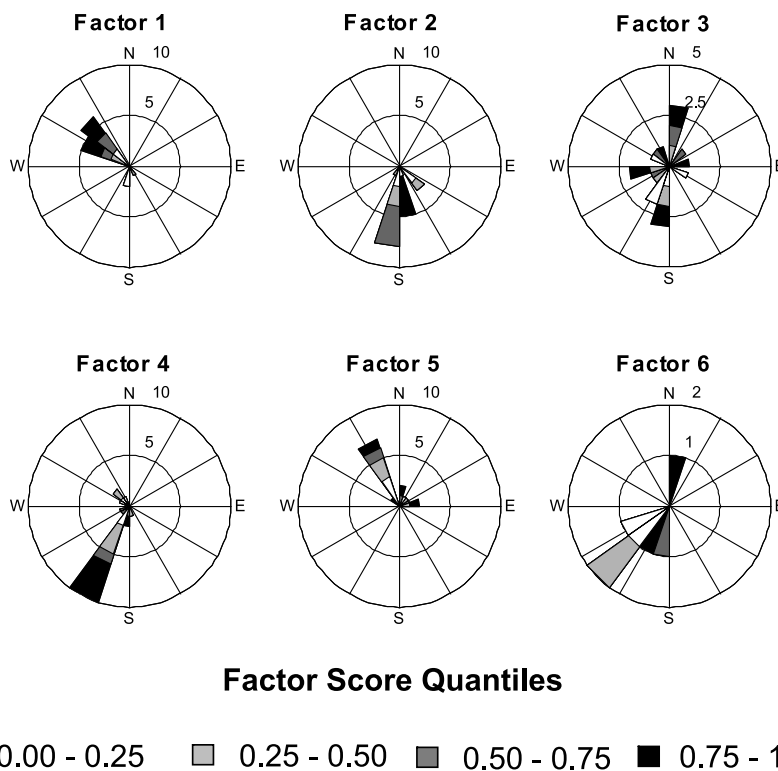


Figure 8. Rose plots of the six aerosol factors using dominant factor $>1\sigma$ impact period criteria. Frequency of observations are represented by the length of each wedge and labeled by concentric rings. Using this impact period criteria, fewer observations are made from northwest winds during factors 1, 3, 5, and 6 events, meaning these sources frequently mix when wind arrives from this direction, resulting in no single dominant source.

between factor 3 and, in the order of highest to lowest correlation, the gas phase local biogenic source, the OVOC + Biomass Burning source, and the Local Anthropogenic source (Table 4), meaning there is likely both biogenic and anthropogenic contribution to these particles which contain large alkanes. All C_{17} – C_{30} alkanes were measured at the site, particularly during factor 3 events, however only a few of these alkanes were included in the top 37 compound list based on abundance. Alkanes smaller than C_{17} appear to be entirely in the gas phase, and alkanes larger than C_{30} appear to be below TAG's detection limits throughout the study.

[29] Factor 4 explains 8% of the variance, and frequently arrives at the site from the south-southwest (Figure 6). Back trajectories (Figure 7) and high average wind speeds (Table 3) similar to factor 2, suggest that this is likely a second U.S. source. The highest loading TAG compound is phthalic acid (Table 2), an aromatic dicarboxylic acid used to make dyes, medicines, and synthetic perfumes. However, phthalic acid is often seen in the atmosphere as a product of naphthalene photo-oxidation [Tuhkanen and Beltran, 1995], which has been observed in urban environments as a product of vehicle exhaust [Fraser et al., 1998; Li et al., 2006], although it can also have origins from phenolic compounds present in sea surface slicks [Kawamura et al., 1996]. There is also a correlation between this factor and O_3 , CO, and BC (Table 4), further indicating an anthropogenic source similar to that seen in factor 2. Factor 2 originates from a specific region of the U.S. which is high in sulfate, perhaps coal-fired power plant emissions, and

factor 4 seems more representative of a general urban corridor U.S. emission source. Factor 4 includes known primary hydrocarbons (i.e., heptadecane, tricosane, methylbis(phenylmethyl)-benzene) that were not apparent in factor 2, suggesting either a slightly closer source, less oxidation, or higher initial concentrations of these primary hydrocarbons from this factor 4 source.

[30] Factor 5 explains 6% of the variance, and frequently arrives at the site from the northwest (Figure 6). Back trajectories (Figure 7) and low average wind speeds (Table 3) similar to factor 3, suggest this is a local source. The highest loading TAG compounds with this factor are pinoaldehyde and phenanthrene (Table 2). Pinoaldehyde is a product of terpene oxidation which partitions between the gas and particle phase. Although terpene emissions from forests are generally highest during the day, being driven by light and temperature, concentrations of terpenes and their oxidation products can often be highest at night, as is observed here at Chebogue Point, because of increased stability in the surface boundary layer [Lamanna and Goldstein, 1999].

[31] Phenanthrene also partitions between the gas and particle phase and has various sources, but is typically considered a petrogenic PAH emitted from incomplete petroleum combustion [Kavouras and Stephanou, 2002]. Factor 5 has a very high correlation with the gas phase local biogenic source described by Millet et al. [2006], and has an above average percentage (77%) of the total aerosol mass attributed to organics, indicating factor 5 is mostly biogenic

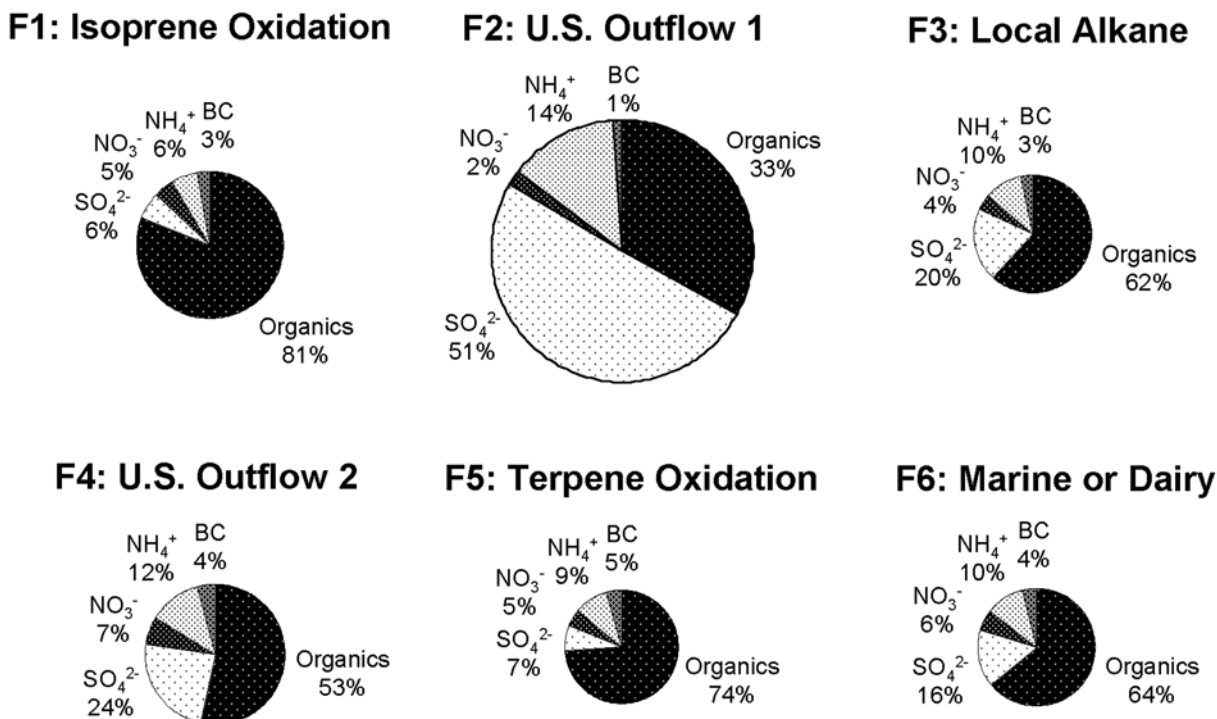


Figure 9. Aerosol composition according to AMS speciation plus black carbon (BC) during dominant factor $>1\sigma$ impact periods for the six aerosol factors. Pie chart areas are scaled to average aerosol concentrations for each factor. These concentrations and a summarized description of each factor are provided in Table 3.

in origin. If the covarying particle phase phenanthrene was emitted from incomplete petroleum combustion, it is likely small-scale combustion occurring near or within the local area. Phenanthrene also loads weakly on factor 3 (0.41), which also correlates with the gas phase local biogenic source. It is clear that these two factors are similar, but differ in chemical composition such that factor 3 contains mostly primary hydrocarbons, and factor 5 has a large contribution from secondary products of terpene oxidation. The analysis performed by *Holzinger et al.* [2007] also concludes that local anthropogenic and local biogenic sources could not be completely separated.

[32] Factor 6 explains 6% of the variance, and frequently arrives at the site from the north-northwest and southwest (Figure 6). Back trajectories (Figure 7) vary during each impact period, but since this factor displays the lowest average wind speed of all six factors (Table 3) it is potentially a local source. There are only five compounds throughout all data sets that correlate with factor 6, all of which are TAG compounds. Of these five compounds, three have been identified. They are, in order of highest to lowest loading in factor 6, δ -undecalactone, δ -lauro lactone, and pristane. Pristane is an isoprenoid that can be found in petroleum products, but typically is accompanied by phytane, another isoprenoid. It is believed that the presence of pristane in the absence of phytane is a signature of marine emissions [*Cripps*, 1989], which is one potential source of factor 6, since all air masses bringing these particles to the site can track back to recently traversing ocean water (Atlantic Ocean to the southwest, and the Bay of Fundy to the north-northwest). Another possibility is that these

particles are produced from processes occurring at the local dairies and dairy processing facilities. There were dairies immediately to the south and to the north of the Chebogue Point field site. Laboratory studies have reported the presence of δ -lactones in industrial and desi ghees (i.e., cream fermentation followed by heat clarification) [*Wadodkar et al.*, 2002]. The heating process involved in making various butters would likely emit the same δ -lactones as in ghee production. This heating process could drive the observed semivolatile δ -undecalactone and δ -lauro lactone from the cream into the gas phase and then ultimately back into the particle phase at atmospheric temperatures. Factor 6 remains the least understood source of organic aerosol measured at Chebogue Point.

[33] By comparing Figure 6, which shows rose plots for all six factors based on $F > 1\sigma$ criteria, and Figure 8, which displays rose plots for all six factors based on dominant factor $>1\sigma$ criteria, it is apparent that most mixing of sources occurs with northwest winds. Figure 6 shows that four factors (i.e., factors 1, 3, 5, and 6) all have sources to the northwest due to an overlap of local forests (factors 3 and 5), the city of Yarmouth (factors 3 and 5), the Bay of Fundy (factor 6), and New Brunswick/Maine/Nova Scotia (factor 1). Many of the northwest wind periods are not included in Figure 8 since all four factors are mixing and none are dominant during such events.

3.4. Total Organics and Inorganic Composition of Aerosols Based on Factors

[34] Differences in particle composition can be further explored on a total mass basis using the 6 previously

defined TAG-based factors to examine AMS species and BC during the factor impact periods. Figure 9 displays the AMS and BC measurements for each of the six TAG factors during the dominant factor $> 1\sigma$ impact periods. The average total mass for each factor is given in Table 3, and the percentage of that total mass due to organics, SO_4^{2-} , NO_3^- , NH_4^+ , and BC is shown in Figure 9. Note that the total aerosol mass described here does not include water and nonvolatile components (e.g., elemental).

[35] Factor 1 periods (isoprene oxidation from New Brunswick/Maine/Nova Scotia) had the highest percentage of organics (81%), and factor 2 periods (U.S. outflow) had the lowest percentage of organics (33%). Factors 2 and 4 (both U.S. outflow) had the largest percentage of sulfate (51% and 24%, respectively), and by mass concentration accounted for the highest BC levels. Ammonium ranged from 6% of the total aerosol during factor 1 events to 14% during factor 2 events. Nitrate was between 2% for factor 2 particles to 7% for factor 4 particles, both of which are associated with U.S. emissions. Note that only periods influenced by the six factors defined here are included in this AMS speciation and BC analysis. Other periods (e.g., marine background) are not included in this report.

[36] The relative contribution to the total aerosol mass flux into the region from each factor is a function of both particle concentration and the duration of that factor's impact periods. The last column of Table 3 makes this clear by comparing the "relative importance for organics" between the six factors based on the product of the average organic aerosol concentration (column 7, Table 3) during an event multiplied by the percentage of the time it contributes to aerosol loading at the site (column 5, Table 3), normalized to the largest single contributor (i.e., factor 1). This analysis shows the most important single factor contributing to organic aerosols at Chebogue Point is factor 1 (isoprene oxidation from New Brunswick/Maine/Nova Scotia). However, the sum of factors 2 and 4, both anthropogenic U.S. outflow aerosol, is larger ($0.84 + 0.43 = 1.27$), thus the sum of U.S. outflow of anthropogenic aerosols represents a large fraction of the total organic aerosol loading at Chebogue Point during our analysis period (26 July to 15 August). Total SOA from biogenic oxidation arriving at the Chebogue Point ground site is estimated as the sum of factor 1 (isoprene oxidation from New Brunswick/Maine/Nova Scotia) and factor 5 (terpene oxidation) ($1 + 0.46 = 1.46$). This biogenic SOA also accounts for a large fraction of the total organic aerosol loading at Chebogue Point. These relative contributions from each factor are meant to provide an estimate of the importance of each factor, and are not meant to be quantitative. Quantification of the overall contribution from each factor is not estimated here because of the nature of the factor analysis used (e.g., nonzero contributions for $F < 1\sigma$).

4. Conclusions

[37] Thermal desorption aerosol GC/MS-FID (TAG) has been used to make the first ever continuous hourly in situ measurements of organic aerosol speciation at the molecular level. These measurements have been used to define aerosol composition for 6 distinct source types contributing to the aerosol composition at the Chebogue Point field site, including two different types of anthropogenic U.S. derived

aerosol, particles formed as a result of isoprene oxidation, particles formed as a result of local terpene oxidation, a locally produced aerosol which contains large alkanes (likely both biogenic and anthropogenic contributions), and a third locally produced aerosol potentially originating from marine or dairy processing sources.

[38] Organic mass dominated the total aerosol composition except during times when U.S. outflow was the dominant source of aerosols. This speaks to the importance of organic aerosols in the unpolluted atmosphere, at least downwind of vegetated regions. Primary compounds were detected in some of the U.S. outflow, but not all, indicating the dominance of secondary organic aerosol over primary organic aerosol just a few days downwind of a major anthropogenic source region like the eastern United States.

[39] This factor analysis is only possible with high time resolution measurements, such as is provided by TAG, to capture the frequent changes in aerosol composition. It was typical of all local sources to have events that lasted as little as 1 hour, which would not be resolved using traditional filter collection. Compound specific measurements (e.g., phthalic acid, pinonaldehyde, δ -lactones, alkanes) have provided information about the sources which could not be otherwise obtained. Furthermore, these high time resolution TAG-defined particle sources have been successfully integrated with other meteorological, gas, and particle phase measurements to examine the contributions that primary and secondary biogenic and anthropogenic sources have on total aerosol concentration and composition.

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