

Emission, oxidation, and secondary organic aerosol formation of volatile organic compounds as observed at Chebogue Point, Nova Scotia

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Received 30 May 2006; revised 2 November 2006; accepted 18 January 2007; published 25 April 2007.

[1] We report the detection of a class of related oxygenated compounds by proton-transfer-reaction mass-spectrometry (PTR-MS) that have rarely or never been observed as a group using in situ instrumentation. Measurements were made as part of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) 2004 in Chebogue Point, Nova Scotia. The detected class of compounds discussed here includes acetic acid, formaldehyde, acetaldehyde, tentatively identified formic acid and hydroxyacetone, and unidentified compounds detected at mass to charge ratios 85, 87, 99, 101, 113, 115, and 129. Typical concentrations were 800, 2500, 450, 700, 85, 25, 50, 50, 60, 35, 20, and 25 ppt, respectively. The uniqueness of this class of compounds is illustrated by showing they were poorly related to trace gases found in the US outflow, local pollution, primary biogenic emissions and other oxygenated compounds such as acetone, methanol, and MEK measured by other in situ instrumentation. On the other hand these oxidized volatile organic compounds were related to chemical species in aerosols and their abundance was high during nucleation events. Thus they likely are gas phase species that are formed in parallel to biogenic secondary organic aerosol production. We clearly show these compounds do not originate from local sources. We also show these compounds match the oxidation products of isoprene observed in smog chamber studies, and we therefore suggest they must be mainly produced by oxidation of biogenic precursor compounds.

Citation: Holzinger, R., D. B. Millet, B. Williams, A. Lee, N. Kreisberg, S. V. Hering, J. Jimenez, J. D. Allan, D. R. Worsnop, and A. H. Goldstein (2007), Emission, oxidation, and secondary organic aerosol formation of volatile organic compounds as observed at Chebogue Point, Nova Scotia, *J. Geophys. Res.*, *112*, D10S24, doi:10.1029/2006JD007599.

1. Introduction

[2] Most primarily emitted anthropogenic and biogenic volatile organic compounds (VOC) are oxidized in the troposphere. There are three possible final stages or outcomes of gas phase oxidation: (1) the production of CO or CO₂, (2) removal from the atmosphere by wet or dry deposition, and (3) the formation of low vapor pressure compounds that partition onto particles, a process commonly known as secondary organic aerosol (SOA) formation. The

removal through formation of SOA may be of similar magnitude to the other pathways [Goldstein and Galbally, 2007], making it a much larger term than previously assumed [e.g., Kanakidou *et al.*, 2005]. The details of this transformation from primary emissions to SOA is poorly understood and intermediate gas phase products have been measured in laboratory experiments only for a few selected compounds [e.g., Odum *et al.*, 1997].

[3] Oxidation products of primary VOC emissions tend to become less volatile and more soluble because of the addition of oxygen atoms to their molecular structures; hence collisions with aerosol particles tend to be more important. Aerosols present an airborne solid or liquid surface of a few to a few hundred square micrometers per cubic centimeter under rural and remote conditions; for example, during this study a range of 21–309 $\mu\text{m}^2/\text{cm}^3$ (10–90% percentiles) was measured. The lower number represents a surface on which $\sim 1 \times 10^{17} \text{ s}^{-1}$ collisions with air molecules occur under standard conditions (1013 hPa, 298 K). This number is 10 times the number of collisions per second that 1.5×10^6 OH radicals would undergo in the same volume, indicating the potential importance of heterogeneous processes.

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[4] The goal of this study was to detect such intermediate compounds under natural conditions in the field and to investigate their relation to the organic fraction of aerosols. We used a PTR-MS instrument in full mass scan mode to measure all species detectable with this technique. In this way a range of largely oxygenated compounds were detected, many of which were only identified by their mass to charge ratio in the PTR-MS. Using statistical methods (factor analysis), the data set of better specified gas phase compounds measured by a GC system [Millet *et al.*, 2006], and aerosol data measured with an AMS (Aerosol mass spectrometer) and other instruments [Jayne *et al.*, 2000; Allan *et al.*, 2004] and the newly developed Thermal Desorption Aerosol GC/MS-FID instrument (TAG) [Williams *et al.*, 2006], we examine the origin and role of these compounds in the troposphere. The analysis identifies a class of compounds that is closely related to aerosols and points out the important role of these compounds as representing a link between the gaseous and solid/liquid phase of the air.

2. Experiment

2.1. Site

[5] As part of the international ICARTT 2004 campaign [Fehsenfeld *et al.*, 2006] a ground based field site was operated at Chebogue Point near the town of Yarmouth, Nova Scotia, Canada. The site was located on a pasture about 100 m from the coastline. Long-range transport of pollution from the US east coast is an important factor that controls the air composition at the site [Millet *et al.*, 2006] which results in high levels of CO, ozone and aerosol mass. Local sources of volatile organic compounds include emissions from a dairy farm located southeast of the site, ship plumes of the ferry connecting Yarmouth with Boston and Bar Harbor, anthropogenic emissions (mostly traffic) from the nearby town of Yarmouth (population nearly 8000 people), biogenic emissions from the sea and nearby tide pools, and biogenic emission from local forests and grasslands. Continuous measurements were performed between 2 July and 15 August 2004.

2.2. PTR-MS

[6] The PTR-MS technique has been described in detail by Lindinger *et al.* [1998]. As far as this study is concerned it is worth mentioning that PTR-MS allows quantification of trace gasses without calibration at accuracy levels of $\pm 40\%$. In principle, all chemical species having proton affinities higher than water can be reliably detected. That includes the vast majority of VOCs with the exception of some alkanes and halogenated compounds [Hunter and Lias, 2005]. In practice there are some issues involved with compounds such as formaldehyde and HCN, the proton affinity of which is just slightly above that of water [Hansel *et al.*, 1997]. Proton transfer is a soft chemical ionization technique that usually does not involve fragmentation of the reactants. If fragmentation does occur it typically follows simple and predictable patterns; for example, upon protonation an alcohol with more than 2 carbon atoms ejects a water molecule and is detected at its molecular weight minus 17 amu.

2.3. Setup

[7] Samples were taken at a height of 10 m from a scaffolding tower around which several air-conditioned con-

tainers housed the instruments. Both the PTR-MS and GC-MS/FID continuously sampled through Teflon tubing (PFA, ID 4 mm, ~ 15 m length) and routinely measured calibration gas standards mixed in 6 cylinders that contained a total of 57 compounds. Details of the GC-MS/FID system are given by Millet *et al.* [2005, 2006]. The line supplying sample air to the PTR-MS was kept several degrees above ambient air temperature (i.e., 25–30°C) with a self-regulating heating cable (SLR3, Omega, 3 W/ft, Tmax 65°C). A flow of ~ 500 sccm was maintained at all times resulting in a response time of ~ 20 s. The line was protected from precipitation and coarse particles by a funnel (PFA) and a filter (PTFE, 2 μm pore size). Next to funnel and filter a solenoid valve (PTFE) provided the option to direct the sample air through a catalytic converter (Platinum coated quartz wool heated to 350°C) thus allowing the quantification of the combined background consisting of both the instrumental background and contamination of the inlet system.

2.4. Sampling Strategy

[8] During the first 30 min of each hour the PTR-MS was set up to monitor concentrations of ~ 50 individual masses in the selected ion mode. During the second 30 min of each hour full mass scans were performed covering the mass range 20–220 amu. In the full mass scan mode ambient air was measured for 15 min followed by another 15 min of background measurement. This setup enabled us to reliably detect trace gases with an average concentration as low as 5 ppt. The mass scan data were evaluated in situ at the beginning of the field campaign and masses with significant signals from VOCs in ambient air were subsequently also monitored in the selected ion mode. In the selected ion mode VOCs can be measured with higher precision and time resolution. In this mode background and gas standards were measured 6 times a day (both for 15 min). Background concentrations were interpolated and subtracted from the ambient air signal on each monitored m/z ratio. Data analyzed and presented here are 30 min averages of the resulting ambient air concentrations; the averaging time (minutes 0–30 of each hour) coincides with the sampling period of the GC-MS/FID and TAG systems.

2.5. Detection of Polar Compounds or Compounds With Low Volatility

[9] As for all methods except open-path optical systems, inlet materials and design are potential sources of artifacts. Polar and condensable compounds can be lost on surfaces in the instrument itself and in the inlet tubing. Along with other sources of contamination, such compounds constitute the monitored background signals: when the system is exposed to clean zero-air from the catalytic converter the sticky compounds still evaporate from internal surfaces and are detected by the PTR-MS. In fact, we consider losses onto internal surfaces to be the major uncertainty. Therefore some compounds might have been completely missed and reported concentrations, especially for unidentified compounds, have to be considered as lower limits.

2.6. Data Analysis

[10] We use factor analysis as statistical tool to interpret and classify the data. Factor analysis attempts to explain the

Table 1. Mean Mixing Ratios of Trace Gases During Times of Highest Dominance (Scores >1) of the Individual Factors^a

m/z	Suggested Identities ^b	F1: Local Anthropogenic, 16%		F2: US Outflow, 12%		F3: Aged Biogenic, 11%		F4: Local Biogenic, 11%		F5: Isoprene Oxidation, 5%		F6: Biomass Burning, 5%	
		Loading	ppt	Loading	ppt	Loading	ppt	Loading	ppt	Loading	ppt	Loading	ppt
GCMS	methylpentanes	0.82	39		21		18		25		23		17
GCMS	o-xylene	0.81	10		3		3		7		6		4
GCMS	m-xylene	0.79	17		3		5		13		11		7
GCMS	hexane	0.78	21		12		11		13		11		10
GCMS	propene	0.76	36		14		17		28		29		18
GCMS	ethylbenzene	0.75	9		5		4		7		7		4
GCMS	p-xylene	0.73	7		3		3		5		5		3
GCMS	pentane	0.73	67		37		32		40		35		25
93	toluene , monoterpene fragments	0.72	66		33		31	0.50	64		50		28
GCMS	isobutane	0.71	125		57		53		75		56		35
107	C8-benzenes	0.58	59		12		26		57		41		38
83	?, (C ₆ H ₁₁ +, C ₅ H ₇ O+) ^c	0.53	37		22		30		33		36		22
121	C ₉ -benzenes, + others	0.42	54		35		43		53		47		43
GCMS	C ₂ Cl ₄		6	0.81	14		6		6		6		6
GCMS	CH ₂ Cl ₂		36	0.76	48		34		33		33		34
GC	CO ^d		131	0.74	163		127		133		131		131
GCMS	MTBE		13	0.72	32		15		6		9		11
73	methylethylketone , methylglyoxal		92	0.65	131	0.54	121		92		100		98
79	benzene		59	0.62	76		57		38		48		47
41	?		102	0.58	122		82		83		85		67
61, 43	acetic acid, glycoaldehyde		349		442	0.88	788		332		496		515
101	? ^c		32		38	0.78	58		33		39		36
113	?		18		12	0.74	35		15		26		19
87	C ₅ -ketones, + others		36	0.50	43	0.73	49		34		38		36
45	acetaldehyde		318	0.48	345	0.70	446		287		358		321
99	? ^c		26		30	0.73	47		26		35		26
31	formaldehyde ^c		1530		1790	0.67	2540		1030		1670		1940
47	formic acid ^c		266		415	0.66	723		85		381		429
75	hydroxyacetone, propionic acid ^c		53		67	0.64	85		53		65		72
129	? ^c		6		5	0.56	16		13		8		11
115	? ^c		12		11	0.54	19		15		12		13
85	? ^c		25		18	0.49	23		22		24		16
123	? ^c		6		9	(0.24)	11	(0.26)	13		12		10
GCMS	α -pinene	0.42	128		8		34	0.85	219		85		46
153	alcohol of a monoterpene		61		18		38	0.84	103		66		34
137, 81	monoterpenes	0.47	325		32		104	0.83	517		239		121
GCMS	β -pinene		92		6		29	0.82	183		50		50
GCMS	Carene		35		2		7	0.80	59		23		12
GCMS	MBO		7		3		5	0.72	14		8		7
139	nopinone ^c		20		6		21	0.56	34		35		9
151	pinonaldehyde ^c		11		6		10	0.50	15		12		8
95	dimethylsulfide, fragments		108		76		99	0.46	175		92		97
71	MVK, MACR		88		33		62		60	0.75	168		43
GCMS	MVK		56		21		41		38	0.73	102		32
GCMS	MACR		38		34		27		29	0.71	65		23
GCMS	isoprene		76		25	(0.35)	72		76	0.57	128		51
69	isoprene , MBO, others		139		60	0.43	137		129	0.53	202		96
63	dimethylsulfide		138		87		165		229	-0.46	89		149
42	acetonitrile		62		63		73		63		59	0.83	92
33	methanol		1820		1350	0.59	2220		2000		1980	0.53	2140
59	acetone		1160	0.45	1210	0.45	1360		1310		1240	0.49	1360
77	PAN, peracetic acid ^c		143		166	0.51	194		166		159	0.40	190

^aFactor loadings are given when their absolute value exceeds 0.4.

^bIntercomparison of GC-MS and PTR-MS confirmed that compounds printed in bold constitute the vast majority (70–100%) of the signal detected at the respective mass.

^cMajor fractions of these compounds could have been lost on surfaces of tubing etc.

^dUnit for CO mixing ratios is ppb.

^eThe uncertainty of formaldehyde concentrations is a factor of ~2.

correlations between observable variables in terms of underlying factors, which are themselves not directly observable. We used the technique of “principal factor estimate”; for details on this technique, see *Harman* [1976] or *Mardia et al.* [1979]. *Millet et al.* [2006] and *Williams et al.* [2007] also present factor analyses for a general air mass

classification on the basis of monitored mixing ratios of gas phase compounds and aerosol parameters, with an emphasis on what could be learned from the gas phase GC-MS/FID measurements and TAG measurements respectively. For the analysis presented here we emphasize the PTR-MS data but otherwise the basal data sets are very similar and so are

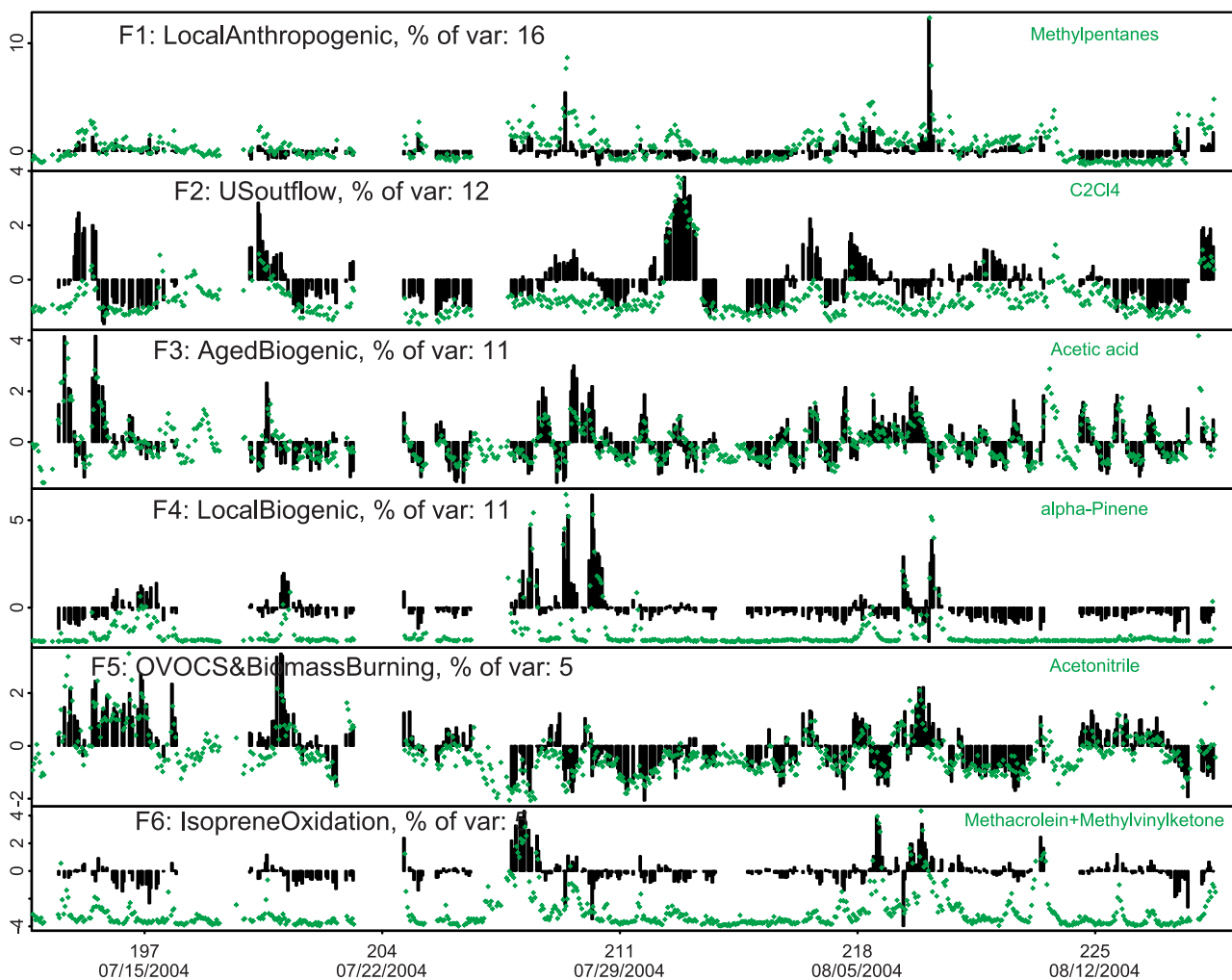


Figure 1. Timeline of factor scores (bars) and mixing ratios (symbols, not labeled) of trace gases with the highest loading on the respective factor. Y axis labels are factor scores.

most of the factors that are produced by the analyses. It is important to recognize that the addition of unique compounds measured by different instruments can add new dimensions to the results. The data set to form the basis of our analysis includes all 32 VOCs that were detected with the PTR-MS instrument (see Table 1), 53 VOCs monitored by the GCMS system, as well as CO, CO₂, H₂O, ozone, and radon. So, the basic data set consists of 90 variables and 940 observations, i.e., hourly mixing ratios covering the entire period of measurement. 358 of these observations were complete (valid values for all 90 variables) and could be used for multivariate modeling. Factor analysis yields independent factors that control the variation of the variables of a data set. Each variable (atmospheric trace gas in our case) is assigned a loading number for each factor that indicates how much a variable is associated with the respective factor; 0 meaning not associated, 1 and -1 meaning 100% associated, correlated or anticorrelated, respectively. For each observation scores can be calculated for each factor; in our case these scores can be regarded as timelines that indicate the relative dominance of a factor at a given time. The factor scores are computed so that their average and

standard deviation over the investigated period is 0 and 1, respectively.

3. Results and Discussion

[11] From a principal factor analysis applied on the basic data set we extracted six factors that together explain 60% of the variation of the data set. As discussed below, these factors can be associated with local combustion (F1), transported pollution from eastern United States (F2), aged air containing high loads of oxidation products likely formed from biogenic precursors (F3), local biogenic emission, mostly terpenes, from forests (F4), isoprene chemistry (F5), and biomass burning (F6). These individual factors explain 16, 12, 11, 11, 5, and 5% of the variation in the data set, respectively. In Figure 1 the scores of all six factors are plotted together with the trace gas having the highest loading on the respective factor; the VOCs and the respective factor scores are clearly correlated with each other. Table 1 gives more information for a larger set of compounds including all species measured with PTR-MS and all other species with loadings of 0.7 or larger on any of the six factors.

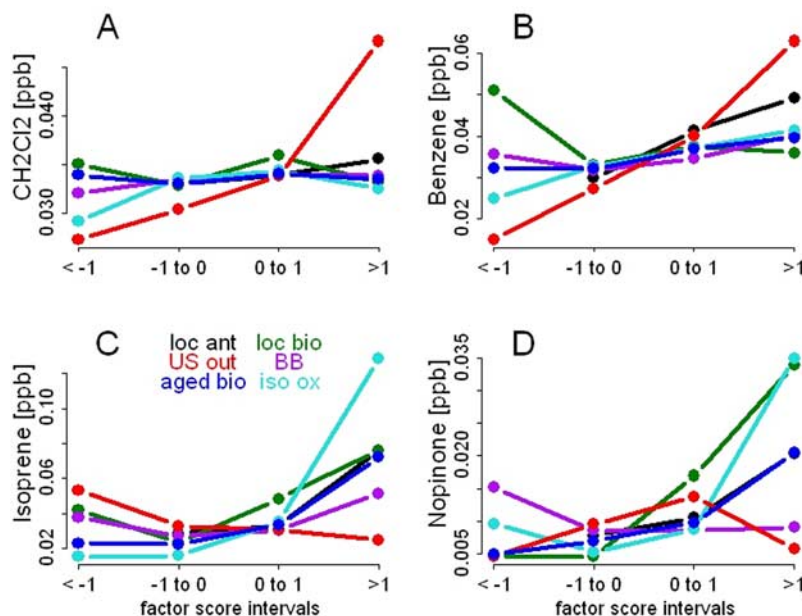


Figure 2. (a) CH_2Cl_2 and (b) benzene as anthropogenic tracers and (c) isoprene and (d) nopinone as biogenic tracer compounds. Mean mixing ratios of each tracer (in ppb) have been calculated for four different regimes of each of the six factors (color coded): Factor scores of -1 or lower, -1 to 0 , 0 to 1 , and above 1 indicate very low, low, strong, and very strong influence of the respective factor on the measured air composition, respectively.

[12] Five of the six factors are very similar to the corresponding factors described by *Millet et al.* [2006] and for a detailed discussion we refer to their paper: reactive emissions from automobile exhaust such as aromatic compounds (excluding benzene), alkanes, and alkenes heavily load on the “local anthropogenic” factor (F1). This factor is associated with local pollution which is transported from the nearby town of Yarmouth. More stable anthropogenic emissions such as benzene, hydrochlorofluorocarbons (HCFCs), and CO exhibit high loadings on the “US outflow” factor (F2) which is associated with long-range transport from densely populated and industrialized areas like Boston and New York. The total load of organic compounds in aerosols is highest during times when this factor is dominant [*Millet et al.*, 2006]. Therefore our results are in agreement with *de Gouw et al.* [2005] who measured closer to the source s of pollution (Boston and New York) and were able to explain the majority of organic carbon by SOA formation from anthropogenic precursor compounds. Biogenic emissions of monoterpenes from nearby forests constitute the “local biogenic” factor (F4); isoprene and its first-order oxidation products methylvinylketone (MVK) and methacrolein (MACR) constitute the “isoprene oxidation” factor (F5); acetonitrile and oxygenated compounds like acetone and methanol have high loadings on the “biomass burning” factor (F6).

[13] The emphasis of this work is the “aged biogenic” factor (F3) that became evident only by including the PTR-MS data set. This factor very much resembles the most dominant factor developed by *Williams et al.* [2007] that explains 38% of the variability of the organic compounds in aerosols measured by the TAG instrument. It is interesting to note that with the exception of acetaldehyde, the compounds making up this factor are entirely missed by the gas

phase GC-MS/FID instrument; yet they constituted one of the four major factors. The reason for this is that these compounds are likely not eluting or not being resolved by the gas chromatograph of the GC-MS/FID system. Many of these compounds are only identified by their mass to charge ratio in the PTR-MS and we can only speculate about their origin and molecular structure. The fact that these species are lost at some point in the GC system already gives an important clue: type “aged biogenic” compounds must be polar or otherwise sticky molecules likely containing one or several oxygen atoms. Among the identified compounds are organic acids, aldehydes and other carbonyls; the unidentified compounds likely are hybrids containing the same type of functional groups.

3.1. What Evidence Links the “Aged Biogenic” Factor to Biogenic Sources?

[14] It is unlikely that the “aged biogenic” compounds are primary emissions transported to the site; no potential biogenic or anthropogenic source is known that would emit such a blend of oxygenated compounds. On the other hand it is known that oxygenated compounds can be easily produced by HO_x and ozone chemistry in the air. Here we present evidence that biogenic rather than anthropogenic emissions are the precursors of the “aged biogenic” compounds. On the range of factor scores 4 intervals can be defined: scores below -1 , -1 to 0 , 0 to 1 , and above 1 indicate periods during which the influence of a factor on the composition of the air was very low, low, strong, and very strong, respectively. Figure 2 shows an evaluation of the six factors with respect to two anthropogenic (dichloromethane and benzene) and two biogenic tracer compounds (isoprene and nopinone, which is a product of β -pinene oxidation). Figure 2 shows mean mixing ratios for the tracer

Table 2. Comparison of Secondary Oxidation Products of Isoprene and Mixing Ratios of Compounds That Highly Load on the “Aged Biogenic” Factor^a

m/z	Identity	Molar Yield of Secondary Products From Isoprene Oxidation, % of Initial Isoprene	Mixing Ratios at Times of High (>1) “Aged Biogenic” Scores, ppt
61	acetic acid, glycoaldehyde	7.0 (1.00)	788 (1.00)
47	formic acid	5.5 (0.79)	723 (0.92)
45	acetaldehyde	2.2 (0.31)	446 (0.57)
73	methylglyoxal	1.8 (0.26)	121 (0.15)
75	hydroxyacetone, propionic acid	1.2 (0.17)	85 (0.11)
113	?	0.6 (0.09)	35 (0.04)
101	?	0.5 (0.07)	58 (0.07)
115	?	0.2 (0.03)	19 (0.02)
129	?	0.01 (0.001)	16 (0.02)

^aThe isoprene oxidation data are from a smog chamber study at the Caltech in Pasadena, California [Lee *et al.*, 2006]. In parentheses are values normalized to acetic acid.

compounds for each interval of each of the six factors. The more atmospheric composition is dominated by the “US outflow” factor, the higher the concentrations of the anthropogenic tracers (Figures 2a and 2b). As benzene is also emitted from local traffic emissions its concentration also increases with increasing dominance of the “local anthropogenic” factor. On the other hand, the anthropogenic tracers show no or a very minor increase as the “aged biogenic” factor becomes more dominant. Therefore Figures 2a and 2b show that anthropogenic pollution is unlikely to explain the “aged biogenic” factor. As for the biogenic tracer compounds: their concentration increases significantly as the importance of the “aged biogenic” factor increases, and thus Figures 2c and 2d indicate that biogenic emissions likely are the largest pool from which the “aged biogenic” compounds are produced. This agrees with findings from 1993 where formaldehyde was measured and analyzed for its ¹⁴C fraction at the same site. Tanner *et al.* [1996] showed that most of the measured formaldehyde could be traced back to secondary production from biogenic isoprene emission. Isoprene oxidation has been recognized to be the major source of formaldehyde over North America, and isoprene sources have been successfully quantified by inverse modeling of space-derived column concentrations of formaldehyde [Palmer *et al.*, 2003]. The biogenic tracers also exhibit high concentrations when the “local anthropogenic” factor is dominant; the local biogenic and anthropogenic sources were in close proximity to each other and the model did not cleanly separate them.

[15] Strong similarities between “aged biogenic” compounds and second-generation products measured during isoprene oxidation provide further evidence indicating their biogenic origins. The isoprene photo-oxidation experiments were performed in a smog chamber at California Institute of Technology (Caltech) in Pasadena, USA. Gas phase organic compounds were measured with a PTR-MS instrument and results have been reported by Lee *et al.* [2006]. All second-generation products from the smog chamber are also associated with the “aged biogenic” factor observed at Chebogue Point. Not only did the identities of the “aged biogenic” compounds match those observed in the smog chamber, but their relative mixing ratios in ambient air were generally consistent with their relative molar yields in the chamber experiment (Table 2). This is striking because the observed mixing ratios are influenced not only by-production from isoprene, but also by-production from the oxidation of other

compounds, and by losses resulting from deposition or oxidation. Many of these product ions were also observed during the photo-oxidation of monoterpenes [Lee *et al.*, 2006], however, their distribution of products and their relative abundance did not match as well. The production of SOA in the chamber experiment was coincident with the oxidation of the first-generation products and the appearance of the second-generation products, represented in Figure 3 by the time series of acetic acid/glycoaldehyde (m/z 61). Second-generation products contributed 81% of the SOA formed from the isoprene photo-oxidation experiment [Ng *et al.*, 2006].

[16] As will be shown below, the oxygenated compounds observed in “aged biogenic” air are also related to the organic fraction of observed aerosols. Together with the time evolution of product ions and SOA observed from the isoprene photo-oxidation experiment, this supports the idea that isoprene contributes to organic aerosol growth in ambient air [Claeys *et al.*, 2004; Kroll *et al.*, 2005; Kourtev *et al.*, 2005].

[17] Assuming that isoprene oxidation accounted for 400 ppt of acetic acid/glycoaldehyde during times of “aged biogenic” influence (~50% of total acetic acid/glycoaldehyde, see Table 1) we can roughly estimate a SOA production of 0.3 $\mu\text{g}/\text{m}^3$ by using yields of 7% and 2% for acetic acid/glycoaldehyde and SOA production, respectively [Lee *et al.*, 2006]. This figure is small compared to the average concentration of organic aerosol matter of 3.9 $\mu\text{g}/\text{m}^3$ during such periods (the median for the whole data set is 1.6 $\mu\text{g}/\text{m}^3$); therefore this may indicate even higher aerosol yields from isoprene oxidation under natural conditions and longer reaction times.

3.2. Is the “Aged Biogenic” of Local or Regional Origin?

[18] Back trajectory calculations using a new wind profiler trajectory tool described by White *et al.* [2006] and FLEXPART simulations [Stohl *et al.*, 1998] suggest areas of origin that spread over mainland Canada (New Brunswick), the northeastern United States, and northwestern Nova Scotia. In order to see if there is also a strong component from local emissions to “aged biogenic” compounds, we use the two local factors, “local anthropogenic” and “local biogenic,” to separate periods where local influence is minimal. Whenever the scores of both local factors were negative, we considered the data only marginally influenced

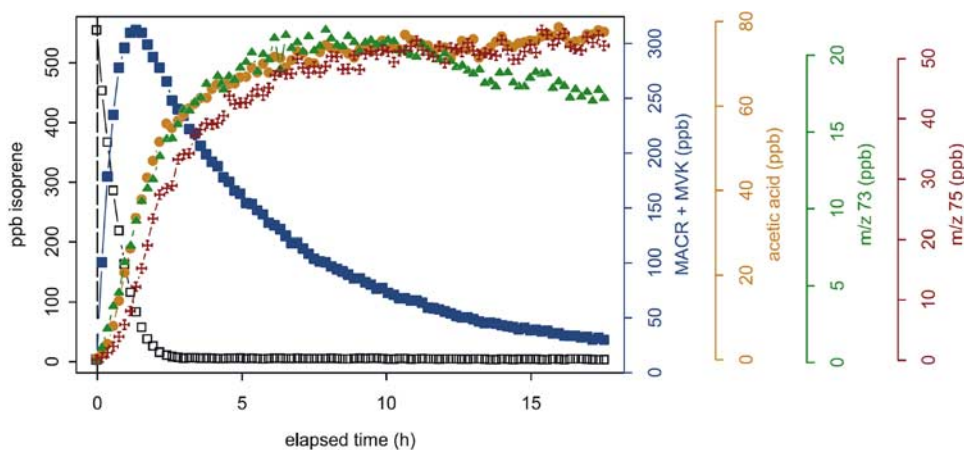


Figure 3. Photo-oxidation of isoprene: evolution of gas phase concentrations of isoprene, primary products (MVK + MACR), and secondary oxidation products (acetic acid, m/z 73, and m/z 75). From *Lee et al.* [2006].

by local sources and thus a nonlocal filter was created. Below we show the usefulness of this filter by exploring the toluene/benzene ratio. Figure 4 shows a scatterplot of benzene versus toluene mixing ratios. When biomass burning emissions of benzene and toluene are negligible, the toluene to benzene ratio can be considered as an indicator of air mass age because the initial emission ratio from gasoline and traffic emissions is relatively well established to be between 2 and 3 [Holzinger *et al.*, 2001]. Acetonitrile mixing ratios can be used as a marker for biomass burning contamination and low mixing ratios of this marker throughout the campaign suggests that biomass burning influence was minor at the site. Toluene degradation occurs on a timescale ~ 5 times faster than benzene oxidation and thus the ratio decreases with time in the atmosphere. Here we define air with a benzene to toluene ratio below 1 as aged (black line in Figure 4). Nonlocal data separated by the above described filter are indicated by large solid red or black circles. The filter reliably segregates aged air from air with recent emissions from local sources as indicated by these data exhibiting the lowest observed toluene/benzene ratios. The nonlocal data include two distinct regions: a narrow distribution of very low benzene and toluene mixing ratios (5–30 and 0–10 ppt, respectively), and a region of higher concentrations and variability of both compounds. These two regions can be cleanly separated using the “US outflow” factor: in Figure 4 data in black are those exhibiting the lowest scores (-0.45 or below) for the “US outflow” factor. We therefore conclude that the nonlocal filter is a reliable tool to isolate data with little local influence.

[19] We use the nonlocal filter to further evaluate the other factors on the basis of the following understanding: if we remove all time periods where the air was strongly impacted by local sources, and if a factor still retains its full spectrum of high and low dominance in the remaining periods of time, we conclude that this factor represents regional rather than local conditions. Figure 5 shows the spectra of the “US outflow,” “aged biogenic,” “isoprene oxidation,” and “biomass burning” factors and their non-local fraction (in red), respectively. Of these four factors only the nonlocal spectrum of the “isoprene oxidation”

factor is significantly reduced, revealing a strong local component of this factor. The spectra of the other factors remain largely conserved if periods of local influence are filtered thus indicating a regional significance of these factors. The regional aspects of the “US outflow” and “biomass burning” factors have also been shown by *Millet et al.* [2006]; the analysis presented here suggests that the “aged biogenic” factor also is of regional significance.

3.3. Processing: Fog and Radiation

[20] Unlike other factors the “aged biogenic” factor is significantly correlated with both solar radiation and fog. The two panels in Figure 6 show scatterplots with photo-synthetically active radiation (PAR) and a fog index. The

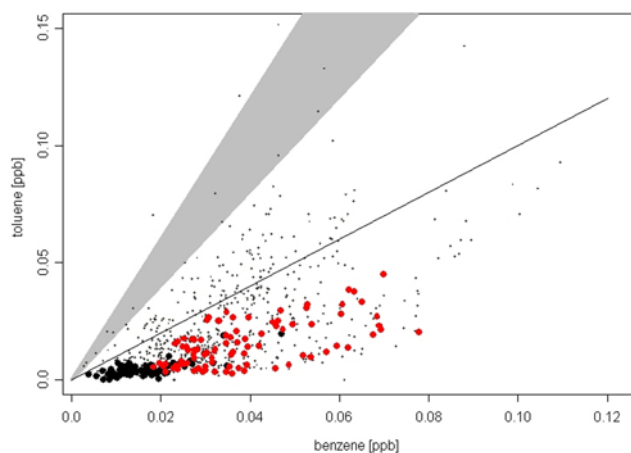


Figure 4. Scatterplot of benzene and toluene. Data printed in black and red are at times with weak local influence; that is, both the “local combustion” and “biogenic terpene” factors are negative. The “US outflow” factor separates red and black points; hence higher concentrations and variability can be explained by transport of air pollution from northeastern United States. The solid black line indicates equal toluene and benzene concentrations, and the grey region indicates ratios of 2–3, which are representative for fresh traffic emissions.

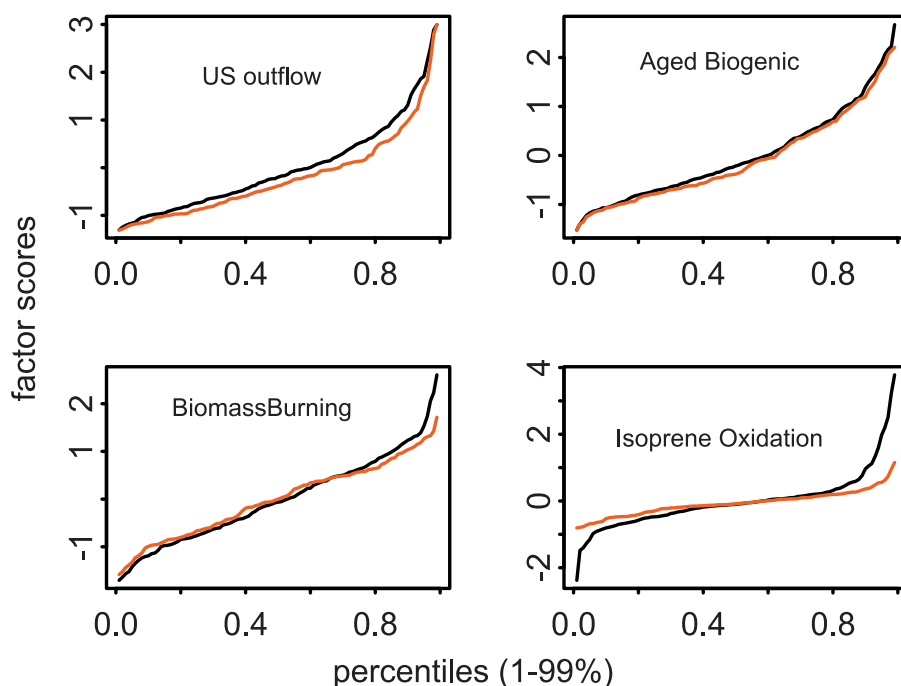


Figure 5. Spectra of the “US outflow,” “aged biogenic,” “biomass burning,” and “isoprene oxidation” factors and their nonlocal fraction in red color. With the exception of the “isoprene oxidation” factor the spectra of the other factors remain largely conserved when times of local influence are cut out. This indicates their regional significance especially for the “aged biogenic” factor.

fog index is the ratio of downward to upward infrared flux; when it is 1 (or nearly 1) it means that the site was surrounded by fog; under clear conditions the index was around 0.75. Figure 6 includes all available daytime data between 0600 and 1800 local time. The positive correlation with PAR suggests photochemical production of “aged biogenic” type compounds on timescales below a few hours. Considering that compounds like formaldehyde load highly on this factor, production on such short timescales is not surprising: the lifetime of formaldehyde with respect to solar radiation is only a few hours. Consequently, the

positive correlation with PAR can only be understood if formaldehyde production from precursor compounds occurs on comparable or shorter timescales. Given the highly oxygenated nature of the “aged biogenic” compounds a negative correlation with fog can also be expected. During fog events highly soluble compounds like acetic acid and hydroxyacetone should be dissolved in fog droplets and eventually removed via wet deposition. However, fog and radiation are also anticorrelated with each other (foggy conditions also reduce the radiation) and it is not easy to show that both these mechanisms independently play a

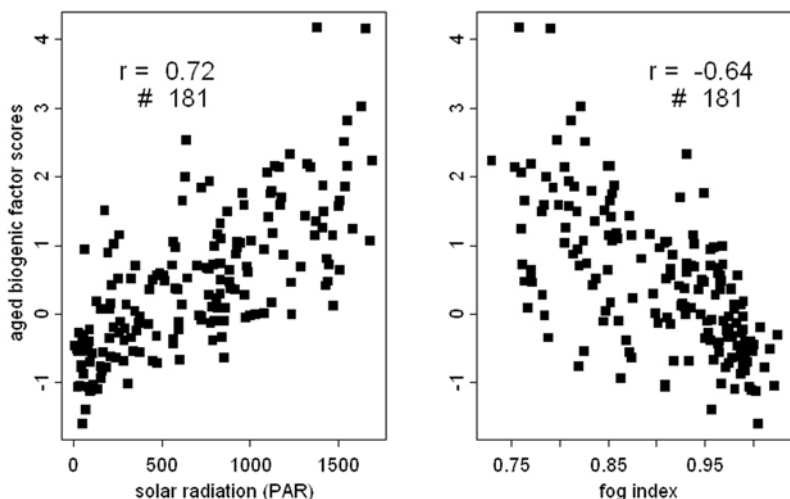


Figure 6. Scatterplot of the “aged biogenic” factor with photosynthetically active radiation (PAR) and fog. All daytime data (0600–1800 local time, 1000–2200 UTC) are included.

Table 3. Correlation Coefficients of “Aged Biogenic” Factor Scores With PAR and the Fog-Index on Hourly Timescales

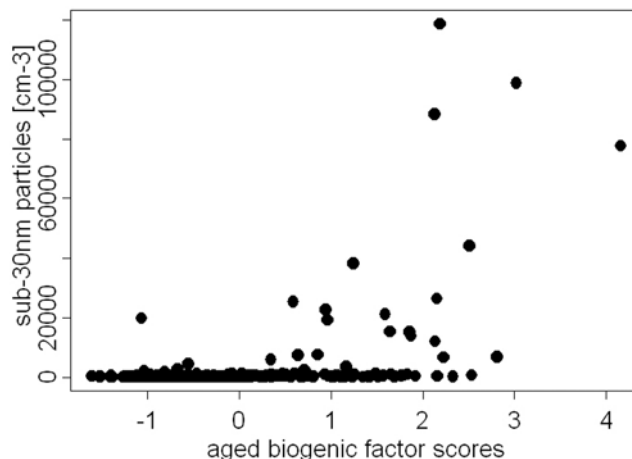
Hour, UTC	Number of Days Included	Correlation With PAR, r_{PAR}	Correlation With Fog, r_{FOG}
1000	22	0.14	-0.24
1200	17	0.49	-0.77
1400	22	0.43	-0.62
1500	19	0.54	-0.53
1600	24	0.68	-0.75
1800	15	0.47	-0.52
1900	15	0.73	-0.71
2000	24	0.5	-0.64
2200	23	0.2	-0.39

significant role. The higher correlation coefficient with PAR suggests that photochemical production of “aged biogenic” compounds may be more important than their removal in fog droplets; on the other hand, this may only reflect that PAR is a more precise measure of sunlight than fog index is of fog. Note that Figure 6 covers a timescale of several hours since all daytime data are included in the scatterplot; if we look at shorter timescales and evaluate each hour separately the pattern changes and the correlation with fog becomes higher (Table 3). Evaluation of the data on these two timescales gives credibility to the idea that both photochemical production and wet deposition during fog events significantly influence mixing ratios of “aged biogenic” compounds.

[21] The connection of the “aged biogenic” factor with radiation and fog can be also shown by means of factor analysis: Loading values of PAR or the fog-index can be obtained if we add their timelines as new variable to the basic data set of atmospheric trace gases and then rerun the principal factor analysis. Table 4 shows the results of this analysis. Fog and PAR, both exhibit high loadings on the “aged biogenic” factor but not on any of the other factors. Interestingly, the fog index is slightly but significantly loaded (loading value of 0.3) on the “local biogenic” factor. It seems that there is a weak correlation between meteorological conditions that produce fog and the conditions which bring local biogenics to the site.

3.4. Role of the “Aged Biogenic” Factor in the Production of Aerosols

[22] Aside from formaldehyde and acetaldehyde, compounds like hydroxyacetone, glycoaldehyde, formic, acetic, and propionic acid are the most dominant species populating this factor. These compounds partition into the aqueous phase of aerosols; and by undergoing transformations in this reservoir they may contribute significantly to the organic fraction of aerosols by mechanisms similar to those proposed by Kalberer *et al.* [2004], Ervens *et al.* [2004], and Carlton *et al.* [2006]. Some of the unidentified compounds may have low enough vapor pressures to trigger the

**Figure 7.** Scatterplot of the “aged biogenic” factor and particles below 30 nm. Nucleation events were unlikely during periods of low dominance of this factor.

production of new airborne particles of measurable sizes, or they may be produced simultaneously with other less volatile oxidation products that do so. Furthermore, all these compounds may have been produced along pathways that also lead to the production of chemical species that predominantly partition into aerosols and thus never reach gas phase concentrations that are accessible with current instrumentation. For these reasons it is of interest to evaluate aerosol information with respect to the six factors developed in this study. Figure 7 shows that events of high number densities of small particles (below 30 nm) usually coincide with high loadings on the “aged biogenic” factor. This connection suggests that the “aged biogenic” factor can be associated with nucleation events as we have speculated above. Allan *et al.* [2005] report that nucleation events occur under conditions of low tide and high solar radiation; they theorize that these nucleation events are triggered by oxidation of iodine compounds emitted from the nearby intertidal zone [O’Dowd *et al.*, 2002; McFiggans *et al.*, 2004]. Our analysis shows that, besides iodine photochemistry, “aged biogenic” compounds (or other oxygenated compounds that are produced along the same lines) are another factor particularly favorable to produce nucleation events. However, it could potentially be that the link is actually with the fog rather than the “aged biogenic” species, as the presence of the fog could be suppressing nucleation through the scattering of sunlight or the uptake of precursors or condensable vapors.

[23] Individual organics in aerosols measured hourly using the newly developed TAG instrument [Williams *et al.*, 2007] were also clearly associated with the “aged biogenic” factor. We evaluated the 37 TAG compounds and other aerosol parameters from other instruments (AMS,

Table 4. Loading Values of Fog and PAR on the Six Factors^a

	Local Anthropogenic	US Outflow	Aged Biogenic	Local Biogenic	Biomass Burning	Isoprene Oxidation
Fog index	-0.02	-0.17	-0.60	0.30	-0.04	-0.01
PAR	-0.10	-0.04	0.76	-0.13	-0.10	0.04

^aSignificant loadings are printed in bold.

Table 5. Factor Loadings of Aerosol Data^a

Parameter	Possible Identity	Local Anthropogenic	US Outflow	Aged Biogenic	Local Biogenic
AMS sulphate			0.36		
AMS organic carbon			0.45	0.45	
AMS ammonium			0.40		
AMS nitrate			0.40	0.21	
MAAP black carbon		0.32	0.61	0.39	
Particle numbers small (<30 nm)				0.48	
Particle numbers, large (>30 nm)			0.47	0.24	
Particle surface, small (<30 nm)				0.46	
Particle surface, large (>30 nm)			0.56	0.41	
TAGa1	5-hexenoic acid, 5-methyl-	0.25		0.51	
TAGb1	hexanoic acid, 9-decen-1-yl ester	0.40		0.48	
TAGc1		0.33		0.54	
TAGd1	5,6-dihydropyran-2-one, 5-acetoxy-6-(1,2-epoxypropyl)-	0.21		0.60	
TAGe1	pinonaldehyde	0.55		0.26	0.45
TAGf1		0.38		0.55	
TAGg1	7-oxabicyclo[2.2.1]heptane-2, 3-dicarboxaldehyde, (2-endo,3-exo)			0.61	
TAGh1	phthalic acid	0.25		0.47	
TAGi1		0.36		0.46	
TAGj1	.delta.undecalactone			0.51	
TAGk1		0.22		0.68	
TAGl1		0.22		0.60	
TAGm1	pelletierine	0.25		0.61	
TAGn1	1,6-dioxaspiro[4,4]nonane-2,7-dione		0.39	0.26	
TAGo1	2H-pyran-2-one, 4-hydroxy-6-pentyl	0.29		0.54	
TAGp1	4-pentenoic acid, 2-acetyl-2, 3-dimethyl-,ethyl ester	0.32		0.53	
TAGq1	2-pentenoic acid, 2-methyl-	0.32		0.55	
TAGr1	4s,6s-dimethyl-7R-acetoxy-3-nonanone (acetyl serricornin)			0.48	
TAGs1				0.39	
TAGt1	2-hydroxy-3,5-dimethylcyclopent- 2-en-1-one			0.43	
TAGu1				0.55	
TAGv1	.delta.-Lauro lactone			0.41	
TAGw1		0.32		0.63	
TAGy1	heptadecane			0.74	
TAGz1	pristane				
TAGaa1		0.57		0.44	0.44
TAGbb1	unknown	0.25		0.45	
TAGcc1		0.28		0.57	
TAGee1	2(3H)-furanone, 3-acetyldihydro-	0.22		0.45	
TAGff1	BHT-aldehyde	0.36		0.43	0.34
TAGhh1	phenanthrene	0.66		0.27	0.39
TAGhh2	tricosane				
TAGii1	methylbis(phenylmethyl)benzene	0.28	0.26	0.39	0.37
TAGii2	tetracosane				
TAGjj1	pentacosane	0.31		0.25	
TAGjj2	hexacosane	0.31		0.38	0.34
TAGjj3	heptacosane	0.33		0.40	0.46

^aAll loadings above 0.2 are printed; loadings above 0.4 are printed in bold.

SMPS, MAAP) by means of factor analysis for the period 26 July to 15 August when TAG was operating. In order to force the aerosol data into the existing set of factors, we added only one aerosol variable at a time to the set of 90 gas phase compounds, reran the program for every new aerosol variable added, and then removed it again from the basic data set. The analysis reliably reproduced the 4 major factors even though the data set was significantly reduced because of the TAG instrument's shorter temporal coverage. Loadings of the aerosol parameters on the "local anthropogenic," "US outflow," "aged biogenic," and "local biogenic" factors are shown in Table 5. Significant loadings above 0.4 were observed for 27, 4, 3, and 0 aerosol compounds on the "aged biogenic," "local anthropogenic,"

local biogenic," and the "US outflow" factor, respectively. So the majority of measured organic compounds in aerosols can be associated with the "aged biogenic" factor and we deduce that these compounds are produced from type "aged biogenic" gas phase precursors as part of secondary organic aerosol. The fact that the TAG instrument is able to detect more compounds in biogenic SOA than anthropogenic SOA is consistent with the lower degree of oxidation of the former reported by the AMS manifested in a lower fraction of CO₂⁺ ions in the organic mass spectra. Compounds which are less oxidized are less likely to stick to the GC column and more likely to be properly resolved in the TAG instrument.

[24] It is remarkable that very few of the TAG compounds loaded on the “US outflow” factor which contrasts the fact that the total aerosol mass is highest when the “US outflow” factor is dominant [Millet *et al.*, 2006]. However, US outflow air is significantly aged so that SOA may have undergone oligomerization processes and individual primary compounds could no longer be detected with the TAG instrument [Williams *et al.*, 2007]. On the other hand, the “aged biogenic” compounds provide a gas phase reservoir from which secondary organic aerosol is continuously produced. Table 5 also includes data on sulphate, organic carbon, ammonium and nitrate measured by an aerosol mass spectrometer (AMS), equivalent black carbon measured using a multi angle absorption photometer (MAAP, Thermo Electron Corporation model 5012) and number densities and surface area for particles below and above a size of 30 nm, measured using a differential mobility particle sizer (DMPS). All AMS parameter and black carbon load on the “US outflow” factor and to a lesser extent on the “aged biogenic” factor. Number densities and surface area of particles below 30 nm exhibit high loadings on the “aged biogenic” factor only, whereas the same parameters of larger particles exhibit higher loadings on the “US outflow” factor. This is in accordance with the discussion of nucleation events above and Millet *et al.* [2006], who report that the majority of aerosol mass is transported in polluted air from the US east coast.

4. Conclusions

[25] During the ICARTT 2004 campaign at the Chebogue Point field site a PTR-MS instrument detected a class of oxygenated compounds that were presumably formed from biogenic precursor compounds. Their significant correlation with radiation indicates photochemical production on time-scales of hours; during fog events they can be removed through wet deposition. Many organic compounds in aerosols are associated with high levels of these compounds. We found no evidence that these oxidized biogenics originate from any local source. As a result, they may be present over larger regions and could be important on regional or even global scales. Through their connection with aerosols we showed that these compounds are a potential atmospheric pool from which particles may acquire organic material, far away from the region of primary emission. Perhaps because of their (with some exceptions) low reactivity, or perhaps because of difficulties in measuring them, these compounds have not received too much attention from atmospheric chemists in the past; our study, however, shows that they may be very “reactive” with respect to aerosol production. A new focus on the role of highly oxygenated compounds in the atmosphere could provide important clues for a better understanding of secondary organic aerosol production. This study would not have been possible without innovative instrumentation such as PTR-MS or the new TAG instrument; further technical developments, especially the reliable measurement of semivolatile compounds, will likely be needed to address questions on the production and chemical and physical properties of organic aerosols.

[26] **Acknowledgments.** This work was funded by NOAA contracts RA133R05SE4459 and RA133R04SE0368. We thank Megan McKay and Jennifer Murphy of the University of California at Berkeley and David Parrish of the NOAA Earth System Research Laboratory for logistical

support. We also thank Elizabeth Andrews and Ellsworth Dutton of the NOAA/ESRL Global Monitoring Division for sharing fog-index data.

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