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Secondary organic aerosols formed from oxidation of biogenic volatile organic compounds in the Sierra Nevada Mountains of California

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[1] Biogenic volatile organic compound (BVOC) emissions, such as isoprene and terpenes, can be oxidized to form less volatile carbonyls, acids, and multifunctional oxygenated products that may condense to form secondary organic aerosols (SOA). This research was designed to assess the contribution of oxidized BVOC emissions to SOA in coniferous forests by collecting high-volume particulate samples for 6 days and 5 nights in the summer of 2003. The samples were analyzed for acids, carbonyls, polyols and alkanes to quantify oxidized BVOCs. Terpene and isoprene oxidation products were among the most abundant chemical species detected with the exception of hexadecanoic acid, octadecanoic acid and two butyl esters of unknown origin. The terpene oxidation products of pinonic acid, pinic acid, nopinone and pinonaldehyde showed clear diurnal cycles with concentrations two- to eight-fold higher at night. These cycles resulted from the diurnal cycles in gaseous terpene concentrations and lower temperatures that enhanced condensation of semivolatile chemicals onto aerosols. The terpene-derived compounds averaged 157 ± 118 ng/m^3 of particulate organic matter while the isoprene oxidation compounds, namely the 2-methyltetrols and 2-methylglyceric acid, accounted for 53 ± 19 ng/m^3. Together, the terpene and isoprene oxidation products represented 36.9% of the identified organic mass of 490 ± 95 ng/m^3. PM_{10} organic matter loadings in the region were approximately 2.1 ± 1.2 μg/m^3, so about 23% of the organic matter was identified and at least 8.6% was oxidized BVOCs. The BVOC oxidation products we measured were significant, but not dominant, contributors to the regional SOA only 75 km downwind of the Sacramento urban area.

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1. Introduction

[2] Aerosols significantly influence the radiative budget of Earth's atmosphere and impact visibility by scattering and absorbing radiation and serving as cloud condensation nuclei. Organic matter typically composes 20–50% of the aerosol mass below 2.5 μm diameter [e.g., *North American Research Strategy for Tropospheric Ozone*, 2003], which includes organic matter that is directly emitted to the atmosphere as well as material formed through gas to particle conversion resulting in secondary organic aerosol (SOA) formation. The organic component of SOA may be derived from either biogenic or anthropogenic precursors, thus it is important to assess the contributions of both sources to understand SOA formation. While global budgets remain highly uncertain, current estimates suggest biogenic SOA sources (8 to 40 Tg yr^{-1}) are much larger than anthropogenic sources (0.3 to 1.8 Tg yr^{-1}) [*Intergovernmental Panel on Climate Change* (*IPCC*), 2001].

[3] Identification of the source of SOA relies on compound-specific measurements of the organic constituents of organic aerosols. Many hundreds of organic compounds have been identified in aerosol samples including alkanes, substituted phenols, alkanals, sugar derivatives, aromatic polycyclic hydrocarbons, monocarboxylic and dicarboxylic acids [*Fine et al.*, 2001; *Nolte et al.*, 1999; *Rogge et al.*, 1993, 1997, 1998]. Often the objective of organic analysis of aerosols is to identify tracers of aerosol sources, but these analyses frequently focus on primary anthropogenic sources rather than biogenic sources. Additionally, the compounds which have been identified generally compose only a fraction of the total organic mass present.

[4] Terrestrial vegetation emits a variety of reactive biogenic volatile organic compounds (BVOCs) including isoprene, alcohols, ketones, monoterpenes, and sesquiterpenes. BVOC emissions are estimated to be approximately a factor of 10 larger than anthropogenic VOC emissions globally [*Seinfeld and Pandis*, 1998]. The BVOCs may be oxidized

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in the atmosphere to form less volatile compounds that may condense onto aerosols and contribute to SOA formation. Terpene and isoprene oxidation products have been observed in aerosols in laboratory oxidation studies and in many forested regions [*Claeys et al.*, 2004a, 2004b; *Kavouras et al.*, 1998, 1999a, 1999b; *Kavouras and Stephanou*, 2002a, 2002b; *Spanke et al.*, 2001; *Yu et al.*, 1999].

[5] The objective of this research was to assess the relative importance of biogenic emissions to organic aerosol composition by collecting particulate samples and analyzing them for a series of organic acids, carbonyls, sugars, polyols and alkanes. In particular, we focused on terpene oxidation products including pinic acid, pinonic acid, norpinic acid, nopinone, and pinonaldehyde, and isoprene oxidation products including 2-methyltetrols, 2-methylglyceric acid and pentenetriols. Measurements were conducted at the Blodgett Forest AmeriFlux site where emissions of BVOCs and their oxidation products have been studied in detail [*Goldstein et al.*, 2004; *Holzinger et al.*, 2005; *Lee et al.*, 2005; *Schade and Goldstein*, 2003; *Schade et al.*, 1999], and fine particle growth events are frequently observed during the day [*Lunden et al.*, 2006]. Separate day and night aerosol samples were collected to test for diurnal variation in organic composition which might provide clues to their sources. Gas-phase VOC and ozone concentrations were also monitored to quantify the variation in precursors to the observed biogenic oxidation products.

2. Materials and Methods

[6] Particulate matter was collected at the Blodgett Forest AmeriFlux site from 9 to 14 September 2003. This site is a secondary-growth Ponderosa pine (*Pinus ponderosa*) plantation located in the Sierra Nevada Mountains of California at an elevation of 1320 m. The region is typical of mixed temperate coniferous forests consisting of *Pinus* and *Abies*. Blodgett Forest is located approximately 75 km downwind of Sacramento, which has a population of nearly 1 million people. The typical meteorology consists of a moderate upslope wind (2.5 to 3 m/s) during the day, which transports pollutants from Sacramento, and a weak downslope flow ($\sim$1.5 m/s) during the night, bringing less polluted air from aloft to the site. The meteorology, gas phase VOC, ozone, carbon dioxide, and humidity were monitored continuously during the study period. Blodgett Forest has been extensively characterized with respect to meteorology and gaseous biogenic emissions and their photochemistry [*Goldstein et al.*, 2000; *Holzinger et al.*, 2005; *Lee et al.*, 2005], thus it provided an ideal setting to study the oxidation products of BVOCs in aerosols.

[7] The gas-phase concentrations of monoterpenes, nopinone, pinonaldehyde, pinonic acid, and methacrolein/methyl vinyl ketone/crotonaldehyde, were monitored in situ using a PTR-MS as has been previously reported [*Holzinger et al.*, 2005; *Lee et al.*, 2005]. During each hour, air was sampled through 6 individual gas inlets, each of which were protected by a Teflon filter (PFA holder, PTFE membrane, pore size 2 μm). One inlet was used to sample air at 12.5 m from 0 to 30 min for eddy covariance flux measurements of total monoterpenes. Five inlets were used to sample vertical gradients at height levels within (1.1 m, 3.1 m, 4.9 m) and above (8.75 m, 12.5 m) the forest canopy, which was approximately 6.5 m high, sequentially for 6 min each during the second 30 min of each hour. The 5 gradient inlets were identically designed; each consisted of 30 m PFA tubing (ID $\sim$4 mm) protected by a Teflon filter and a sample flow of 1 L/min was maintained at all times through each inlet. Since the particulate matter was sampled at a height of $\sim$3 m, only data from the 3.1 m inlet were utilized for comparisons to aerosol data. The PTR-MS instrument was operated under standard conditions (a pressure of 2.1 mbar in the reaction chamber and an electrical field of 66 V/cm), typical primary ion signals were 3–5 million counts per second; see *Holzinger et al.* [2005] for details.

[8] Particulate matter was collected onto 20.3 $\times$ 25.4 cm Tissuquartz^{tm} filters (PALL Life Sciences, Ann Arbor, Michigan) by an Andersen High-volume total suspended particulate sampler (model GBM2000H, Andersen Instruments Inc., Georgia, USA). The sampler was modified by creating a 3 m high "snorkel" from 10.2 cm ID diameter aluminum ducting in an effort to sample forest canopy air more than ground-level air. The flow rate of the sampler was set to 30 m^3/h for all samples. Separate samples were collected during the day (0830 to 2030 local time (LT)) and night (2200 to 0800 LT) to test for diurnal cycles in particulate concentrations. A total of 6 day and 5 night samples were collected sequentially during the study. The quartz filters were baked at 800°C for 8 hours prior to use to remove organic contaminants. Two field blanks were prepared by randomly selecting two filters from the same batch used in sampling, mounting them in the sampler but not turning the vacuum pumps on, removing them from the sampler, and storing them with the field samples. An additional filter was used as a laboratory blank that did not undergo transport and handling in the field.

[9] After sample collection, the filters were cut in half. The first half of the filter was extracted by a Soxhlet apparatus while the second half was archived. Prior to extraction, butanedioic-$^{13}C_2$ acid (Cambridge Isotope Laboratories, Inc. Andover, MA), dodecanoic-$^{13}C_1$ acid, glucose-d_2, 6-fluorochromanone (Sigma-Aldrich chemical Co., Milwaukee, Wisconsin), and pinonaldehyde-$^{13}C_1$ (synthesized at University of California, Davis) were added to the filter to determine extraction efficiencies of the chemicals from the actual field samples. These spiking chemicals were dissolved in methanol and then blotted onto the filter in several locations and then allowed to air dry to remove the methanol solvent. In addition, three blank filters were used for spike-recovery trials to determine extraction efficiencies of a wider range of chemicals. The acids were represented by pentanoic, decanoic, pentadecanoic, pentanedioic, *cis*-pinonic, pinic, and *trans*-norpinic acids (Sigma-Aldrich Chemical Co.). The carbonyls were represented by 2-decanone, 2-indanone, nonanal, 3,5-heptanedione and unlabeled pinonaldehyde (Sigma-Aldrich Chemical Co.). The filters were Soxhlet-extracted by 50:50 acetonitrile (ACN, Optima grade, Fisher Scientific, Pittsburgh, Pennsylvania) and dichloromethane (DCM, B&J CG^2 grade, Honeywell International, Inc., Muskegon, Michigan) for 24 hours followed by an additional 24 hour extraction with methanol (Purge and Trap grade, Fisher Scientific). The extracts where then concentrated by roto-evaporation to $\sim$3 ml and transferred to a graduated centrifuge tube, along with

two rinses of the round bottom flask, for nitrogen evaporation to a final volume of 2 ml.

[10] The study investigated five classes of compounds that required different derivatization methods. The first class of chemicals was the acids, which included 35 target analytes. The acids were derivatized by adding *N*,*O*-bis (trimethylsilyl)trifluoroacetamide (BSTFA, Supelco, Bellefonte, Pennsylvania) as a silylation reagent. In this case, aliquots of the ACN:DCM and methanol extracts were combined and evaporated to dryness and then reconstituted into 200 μl DCM. The internal standards of hexanoic-d_{11} and benzoic-d_5 acids (Sigma-Aldrich Chemical Co.) were then added to the samples. Twenty microliters of BSTFA: chlorotrimethylsilane (10:1 v/v) were added to the samples which were then heated at 45°C for 24 hours. The samples were then analyzed without further cleanup. The second class of chemicals studied was the carbonyls. Only the ACN:DCM extract was used since it contained the less polar carbonyls while avoiding the more polar interferences. In this case, benzaldehyde-d_6 (Cambridge Isotope Laboratories) was used an internal standard. The carbonyls were derivatized by adding 20 μl of a 50 mM pentafluorobenzylhydroxylamine (PFBHA, Sigma-Aldrich Chemical Co.) solution to a 200 μl aliquot of the sample extract. The samples were then allowed to react for 24 hours at room temperature (22°C) after which they were ready for analysis. The third group of chemicals investigated were the sugars and sugar-derived compounds (8 compounds), which were also derivatized by BSTFA, but the derivatization was more aggressive. Aliquots of the ACN:DCM and methanol extracts were combined and evaporated to dryness. The samples were reconstituted and derivatized in a 50:50 solution of BSTFA and pyridine (Sigma-Aldrich Chemical Co.), which is similar to previously used approaches [*Pashynska et al.*, 2002]. The samples were heated at 45°C for 24 hours and then injected on the instrument. The fourth group of chemicals was the polyols, which consisted of the 2-methyltetrols, 2-methylglyceric acid, and three pentenetriols. The 2-methyltetrols and 2-methylglyceric acid are isoprene oxidation products [*Claeys et al.*, 2004a]. The standards for the two methyltetrols were obtained from Dr. Claeys who synthesized them. These chemicals were derivatized in an identical fashion as the sugars with a 50:50 mix of BSTFA and pyridine. The last group was the "native" analysis, which consisted of 21 *n*-alkanes that required no derivatization. In this case, the sample extract was added to a GC vial along with the internal standards of tetracosane-d_{50}, and hexatriacontane-d_{74} (Cambridge Isotope Laboratories).

[11] In addition to the filter samples, surface soil, Ponderosa pine needle and Ponderosa pine wood samples were collected from Blodgett forest to try to identify the source of two unexpected nonpolar analytes, namely the butyl ester of hexadecanoic acid and the butyl ester of octadecanoic acid. Two aliquots (105 mg and 210 mg, wet weight) of the surface soil sample were added to a centrifuge tube along with sodium sulfate to dry the soil. The samples were shaken three times with 3 ml of hexane each time and the extract was evaporated to 200 μl. The pine needles and wood were simply shaken in hexane to give a qualitative presence/absence of the butyl esters in the samples. In addition, two 2 cm^2 patches from an archived filter, one from the edge and one from the center of the filter, were also extracted by shaking them in hexane to ensure that butyl esters were not formed as a result of the Soxhlet extraction procedure.

[12] All analyses were conducted by a Varian 3400 gas chromatograph coupled to a Saturn 2000 ion trap mass spectrometer (Varian Inc. Walnut Creek, California). Five microliters of the samples were injected into an injection port packed with silanized glass wool that was maintained at 5°C below the boiling point of the sample solvent. The injection port was then heated to 275°C to volatilize the chemicals from the injector port onto the analytical column. Chromatographic separation was conducted with a DB-XLBMSD column (5% phenyl substituted, 30 m length, 0.25 mm ID, 0.25 μm film thickness, Agilent Technologies, Wilmington, Delaware) using helium as a carrier gas at 37 cm/s. The initial column temperature was 35°C for the acid and sugar analyses while it was 64°C for the native and carbonyl analyses. The column was then heated at 5°C/min to 330°C where it was held for 8 minutes. The ion trap mass spectrometer conditions were a 270°C transfer line temperature and a 220°C trap temperature. Electron ionization (EI) was used for sample detection and quantification while methane chemical ionization (CI) was used for analyte confirmation as well as structural elucidation of unknown chemicals. The EI and CI analyzes used were the Varian default parameters except that the target ion count in EI was reduced to 10,000 from 20,000 to improve the spectra in dirty matrices.

[13] Quantification was conducted using a 6-point calibration curve which was obtained by derivatizing standard mixtures alongside the samples for each of the chemical classes investigated. If a field sample exceeded the calibration curve, then a new aliquot of the sample extract was diluted and derivatized along with a new calibration curve. The limit of detection was defined as the field blank plus three standard deviations of the field blank (blank + 3·SD) while the limit of quantification was defined as the field blank plus six standard deviations of the blank (blank + 6S·D). All concentration results were rounded to two significant digits of accuracy after all calculations were completed.

3. Results

3.1. Gaseous Results

[14] The meteorological and ozone data showed diurnal cycles during the sampling period that are typical for this site and time of year for the western slope of the Sierra Nevada Mountains (Figure 1). The ambient temperature data showed a clear daily cycle with an average daytime temperature of 21.3°C and an average nighttime temperature of 12.9°C during the sampling period. The wind speed also showed a diurnal cycle with the highest wind speed occurring during the daytime. The prevailing daytime "upslope" wind may also bring anthropogenic contaminants from the urban areas in the Central Valley. The concentration of ozone was slightly higher during the day (average = 57.0 ± 11.7 ppbv, n = 144) compared to the night (avg = 45.6 ± 10.2 ppbv, n = 120). Therefore we would not expect more than a factor of ~2 differences in the rate of BVOC oxidation product formation based on varying con-

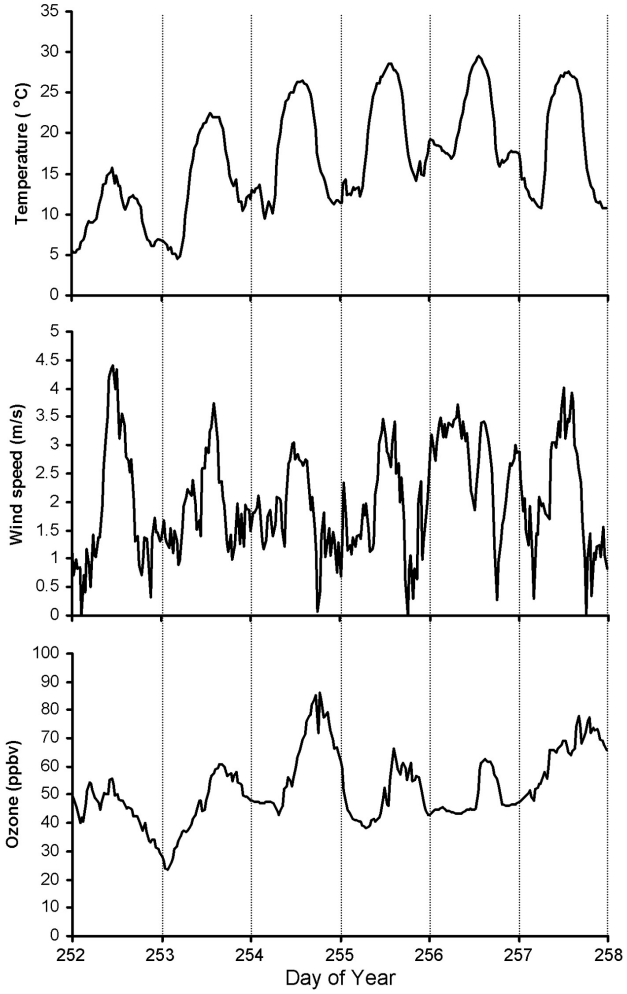

Figure 1. Temperature, wind and ozone data during sampling the period.

centrations of ozone. However, there could be substantial differences in oxidation rates for reactions with hydroxyl (maximum during the day) or nitrate (maximum at night) radicals.

[15] The gaseous concentrations of the monoterpenes, nopinone, pinonaldehyde, pinonic acid, benzene and methacrolein/methyl vinyl ketone/crotonaldehyde were determined alongside the particulate air sampler. The results showed that the monoterpene concentrations were approximately twice as high at night (6000 ± 2400 ng/m^3 or 1.2 ± 0.52 ppbv; n = 50) compared to the day (3200 ± 1100 ng/m^3 or 0.67 ± 0.24 ppbv; n = 36) (Figure 2). The higher nighttime concentrations of the monoterpenes, which is due to more vertical stability and slower oxidation rates compared to daytime conditions, is regularly observed at Blodgett Forest [*Holzinger et al.*, 2005]. The gas-phase concentrations of nopinone were not significantly different between day (570 ± 200 ng/m^3 or 0.12 ± 0.042 ppb; n = 36) and night (580 ± 180 ng/m^3 or 0.12 ± 0.036 ppb; n = 50) during the sampling period. The lack of a strong diurnal cycle in gas phase concentrations of nopinone was also consistent with previous research at this site [*Holzinger et al.*, 2005]. Gaseous pinonaldehyde was sporadically detected with concentrations near the detection limit. When pinonaldehyde was detected, its concentrations were in the 29 to 175 ng/m^3 (0.050 to 0.30 ppbv) range. Pinonic acid was not detected in the gas phase during this study. The observation that the less volatile compounds of pinonaldehyde and pinonic acid were either not detected or present at low concentrations in the gas phase was not surprising since these chemicals were expected to condense onto particulate matter and thus not be present in the gas phase to any considerable degree. Lastly, benzene was also monitored to give an indication of influence from anthropogenic sources from the Central Valley. The concentrations of benzene were highest during the day, which corresponded to the upslope airflow (Figure 2).

3.2. Particulate Results

[16] The results from the spike-recovery trials and labeled surrogate compounds added to the field samples showed that the extraction method was generally good (between 70 and 120%) for most of the chemicals investigated (Table 1). For the acids, the exceptions were pentanoic acid that evaporated during the drying step and decanoic acid which seemed to suffer from contamination. Butanedioic-$^{13}C_2$ acid

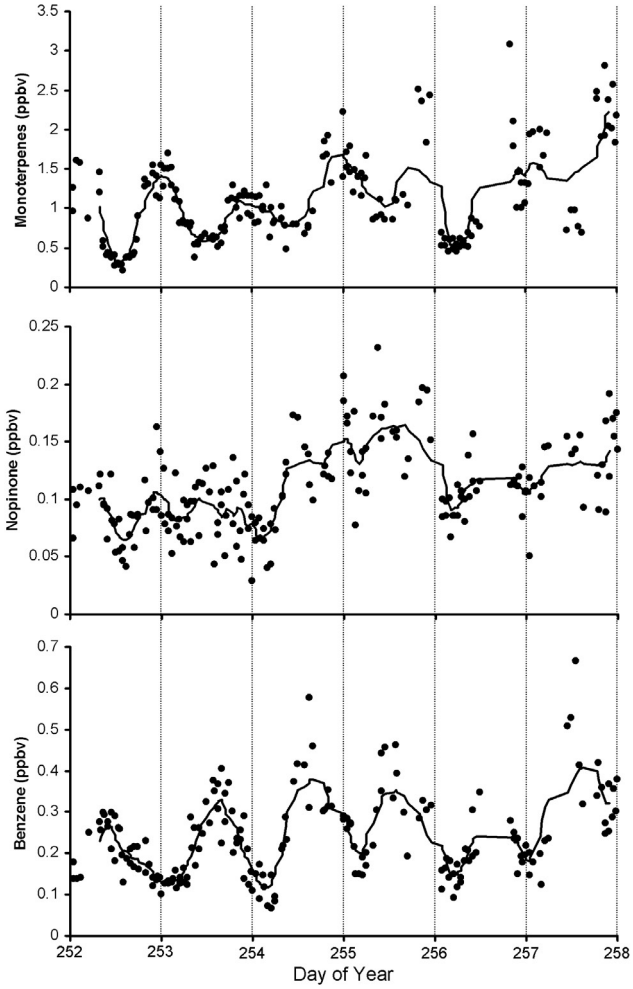

Figure 2. Gaseous concentrations of monoterpenes, nopinone and benzene as determined by PTR-MS during the course of particulate sampling period. The line represents the 10-point moving average of the data.

Table 1. Recovery of Typical Analytes From High-Volume Air Filters as Determined by Three Spike Recovery Trials and Surrogate Compounds Added to Field Samples

Compound	Average Recovery, %	SD (n = 3)
Spike-recovery trials (n = 3)		
Acids		
Pentanoic acid	0.0	0.0
Decanoic acid	150	26
Pentadecanoic acid	110	7.5
Pentanedioic acid	77	11
Cis-pinonic acid	97	9.0
Pinic acid (two isomers)	81	9.5
Trans-norpinic acid	72	5.2
Carbonyls		
2-decanone	71	14
2-indanone	28	17
Nonanal	84	17
3,5-heptanedione	35	8.3
Pinonaldehyde	80	15
Field sample surrogates (n = 11)		
Dodecanoic-$^{13}C_1$ acid	134	30
Butanedioic-$^{13}C_2$ acid	64	17
Glucose-d_2	75	17
6-fluorochromanone	110	7.4
Pinonaldehyde-$^{13}C_1$	see note[a]	

[a]Large amounts of native pinonaldehyde in the samples contributed significant fraction amount of pinonaldehyde-$^{13}C_1$, thus obscuring the labeled compound added to the samples.

recovery from the field samples averaged 64%, which was still reasonable but lower than expected on the basis of the pentanedioic acid spike recovery results. Dodecanoic-$^{13}C_1$ acid recovery from field samples was high at 134 ± 30%, which may be partly due to natural ^{13}C isotopes present in native dodecanoic acid. For the carbonyls, 2-indanone and 3,5-heptanedione showed poor recoveries with 28 and 35% for reasons that are not completely clear. Overall, the recovery of terpene oxidation products, such as *cis*-pinonic acid (97 ± 9.0%), pinic acid (81 ± 9.5%), *trans*-norpinic acid (72 ± 5.2%) and pinonaldehyde (80 ± 15%), were good for this extraction procedure. These extraction experiments were used to validate the efficiency of the extraction methodology, but we did not use the spike-recovery data to correct the observed field concentrations.

[17] The field blanks proved the substrates were largely free of the analytes of interest or were at low enough concentrations as not to interfere with field sample quantification. For the acids, the exceptions were benzoic (MQL = 2.1 ng/m^3), hexanoic (MQL = 5.2 ng/m^3), heptanoic (MQL = 0.57 ng/m^3) and oxalic acids, where oxalic acid suffered from instrumental problems. For the sugars, the exceptions were sucrose (MQL = 1.7 ng/m^3) and inositol (MQL = 0.40 ng/m^3), which interfered with the quantification of 7 and 9 of the 11 samples, respectively. For the carbonyls where quantification was attempted, only decanal (MQL = 0.97 ng/m^3) showed an appreciable contamination in the field blank, although some of the lighter carbonyls, such as acetone, also showed significant blanks, but these volatile species were not quantified since they were not expected to be retained on a filter. Unfortunately, most of the targeted *n*-alkanes from C_{20} to C_{36} showed enough contamination in the field blanks to make the quantification unreliable, so only three *n*-alkanes were quantified.

3.3. Acid Results

[18] The first class of chemicals investigated for biogenic contributions to aerosols were the acids since these compounds were expected to condense onto aerosol because of their lower vapor pressures (Table 2). Overall, the sum of 24 detected acid species ranged from 150 to 510 ng/m^3 with hexadecanoic (avg = 94 ng/m^3), octadecanoic (avg = 22 ng/m^3), *cis*-pinonic (avg = 14 ng/m^3) and glyoxylic (avg = 13 ng/m^3) being the most abundant acids. *Cis*-pinonic and pinic acids are products of ozone oxidation of α-pinene, β-pinene, and in the case of pinic acid, sabinene and Δ^3-carene as well [*Yu et al.*, 1999], thus these chemicals have a oxidized BVOC source. We did not detect *trans*-norpinic acid. However, *Yu et al.* [1999] observed that norpinic acid had a low product yield as a result of ozone interacting with α-pinene and β-pinene, so the lack of detection in the field is likely correct and indicative of low concentrations. The concentrations of the terpene-derived acids detected in Blodgett Forest were comparable to other studies (Table 3) [*Kavouras et al.*, 1998, 1999b; *Kavouras and Stephanou*, 2002a, 2002b; *Spanke et al.*, 2001]. The alkanoic acid series from decanoic to nonadecanoic acids showed that the even carbon numbered acids were far more prevalent than the odd carbon number acids (Table 2). The general trend of the alkanoic acids and alkanedioic acids were similar to those observed by *Yue and Fraser* [2004] around Houston, Texas, except that hexadecanoic acid was the predominant acid in this study while octadecanoic acid was the most abundant acid in their research.

[19] The acids results showed significant day/night differences in concentrations of *cis*-pinonic (Figure 3), pinic and octadecanoic acids (Table 2). In the case of pinic and *cis*-pinonic acids, the concentrations were significantly higher at night while octadecanoic acid was higher during the day (*t*-test, $P < 0.05$). The gas-phase monoterpene data showed approximately two-fold higher monoterpene concentrations at night. In addition, the nighttime samples would experience cooler sampling conditions that should shift the gas-particle partitioning of the chemicals into the particulate phase [*Janson et al.*, 2001; *Kavouras et al.*, 1999a] or allow gas-phase chemicals to adhere and be more retained by the filter. Thus the higher concentrations of the terpene-derived acids at night were reasonable.

3.4. Carbonyl Results

[20] The second class of chemicals that may have biogenic sources through oxidation of terpenes are the carbonyls. Only 19 of the 113 carbonyls in our calibration standards were detected in the filter samples. Furthermore, the majority of the detected compounds were volatile species (e.g., acetone, methacrolein, methyl vinyl ketone, etc.) that were unlikely to be retained on a filter for any extended period of time during sampling. If only the less volatile species are considered, then the number of detected compounds drops to 7 (Table 4), of which most are still semivolatile (e.g., nopinone) and were more abundant in the gas phase than the particulate phase [*Yu et al.*, 1999]. Therefore the particulate numbers are likely to be underestimates because of blow-off. The most abundant carbonyl species detected were pinonaldehyde with an average concentration of 110 ng/m^3 followed by methylglyoxal (avg = 29 ng/m^3), glyoxal (avg = 9.5 ng/m^3) and nopinone (avg =

Table 2. Concentrations of Acids (ng/m^3) Collected on High-Volume Quartz Filters[a]

Compound	Overall Average ± SD	Daytime Average ± SD	Nighttime Average ± SD	*t*-Test (*P*-Value)
Decanoic acid	0.7 ± 0.4	0.8 ± 0.3	0.6 ± 0.5	NS
Undecanoic acid	1.7 ± 1.2	1.4 ± 1.0	2.0 ± 1.4	NS
Dodecanoic acid	9.8 ± 7.8	7.0 ± 8.5	13 ± 6.0	NS
Tridecanoic acid	1.7 ± 0.8	1.3 ± 0.5	2.2 ± 0.7	0.036
Tetradecanoic acid	7.9 ± 3.1	7.8 ± 3.6	8.1 ± 2.7	NS
Pentadecanoic acid	2.1 ± 0.7	2.3 ± 0.8	1.8 ± 0.4	NS
Hexadecanoic acid	94 ± 100	140 ± 120	39 ± 22	NS
Heptadecanoic acid	1.5 ± 1.0	1.7 ± 1.2	1.2 ± 0.6	NS
Octadecanoic acid	22 ± 14	31 ± 14	12 ± 4.5	0.019
Nonadecanoic acid	4.5 ± 2.6	5.0 ± 1.6	3.9 ± 3.5	NS
9-octadecenoic acid	6.9 ± 2.8	7.4 ± 2.3	6.5 ± 3.4	NS
Oxalic acid	see note[b]	see note[b]	see note[b]	···
Propanedioic acid	see note[c]	see note[c]	see note[c]	···
Butanedioic acid	5.5 ± 1.6	5.9 ± 2.0	5.0 ± 0.8	NS
Pentanedioic acid	5.8 ± 9.7	6.1 ± 11	5.4 ± 9.0	NS
Hexanedioic acid	see note[c]	see note[c]	see note[c]	···
Heptanedioic acid	0.7 ± 0.4	0.7 ± 0.4	0.7 ± 0.4	NS
Octanedioic acid	see note[c]	see note[c]	see note[c]	···
Nonanedioic acid	5.8 ± 2.1	5.8 ± 2.9	5.8 ± 0.7	NS
Decanedioic acid	3.5 ± 2.4	3.8 ± 3.0	3.1 ± 1.7	NS
L-tartaric acid	see note[c]	see note[c]	see note[c]	···
DL-malic acid	2.2 ± 2.2	2.6 ± 2.9	1.8 ± 1.1	NS
Fumaric acid	0.4 ± 0.2	0.3 ± 0.2	0.5 ± 0.1	NS
Maleic acid	see note[b]	see note[b]	see note[b]	···
Glycolic acid	2.1 ± 2.0	2.7 ± 2.5	1.3 ± 0.8	NS
Citraconic acid	see note[c]	see note[c]	see note[c]	···
Glyoxylic acid	13 ± 5.6	17 ± 5.3	10 ± 4.2	NS
Benzoic acid	see note[c]	see note[c]	see note[b]	···
Cis-pinonic acid	14 ± 14	3.6 ± 0.7	27 ± 9.1	0.004
Pinic acid	4.3 ± 3.0	2.2 ± 0.5	6.9 ± 2.7	0.018
Trans-norpinic acid	see note[b]	see note[b]	see note[b]	···
2-Methylglyceric acid[d]	8.2 ± 7.4	11 ± 8.6	4.7 ± 4.2	NS

[a]The average concentration (±SD) is given for all the samples, then only the daytime samples (n = 6), and then only the nighttime samples (n = 5). A Student's *t*-test ($P < 0.05$) was used to test for differences in concentrations between the day and night samples where "NS" indicates that the compound was not statistically different.
[b]This compound was not detected in any samples either because of low concentrations or high field blank values.
[c]This compound was below the limit of quantification in more than half of the samples, so no average was calculated.
[d]No standard was available, hence quantification was conducted assuming similar instrumental response similar to glycolic acid. Identification was based on a match of the mass spectrum with spectrum presented by *Edney et al.* [2005] and similar retention time.

2.8 ng/m^3). The concentration of pinonaldehyde in the gas and particulate phases were comparable while the particulate concentration of nopinone was considerably lower than the average gas phase with concentrations of 670 ng/m^3. Furthermore, Kavouras et al. [*Kavouras et al.*, 1999a; *Kavouras and Stephanou*, 2002a] also showed higher gas phase concentrations of pinonaldehyde and nopinine in field samples. Both nopinone and pinonaldehyde are products from the ozone degradation of β-pinene. [*Yu et al.*, 1999] showed that pinonaldehyde was the most abundant species

Table 3. Concentrations of Particulate Monoterpene Oxidation Products (ng/m^3) Observed in This Study Compared to Previous Research[a]

Compound	Day Average ± SD	Night Average ± SD	Overall Range	Literature
Cis-pinonic acid	3.6 ± 0.7	27 ± 9.1	2.6–37	0.2–71.0,[b] 1.0–25.7,[c] 7.05–97.74,[d] 9.68 ± 7.96 (0600–1200 LT),[e] 1.16 ± 0.91 (1200–1800 LT),[e] 3.99 ± 2.45 (1800–0600 LT)[e]
Pinic acid (sum of two isomers)	2.2 ± 0.5	6.9 ± 2.7	1.7–10	0.8–4.0,[f] 0.4–4.4,[c] 0.39–82.72,[d] 2.38 ± 1.53 (0600–1200 LT),[e] 0.49 ± 0.46 (1200–1800 LT),[e] 3.03 ± 1.55 (1800–0600 LT)[e]
Trans-norpinic acid	not detected[g]	not detected[g]	···	0.4–5.4,[c] 0.0–13.85,[d] 1.94 ± 1.92 (0600–1200 LT),[e] 0.14 ± 0.09 (1200–1800),[e] 1.51 ± 1.02 (1800–0600 LT)[e]
Nopinone	1.8 ± 0.4	3.9 ± 1.0	1.5–5.1	0.2–13.0,[b] 0.1–0.5,[c] 0.0–13.24,[d] 0.17 ± 0.22 (0600–1200 LT),[e] 0.02 ± 0.03 (1200–1800),[e] 0.24 ± 0.14 (1800–0600 LT)[e]
Pinonaldehyde	35 ± 34	200 ± 98	16–320	0.2–32.0,[b] 0.3–1.2,[c] 0.17–32.12,[d] 0.78 ± 0.54 (0600–1200 LT),[e] 0.27 ± 0.28 (1200–1800),[e] 0.88 ± 0.50 (1800–0600 LT)[e]

[a]The concentrations are divided into day (n = 6) and night (n = 5) samples since the concentrations between these two time classes are significantly different.
[b]*Kavouras and Stephanou* [2002b].
[c]*Kavouras et al.* [1998]. The nopinone and pinonaldehyde values were estimated from a figure.
[d]*Kavouras et al.* [1999b].
[e]*Kavouras and Stephanou* [2002a]. Values are presented for different times of the day.
[f]Sum of pinic and pinonic acids presented by *Spanke et al.* [2001].
[g]The limit of quantification was 0.48 ng/m^3.

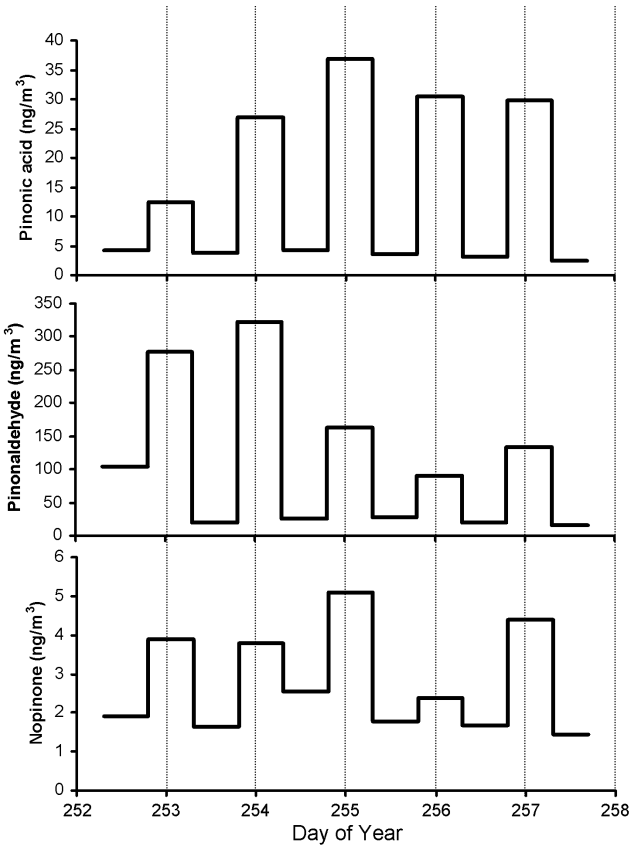

Figure 3. Diurnal cycle in particulate concentrations of the monoterpene oxidation products of pinonic acid, pinonaldehyde and nopinone.

formed in their laboratory experiments, which was consistent with the field measurements. The observed pinonaldehyde concentrations in this study were considerably higher than *cis*-pinonic and pinic acid concentrations, which is also in agreement with the laboratory experiments [*Yu et al.*, 1999]. While the concentrations of particulate-associated nopinone observed in this study were consistent with previous research, the concentrations of pinonaldehyde were considerably higher (Table 3) [*Kavouras et al.*, 1998, 1999b; *Kavouras and Stephanou*, 2002a, 2002b].

Table 4. Concentrations of Carbonyls (ng/m^3) Collected on High-Volume Quartz Filters[a]

Compound	Overall Average ± SD	Daytime Average ± SD	Nighttime Average ± SD	*t*-Test (*P*-Value)
Glyoxal	9.5 ± 6.5	11 ± 7.3	8.3 ± 5.8	NS
Methylglyoxal	29 ± 10	26 ± 5.2	33 ± 14	NS
Decanal	1.3 ± 0.8	1.6 ± 1.0	1.0 ± 0.3	NS
2,5-hexanedione	0.5 ± 0.1	0.5 ± 0.2	0.4 ± 0.1	NS
Benzophenone	0.2 ± 0.3	0.1 ± 0.1	0.3 ± 0.4	NS
Nopinone	2.8 ± 1.3	1.8 ± 0.4	3.9 ± 1.0	0.007
Pinonaldehyde	110 ± 110	35 ± 34	200 ± 98	0.018

[a]The average concentration (±SD) is given for all the samples, then only the daytime sample, and then only the nighttime samples. A Student's *t*-test was used to test for differences in concentrations between the day and night samples. Statistical differences were defined at the $P < 0.05$ level while "NS" indicates that the compound was not statistically different.

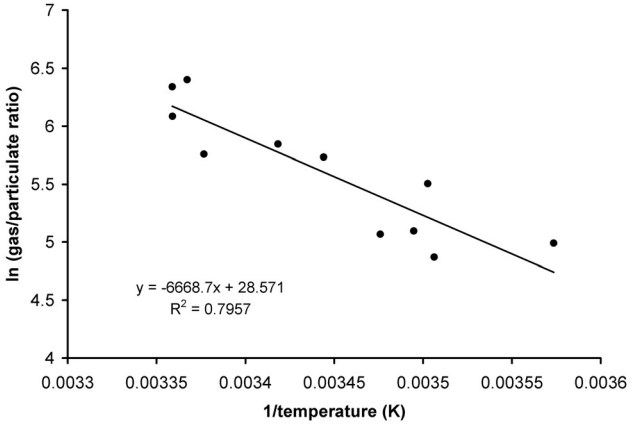

Figure 4. Correlation ($R^2 = 0.79$) between the ambient temperature expressed as inverse temperature in Kelvin and the natural logarithm of gas-particulate ratio of nopinone. The Clausius-Clayperon plot predicts the ΔH_{vap} for nopinone to be 55.4 KJ/mol. The results showed that increasing temperature caused a shift of the partitioning of nopinone to the gas phase.

This may be the result of differences in vegetation types between different study sites.

[21] The terpene-derived carbonyl oxidation products (Table 4) showed a strong diurnal cycle in a similar fashion as the terpene-derived acids (Figure 3). Pinonaldehyde concentrations at night were approximately 5.7-fold higher than the daytime concentrations while nopinone concentrations were 2.2-fold higher at night. Once again, the higher concentrations of pinonaldehyde and nopinone in the aerosol at night were probably the result of slower vertical mixing and heterogeneous-condensation from the gas phase onto particles at cooler temperatures [*Janson et al.*, 2001; *Kavouras and Stephanou*, 2002a]. The gas to particulate ratio for nopinone showed a strong dependence on ambient temperature (Figure 4), with increasing partitioning of nopinone into particulate matter as temperatures decreased. The gas-particulate ratio varied with ambient temperature following a Clausius-Clayperon relationship with an apparent ΔH_{vap} for nopinone of 55.4 KJ/mol. This comparison quantifies how important temperature is for heterogeneous condensation of this terpene oxidation product onto aerosols, and provides the first measure of an effective enthalpy of vaporization that can be used in atmospheric chemistry models for nopinone.

3.5. Sugars and Sugar-Derived Compounds

[22] The results from the sugar analysis (Table 5) procedure showed that levoglucosan (avg = 16 ng/m^3) was the most abundant compound detected followed by glucose (avg = 13 ng/m^3). The sum of the sugar mass was 53 ± 15 ng/m^3, which was comparable to the sugars observed in the Howland Experimental Forest in Maine, USA, which is also a predominately conifer-based forest [*Medeiros et al.*, 2006]. Levoglucosan is a known wood combustion product [*Simoneit et al.*, 1999; *Simpson et al.*, 2004], which implies that the site had wood smoke traces in the samples. However, the concentrations were generally much lower than those observed by other research groups such as *Nolte et al.* [2002] at Kern Wildlife refuge (106 ng/m^3); Bakers-

Table 5. Average (±SD, n = 11) Concentrations (ng/m^3) of Sugars and Polyols Collected on High-Volume Quartz Filters[a]

Compound	Overall Average ± SD
Sugars	
Methyl-β-L-arabinopyranoside	see note[b]
D-arabitol	7.6 ± 2.6
Levoglucosan	16 ± 13
Fructose	4.9 ± 2.5
Glucose	13 ± 5.2
Mannitol	8.8 ± 3.4
Inositol	see note[c]
Sucrose	see note[c]
Sum of sugars	53 ± 15
Polyols	
2-methylthreitol	13 ± 3.8
2-methylerythritol	32 ± 9.6
2-methylglyceric acid[d]	8.2 ± 7.4
Pentenetriol (first eluting)[e]	1.1 ± 0.43
Pentenetriol (second eluting)[e]	0.47 ± 0.11
Pentenetriol (third eluting)[e]	1.9 ± 1.1
Sum of polyols	57 ± 19

[a]No statistical differences (*t*-test, $P > 0.05$) were observed between day and night samples, so only an overall concentration is presented for the study.
[b]This compound was not detected in any samples.
[c]This compound was below the limit of quantification in more than half of the samples, so no average is calculated.
[d]No standard was available, so quantification was based on assuming a similar instrumental response as glycolic acid.
[e]No standard was available, so quantification was based on assuming a similar instrumental response as 2-methylerythritol.

field (2390 ng/m^3); Fresno (2980 ng/m^3); *Pashynska et al.* [2002] in Ghent, Belgium (summer avg = 19.1 and winter avg = 420 ng/m^3); *Yue and Fraser* [2004] around Houston before and after a smoke episode (20.8 to 663.4 ng/m^3); and *Simpson et al.* [2004] in the Seattle area (10 to 760 ng/m^3). Considering the site is located in the Sierra Nevada Mountains where wood fire places are frequently used for heating homes and fire is often used to dispose of logging debris, it is reasonable to expect periodic observations of levoglucosan. Unlike the terpene oxidation products, the sugars and sugar derivatives did not show clear diurnal cycles (Figure 5). The source of these chemicals was probably primary particulate emissions since these chemicals are essentially nonvolatile and not present in the ambient gas phase of the atmosphere. It should be noted that the sampler used was a total suspended particulate sampler that would collect coarse biological particulate matter, such as plant detritus, microbes and spores, that may contain sugars [*Medeiros et al.*, 2006].

3.6. Polyols

[23] The polyols, namely the 2-methyltetrols, 2-methylglyceric acid and pentenetriols (i.e., cis and trans 2-methyl-1,3,4-trihydroxy-1-butene and 3-methyl-2,3,4-trihydroxy-1-butene), have recently been recently identified as marker compounds for photo-oxidation of isoprene in aerosols [*Claeys et al.*, 2004a; *Edney et al.*, 2005; *Wang et al.*, 2005]. Two diastereoisomeric 2-methyltetrols were detected in the samples with 2-methylerythritol being about 2.5-fold more abundant than 2-methylthreitol (Table 5), which is a similar ratio as observed in other studies in the Amazon [*Claeys et al.*, 2004a], K-puszta, Hungary [*Ion et al.*, 2005] and boreal forests in Finland [*Kourtchev et al.*, 2005]. The two 2-methyltetrols combined had an average mass loading of 45 ± 13 ng/m^3, which is comparable to concentrations observed in the Amazon, Hungary and Finland in the summer [*Claeys et al.*, 2004a; *Ion et al.*, 2005; *Kourtchev et al.*, 2005]. This confirms the ubiquitous nature of the 2-methyltetrols in SOA from vastly different geographic regions.

[24] Although the 2-methyltetrols were expected to be photochemically produced, they did not show clear diurnal cycles (Figure 5) like some of the monoterpene oxidation products such as pinonic acid and pinonaldehyde (Figure 3). This contrasts with *Ion et al.* [2005] who observed a clear diurnal cycle with higher concentrations during the day. These differences are likely due to different meteorology at the sites. A comparison between the 2-methyltetrols and the other chemicals showed that tetrols correlated best with ozone followed by glucose and fructose (Figure 6). It is intriguing that the 2-methyltetrols correlated well with the sugars. It may be possible that the 2-methyltetrols may arise directly from a similar biological source as the sugars in addition to the well documented photochemical pathway. The poor correlation with the monoterpene oxidation products (Figure 6) would suggest the 2-methyltetrols would have a different source, but the strong correlation with ozone and other highly oxidized compounds, such as glyoxal, supports an atmospheric oxidation formation path-

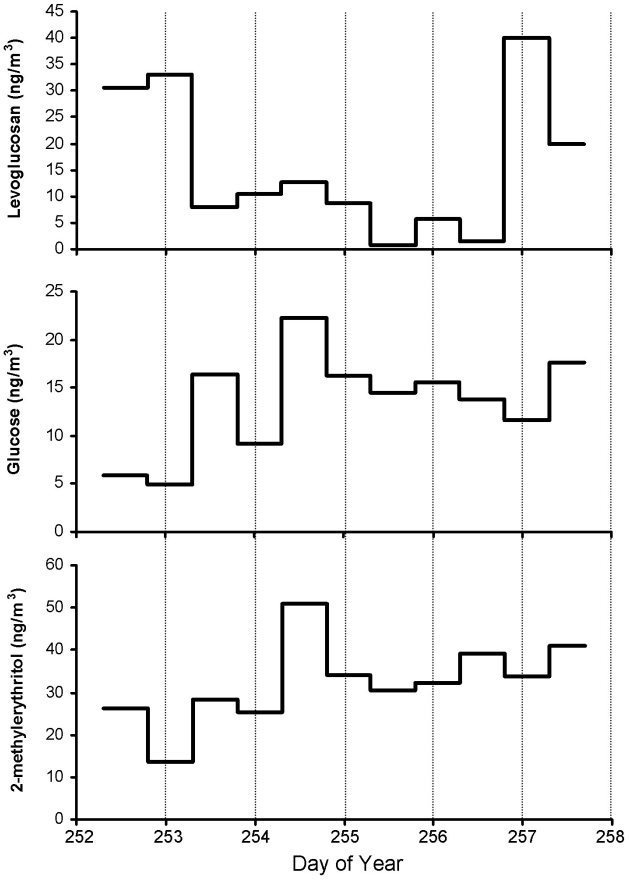

Figure 5. Day and night particulate concentrations of levoglucosan, glucose and 2-methylerythritol.

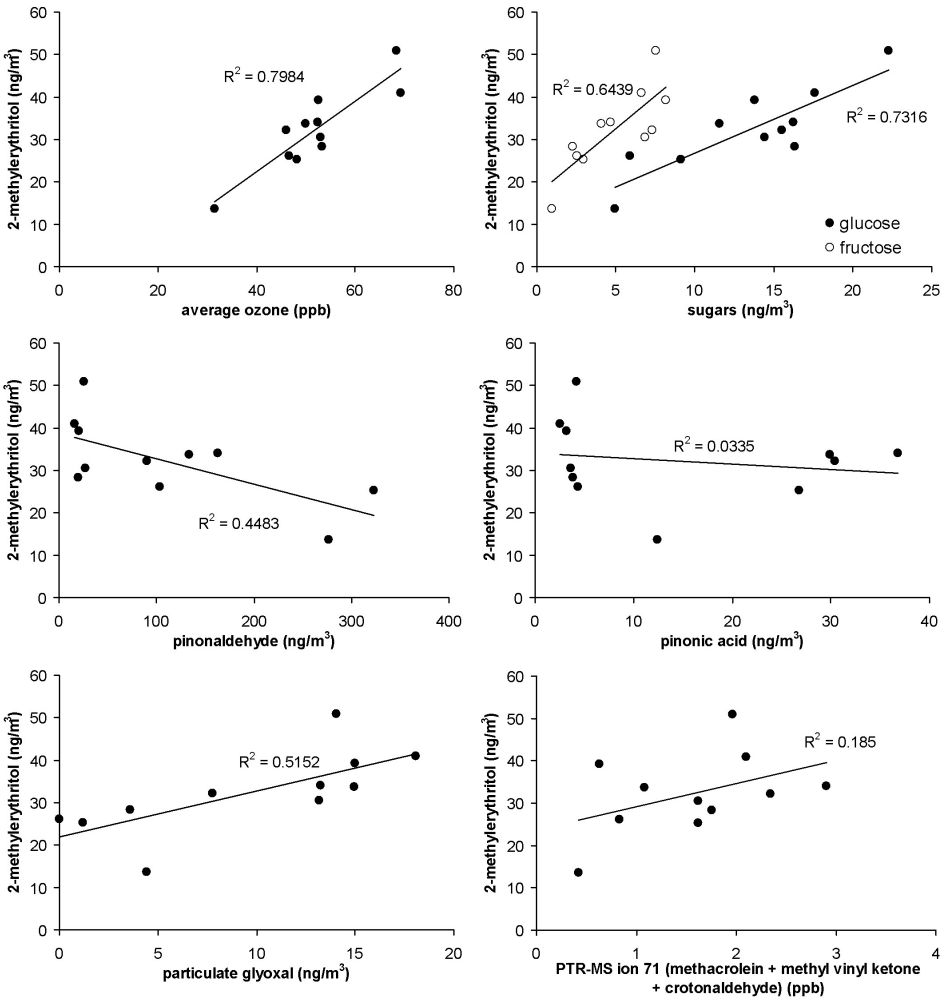

Figure 6. Correlation between several different chemicals and 2-methylerythritol. The strongest correlations observed were with ozone, glucose and fructose.

way. The weak correlation between PTR-MS results for ion $[71]^+$, which corresponds to methacrolein, methyl vinyl ketone and crotonaldehyde, and the 2-methyltetrols was expected since both methacrolein and methyl vinyl ketone are also oxidation products of isoprene and have been shown to correlate with ozone production from isoprene oxidation at this site [*Dreyfus et al.*, 2002]. The lack of correlation between the pinene-derived compounds and the isoprene-derived compounds results from the regional biomass distribution and meteorology. Isoprene emission in the region is dominated by oak trees found at lower elevations and transported upslope in rising air masses during the daytime. The monoterpene emissions occur mainly from the local mixed conifer forests and have maximum concentrations when atmospheric mixing is the lowest, so their maximum concentrations occur at night.

[25] In addition to the 2-methyltetrols, 2-methylglyceric acid (2,3-dihydroxypropanoic acid), which is an oxidation product of methacrolein, a first-generation photo-oxidation product of isoprene [*Claeys et al.*, 2004b] was also observed. The 2-methylglyceric acid correlated well with glycolic acid ($R^2 = 0.72$), ozone ($R^2 = 0.54$), 2-methyltetrols ($R^2 = 0.38$) and glucose ($R^2 = 0.32$). The strong correlation with glycolic acid (or hydroxyacetic acid) was unexpected, but the correlation is intriguing since these two chemicals are structurally very similar in that they differ by only a CH-OH group. This implies that these compounds may have similar sources. Overall, the 2-methylglyceric acid was approximately four-fold more abundant than glycolic acid, although quantification is tenuous since we lacked a standard for 2-methylglyceric acid and assumed it had the same relative response as glycolic acid.

[26] The last group of polyols investigated were the pentenetriols, of which three were detected (Table 5). Standards were not available for these compounds, so identification was based on the mass spectra and relative retention time presented by *Wang et al.* [2005]. Quantification was conducted assuming a similar relative response to the 2-methyltetrols. Although the pentenetriols are believed to be related to the 2-methyltetrols [*Wang et al.*, 2005], the pentenetriols and 2-methyltetrols showed a relatively weak correlation ($R^2 = 0.16$). Moreover, the pentenetriols did not correlate well with any other chemical but the strongest correlations were observed with levoglucosan ($R^2 = 0.40$), glycolic acid ($R^2 = 0.20$), particulate methylglyoxal ($R^2 = 0.19$) and the 2-methyltetrols ($R^2 = 0.16$). The pentenetriols

Table 6. Concentrations of *n*-Alkanes and Butyl Esters (ng/m^3) Collected on High-Volume Quartz Filters[a]

Compound	Overall Average ± SD	Daytime Average ± SD	Nighttime Average ± SD	*t*-Test (*P*-Value)	LOQ, ng/m^3
n-alkanes					
C_{25} *n*-alkane	2.0 ± 1.4	2.9 ± 1.3	0.87 ± 0.32	0.014	0.23
C_{26} *n*-alkane	1.4 ± 1.3	2.1 ± 1.3	0.43 ± 0.38	0.02	0.27
C_{27} *n*-alkane	see note[b]	see note[b]	see note[b]	···	1.82
C_{28} *n*-alkane	see note[b]	see note[b]	see note[b]	···	4.67
C_{29} *n*-alkane	see note[b]	see note[b]	see note[b]	···	6.00
C_{30} *n*-alkane	see note[b]	see note[b]	see note[b]	···	2.89
C_{31} *n*-alkane	1.0 ± 1.2	1.3 ± 1.5	0.69 ± 0.74	NS	0.61
C_{32} *n*-alkane	see note[b]	see note[b]	see note[b]		0.13
C_{33} *n*-alkane	see note[b]	see note[b]	see note[b]	···	0.80
C_{34} *n*-alkane	see note[b]	see note[b]	see note[b]	···	0.15
C_{35} *n*-alkane	see note[b]	see note[b]	see note[b]	···	0.15
C_{36} *n*-alkane	see note[c]	see note[c]	see note[c]	···	0.15
Sum of quantified alkanes[d]	7.2 ± 8.3	10 ± 10	3.2 ± 2.8	NS	
Upper limit of alkane mass[e]	22 ± 4.9	···	···	···	
Butyl esters					
Hexadecanoic acid, butyl ester	8400 ± 5100	12000 ± 4200	4400 ± 2500	0.007	
Octadecanoic acid, butyl ester	5000 ± 5200	8200 ± 5100	1100 ± 750	0.018	

[a]The average concentration (±SD) is given for all the samples, then only the daytime sample, and then only the nighttime samples. A Student's *t*-test was used to test for differences in concentrations between the day and night samples. Statistical differences were defined at the $P < 0.05$ level.
[b]The compound was either not detected or below the limit of quantification, defined as the mean field blank + 6 SD of the blank, in more than half the samples, so no average value is presented.
[c]This compound was not detected in any samples.
[d]The sum of quantified mass includes all chemical species above the LOQ including chemicals that were sporadically detected, hence this value is higher than sum of the C_{25}, C_{26}, and C_{31} *n*-alkanes.
[e]The upper limit of alkane mass was defined as the quantified chemicals plus the limit of quantification for the chemicals that fell below the LOQ.

did not correlate with ozone ($R^2 = 0.091$) or temperature ($R^2 = 0.0004$) as was the case with the methyltetrols.

3.7. Alkanes and Butyl Esters

[27] The last class of chemicals investigated was the "native" hydrocarbons that did not require any derivatization. The target analytes were the C_{20} through C_{36} *n*-alkanes. Unfortunately, the field blanks showed sufficient contamination to make quantification unreliable except for the C_{25}, C_{26}, and C_{31} alkanes (Table 6). The C_{20} to C_{24} alkanes could not be quantified because of coelution with the butyl ester series (see below) since the alkanes lacked a strong, unique ion for quantification. Overall, the alkanes contributed relatively little mass to the particulate matter with a total quantified mass of 7.2 ± 8.3 ng/m^3. The maximum amount of alkanes that could have been present was estimated to be 22 ± 4.9 ng/m^3 by summing the quantified compounds and the limit of quantification for the chemicals that fell below the LOQ. Even this maximum possible amount of alkanes was still relatively minor compared to the biogenic chemicals. Unlike the terpene-derived compounds, the observed alkanes showed diurnal cycles with higher concentrations during the day. This is most likely the result of transport from the Sacramento urban area, which was demonstrated by the increase in gaseous benzene concentrations during the day.

[28] An unexpected observation was the presence of two peaks that dominated the chromatograms. These two compounds were absent from the field blanks, indicating that they were not the result of contamination from the substrate, reagents, handling or storage of the samples. Both the electron ionization and methane chemical ionization mass spectra were used to identify the compounds as the butyl ester of hexadecanoic acid (hereafter C_{16}-butyl ester) and the butyl ester of octadecanoic acid (C_{18}-butyl ester). Authentic standards were purchased from Chem Service (West Chester, Pennsylvania) to confirm compound elution time as well as the EI and CI mass spectra, which proved the identity of these analytes. A third peak in the chromatogram had a similar fragmentation pattern as the C_{16} butyl ester, but it was smaller by 28 mass units (probably C_2H_4), so we believe that it is the C_{14}-butyl ester, but the lack of an authentic standard prevents confirmation of this compound.

[29] The field samples were re-analyzed with a calibration curve to quantify the C_{16} and C_{18} butyl esters. The results showed very high concentrations of C_{16}-butyl ester (avg = 8400 ng/m^3) and the C_{18}-butyl ester (avg = 5000 ng/m^3) (Table 6). These two compounds by themselves exceed the extractable organic matter found in previous high-volume air sampling conducted in the region [*Simoneit*, 1984] and the total organic matter as determined by the Interagency Monitoring of Protected Visual Environments (IMPROVE) network at Bliss State Park (available at http://vista.cira.colostate.edu/IMPROVE/). Therefore we consider these values suspect. Furthermore, these two butyl esters should have been observed in the previous extraction and analytical procedures if they were present [*Simoneit*, 1984].

[30] While we were confident in the identification and quantification of the butyl esters, questions remain regarding the potential origin of these two compounds that were very abundant in our samples but not the field blanks. Analysis of soil, Ponderosa pine needles and Ponderosa pine wood from Blodgett Forest did not show any butyl esters. The filter patches extracted by shaking the samples in hexane rather than extracted by Soxhlet also showed high concentrations of the butyl esters, which eliminates the possible formation of the butyl esters during the extraction procedure. Currently, we do not know the source of the C_{16} and C_{18} butyl esters, so additional experiments will be necessary to determine if the butyl esters are an artifact

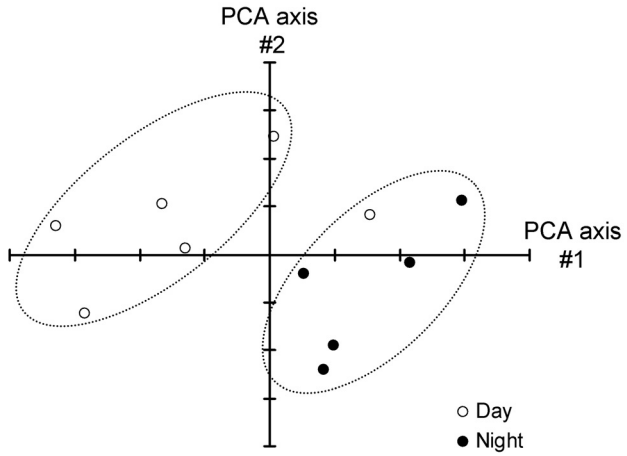

Figure 7. Plot of the principal component analysis (PCA) scores for samples collected during the study period. The samples fell into two clusters, generally corresponding to day and night samples, along the first PCA axis.

arising from other equipment at the sampling site or if they are arising from another local source (e.g., pollen).

4. Principal Component Analysis

[31] The particulate data were used to investigate the potential source of different chemical classes through correlations as previously shown. However, the large number of potential correlations between the different chemicals makes the data set more suited to multivariate statistical analysis. Therefore we conducted a principal component analysis (PCA, Minitab Statistical Software version 13.20) where all chemical species that were detected in at least 6 of the 11 samples were treated as variables along with the gas-phase PTR-MS chemical results, ozone and temperature (Figure 7). Typically PCA analyses are conducted on larger data sets, so the limited number of samples (n = 11) makes the current PCA analysis more tentative than studies with larger sample sets. However, the results are useful in an exploratory fashion and to support previous observations from the regression analyses.

[32] The results showed that the samples formed two groups along the first PCA axis based on diurnal differences, which was expected on the basis of meteorology suspected sources of particulate chemicals. A single daytime sample fell into the nighttime grouping, but this sample was taken on the first day when it was cool and cloudy and therefore was not typical of the other daytime samples (Figure 1).

[33] The PCA coefficients for the different chemicals and conditions showed that diurnal differences were largely responsible for most of the variation along the first PCA axis (Figure 8) where chemicals with higher concentrations at night had larger positive PCA coefficients while chemicals that where higher in the day had negative values along PCA axis 1. The second PCA axis appeared to differentiate between biogenic and anthropogenic chemicals, but the separation is not as clear as the first PCA axis. Four chemical groupings were observed in the plot of the PCA variable coefficients although there were chemicals spread throughout the plot (Figure 8). The first small group consisted of gaseous monoterpenes and the terpene oxidation products, although tridecanoic acid also fell into this group and pinonaldehyde fell outside the group. The relatively tight cluster of the monoterpenes and terpene oxidation products away from the temperature and ozone parameters suggest that the gaseous monoterpene concentrations were a more important parameter in controlling the terpene oxidation product concentrations than ozone or temperature. The terpene oxidation product abundance in the aerosols were inversely related to air temperature as shown for nopinone. The second cluster was very tight and consisted of temperature, gaseous benzene, the butyl esters, octadecanoic acid, the C_{25} and C_{26} n-alkanes. This group of chemicals likely indicates transport of air pollution from the Sacramento urban area, as evidenced by the gaseous benzene. The third grouping consists of a series of alkanoic and alkanedioic acids that are relatively independent of diurnal cycle. It is interesting that the majority of the alkanoic and alkanedioic acids grouped together away from other chemicals. The last group is composed of ozone and a series of oxidized chemicals as well as glucose and fructose. The close proximity of the 2-methyltetrols to glucose and fructose may be a statistical fluke, but it might also be suggestive of a similar source for these chemicals. However, the presence of ozone and some other highly oxidized species (e.g., glyoxal) is consistent with oxidation being an important source for this group of chemicals as has been previously observed.

5. Discussion

[34] The objective of this research was to assess the importance of oxidized biogenic emissions for organic aerosol concentrations by collecting a series of high-volume particulate samples over 5 days and nights in Blodgett Forest. The results clearly show that terpene and isoprene oxidation products represent the more abundant chemicals on the filters with the exceptions of the butyl esters, whose source is not known, and the C_{16} and C_{18} alkanoic acids (Table 7). Pinonaldehyde was the most abundant chemical quantified, excluding the butyl esters, accounting for 22% of the identified organic aerosol mass over the entire study, and 39% of the aerosol mass during the nighttime samples. *Cis*-pinonic acid was the third most abundant acid and represented 2.9% of the overall quantified organic species mass while 2-methylglyceric acid was the 6th most abundant acid. Overall, the terpene oxidation products constituted 27% of the average identified aerosol organic constituents, excluding the two butyl esters, while the isoprene oxidation products of the 2-methyltetrols and 2-methylglyceric acid represented 11% identified aerosol mass during the study. In total, the oxidation products of terpenes and isoprene accounted for 180 ng/m^3 of organic aerosol during the course of the study and 280 ng/m^3 at night. This result clearly highlights the importance of oxidized BVOC sources for secondary organic aerosols in this and similar forested regions with strong BVOC emissions.

[35] The mass of identified organic material in this study can be compared to total organic carbon measurements in the region conducted by the IMPROVE network

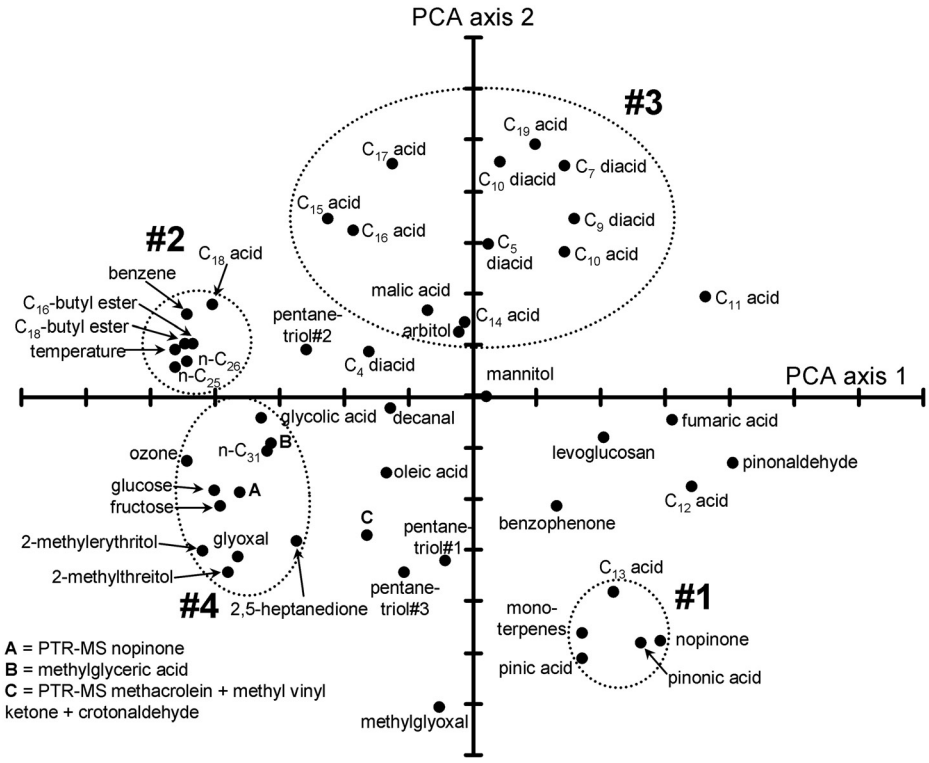

Figure 8. Plot of the principal component analysis coefficients for the chemicals observed at Blodgett Forest. In general, compounds that are higher during the daytime are on the left side of PCA axis 1 while chemicals higher at night are on the right-hand side. It appears that recently biologically derived compounds have low scores on the second PCA axis. Group 1 mostly consists of monoterpenes and monoterpene derived chemicals. Group 2 contains gaseous benzene, which is a marker of transport from urban areas, and the butyl esters and a couple alkanes. Group 3 consists solely of alkanoic acids, alkanedioic acids, malic acid and arbitol. Group 4 contains ozone, glucose, fructose, the 2-methyltetrols and 2-methylglyceric acid.

at Bliss State Park. The Bliss site is located approximately 46 km east of Blodgett Forest at an elevation 2100 m, but it is representative of aerosols on the west side of the Sierra Nevada Mountains [*Cahill et al.*, 1996]. The organic carbon data, as determined by combustion, from the IMPROVE Bliss site in September 2002 was 1.4 ± 0.78 $\mu g/m^3$ in 2002 (http://vista.cira.colostate.edu/IMPROVE/), which approximately corresponds to 2.1 ± 1.2 $\mu g/m^3$ of organic matter (Table 7). The Bliss site was impacted by forest fires in September 2003, hence that data cannot be used for comparisons. If one assumes the sites are sampling a similar air mass and that there is little difference between our TSP aerosol collection and the IMPROVE PM_{10} collection with respect to semivolatile organics, then approximately 23% of the total organic matter was identified during this study and BVOC oxidation products accounted for approximately 8.6% of the total organic material.

[36] It should be noted that quartz filters are subject to both positive artifacts, resulting from the adsorption of gases [*Kirchstetter et al.*, 2001; *Turpin et al.*, 1994], and negative artifacts due to volatilization of semivolatile chemicals [*Subramanian et al.*, 2004]. Since the IMPROVE network also used quartz filters for the organic carbon determinations, the data sets should be relatively comparable. The three main differences are (1) the high-volume sampler employed in this study was a TSP sampler compared to the IMPROVE PM_{10} sampler, (2) the samples collected herein were 11.5 h samples instead of 24 hour samples and (3) the face velocity of the air through the filter was 16.2 cm/s in this study compared to approximately 80 cm/s in the IMPROVE samplers. The difference in size fractions collected may result in more organic matter being collected in the PM_{10} to $\sim PM_{30}$ faction while the second and third differences in sampling approaches would result in less loss of semivolatile organics from the entrained particulate matter since there is less air passing by the collected aerosols for a shorter period of time. However, the shorter sampling period may give a greater bias because of the adsorption of *F* gases to the filters since the filter may not be at equilibrium with the incoming air stream [*Subramanian et al.*, 2004; *Turpin et al.*, 1994].

[37] Another consideration in assessing the potential contribution of oxidized biogenic chemicals to SOA formation is the potential for organic acids to form oligomers. [*Gao et al.*, 2004] estimated that 50% of the SOA mass from α-pinene ozonolysis was oligomers consisting mainly of dimers, although up to pentamers were observed. If polymerization of biogenic oxidation products is also significant in our samples, then the contribution of oxidized biogenic compounds would have an even greater contribu-

Table 7. Summary of the Composition of the Total Identified and Quantified Organic Mass (Excluding the Butyl Esters Whose Source Was Unknown) Represented by Different Chemical Classes or Specific Compounds

	Overall	Daytime (0830 to 2030 LT)	Nighttime (2200 to 0800 LT)
Sum of identified organics, ng/m^3	490 ± 93	480 ± 120	520 ± 57
Percent acids	46.0	56.3	33.6
Percent sugars	11.0	11.4	10.5
Percent carbonyls	30.9	17.7	46.6
Percent polyols	12.1	14.5	9.3
Percent alkanes	1.5	2.3	0.6
pinonaldehyde	110 ± 110	35 ± 34	200 ± 100
nopinone	2.8 ± 1.3	1.8 ± 0.4	3.9 ± 1.0
cis-pinonic acid	14 ± 14	3.6 ± 0.7	27.3 ± 9.1
pinic acids (two isomers)	4.3 ± 3.0	2.2 ± 0.5	6.9 ± 2.7
2-methyltetrols + 2-methylglyceric acid	53 ± 19	61 ± 20	44 ± 13
Sum of biogenic oxidation products, ng/m^3	180 ± 110	100 ± 33	280 ± 90
Sum of biogenic oxidation products, %	36.9%	23.3%	53.2%
Organic carbon at Bliss, Sep 2002,[a] μg/m^3	1.4 ± 0.78		
Estimated organic matter,[b] μg/m^3	2.1 ± 1.2		
Approximate % of organic matter identified	23%		
Approximate % contribution of oxidized BVOCs to organic matter	8.6%		

[a]PM_{10} carbon measurements determine by the IMPROVE network at Bliss State Park (http://vista.cira.colostate.edu/IMPROVE/). Organic carbon was determined by combustion and elemental carbon by light adsorption. Data from 2002 were used instead of 2003 since a forest fire impacted the Bliss site during September 2003, so the organic carbon number would not be representative.

[b]Organic matter was estimated as 1.5 × (Organic carbon) as suggested by *Wolff et al.* [1991].

tion to SOA than was determined from the single acids species determined in this research.

[38] The higher concentrations of terpene oxidation products at night can be explained by the following three factors: (1) lower vertical mixing rates at night cause higher concentrations of terpene-precursors despite reduced emission due to lower temperature; (2) lower temperatures cause increased condensation of the semivolatile organic species onto aerosols; and (3) changing oxidant concentrations; while ozone measurements confirm similar levels during day and night, OH levels should be much lower at night, and nitrate may contribute additional oxidation capacity during night. The results from the gas-phase characterization of the site showed that the monoterpene concentrations were approximately two-fold higher at night, which would indicate that the oxidation products should also be about two-fold higher at night if factors 2 and 3 above are insignificant. The close proximity of the gaseous monoterpenes to the oxidation products in the PCA analysis certainly suggests a strong relationship between the two groups of chemicals. However, the nighttime concentration of nopinone, pinonaldehyde, *cis*-pinonic acid and pinic acid were 2.1, 5.7, 7.5 and 3.1-fold higher than the daytime concentrations, respectively. An investigation of the nopinone concentrations in the gas phase and the particulate phase clearly shows the effect of temperature on gas/particle partitioning as shown by Figure 4 (factor 2), providing a useful measure of the apparent enthalpy of vaporization which can be applied in atmospheric chemistry modeling of secondary aerosols. Therefore we conclude that the higher particulate concentrations at night are the result of multiple processes.

[39] The clear implication of these findings is that oxidized biogenic emissions contribute a significant fraction of organic matter to ambient aerosols, thus these terpene and isoprene oxidation products need to be considered as important components of aerosols even at this site which is 75 km downwind of Sacramento, a major urban area.

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