Probing molecular associations of field-collected and laboratory-generated SOA with nano-DESI high-resolution mass spectrometry

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[1] Aerosol samples from the 2010 CalNex field study in Bakersfield (BF) and Pasadena (LA) were analyzed using positive mode nanospray-desorption electrospray ionization mass spectrometry. Secondary organic aerosol (SOA) produced in a photochemical chamber by photooxidation of diesel (DSL) fuel and isoprene (ISO) under humid, high-NOx conditions, was analyzed for comparison. Three groups of organic compounds with zero, one, or two nitrogen atoms in their molecular formulas (0N, 1N, 2N) were compared in detail. The composition of ambient SOA exhibited greater overlap with DSL than with ISO. The overlap of the chamber experiments with the BF data was relatively consistent throughout the day while the overlap with LA data increased significantly in the noon to 6 P.M. sample, consistent with the SOA plume arriving from downtown Los Angeles. BF samples were more oxidized, contained more organic nitrogen, and had more overlap with the chamber data compared to LA samples. The addition of gaseous ammonia (NH3) to the DSL experiment was necessary to generate many of the 2N compounds observed in BF. This analysis demonstrates that DSL and ISO were important sources but cannot account for all of the observed ambient compounds indicating that other sources of organics were also likely important.


1. Introduction

[2] Organic aerosols (OA), a major fraction of fine (< 2.5 µm) particulate matter, significantly affect visibility, climate, and human health [Charlson et al., 1992; Kanakidou...]

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formed under different relative humidity and NO chemical composition of isoprene SOA changed when it was under different experimental conditions. For example, the ular composition of SOA formed from different precursors, and high-MW SOA compounds in chamber studies. The mass cycloalkenes [Gao et al., 2004; Tolocka et al., 2004; Reinhardt et al., 2007], limonene [Walser et al., 2008; Laskin et al., 2010], and anthropogenic precursors, such as 1,3,5-trimethylbenzene [Kalberer et al., 2004; Baltensperger et al., 2005], and cycloalkenes [Gao et al., 2004] have all been found to form high-MW SOA compounds in chamber studies. The mass spectra reported in these studies show differences in the molecular composition of SOA formed from different precursors, and under different experimental conditions. For example, the chemical composition of isoprene SOA changed when it was formed under different relative humidity and NO\textsubscript{2} concentrations [Nguyen et al., 2011; Zhang et al., 2011]. Kalberer et al. compared the composition of ambient SOA to that of chamber SOA generated using different precursors illustrating the potential for comparison studies to provide insights into the sources and chemistry of SOA [Kalberer et al., 2006].

In ESI-MS studies, the aerosol sample is first extracted into an organic solvent and then electrospayed into the mass spectrometer inlet. Potential solvent-analyte interactions introduced by the extraction step [Bateman et al., 2008] can be alleviated by quick dissolution and ionization of the sample directly from the substrate. A novel technique for this type of analysis is nano-desorption electrospray ionization (nano-DESI) mass spectrometry [Roach et al., 2010b]. Laskin and coworkers have demonstrated the utility of nano-DESI for the soft ionization of complex mixtures on substrates with the potential preservation of some labile species and no sample preparation [Roach et al., 2010a; Eckert et al., 2012].

There have been numerous applications of HR-MS to chamber studies of SOA and the number of field-applications of HR-MS is also growing quickly [Laskin et al., 2012]. However, no systematic studies have been performed on the degree of overlap between molecular level composition of OA collected in the field and OA generated in lab studies. In this work, we present the molecular characterization of organic compounds inferred from nano-DESI/HR-MS analysis of aerosol samples collected in Bakersfield (BF) and Los Angeles (LA) California during the 2010 CalNex campaign. We compare the ambient chemical composition with SOA samples generated in a smog chamber under high NO\textsubscript{x} conditions with diesel fuel (DSL) and isoprene (ISO) precursors, and analyzed using the same nano-DESI/HR-MS approach. DSL and ISO SOA were chosen to represent potentially significant anthropogenic and biogenic influences, respectively, at the BF and LA site. Isoprene and diesel are both known sources for SOA [Carlton et al., 2009; Weitkamp et al., 2007]. The nearby vegetation and the prevalence of diesel use near both urban centers suggested that both diesel and isoprene were likely to be important sources at the two field sites. The BF site is also characterized by elevated mixing ratios of ammonia (NH\textsubscript{3}) (M. Z. Markovic et al., Measurements and modeling of water-soluble Q12 composition of PM2.5 and associated precursor gases in Bakersfield, CA during CalNex 2010, J. Geophys. Res.-Atmos., manuscript in preparation, 2012) and additional chamber experiments were performed including the oxidation of DSL in the presence of NH\textsubscript{3}. Hereinafter, the high-NO\textsubscript{x} photooxidation of DSL and ISO are referred to as “DSL-NO\textsubscript{x}” and “ISO-NO\textsubscript{x}”. Respectively, and the high-NO\textsubscript{x} photooxidation of diesel in the presence of NH\textsubscript{3} is referred to as “DSL-NO\textsubscript{x}-NH\textsubscript{3}.” Composition differences in the ambient SOA samples throughout the day were inferred from the high resolution mass spectra. The contributions of DSL and ISO to SOA formation BF and LA were investigated and while both were found to be important SOA sources, contributions from other sources, such as gasoline [Bahreini et al., 2012; P. L. Hayes et al., Aerosol Composition and Sources in Los Angeles During the 2010 CalNex Campaign, J. Geophys. Res.-Atmos., submitted manuscript, 2012] and terpenes [Pandis et al., 1991; Griffin et al., 1999], were also indicated.

2. Experimental
2.1. Sampling and Instrumentation

[7] The 2010 CalNex campaign had ground sites in BF and LA as well as aerial and ship-based measurements [National Oceanic and Atmospheric Administration, 2008]. A summary of the field sites, the ambient sampling, and the chamber studies is provided in Section A of the auxiliary material (auxiliary materials are available in the HTML doi:10.1029/ 2012JD018558). Briefly, the samples were collected at the BF (35.35°N, 118.97°W) and LA (34.14°N, 118.12°W) sampling sites. 5 June and 23 June were chosen for in-depth analysis, in LA and BF, respectively, because concurrent measurements with an aerosol mass spectrometer (AMS) indicated high SOA loadings on those days (P. L. Hayes et al., submitted manuscript, 2012). For these 2 days the diurnal patterns of the organic fraction from AMS measurements at each site were similar to the average diurnal pattern over the whole campaign. This suggests that these days can be taken as representative of the average trends observed at each site. Samples were collected on aluminum foil substrates using an 8 stage (BF) nonrotating and a 10 stage (LA) rotating Micro-Orifice Uniform Deposit Impactor (MOUDI, MSP Corp.) at ~30 standard liters per minute. BF samples were stored in a ~20 °C freezer at the site and a ~80 °C freezer at the lab, and LA samples were stored in a ~20 °C freezer. Samples on the eighth stage of the MOUDI, (size range of 0.18–0.32 μm aerodynamic diameter), showed the largest number of compounds in the MS of the BF samples and were chosen for intensive analysis. For consistency, the same stage was used for the LA samples, which corresponds to the middle of the accumulation mode mass distribution there (P. L. Hayes et al., submitted manuscript, 2012). All times discussed here are in local time (PDT). Online composition of the nonrefractory components of the aerosol was measured using an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) at both sites [DeCarlo et al., 2006]. In LA, the size resolved O/C was estimated from HR-ToF-AMS measurements using the relationship O/C = 3.25(f\textsubscript{iso}) + 0.001 where f\textsubscript{iso} is the fraction of the total organic signal at m/z 44 (P. L. Hayes et al., submitted manuscript, 2012). A similar relationship of O/C and f\textsubscript{iso} was found for Bakersfield: O/C = 3.02 (f\textsubscript{iso}) + 0.043
the sample-free area were identified and removed from the mass spectra recorded when the probe was positioned over the sample area with deposited particulate matter [Roach et al., 2010a]. Mass spectral features with a signal-to-noise ratio higher than 3 and a minimum background ratio of 5 were extracted from raw spectra using Decon2LS [Jaitly et al., 2009]. The signal-to-noise ratio was defined as the ratio of the intensity of the peak to the average intensity at the valleys of the peak. The background intensity was defined as the average intensity of the points that are within five standard deviations of the average of all the points in the spectrum. Molecular assignments of the observed ions were performed using MIDAS molecular formula calculator (http://magnet.fsu.edu/~midas/) with the following constraints C ≤ 100, H ≤ 200, O ≤ 50, N ≤ 3, S ≤ 1, Na ≤ 1. Approximately 80–90% of the peaks could be assigned molecular formulas and assignments were aided by Kendrick analyses [Kendrick, 1963; Stenson et al., 2003] using O and C3H4O2 as base units, and a second-order Kendrick analysis using a sequence of CH2 and H2 base units [Roach et al., 2011]. The formula C2H5O2 has been found to be a common base unit in atmospheric samples [Altieri et al., 2008; Mazzoleni et al., 2010] and was used here to aid in the identification of molecules that did not fall in families with the other Kendrick base units. No seed particles were used in the chamber studies and no sulfur compounds were observed. Thus, we limit our discussion of the comparisons to C2H5O2Nn compounds. The mass spectra were acquired over the mass range of m/z 100–1000. However, in this work we limit our discussion to peaks in the 100–400 Da range because they can be unambiguously assigned for C2H5O2Nn compounds given the mass accuracy and resolution used in this study.

[11] To resolve and identify elemental compositions in complex mixtures such as aerosol, petroleum, and dissolved organic matter samples, both high mass resolution and high mass accuracy are required [Marshall et al., 2006; Reemtsma et al., 2006; Schmitt-Kopplin et al., 2010]. High resolution enables the separation of closely-spaced peaks while high accuracy enables the determination of the elemental composition based on the exact mass. It has been demonstrated through mathematical modeling that ~0.1–0.5 mDa mass accuracy is necessary to determine unique elemental compositions for typical organic compounds up to 500 Da (and higher when combined with Kendrick analysis) [Marshall et al., 2006]. In an analysis of extracted aerosol filter samples using negative mode ESI, Schmitt-Kopplin and coworkers showed that closely-spaced CHO and CHOS compounds (C3 vs. SH4) at ~400 Da were resolved with an instrument resolution of ~150,000 [Schmitt-Kopplin et al., 2010]. Compared to their study, we used a relatively lower mass resolution of 60,000 m/Δm at m/z 400. However, we can still confidently identify peaks over a broad mass range based on the accurate mass measurements. Kendrick analysis aids identification by grouping higher mass peaks into families with lower mass peaks that can be unambiguously identified. The second-order transformation introduced recently [Roach et al., 2011], and used here, enables even more efficient grouping, which facilitates identification of higher-mass peaks within each group that cannot be unambiguously identified using traditional first-order Kendrick analysis. Mass accuracy can be affected by the presence of overlapping, unresolved peaks if the peaks have similar abundance. For
example, an unresolved CHO/CHOS doublet (e.g., C₁₀H₂₈O₁₀S vs. C₁₀H₂₈O₁₀) with equivalent abundances would result in an error of ~1.7 mDa for either assignment. In contrast, when the relative abundance of one of the peaks in the unresolved doublet is low, the measured mass is very close to the exact mass of the more abundant peak. Under these conditions, while lower abundance species are unresolved and unassigned, the dominant species are accurately identified. In this study the majority (~75–80%) of our assignments had mass accuracy within ±0.35 mDa. Some higher mass peaks had both C₆H₇OS₄ and C₆H₇O₃SNa as possible assignments within this mass accuracy. These peaks were assigned as sodiated through the use Kendrick analyses with oxygen and C₆H₇O₂ base units. These assignments are consistent with results from Lin et al. [2012] showing low numbers of sulfur containing compounds in ambient aerosol samples measured with positive mode ESI. While we do not necessarily resolve all of the peaks in the spectrum, the assignments are accurate as indicated by the absolute error.

[12] The analyte molecules were observed as either protonated ([M+H]⁺) or sodiated ([M+Na]⁺) species. The assigned ionic formulas were converted to neutral formulas by subtracting either the exact mass of a proton or a sodium ion. Approximately 0–10% of the compounds in each sample were detected as both sodiated and protonated species. For these peaks, the average intensity was used. In this work, compounds containing zero, one, or two nitrogen atoms (0N, 1N, 2N, respectively) were compared. While analysis focused on positive mode spectra, elemental ratios from analysis of the negative mode spectra were included for comparison with AMS data.

[13] There are many ways to look at the overlap between two measurements. We opted to use the percentage of peaks found in ambient samples that were also found in the chamber studies. The percentage of overlap between the ambient samples and the chamber studies was determined using equation (1).

\[
\text{\% overlap} = \frac{\text{number of matching peaks}}{\text{number of peaks in ambient sample}} \times 100
\]

where the “matching peaks” are compounds that have the same observed molecular formulas in both the ambient and the chamber study samples. The relative intensities are not included in the overlap calculations due to the variability of ion intensities inherent in ESI. In equation (1) the overlap is divided by the number of peaks in the ambient sample, thus, the relative extent of overlap is not weighted by the number of observed compounds. The number of conceivable molecular formulas of the type C₆H₇O₃Nₓ that satisfy valence rules and weigh under 400 Da exceeds 10⁴, whereas the number of observed peaks in the field and lab samples was of order 10³. The probability of a random match between the samples at the overlap level observed in this work is small. A caveat to this approach is that the chemical formula may correspond to multiple isomers, thus percent overlaps include molecules having the same elemental composition regardless of their structure. This means that a match between two samples does not necessarily indicate that the compound originates from that source. However, a match found for a large fraction of peaks increases the level of confidence in the apportionment. In this study only the elemental formulas are obtained, however, to aid discussion the terms “molecules” and “compounds” are used here to refer to all the possible isomers with a given molecular formula.

3. Results and Discussion

3.1. Comparing Ambient to Chamber Data

[14] Figure 1 shows a comparison of the high resolution mass spectra from the ambient samples for each location exhibiting the best overlap with DSL-NOₓ. The peaks in the mass spectra are color-coded as 0N, 1N, and 2N compounds with molecular formulas C₆H₇O₄N, C₆H₇O₃N, and C₆H₇O₂N₂, respectively. Similar comparison mass spectra of all the BF and LA samples with DSL-NOₓ, DSL-NOₓ-NH₃, and ISO-NOₓ are provided in Figures S2 through S7 in the auxiliary material. The measured peak intensities do not necessarily correlate to the absolute concentrations of the corresponding compounds in the sample. However, larger concentrations generally result in larger relative peak intensities for structurally related compounds, and therefore, qualitative comparison of the peak intensity distributions (overall shapes) in mass spectra is still valuable. The relative intensities were calculated by dividing the measured intensity by the maximum intensity observed in that sample, except where noted. Figure 1a shows that the intensity distributions of the BF sample collected from 6 A.M. to noon and the DSL-NOₓ sample were similar, e.g., the maximum intensities occurred over roughly the same mass range and the mass ranges of the

\[
\begin{align*}
\text{Relative intensities} & \quad 0N \quad \text{BF 6am-noon} \\
\text{Relative intensities} & \quad 1N \quad \text{DSL-NOₓ} \\
\text{Relative intensities} & \quad 2N \\
\end{align*}
\]

\[
\begin{align*}
\text{Relative intensities} & \quad 0N \quad \text{LA noon-6pm} \\
\text{Relative intensities} & \quad 1N \quad \text{DSL-NOₓ} \\
\text{Relative intensities} & \quad 2N \\
\end{align*}
\]

Figure 1. Comparison of the mass spectra of the ambient samples from each site with the best DSL-NOₓ overlap: (a) BF 6 A.M. to noon and (b) LA noon to 6 P.M. The DSL-NOₓ mass spectra are plotted with negative relative intensities to aid comparison. The colors correspond to the number of N atoms in the chemical formula with black = 0N, red = 1N, blue = 2N. The two starred peaks in the LA noon to 6 P.M. sample have intensities of 260 and 250 on this scale.
different subgroups (0N vs. 1N) correlated reasonably well. In contrast, Figure 1b shows that the LA sample collected from noon to 6 P.M. and the DSL-NO\textsubscript{x} sample appeared quite different in terms of the intensity distribution of mass spectral signals. In the LA sample, the intensity distribution was still increasing up to ~400 Da compared to a maximum at ~250 Da for the DSL-NO\textsubscript{x} sample. Additionally, there were significantly fewer 1N and 2N compounds compared to the DSL-NO\textsubscript{x} sample. A visual comparison of the BF 6 A.M. to noon with the LA noon to 6 P.M. sample (Figures 1a and 1b) shows a dramatically different intensity distribution, likely indicating different source composition/contributions and/or chemistry at the two sites.

Figure 2 shows how the distribution of 0N, 1N, and 2N compounds assigned for each sample changes with the measurement location and time. The total number of compounds in each sample is written above the corresponding column. The BF samples had a relatively consistent number of detected compounds in the night and early morning samples with a decrease in the afternoon (noon to 6 P.M.). In contrast, the LA data had lower numbers of compounds in the night samples and higher numbers of compounds during the day. In all cases, the majority of species were 0N or 1N compounds. The percentage of 2N compounds was below 10% in all samples, and averaged ~4%. The number of 1N or 2N compounds was significantly lower in the LA samples compared to both the BF and the chamber samples.

Figure 3 compares the overlap percentage (equation (1)) of the chamber and ambient sample data. The chamber experiment with the highest percent overlap with BF data was the DSL-NO\textsubscript{x} sample (Figure 3a) where 60 to 65% of the compounds identified in the BF sample were also observed in the laboratory SOA. The DSL-NO\textsubscript{x}-NH\textsubscript{3} data had the second highest overlap and the ISO-NO\textsubscript{x} had the lowest overlap. Within the day in BF, the 6 a.m. to noon sample had the highest percent overlap with the DSL-NO\textsubscript{x} and DSL-NO\textsubscript{x}-NH\textsubscript{3} samples at 65% and 59%, respectively. The overlap with ISO-NO\textsubscript{x} was relatively consistent throughout the day, between 37 and 40%. The BF noon to 6 P.M. sample had the lowest percent overlap with the DSL-NO\textsubscript{x} data, even though this sample had the lowest number of identified peaks and thus, would be expected to have the highest overlap if the samples were very similar because in the overlap comparison we divided by the number of peaks in the ambient sample. The total number of overlapping compounds was the lowest for this sample (Table S1), which suggests that either these sources, DSL and ISO, had the least impact on this sample or this sample was affected by different chemistry. Generally, the BF samples showed more overlap with the DSL sample and there were small changes in the overlap with the DSL sample throughout the day. The small changes in overlap could be due to either variations in local sources such as gasoline, diesel, terpenes, etc., or to variations in atmospheric chemistry such as those due to changes in ozone and liquid water content. However, the extent to which variation in either sources or chemistry contributed to the observations cannot be determined from these data. The percent overlap of BF with ISO-NO\textsubscript{x} was slightly more constant throughout the day perhaps indicating a more distant, but broadly arrayed, source resulting in a more stable signal, consistent with the high isoprene-emitting oak trees prevalent in the hills surrounding the San Joaquin Valley.

The LA data generally had less overlap with the chamber study data than BF (Figure 3b). The percent overlap between LA and the chamber studies followed the same trend with the highest overlap observed with DSL-NO\textsubscript{x} and the lowest overlap observed with ISO-NO\textsubscript{x}. The percent overlap varied more within the day in LA, with the DSL-NO\textsubscript{x} sample matching ~31% of the compounds from 6 A.M. to noon and ~51% of the compounds from noon to 6 P.M. The much higher percent overlap for the noon to 6 P.M. sample is consistent with the arrival of the afternoon SOA from both DSL and ISO influenced sources. The concentration of elemental carbon and the photochemical age both peaked during the noon to 6 P.M. period also consistent with SOA influenced by DSL sources (P. L. Hayes et al., submitted manuscript, 2012). The percent overlap of the LA noon to 6 P.M. sample with the chamber samples was lower than any of the BF data. This difference was likely due to the presence (or the increased concentrations) of other sources in LA, including gasoline SOA which has been asserted to be a dominant source there [Bahreini et al., 2012; P. L. Hayes et al., submitted manuscript, 2012], and/or a
potentially shorter photochemical processing time relative to both BF and the chamber studies.

[16] The bulk H/C, O/C, and N/C elemental ratios are commonly used to characterize SOA, and the corresponding averaged values for all samples, weighted by relative intensities [Bateman et al., 2009; Nguyen et al., 2010], are listed in Table 1. These bulk elemental ratios can be compared with other concurrent measurements obtained using more established methods to support the results from this novel technique. Collocated HR-ToF-AMS were used in both field studies to measure the composition of the aerosol in real time and the uncertainties listed for the AMS data in Table 1 follow those suggested by Aiken et al. [2008]. The H/C ratio measured by the nano-DESI method was fairly consistent throughout all of the field and laboratory samples ranging from 1.7 to 1.4 in the LA afternoon (6 P.M. to midnight) and midnight to 6 A.M. samples, respectively. The H/C ratio measured by the AMS was somewhat lower, ranging from 1.3 to 1.5 (Table 1). The O/C ratios measured with the nano-DESI analysis had a slightly larger range with the lowest values measured in the LA samples, between 0.13 and 0.24, and the highest value, 0.46, observed in the ISO-NOx sample. A comparison of the O/C and N/C values to AMS data must be considered with caution because selective ionization in ESI may lead, on the sample and the ionization mode, to either an overestimation or an underestimation of the <O/C> value. In addition, we analyzed only the 0.18–0.32 μm size fraction in the ambient samples which is smaller than the size range sampled by AMS (0.05–1.0 μm). In BF, no dependence of the <O/C> on the aerosol size was found from an analysis of the AMS data so the AMS <O/C> for the ensemble submicron particles is used to represent the <O/C> in the 0.18–0.32 μm size range. The BF <O/C> values of 0.32–0.35 for the positive mode data and 0.56–0.76 for the negative mode data were comparable to the <O/C> values of 0.28–0.44 measured by the AMS on the same day (Tables 1 and S2). Because AMS and nano-DESI-MS employ different ionization techniques, we do not expect a perfect overlap in the bulk elemental ratios between the two data sets. The fact that the majority of the AMS results lie between the results from the two nano-DESI ionization modes suggests that the aerosol elemental compositions measured by both techniques are similar [Bateman et al., 2012]. In contrast, AMS measurements showed that the <O/C> values in LA were lower and depended on the size of the aerosol (Table S3). The LA data for the nano-DESI-MS analysis had <O/C> values ranging from 0.13 to 0.24 in the positive mode and 0.27–0.63 in the negative mode (Tables 1 and S2). These two ranges bracket the AMS <O/C> values of 0.31–0.39 for the same aerosol size range (Table 1). For the positive mode data, the <N/C> values from BF were about 4 to 14 times higher than average N/C values measured with AMS. In LA, the AMS values were about 0.5 to 9 times higher than the nano-DESI values (Table 1). The AMS N/C values are not size resolved which could explain some, but likely not all, of the differences. More work comparing the responses of the two different techniques to nitrogen containing compounds is necessary to fully understand these observations. The much lower <N/C> values measured in the LA samples with nano-DESI-MS further indicate differences in chemistry between the two sites. Because both the LA and BF regions have plenty of NOx this difference in the <N/C> is likely indicative of both different aerosol ages and different chemistry leading to nitrogen containing species, as we discuss below.

3.2. Comparing LA to BF

[19] Significant differences were observed in the mass spectral overlap and the <O/C> and <N/C> ratios between the LA and BF samples. The degree of overlap between LA and BF was calculated using equation 2.

\[
\text{overlap} = \frac{\text{number of matching peaks}}{\text{number of peaks detected in LA sample}} \times 100
\]

where “matching peaks” were those identified in both samples. Similar trends were observed with either BF or LA sample placed in the denominator, for brevity only comparisons against LA are discussed. The LA samples with the highest percent overlap with BF data were the two afternoon samples (noon-midnight) and the percent overlap of the four LA samples with each of the BF samples followed a similar pattern as observed in the overlap between LA and the chamber data (Figures 3 and S12). Insights into the differences in SOA composition characteristic for the two locations can be gained from examining the compounds.

<p>| Table 1. Ensemble Average, Intensity Weighted H/C, O/C, and N/C Values of the Compounds Observed for Each Sample and the AMS Values Averaged Over the Same Sample Time Periods. Only the LA AMS O/C Values are Size Resolved |</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>Nano-DESI</th>
<th>AMS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H/C</td>
<td>O/C</td>
</tr>
<tr>
<td>Diesel-NOₓ</td>
<td>1.7</td>
<td>0.28</td>
</tr>
<tr>
<td>Diesel-NOₓ-NH₃</td>
<td>1.6</td>
<td>0.32</td>
</tr>
<tr>
<td>Isoprene-NOₓ</td>
<td>1.7</td>
<td>0.46</td>
</tr>
<tr>
<td>BF midnight to 6 A.M.</td>
<td>1.6</td>
<td>0.33</td>
</tr>
<tr>
<td>BF 6 A.M. to noon</td>
<td>1.6</td>
<td>0.32</td>
</tr>
<tr>
<td>BF noon to 6 P.M.</td>
<td>1.5</td>
<td>0.35</td>
</tr>
<tr>
<td>BF 6 P.M. to midnight</td>
<td>1.5</td>
<td>0.35</td>
</tr>
<tr>
<td>LA midnight to 6 A.M.</td>
<td>1.4</td>
<td>0.19</td>
</tr>
<tr>
<td>LA 6 A.M. to noon</td>
<td>1.5</td>
<td>0.13</td>
</tr>
<tr>
<td>LA noon to 6 P.M.</td>
<td>1.7</td>
<td>0.24</td>
</tr>
<tr>
<td>LA 6 P.M. to midnight</td>
<td>1.7</td>
<td>0.23</td>
</tr>
</tbody>
</table>
than the unique compounds in LA. The aromaticity index (AI)
unsaturated (average 11% vs. 8%) and had higher O/C values
ranged from 0 to around 25% and generally decreased with
unsaturation for the BF sample in this region is thus largely
zero, suggesting that many of the double bonds were carbonyls
compounds above 200 Da had aromaticity index values of
higher unsaturation values in BF. Approximately 62% of the
to investigate the type of double bonds indicated by the
C = C double bonds, was calculated for the unique BF data

\[
DBE = 1 + c - (h/2) + (n/2)
\]

where \( c, h, \) and \( n \) refer to the number of carbon, hydrogen,
and nitrogen atoms in the identified species, respectively. This equation assumes a valence of 3 for nitrogen; the
calculated DBE will be slightly higher if most of the nitrogen-containing compounds have valence of 5. The percent of
unsaturation was calculated by dividing the DBE values for
each compound by the number of single bonds in a saturated
hydrocarbon with the same number of carbon atoms [Smith
et al., 2009]. Figure 4 shows a comparison of the percent
unsaturation of the BF and LA noon to 6 P.M. samples which
 ranged from 0 to around 25% and generally decreased with
increasing mass. The unique compounds in BF were more
unsaturated (average 11% vs. 8%) and had higher O/C values
than the unique compounds in LA. The aromaticity index (AI)
[Koch and Dittmar, 2006], an estimation of the number of

\[
C = C \text{ double bonds, was calculated for the unique BF data}
\]
to investigate the type of double bonds indicated by the
higher unsaturation values in BF. Approximately 62% of the
compounds above 200 Da had aromaticity index values of
zero, suggesting that many of the double bonds were carbonyls
and nitrogen-oxygen functional groups. The higher percent
unsaturation for the BF sample in this region is thus largely
driven by the increased number of oxygen atoms.

[20] The lower oxidation level of the compounds in LA
(Figure 4) suggests this SOA was younger and had undergone
less heterogeneous, homogenous, and/or photolytic
[Bateman et al., 2011] processing. Since aerosols can grow
in size as they age, the observation of younger aerosol in
LA is consistent with the AMS results showing that the
average O/C value increased with increasing aerosol size
(Table S3). The aerosol sample measured here, in the
0.18–0.32 \( \mu \)m range, was less oxidized than the more
processed aerosols found in larger size fractions, although
a caveat is that primary aerosols are generally concentrated
in the smaller size fractions (P. L. Hayes et al., submitted
manuscript, 2012). The compounds with low O/C values
unique to the LA samples may also indicate different sources
between the two sites.

[21] The younger age of the aerosol can also explain the very
low number of nitrogen containing compounds observed in the
LA samples despite high NO\(_x\) levels. If the aerosol sample in the
0.18–0.32 \( \mu \)m range in LA was only a few hours old then
there was less time for organonitrates to form and partition into
the particle phase. AMS measurements in LA suggested low
concentrations of organonitrates over the whole size range
(0.05–1.0 \( \mu \)m) (P. L. Hayes et al., submitted manuscript,
2012). Lower concentrations of organonitrates (PM 2.5) in
LA vs. BF were also observed with FTIR analysis. In BF on
23 June, the organonitrates group concentration from FTIR
was 0.2 \( \mu \)g/m\(^3\) compared to 0.09 \( \mu \)g/m\(^3\) in LA on 5 June. Thus,
the amount of organonitrates was lower overall in LA
compared to BF. Also, the much higher nitrogen content in
BF could have been driven by the high ammonia levels there
(average value of 20 ppb with an hourly maximum of
65 ppb) (M. Z. Markovic et al., manuscript in preparation,
2012), which can result in production of reduced nitrogen
compounds [Laskin et al., 2010; Wang et al., 2010].

3.3. Comparing Unique Species Observed in Chamber
and Ambient Samples

[22] A comparison of the unique compounds between the
chamber experiments can help elucidate their relative
contributions to the ambient samples. The hypothesis is that each
type of chamber-generated SOA may have a set of unique
and reproducible “signature” peaks, which could be used
for source apportionment of the field data. An analysis of
the overlap between the ISO-NO\(_x\) sample (504 total peaks)
and the DSL-NO\(_x\) sample (732 total peaks) resulted in 401
(55% with respect to the total number of peaks in this
sample) unique DSL-NO\(_x\) compounds, 173 (34%) unique
ISO-NO\(_x\) compounds, and 331 compounds that were common
to both DSL-NO\(_x\) and ISO-NO\(_x\) samples. These results
demonstrate that there is an overlap in the elemental
formulas of the molecules that are formed, after oxidation
and oligomerization reactions, from both isoprene and diesel
precursors. Approximately 25-30% of the unique DSL-NO\(_x\)
compounds and approximately 3–5% of the unique ISO-NO\(_x\)
compounds overlapped (Equation 1) with BF (Figure S14).
Since the majority of the overlap between ISO-NO\(_x\)
and BF consisted of compounds that are common to both
ISO-NO\(_x\) and DSL-NO\(_x\), we cannot separate the relative
ccontributions of the two sources well. However, given
the greater overlap with unique compounds in DSL, it is
likely that BF was more influenced by anthropogenic
diesel-like sources than by biogenic isoprene-like sources.
Part of the difficulty in separating ISO and DSL sources is
that many molecular formulas, such as C\(_3\)H\(_7\)O\(_2\) (methyl- glyoxal), are common to the oxidation of both isoprene
and aromatic compounds.

![Figure 4](image-url)
The percent overlap of the three chamber experiments each showed each sample (Figure 2). The percent overlap of the ambient and DSL-NO$_x$-NH$_3$ compounds obtained from our comparison are consistent with the expectations in producing SOA in LA than reduced nitrogen (e.g., amines, imines, heterocyclic N-containing compounds). The results in producing SOA in LA than reduced nitrogen (e.g., amines, imines, heterocyclic N-containing compounds). The results obtained from our comparison are consistent with the expectation that urban sites like LA have much lower influence of NH$_3$ relative to rural/urban sites like BF [Hughes et al., 2000]. Based on other concurrent measurements at the two sites, the mixing ratios of NH$_3$ in BF were on average ~10 times higher than in LA (M. Z. Markovic et al., manuscript in preparation, 2012; R. A. Ellis et al., Gas-particle partitioning of ammonia at the CalNex-LA ground site and the influence of aerosol pH, J. Geophys.Res.-Atmos., manuscript in preparation, 2012). The higher overlap with the 2N compounds for the unique DSL-NO$_x$-NH$_3$ sample was slightly higher for 1N compounds than for 0N; however, there was no overlap with the 2N compounds. The unique DSL-NO$_x$-NH$_3$ overlap was always lower than the unique DSL-NO$_x$ in LA, suggesting that oxidized nitrogen (e.g., nitric acid esters) played a bigger role in producing SOA in LA than reduced nitrogen (e.g., amines, imines, heterocyclic N-containing compounds). The results obtained from our comparison are consistent with the expectation that urban sites like LA have much lower influence of NH$_3$ relative to rural/urban sites like BF [Hughes et al., 2000]. Based on other concurrent measurements at the two sites, the mixing ratios of NH$_3$ in BF were on average ~10 times higher than in LA (M. Z. Markovic et al., manuscript in preparation, 2012; R. A. Ellis et al., Gas-particle partitioning of ammonia at the CalNex-LA ground site and the influence of aerosol pH, J. Geophys.Res.-Atmos., manuscript in preparation, 2012). The higher overlap with the 2N compounds for the unique DSL-NO$_x$-NH$_3$ with BF data suggests that some of the 2N compounds observed in BF were formed through reactions of organic compounds with gaseous NH$_3$ [Laskin et al., 2010; Wang et al., 2010].

4. Conclusions

The molecular composition of aerosol samples collected from chamber studies and in BF and LA during CalNex were investigated using high resolution mass spectrometry. Between 100 and 800 unique compounds were identified in each sample (Figure 2). The percent overlap of the ambient samples with the three chamber experiments each showed the same trend: DSL-NO$_x$ had the highest overlap followed by DSL-NO$_x$-NH$_3$ and ISO-NO$_x$ (Figure 3). The number of peaks identified for the LA night samples was lower than the number identified for the LA day samples. The highest overlaps with the chamber experiments were observed for the noon-6 P.M. sample, consistent with the SOA plume arriving from downtown LA.

There were significant differences in the mass spectra measured for the LA and BF samples (Figures 1 and S2–S7). A comparison of the molecular compositions in LA and BF showed compounds with higher O/C values and higher percent saturation for BF. The higher oxidation level of the BF samples may indicate a fresher LA sample and/or different sources at the two sites. The DSL-NO$_x$-NH$_3$ sample had significantly more overlap with the 2N compounds in each BF sample than the DSL-NO$_x$ sample. This suggests that some of the nitrogen containing compounds in BF were formed by NH$_3$ chemistry. There were significantly more nitrogen containing compounds in the BF samples than in the LA samples consistent with AMS and FTIR results showing low levels of organonitrates in LA. Additionally, the higher number of CHON compounds in BF could have been driven by the higher concentrations of NH$_3$ in BF.

Combining all the compounds observed in chamber experiments with diesel and isoprene oxidation results in overlap with 70% or less of the ambient compounds. The inherent differences between ambient and chamber experiments, including the increased time for oxidation available in an ambient environment, could explain some of these differences. However, it is evident that diesel and isoprene do not cover the full range of sources contributing to SOA in either BF or LA. The utility of this comparative approach indicates that a more complete assessment of expected sources to the high-MW fraction of the aerosol, including chamber experiments with other SOA precursors such as gasoline [Bahreini et al., 2012; P. L. Hayes et al., submitted manuscript, 2012], terpenes [Pandis et al., 1991; Griffin et al., 1999], and petroleum and cooking emissions [Liu et al., 2012] could be useful in the source apportionment of ambient aerosols.

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