Characterization of urban aerosol using aerosol mass spectrometry and proton nuclear magnetic resonance spectroscopy

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1. Introduction

Atmospheric fine (diameter less than 2.5 μm) particulate matter (PM) is important because of its role in determining the global radiation budget directly through scattering and indirectly through serving as cloud condensation nuclei (IPCC, 2007). These cloud-aerosol effects have “medium to low” scientific understanding (IPCC, 2007), underscoring the need to identify accurately atmospheric particle characteristics in order to improve regional and global models. In addition, increased levels of PM cause increased rates of cardiovascular health problems and premature mortality (Pope, 2000). PM affects visibility, transports material through different environmental media, and makes available surface area for heterogeneous reactions.

Aerosols are emitted directly to the atmosphere (primary) or formed via chemical reactions (secondary). The processes leading to secondary inorganic aerosol production are relatively well understood. Those leading to formation of secondary organic aerosol (SOA) remain poorly characterized due to the large number of volatile organic compounds (VOCs) that are SOA precursors and the large number of potential reaction and partitioning pathways.

Organics ubiquitously constitute a significant fraction of aerosol mass (Zhang et al., 2007; de Gouw et al., 2008). Use of a quadrupole aerosol mass spectrometer (Q-AMS) allows separation of components of organic aerosol (OA), namely hydrocarbon-like organic aerosol (HOA, a proxy for primary OA (POA)) and different types of oxidized organic aerosol (OOA, a proxy for SOA) (Zhang et al., 2005a, b).

Recent efforts to better understand aerosol organic carbon (OC) have utilized proton nuclear magnetic resonance (1H NMR) spectroscopy. Based on chosen extraction techniques, 1H NMR characterizes a subset of OC sampled on a filter. For example, 1H NMR performed on a water extract characterizes the water-soluble OC (WSOC). WSOC comprises of 20–70% of aerosol carbon and impacts PM hygroscopicity (Saxena and Hildemann, 1996). In some cases, WSOC appears to be another proxy for SOA (Hennigan et al., 2008a). Specifically, 1H NMR illustrates changes in the oxidation state of aerosol through differences in the organic functional group budget (Moretti et al., 2008), which can be used to source apportion...
different types of OA (Decesari et al., 2007). To date, little research has used synchronous and co-located AMS and 1H NMR data.

In an industrially influenced urban center such as Houston, primary emission sources are abundant, especially related to power generation and petrochemical facilities along the Houston Ship Channel (HSC). Air quality in Houston exhibits high levels of ozone (Kleinmann et al., 2002) and submicron PM (Bates et al., 2008). Flight measurements from summer of 2006 reveal that over 60% of the aerosol mass in plumes from the HSC is organic (Bahreini et al., 2009). This research will provide additional understanding of the nature and dynamics of OA in Houston.

2. Methods

2.1. Field site

Measurements were made from August 15 through September 28, 2006 during the Texas Air Quality Study II (TexAQSII) Radical and Aerosol Measurement Project (TRAMP) (Lefer and Rappenglück, 2010). All instrumentation was located atop the North Moody Tower, an 18-story residence hall located on the University of Houston (UH) campus, which is located centrally within Houston. It is encircled by the regional highway network and is situated a few kilometers southeast of downtown and southwest of the HSC. The campaign was characterized by high temperatures, high relative humidity, and strong insolation. All times are in Central Standard Time (CST).

2.2. Q-AMS

Ten-minute average particle size and non-refractory mass concentrations were measured with an Aerodyne quadrupole Q-AMS (Jayne et al., 2000; Jimenez et al., 2003; Canagaratna et al., 2007). Operating conditions are described in Ziemba et al. (2010) and Cottrell et al. (2008). Briefly, particles with diameters between 0.04 μm and 1.0 μm are focused into a narrow beam by an aerodynamic lens and accelerated into a vacuum time-of-flight (ToF) chamber. Particle vacuum aerodynamic diameter is determined by the time taken by each particle to traverse this chamber. From each filter, two 1.5-cm² punches were soaked in 5 mL of ultrapure (milliQ) water for 10 min then centrifuged for 10 min. The 5 mL of centrifuged solution was freeze-dried until all liquid had evaporated and then re-dissolved with 0.8 mL of high purity (99.999%) D₂O.

1H NMR analysis was performed on each reconstituted sample using a Varian Inova 500 MHz NMR with an inverse probe. All samples were run for 1024 scans using a PRESAT pulse sequence to suppress the residual HOD peak. A 0.5-Hz line-broadening function was applied, as were six sequential polynomial baseline corrections. The spectra were integrated in specific regions to quantify hydrogen atoms and the resulting functional groups based on the analysis of Tagliavini et al. (2006). The functional groups are as follows: 0.60–1.80 ppm (aliphatic hydrogens, R–H; 1.80–3.20 ppm (hydrogens in z-position to unsaturated carbons, –C=–C–H; 3.20–4.40 ppm (hydrogens bound to alcoholic, ethereal, or esteral carbons, O–C–H; 5.00–5.50 ppm (acetal and vinylic hydrogens, O–CH–O and –C=–H); and 6.50–8.20 ppm (aryl hydrogens, Ar–H). Here, the contribution of a functional group within a sample is normalized to the total signal. Blank spectra were generated for both the ultrapure water alone and for the extract of a filter placed in the VAPS without initiating sample flow. Similar to the blank shown in Shakya et al. (2012), signals in the blank runs were significantly smaller than those in the spectra for actual samples.

The concentrations of organic hydrogen determined by 1H NMR spectroscopy were converted to organic carbon concentrations using hydrogen-to-carbon (H/C) ratios provided by Decesari et al. (2007). Additionally, the contribution of ketone and carboxylic
aliphatic groups (H–C–C=O) was estimated by taking the difference between the measured H–C–C= signal and the contribution of benzyl groups to the H–C–C= signal (assumed to be 16.7% of the measured H–Ar signal). In this way, if H–Ar is small, most of the signal for H–C–C= is attributed to H–C–C=O. Similar methods can be used to calculate oxygen-to-carbon (O/C) ratios. In this study, the two oxygenated functional groups (H–C–C=O and O–C–H) were utilized to estimate the O/C ratios for the water-soluble fraction. Ratios of 1.5 and 1.0 were applied to the H–C–C=O and O–C–H groups, respectively.

2.4. Supplementary measurements

Additional supporting gas-phase and meteorological data were acquired (Lefer and Rappenglück, 2010). A 10-m sampling tower at the top of the facility housed all meteorological instrumentation as well as inlets for chemical measurements. Carbon monoxide (CO) data were collected with a TE 48c trace-level enhanced gas filter correlation wheel instrument, and sulfur dioxide (SO2) was measured with a modified TE 43 s pulsed fluorescence detector (Lefer and Rappenglück, 2010; Luke et al., 2010). WSOC data were measured with a Sievers 800 TOC Analyzer (General Electric, Boulder, CO) with 30–60 min sampling periods (Anderson et al., 2008).

3. Results and discussion

3.1. AMS aerosol composition

Table 1 lists statistics for ammonium, nitrate, sulfate, organics, and chloride. The aerosol composition is dominated by sulfate and organics. All species have a mode in the mass-based size distribution at approximately 300 nm in vacuum aerodynamic diameter (with occasional smaller modes ranging from 100 nm to 150 nm, and for organics, even down to 70 nm). Large mass loadings of organics and sulfate often occur during the same periods, but some occasions indicate sulfate dominating without a corresponding organic signal. Ammonium correlates strongly to sulfate for the campaign (Fig. 1), with a regression indicating ammonium that is not fully neutralized with respect to ammonium (the 1:2 line).

3.2. Sulfate

Sulfate accounts for an average of 38% of the total measured mass (mean 4.1 ± 2.6 (1σ) µg m⁻³). The mean to median ratio of 1.2 indicates the regional nature of the sulfate aerosol and that Moody Tower is not unduly influenced by a specific source. However, there are times when increases in SO2 and sulfate occur concurrently, indicating local sulfate formation. These times are not representative of the majority of the dataset. Hourly medians show a distinct diurnal profile (not shown), with an increase beginning at 1100 CST and remaining elevated until 1400 CST, when it begins to decrease. The minimum occurs at night at 2300 CST. Nighttime medians remain reasonably constant and see little variation until morning rush hour, which is echoed by SO2 data (Luke et al., 2010). The afternoon peak is consistent with sulfate forming through photochemical channels.

3.3. Ammonium

Ammonium comprises on average 8.5% of the total measured mass (mean 0.9 ± 0.5 µg m⁻³). The mean to median ratio is 1.1, similar to that of sulfate. A regression between the molar concentrations of ammonium and sulfate produce a slope of 0.9 (Fig. 1), indicating an aerosol more like ammonium bisulfate (slope of 1) than ammonium sulfate (slope of 0.5). Production of ammonium bisulfate is representative of aerosols that are likely acidic; here, the aerosols sampled are less neutralized with respect to ammonium than those measured with a Q-AMS in Pittsburgh and New Hampshire (Zhang et al., 2005b; Cottrell et al., 2008).

3.4. Nitrate

Nitrate concentrations were small (mean 0.4 ± 0.5 µg m⁻³), accounting for only 6% of the average measured mass. Ammonium nitrate would not be expected to form to any significant extent due to the acidic nature of the aerosols in Houston and the high temperatures in this location during the summer. More evidence that this nitrate is not ammonium nitrate is demonstrated in the ratio of the signal at m/z 46 to that at m/z 30. For ammonium nitrate, this ratio is approximately 1:2; deviations from this value signify the contribution of other forms of nitrate. For organic nitrates, this ratio has been shown to decrease considerably, with a ratio of approximately 1:10 for SOA formed from the nitrate radical–NH3 reaction (Fry et al., 2009) and 1:5 and 1:8 for SOA formed from photooxidation of α-pinene and 1-3-5 trime-thylbenzene, respectively, in the presence of nitrogen oxides (Alfarra et al., 2006). The average ratio during TRAMP is 1:4.5. Observed increases in nitrate mass during morning rush hour were not accompanied by corresponding increases in ammonium, which would impact the 46/30 ratio and points to organic nitrates or to a process in which nitric acid is taken up on organic surfaces.
Additionally, the relationship between the molar nitrate concentration and the ratio of the molar concentrations of ammonium to sulfate indicate that significant, if not most, nitrate mass is forming when the ammonium to sulfate ratio is less than two. This result has been observed in other locations (Cottrell et al., 2008) and suggests that traditional thermodynamics cannot be used solely to predict nitrate formation.

3.5. Organics

Organics constituted the majority of the PM measured by the Q-AMS (mean 5.5 ± 4.0 μg m⁻³), accounting for slightly more than 50% of the total average mass. The mean to median ratio is close to unity, likely indicating the prevalence of organic aerosol from all upwind directions. Total mass of organic material showed a diurnal trend (not shown) with hourly means and medians approximately equal. A distinct peak in mass is evident at 0800 CST, concurrent with large POA emissions due to morning traffic. A smaller peak occurs at 1500 CST, the height of photochemical oxidation.

The average organic mass spectrum for the entire campaign is presented in Fig. 2. Enhanced signals at m/z 27, 29, 41, 43, 55, 57, and 69 are consistent with those from urban environments (Zhang et al., 2005a). The enhanced signal at m/z 44 indicates the presence of OOA. The comparable signals at these m/z indicate the mixed POA and SOA contributions to overall OA burdens in Houston.

3.6. OOA/HOA analysis

Time series of HOA and OOA are presented in Fig. 3. The average HOA is 1.7 ± 1.9 μg m⁻³, accounting for 32% of the total OA. The average OOA concentration is 3.7 ± 2.6 μg m⁻³. Diurnal trends in the data are observed, with HOA strongly peaking at approximately 0800 CST, coinciding with morning rush hour (Fig. 4). OOA has a less pronounced diurnal trend, with small increases at approximately 0800 CST and again at 1500 CST, when photochemical oxidation is at its strongest. OOA comprises approximately 80% of the total OA during the afternoon. It should be noted that these increases in OOA occur during the times of the deepest boundary layer, indicating the importance of photochemical aerosol formation and/or processing at this location. To further emphasize this, the diurnal variation of the ratio of OOA to CO is displayed in Fig. 4. Utilizing CO to normalize OOA values accounts for dilution and fluctuations in primary emissions (de Gouw et al., 2009). The ratio is small in the morning as result of primary emissions and climbs in the afternoon due to both secondary formation and decreased CO emissions, similar to OOA to CO ratios calculated by de Gouw et al. (2009) during MILAGRO. The increase in the evening ratio is likely related to residual OOA material and a decrease in CO emissions as automobile activity decreases.

Also included in Fig. 4 is the diurnal concentration profile for WSOC. WSOC strongly increases between 0800 and 1000 CST to a peak of 3.7 μg m⁻³ but is fairly constant for the rest of the day (average 2.1 μg C m⁻³). It should be noted that the measurements during the 0800 to 1000 CST period showed the largest variability. Again, a similar pattern was observed during MILAGRO, where increases in WSOC occurred between 0800 and 1100 CST, coinciding with an increase in particulate nitrate and RH (Hennigan et al., 2008b). It has been theorized that particulate WSOC production in the morning occurs via mechanisms different than those associated with WSOC increases in the afternoon (Ervens et al., 2011).

In Table 2, results of linear regressions of the average HOA and OOA spectra with common POA and SOA spectra are shown. The coefficients (r²) for regressions between HOA and published Pittsburgh HOA values, diesel exhaust aerosols, lubricating oil, and diesel fuel from a laboratory study are all 0.77 or greater. Additionally, time series data for HOA were regressed against those of Q-AMS-measured sulfate, ammonium, and nitrate as well as CO, a tracer of motor vehicular emissions. The HOA time series tracks CO (r² = 0.51) and nitrate (r² = 0.45), and the HOA spectra exhibits enhanced signals at m/z 43, 55 and 57, consistent with POA (Zhang et al., 2005a, b).

The r² for the OOA spectra versus spectra from Pittsburgh OOA, chamber SOA, rural OA from Vancouver, Canada, and fulvic acid all are 0.81 or greater, representative of aerosol that is likely secondary. However, the HOA time series shows a weak correlation with sulfate (r² = 0.23), possibly indicating that Houston OOA is less processed and less regional in nature. This is exemplified by a stronger correlation between nitrate and OOA (r² = 0.41). Regression between OOA and sulfate yields r² values of 0.75 and 0.74 for Pittsburgh (Zhang et al., 2005b) and rural New Hampshire (Cottrell et al., 2008), respectively, typical for locations to which highly processed aerosols are advected. Decreased signals at m/z 18, 44, and 55 compared to rural OA also indicate less oxidized OOA. It is most likely that Houston OOA, while still secondary, is significantly less processed, which has been suggested previously by Russell et al. (2009) based on O/C ratios for samples collected on the RV Ronald H. Brown during TexAQSII.

3.7. 1H NMR analysis

Example 1H NMR spectra are shown in Fig. S1. 1H NMR spectra from collected samples display large intensities in the aliphatic portion of the spectrum. Maxima occur in most samples at approximately 0.9 ppm and 1.2 ppm, falling within the ranges for methyl groups (0.7–1.0 ppm) and chain methylene groups (1.2–1.8 ppm), respectively (Décérsi et al., 2000). These correspond to alkyl carbon with low reactivity with respect to most atmospheric oxidants except hydroxyl radical (Moretti et al., 2008). These maxima are consistent with the enhanced relative mixing ratios of alkanes observed during TRAMP (Leuchner and Rappenglück, 2010). Smaller intensities are seen between 1.8 and 4.4 ppm, which includes hydrogen attached to carbon in the α-position to unsaturated carbons (C=O–) and hydrogen bound to carbon associated with alcohols, esters, and ethers (O–C–H). Trace signals of anomic (three samples) and aromatic (seven samples) hydrogen exist only occasionally. Of the seven samples with aromatic content, six were collected during the day. Trace levels of
aromatics were associated with the three samples in which anomeric carbon was measured.

Though observation of small contributions of anomeric hydrogen has been documented, larger contributions from aromatics are common (Decesari et al., 2000, 2007; Tagliavini et al., 2006; Moretti et al., 2008). In Houston, it is possible that heterogeneous reactions involving aromatics in water-soluble POA occurred quickly and that the products of these reactions did not retain their aromatic structure. Given the relatively slow heterogeneous oxidation rates (lifetimes approaching several days) thought to occur in the atmosphere (Weitkamp et al., 2008), this seems unlikely. The low solubility of non-functionalized aromatic species in POA that have not undergone oxidation also could contribute to the lack of an aromatic signal. It is also possible that water-soluble SOA formed from aromatic VOCs is comprised of products that do not retain their aromatic nature. Non-aromatic SOA species from aromatic parent VOCs have been noted in chamber studies (Forstner et al., 1997; Kalberer et al., 2004). The lack of aromatic WSOC also may indicate that biomass burning had little to no influence on WSOC in Houston at these times. The AMS spectrum in Fig. 2 does not indicate a large contribution of m/z 60, which acts as a marker of the local biomass burning tracer levoglucosan (Hennigan et al., 2010). Shakya et al. (2011) also observed very little influence of biomass burning in particles collected at Moody Tower during 2010.

The aromatic samples correspond to days marked by winds from the north to east region (from the HSC), which agrees with Leuchner and Rappenglück (2010), who observed enhanced aromatic VOCs from this direction. The samples with aromatic carbon are compared to the campaign average in Table 3. No change in aliphatic carbon is observed, yet a large decrease in the H–C–C–O group is noted. A corresponding increase is shown in the O–C–H group. These characteristics correlate with aerosol that is fresh and unprocessed (Moretti et al., 2008).

Aerosols analyzed using 1H NMR from a site outside of London showed large contributions from alkyl carbon and hydroxyl groups, while biogenic SOA displayed decreased levels of hydroxyl groups (Decesari et al., 2007). In general, Houston samples appear to be dominated by anthropogenic sources, with large contributions from alkyl and O–C–H groups. The contribution of alkyl content remains steady in most of the measured samples, comprising approximately 63 ± 0.04% of the aliphatic carbon signal (sum of alkyl, H–C–C–O, O–C–H, and aromatics). In comparison, the contribution of the H–C–C–O group fluctuated significantly from sample to sample (between 0 and 40% of the measured signal). Lastly, the O–C–H content varied between 8 and 45% of the measured signal. This is partially consistent with the findings of Decesari et al. (2007) who reported large variability in the O–C–H content but limited changes in the level of H–C–C–O.

Average day and night intensities were considered despite the large variability discussed above. Nearly equal numbers of daytime and night samples are included in these calculations, but the samples were not always chosen from the same specific day. Aliphatic carbon shows no enhancement or depletion based on the time of day. For H–C–C–O, there is a pronounced relative nighttime enhancement and resulting daytime depletion, opposite what is observed for O–C–H. Based on Moretti et al. (2008), it appears that daytime water-soluble aerosols in Houston are influenced to...
calculated H from Decesari et al. (2007) in Fig. 5. The points in this TRAMP, and results are plotted with corresponding source boxes shaded using the 1H-NMR-calculated O/C ratios.

Large organic mass to organic carbon ratios (in the range of underscoring the lack of oxidation. This is emphasized by the 1H-NMR spectra that indicate that the relative amount of aromatics increases at night for the limited number of samples. Instead, there appears to be no relationship between the H–C–C=O signal and the Q-AMS-derived O/C ratios. The data show considerable variability in the Q-AMS O/C ratios, with a minimum of 0.003 and a maximum of 0.87 for the entire dataset, both of which occurred at night. The range of values between these extremes include aerosol that would be characterized as fresh HOA and as aged OOA (Aiken et al., 2008). These values are consistent with those calculated on the RV Ronald H. Brown during TexAQSII (Russell et al., 2009). Russell et al. (2009) suggested that aging of aerosols in Houston, while not extensive, occurs rapidly and is not photochemically limited. The results from this analysis corroborate this theory.

**Table 2**
The $r^2$ coefficients between HOA/OOA spectra and common POA/SOA spectra (Zhang et al., 2005a, b). Miscellaneous includes $r^2$ coefficients between the time series of other measured data and the HOA/OOA time series.

<table>
<thead>
<tr>
<th></th>
<th>HOA ($r^2$)</th>
<th>OOA ($r^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POA</td>
<td>0.97</td>
<td>--</td>
</tr>
<tr>
<td>Pittsburg HOA</td>
<td>0.91</td>
<td>--</td>
</tr>
<tr>
<td>Diesel Exhaust Aerosol</td>
<td>0.97</td>
<td>--</td>
</tr>
<tr>
<td>Lubricating Oil</td>
<td>0.91</td>
<td>--</td>
</tr>
<tr>
<td>Diesel Fuel</td>
<td>0.77</td>
<td>--</td>
</tr>
<tr>
<td>SOA</td>
<td>--</td>
<td>0.99</td>
</tr>
<tr>
<td>Pittsburg OOA</td>
<td>--</td>
<td>0.94</td>
</tr>
<tr>
<td>m-Xylene + hv SOA</td>
<td>--</td>
<td>0.90</td>
</tr>
<tr>
<td>Rural OA</td>
<td>--</td>
<td>0.81</td>
</tr>
<tr>
<td>Fulvic Acid</td>
<td>--</td>
<td>0.34</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>--</td>
<td>0.23</td>
</tr>
<tr>
<td>CO</td>
<td>0.51</td>
<td>0.23</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.004</td>
<td>0.23</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0.04</td>
<td>0.33</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.45</td>
<td>0.41</td>
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</tbody>
</table>

Po Valley in Italy) showed more variability in both the H–C–C=O and O–C–H fractions than all other locations studied. Additionally, while the Po Valley is influenced to a great extent by pollution, it does not have the same level of extreme petrochemical industrial activity that characterizes Houston. Therefore, the variability in the 1H NMR spectra for samples collected during TRAMP is intriguing but not completely unexpected.

3.8. Q-AMS-1H NMR comparison

O/C ratios calculated using Q-AMS data (Aiken et al., 2008) are different than those obtained using 1H NMR spectra, which pertain to WSOC only. The diurnal pattern in the Q-AMS-derived O/C for the sampling periods associated with the 1H NMR samples shows an average daytime ratio of 0.44 and an average nighttime ratio of 0.37, indicating slightly less oxidation at night. This is contrary to the 1H NMR spectra that indicate that the relative amount of H–C–C=O increases at night for the limited number of samples. Instead, there appears to be no relationship between the H–C–C=O signal and the Q-AMS-derived O/C ratios. The data show considerable variability in the Q-AMS O/C ratios, with a minimum of 0.003 and a maximum of 0.87 for the entire dataset, both of which occurred at night. The range of values between these extremes include aerosol that would be characterized as fresh HOA and as aged OOA (Aiken et al., 2008). These values are consistent with those calculated on the RV Ronald H. Brown during TexAQSII (Russell et al., 2009). Russell et al. (2009) suggested that aging of aerosols in Houston, while not extensive, occurs rapidly and is not photochemically limited. The results from this analysis corroborate this theory.
Generally, the Q-AMS O/C ratios were larger than the $^1$H NMR O/C values, with an average Q-AMS/$^1$H NMR ratio of 1.7. The $^1$H NMR O/C values range from 0.08 to 0.49, while the corresponding Q-AMS O/C values for the specific filter periods vary between 0.23 and 0.49. This indicates a water-insoluble (based on the extraction method used) OA component with significant O/C being measured by the Q-AMS. This is corroborated by constant WSOCE particulate concentrations, except in mid-morning (Fig. 4). This phenomenon is interesting and should be investigated further as enhanced O/C should generally increase water solubility. It should be noted that slight differences in particle size sampled could cause differences in the results.

4. Conclusions

Aerosol measurements made with a Q-AMS during TRAMP indicate aerosols comprised primarily of organic material and sulfate, with smaller fractions of ammonium and nitrate. Sulfate and ammonium aerosols in Houston track each other closely, while nitrate and OA are correlated, though not as strongly. Analysis of the organic spectra with a two-component analysis yields an average OA composition of approximately 2/3 OOA and 1/3 HOA. HOA correlates well with common POA tracers, and its spectrum is similar to those for proxies for POA. Similarly, OOA appears to be spectrally similar to proxies for SOA. The OOA appears to be formed locally. $^1$H NMR analysis was performed on 29 samples from the campaign. Large variability in comparison to previous studies was noted in the $H-C-C=O$ and $O-C=H$ groups, which tended to co-vary inversely in magnitude in most of the samples. The aliphatic content of the samples remained consistent. Only trace amounts of both anomic and aromatic carbon were measured, possibly due to the low water solubility of these groups.

Day and night samples were compared. While it is expected that daytime photochemical activity should result in more $H-C-C=O$ relative to $O-C=H$, the reverse trend was observed. However, calculated O/C ratios for the samples show small changes between day and night and provide little evidence for a diurnal cycle. Therefore, any true diurnal trends may be obscured in Houston by the constant presence of industrial emissions, residual material at night, and the specific samples chosen.

The spectra were compared to $^1$H NMR source apportionment fingerprints established for marine OA, SOA, and BBOA (DeCesari et al., 2007). The TRAMP samples displayed a significantly smaller contribution of $H-C-C=O$ groups due to the lower level of oxidation. However, the fraction of aliphatic carbon composed of $O-C=H$ groups exhibited as much variability as all of the sites in the study of DeCesari et al. (2007). As Houston is the most industrially influenced site to be examined using $^1$H NMR to date, the increased variability and lack of oxidation present in the samples is not completely unexpected. However, it is recommended this analysis be repeated in other similarly polluted locations. Further refinement of the marine OA, SOA, and BBOA fingerprints originally established by DeCesari et al. (2007) will further the evolution of $^1$H NMR as a robust technique for source apportionment of WSOCE.

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Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2012.02.074.

References


