Airmass aging metrics derived from particle and other measurements near Fort Worth

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Highlights

• OA/ΔCO and aging metrics for hydrocarbons and NO₅ are correlated

• OA/ΔCO is not correlated to a sulfur aging metric

• More rapid OA enhancement is observed with lower values of the NO₅ aging metric

• Increasing OA/ΔCO with photochemical age is valid only up to approximately 30 hours
Abstract

The composition, concentration, and size of submicron particulate matter (PM$_{1}$) were measured at five-minute resolution by an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) at a semi-rural location northwest of the Dallas-Fort Worth, TX, area during June 2011. Because of increased organic aerosol (OA) levels, focus here is placed on the period from June 17-30. The total measured PM$_{1}$ mass concentration ranged between 1.1 and 16.5 µg m$^{-3}$, with a mean of 4.4 ± 2.6 (one s.d.) µg m$^{-3}$. Significant variability is observed in the time series of total PM$_{1}$ and of four individual HR-ToF-AMS species, particularly between June 21 and 25. The average PM$_{1}$ composition was dominated by OA (55.0 ± 14.8%) and sulfate (30.7 ± 12.3%). Organic aerosol concentrations were correlated positively with carbon monoxide (CO) (R = 0.81). This study uses a variety of aging metrics and their relations to OA/ΔCO to characterize secondary organic aerosol. Photochemical age is estimated by using the toluene to benzene ratio. The average photochemical age was 26.7 ± 5.3 hours. Other metrics of age used in this work include the ratio of sulfate to total sulfur and the ratio of nitrogen oxides to total reactive nitrogen. The correlations between the OA/ΔCO and nitrogen aging metrics indicate consistent aging. However, the relationship between photochemical age and OA/ΔCO shows a peak at approximately 30 hours, which could be indicative of dilution by air with high levels of CO or of reaching a point in time at which further oxidation leads to a decrease in aerosol mass due to material repartitioning to the gas phase.

**Keywords:** organic aerosol; photochemical age; Fort Worth
1. Introduction

Despite established National Ambient Air Quality Standards, high concentrations of particulate matter (PM) still occur in some regions of the United States. The presence of PM in the troposphere impacts climate, visibility, and public health. Aerosols affect Earth’s climate directly by scattering (cooling effect) or absorbing (warming effect) radiation, and they can serve as condensation and ice nuclei for cloud formation, leading to indirect climate impacts (Forster et al., 2007). Aerosols cause visibility reduction through the extinction of visible light. Elevated concentrations of PM also have been correlated strongly to increased rates of human respiratory and allergic illnesses and death (Pope et al., 2002).

Organic aerosol (OA) accounts for a large fraction of atmospheric fine PM and can be divided generally into two categories: primary OA (POA) that is emitted directly into the atmosphere from natural or anthropogenic sources and secondary OA (SOA) that is formed in the atmosphere through the oxidation of natural or anthropogenic volatile organic compounds (VOCs) and subsequent partitioning of the products (Zhang et al., 2007). Although the importance of aerosols in climate, visibility, and public health is well known, the quantification of these impacts includes significant uncertainties because of deficiencies in the understanding of the sources, formation mechanisms, and aging processes associated with SOA (Jimenez et al., 2009).

A temporary ground-based photochemical “supersite” was established at the Eagle Mountain Lake (EML) Texas Commission on Environmental Quality (TCEQ) monitoring site in the Dallas-Fort Worth (DFW) area during June 2011. The goal of the campaign was to investigate the influence that oil and natural gas operations in this area have on local air quality. As part of this, PM measurements were made to help differentiate locally emitted and transported POA and
SOA. This specific work describes efforts to investigate relationships between enhanced OA concentrations and aging processes at the site. Organic aerosol data were analyzed in the context of OA enhancements with respect to excess carbon monoxide (CO), the ratio of which can be used to investigate the relative importance of SOA (DeCarlo et al., 2010; Hayes et al., 2013). Photochemical age estimated from toluene to benzene ratios, the ratio of sulfate (SO$_4^{2-}$) to total sulfur, and the ratio of nitrogen oxides (NO$_x$ = nitric oxide (NO) plus nitrogen dioxide (NO$_2$)) to total reactive nitrogen (NO$_y$) also were used as airmass age indicators to help characterize processes relevant to OA at the site and to allow comparison between various metrics of age.

### 2. Experimental

#### 2.1 Sampling site and meteorology

Measurements were performed continuously in June 2011 at the EML TCEQ monitoring site, which is located 226 m above sea level, in Fort Worth, TX, at 32° 59’16” N, 97° 28’ 37” W. Due to increased pollution levels, only the second half of the month is considered in this study. The site is in a semi-rural area and is ~40 km northwest of downtown Fort Worth. The combined DFW area is the largest metropolitan area in Texas and the fourth largest metropolitan area in the United States, with a population of approximately 6.5 million people. The site is flat and includes various grasses and shrubs. It is located a few kilometers west of a minor state highway and near abundant natural gas and oil operations. The land on which the site sits is owned by the United States National Guard and is used as rangeland for cattle.

Meteorology is described in detail in Rutter et al. (2015); a brief overview is given here. During the campaign, the wind speed and direction were fairly stable. The average wind speed was 7.9 m s$^{-1}$, and the wind direction was almost continuously southerly and southeasterly.
throughout the campaign, which placed the site downwind of the DFW metropolitan area. There was thunderstorm activity during the night of June 21, which was the only time during the campaign with measurable precipitation. The temperature varied from 17.7 to 39.6 °C, and the relative humidity (RH) ranged from 13.8% to 93.3% during the sampling time. Temperature and RH each varied diurnally. Days were generally cloud-free.

2.2 Instrumentation

Particles were sampled from a main copper tubing inlet. An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and a Brechtel Manufacturing, Inc. (BMI) particle-into-liquid sampler (PILS) connected to Dionex ion chromatographs (IC) subsampled from the main inlet, which was equipped with a 2.5-µm cyclone. The main inlet extended approximately 5 m above ground level. Rutter et al. (2015) describe instrumentation in more detail so overviews of only the HR-ToF-AMS and PILS are given here.

The HR-ToF-AMS (DeCarlo et al., 2006) is an online measurement of size-resolved chemistry of submicron non-refractory atmospheric aerosol. Air is sampled through a critical orifice and enters an aerodynamic lens that forces particles to focus into a narrow beam that is accelerated into a vacuum chamber. The size of the particle is measured by particle time of flight (PToF) through this region. After the particles pass through the PToF region, they are vaporized after impacting on a heated surface (600 °C); vaporized material is ionized by electron impact. The resultant ions are detected by a time-of-flight mass spectrometer and attributed to specific aerosol species (sulfate, nitrate, chloride, ammonium, and organic material) based on their mass-to-charge (m/z) ratios. Based on spectral characteristics, organic material is attributed to various types of OA including hydrocarbon-like OA (HOA, thought to be a proxy for combustion-derived POA) and various types of oxidized OA (OOA), thought to be proxies for SOA or
processed POA (Zhang et al., 2005; Jimenez et al., 2009; Ulbrich et al., 2009; Huang et al., 2010). In this case, LV-OOA (termed OOAI in previous studies) represents the factor that exhibits a greater extent of oxidation, and SV-OOA (termed OOAII in previous studies) is that which is less oxidized. As a proxy for SOA mass concentration, pSOA is calculated as the sum of LV-OOA and SV-OOA.

The PILS provides an online measurement of water-soluble ionic aerosol chemical composition at a resolution of 16 minutes. The PILS collects particles by growing them through exposure to a saturated steam environment and then causing their impaction on a surface. A solution containing aerosol species for injection to the ICs (Dionex ICS 1600) is generated by washing the impaction surface with deionized water (Weber et al., 2001; Orsini et al., 2003). A BMI, Inc. Model 8003 impactor was used to remove particles with diameters larger than 1 micron. Sulfate ion concentrations measured with the PILS-ICs are used to determine the collection efficiency of the HR-ToF-AMS. All data shown have been corrected for this assumed constant efficiency of 69%.

Gas-phase species were sampled from separate inlets attached to a walk-up scaffold that reached approximately 20 m above ground level. Except for the VOC measurements, trace gases were sampled through a common ¼” stainless steel tube from which instruments subsampled. The VOC inlet required ¼” PFA tubing. A Thermo Electron Corp. (TECO) 48C Trace Level CO Analyzer (gas filter correlation), a TECO 42C Trace Level nitrogen oxide (NO and NO₂) Analyzer (chemiluminescence), a TECO 42C-Y total reactive nitrogen (NOₓ) Analyzer (molybdenum converter), a TECO 49C ozone (O₃) Analyzer (ultraviolet), a TECO 43C Trace Level sulfur dioxide (SO₂) Analyzer (Pulsed Fluorescence), and an IONICON Analytik Proton Transfer Reaction-Time of Flight- Mass Spectrometer (PTR-ToF-MS) were deployed to measure
trace gases including CO, NO₂, NO, NO₃, O₃, SO₂, and VOCs, respectively. Meteorological data including planetary boundary layer height, temperature, wind speed, and wind direction were tracked with a Vaisala DigiCORA tethersonde system, a Campbell Scientific HMP45C platinum resistance thermometer, and a Campbell Scientific 05103 R. M. Young wind monitor.

3. Results and Discussion

3.1 PM₁ overview

The total observed HR-ToF-AMS PM₁ mass concentration ranged between 1.1 and 16.5 µg m⁻³, with a mean of 4.4 ± 2.6 (one s.d.) µg m⁻³. Significant variability is observed in the time series of total PM₁ and of all species (Figure S1). The average aerosol composition was dominated by organic matter (55.0 ± 14.8%) and sulfate (30.7 ± 12.3%), followed by smaller contributions from ammonium (10.7 ± 3.8%), and nitrate (3.1 ± 1.5%). Over the campaign, the average sulfate mass concentration was 1.2 ± 0.8 µg m⁻³, with a range of 0.2 to 6.7 µg m⁻³. The rapid increase in the sulfate concentration on the night of June 24 also is observed in SO₂ mixing ratios and particle number concentrations (not shown) (Figure S2). The time series of ammonium and sulfate are well correlated (R = 0.98, Figure S3), indicating the predominance of ammonium sulfate relative to ammonium nitrate. This is expected due to the high temperatures during the sampling period and indicates the general aged quality of the inorganic aerosol.

Large spikes in concentrations are observed, particularly between June 21 and 25. The large spikes are mostly driven by increases in OA. The average OA concentration was 2.6 ± 1.9 µg m⁻³, with a wide range of 0.3 to 12.8 µg m⁻³. Organic aerosol was correlated positively with CO, likely indicating a relationship between OA and combustion activities (R=0.81).
The mean OA concentration diurnal profile (Figure 1) during daytime shows a slight increase starting from 1030 CST to 1830 CST, likely as a result of photochemical processing, with the diurnal profile more pronounced for median values. The ratios of the mean to the median OA concentrations are closer to unity between 1000 CST to 1600 CST, indicating significant variability in OA during early morning and at night. Because of the predominance of OA and its diurnal profile, significant attention is paid to OA here.

![Diurnal profile plots of OA (µg m⁻³), CO (ppbv), and OA/ΔCO (µg m⁻³ ppmv⁻¹). The points in the middle show the mean (solid) and median, and the bottom and the top of the whiskers represent the 25th and 75th percentiles, respectively.](image)

**Figure 1.** Diurnal profile plots of OA (µg m⁻³), CO (ppbv), and OA/ΔCO (µg m⁻³ ppmv⁻¹). The points in the middle show the mean (solid) and median, and the bottom and the top of the whiskers represent the 25th and 75th percentiles, respectively.

### 3.2 OA Characterization

Both O₃ and the quantity Oₓ (Oₓ = O₃ + NO₂) are driven photochemically. However, Oₓ is a better tracer than O₃ because the reaction between NO and O₃ forms NO₂, the photolysis of which
eventually reproduces O₃. Previous studies have reported correlation between O₃ and pSOA during periods of pSOA formation due to both requiring photochemical oxidation (Cabada et al., 2004; Liu et al., 2011). The positive correlation between Oₓ and pSOA also has been reported in air masses affected on relatively short timescales (less than eight hours) and with no significant local NO₂ sources (Herndon et al., 2008; Wood et al., 2010).

The times series for pSOA, O₃, and Oₓ track each other well for the DFW campaign. Correlation coefficients (R) are 0.64 and 0.71 for O₃ and Oₓ, respectively, with pSOA (Figure 2). The correlation of pSOA with O₃ and Oₓ confirms photochemically driven SOA formation.

Figure 2. a. pSOA mass concentration (µg m⁻³) versus mixing ratio of Oₓ (ppbv). b. Time series of pSOA mass concentration (black, µg m⁻³), mixing ratio of Oₓ (dashed, ppbv), and mixing ratio of O₃ (gray, ppbv).
The O:C and H:C elemental ratios of ambient OA can be estimated by summation of the contribution of each element within each ion (Aiken et al., 2008). The average of O:C is $0.5 \pm 0.1$ and reaches a value up to 0.9; the average value of H:C is $1.3 \pm 0.1$. The van Krevelen diagram (H:C versus O:C) indicates the oxidation mechanisms of relevance to the OA. Slopes of -2, -0.5, and 0 correspond to the addition of ketone/aldehyde, carboxylic acid, and alcohol/peroxide groups to an aliphatic (unfunctionalized) carbon, respectively (Heald et al., 2010). The slope of H:C versus O:C for DFW is -0.6 ($R = 0.7$); this slope falls between those for ketone/aldehyde and carboxylic acid but closer to that for carboxylic acid (Figure S4). It should be noted that the slope on the diagram can be a result of different combinations of reactions; therefore, the slope only gives information on the range of oxidation processes that are responsible for the aging of the OA. Slopes of ambient data usually range between -0.5 to -1. The slope observed in DFW is similar to those observed in Pasadena, CA (-0.64) (Hayes et al., 2013) and Changdao, China (-0.63) (Hu et al., 2013).

Carbon oxidation state ($O_{Sc} = 2*O:C - H:C$) describes the extent of OA processing and usually ranges between -2 to +1 for observed OA (Kroll et al., 2011). Lower $O_{Sc}$ represents HOA (between -1.7 to -1.6), while OOA typically has an $O_{Sc}$ between -0.5 to +0.9 (Kroll et al., 2011). In this dataset most of the $O_{Sc}$ values fall between -0.5 and +0.5, with a mean of -0.2. The mean and median values are close to each other, which suggests relatively little impact of events characterized by atypical levels of either type of OA. Figure S5 shows the diurnal profile of $O_{Sc}$ values. $O_{Sc}$ starts increasing in the morning at 830 CST and shows a decrease after 1930 CST suggesting a higher oxidation state during daytime, as expected.
3.3 OA/\Delta CO Analysis

Analysis of the ratio of OA to CO has been used previously to investigate the aging and formation of SOA (Kleinman et al., 2008; DeCarlo et al., 2010; Hayes et al., 2013). Carbon monoxide is a fairly conservative pollutant with a lifetime with respect to hydroxyl radical (OH) oxidation on the order of two months. Therefore, any dilution effect on the time scale of hours to days can be minimized by analyzing the ratio of OA to CO (Hodzic and Jimenez, 2011).

Because CO and POA generally have similar emission sources, their concentration ratios are expected to be somewhat constant in a source region over a short timeframe (Hodzic and Jimenez, 2011). Consequently, any increases in the ratio of OA to \Delta CO (measured CO minus background CO) can be used as an indicator of SOA formation.

To calculate the OA/\Delta CO (\mu g m^{-3} ppmv^{-1}) ratio, the fifth percentile of CO mixing ratio (ppmv) is used as a background level (0.085 ppmv) and subtracted from measured values in this study (Cottrell et al., 2008). Fifth and 95th percentiles of OA/\Delta CO values were calculated, and any values smaller or larger than those values were removed.

OA mass concentrations and CO mixing ratios generally track each other (Figure 3). A diurnal trend can be observed in OA time series, except the period with large spikes between June 21 and 25. The OA/\Delta CO time series shows greater variability than the individual OA and CO time series, with lower values between June 21 and June 25 despite both species being enhanced.

The average OA/\Delta CO in the DFW region was 113.9 \pm 60.8 \mu g m^{-3} ppmv^{-1}, with a range of 23.9 and 346.9 \mu g m^{-3} ppmv^{-1} (Table 1). Figure 1 shows a diurnal profile of the ratio, along with diurnal profiles of OA and CO alone. Organic aerosol enhancement with respect to CO starts in the morning (increased photochemical activity) at 830 CST and shows a decrease after sunset.
1830 CST. However, values remain relatively consistent overnight. If the premise of this approach regarding co-location of CO and POA emissions is correct, this consistency at night potentially can be explained by OA formation at night to counter particle deposition and enhancement of CO in the shallower nocturnal boundary layer. An increase of OOA/∆CO at night was observed during a field campaign in Houston in 2006 (Cleveland et al., 2012). The CO diurnal profile shows its first peak during morning rush hour between 0530 CST and 0930 CST, starts increasing at 1430 CST, keeps increasing until midnight, and then remains low.

Figure 3. Time series of OOA/∆CO (gray, μg m⁻³ ppmv⁻¹), mass concentrations of OA (black, μg m⁻³), and the mixing ratio of CO (ppbv).
Table 1. Statistics of OA/ΔCO and other aging metrics.

<table>
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<th></th>
<th>OA/ΔCO (µg m⁻³ ppmv⁻¹)</th>
<th>-log(NOₓ/NOᵧ)</th>
<th>SO₄²⁻ / (SO₂ + SO₄²⁻)</th>
<th>Photochemical Age (hr)</th>
</tr>
</thead>
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<tr>
<td>Mean</td>
<td>113.9</td>
<td>0.3</td>
<td>0.6</td>
<td>26.7</td>
</tr>
<tr>
<td>Median</td>
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<td>0.3</td>
<td>0.7</td>
<td>26.9</td>
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<td>0.2</td>
<td>0.1</td>
<td>5.3</td>
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<tr>
<td>Std Error</td>
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<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Min</td>
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<td>0.4</td>
<td>13.9</td>
</tr>
<tr>
<td>Max</td>
<td>346.9</td>
<td>0.8</td>
<td>0.8</td>
<td>38.1</td>
</tr>
</tbody>
</table>

3.4 Airmass Aging Metrics

Photochemical age and other aging surrogates were used to evaluate the extent of processing and for intercomparison in the DFW area. It is important to note that these values are only approximations/proxies of the airmass age because the calculation of the real age is more complicated, requires reaction rates and oxidant levels, and depends on atmospheric conditions. However, it should be noted that all metrics presented here are expected to increase with airmass aging. In addition, it is hypothesized that relationships between OA/ΔCO and any of these age metrics may allow insight into processes relevant for pSOA. An error and statistical analysis is presented in the supplemental information.

3.4.1 Sulfur

The processing of the observed airmasses with respect to SO₂ is calculated by the ratio of sulfate from the HR-ToF-AMS to total sulfur (assuming sulfate and SO₂ constitute total sulfur), SO₄²⁻ / (SO₄²⁻+SO₂), because over time emitted SO₂ is oxidized to sulfuric acid which then forms SO₄²⁻ (Quinn et al., 2005). The photochemical age is expected to increase with the increase in the ratio of SO₄²⁻ / (SO₄²⁻+SO₂). Because sulfur is predominantly emitted from coal-burning power plants, this aging metric is similar to the concept of plume age (Springston et al., 2005).
The $\text{SO}_4^{2-}/(\text{SO}_4^{2-}+\text{SO}_2)$ values range between 0.4 and 0.8, and no significant diurnal profile is observed. The average sulfate aging metric is $0.6 \pm 0.1$ (Table 1). The observed sulfate aging metric values were comparable to those measured in Ontario, Canada (Hayden et al., 2011).

Figure 4a shows the time series of $\text{OA}/\Delta\text{CO}$ as a function of the sulfate aging metric. Most $\text{SO}_4^{2-}/(\text{SO}_4^{2-}+\text{SO}_2)$ data fall near the average value, and no consistent monotonic linear relationship between the $\Delta\text{OA}/\Delta\text{CO}$ values and the sulfate aging metric can be observed (Figure 4a). As illustrated Figure 4b, overall only a very slight positive correlation can be observed between the two metrics when $\text{OA}/\Delta\text{CO}$ values are averaged within binned values of the sulfur aging metric. This suggests that processing mechanisms required for sulfate formation likely contribute to enhancements in OA indirectly by altering the nature of the aerosol. The poor correlation also can be explained by the relatively long lifetimes of $\text{SO}_2$ with respect to aqueous- and gas-phase oxidation, which are approximately 70 hours and 7 days, respectively (Wojcik and Chang, 1997). The sulfur aging metric therefore does not reflect more local processes.
Figure 4.  a.) OA/\Delta CO (\mu g m^{-3} ppmv^{-1}) ratios color coded by \( \text{SO}_4^{2-}/(\text{SO}_2 + \text{SO}_4^{2-}) \) b.) OA/\Delta CO (\mu g m^{-3} ppmv^{-1}) vs. \( \text{SO}_4^{2-}/(\text{SO}_2 + \text{SO}_4^{2-}) \). The OA/\Delta CO ratios are averaged into 10 bins according to \( \text{SO}_4^{2-}/(\text{SO}_2 + \text{SO}_4^{2-}) \). The lack of data points that approach zero for the x-axis indicates consistently aged air with respect to sulfur. Error bars show the range of data.

3.4.2 NO\textsubscript{x}/NO\textsubscript{y}

The processing of the airmass with respect to NO\textsubscript{x} is approximated with the value of \(-\log(\text{NO}_\text{x}/\text{NO}_\text{y})\). Nitrogen oxides, which are emitted mostly by fossil fuel combustion, are oxidized to species such as nitric acid, nitrous acid, nitrate radical, dinitrogen pentoxide, peroxyacétique nitrite, and peroxyacetyl nitrate (and its analogs) as the air is processed photochemically. Because NO\textsubscript{y} includes both NO\textsubscript{x} and all of its oxidation products, photochemical age increases with the increase of \(-\log(\text{NO}_\text{x}/\text{NO}_\text{y})\) ratio, and smaller values represent fresh emissions (Kleinman et al., 2007; DeCarlo et al., 2008; Slowik et al., 2011). For fresh emissions, \(-\log(\text{NO}_\text{x}/\text{NO}_\text{y}) = 0\), and when NO\textsubscript{x} is 10% of NO\textsubscript{y}, \(-\log(\text{NO}_\text{x}/\text{NO}_\text{y}) = 1\) (Kleinman et al., 2008). This metric represents aging with respect to a combustion source.

The \(-\log(\text{NO}_\text{x}/\text{NO}_\text{y})\) ranged between 0.0 and 0.8 and showed a significant diurnal profile (not shown). The aging metric starts to increases at 0630 CST, peaks around 1530 CST, and keeps
decreasing overnight. The average metric value was 0.3 ± 0.2 (Table 1). The observed -
log(NOx/NOy) values were similar to those observed by Slowik et al. (2011) in southwestern
Ontario and smaller than those observed by Kleinman et al. (2007) in New England. The time
series of NOx and NOy (Figure S6) are included as supplementary information.

Figure 5a shows the same OA/ΔCO time series but colored by the aging metric with respect
to NOx. As illustrated in Figure 5a, values smaller than 0.2 are more likely when low OA/ΔCO
ratios are observed; accordingly, values higher than 0.4 mostly correspond to higher OA/ΔCO
values. This is intuitive as one would expect less OA enhancement in fresher airmasses. A
significant positive correlation exists between -log (NOx/NOy) and OA/ΔCO (Figure 5b), but the
slope of this relationship changes when −log(NOx/NOy) lies between 0.2 and 0.3. A steeper
slope indicates that enhancement in OA occurs more rapidly as the airmass ages; a more gentle
slope indicates slower OA enhancement as the airmass ages. The larger slope in this case occurs
with fresher airmass age, likely signifying that OA processing and formation are more rapid in
fresher airmasses. Compared to the sulfur aging metric, the NOx aging metric is more likely to
reflect local processes. Kleinman et al. (2007, 2008) observed similar trends in New England
and Mexico City.
3.4.3 Photochemical Age

Photochemical age, $\Delta t$, with respect to hydrocarbons (toluene and benzene) is estimated as (Roberts et al., 1984).

$$\Delta t = \frac{1}{[\text{OH}](k_t-k_b)} \times \left[ \ln \left( \frac{[\text{toluene}]}{[\text{benzene}]} | t = 0 \right) - \ln \left( \frac{[\text{toluene}]}{[\text{benzene}]} \right) \right]$$  

(1)

where brackets represent mixing ratios (PTR-ToF-MS ambient measurements in ppb for toluene and benzene) or number densities (for OH, assumed for the entire data set to be $3 \times 10^6$ molecules cm$^{-3}$) and $k_t$ and $k_b$ are the rate coefficients (not temperature-corrected) for the reaction of OH with toluene ($5.63 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) and benzene ($1.22 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$), respectively (Atkinson and Arey, 2003; de Gouw et al., 2005). The initial ratio of toluene to benzene is assumed to be 1.4 based on Texas emission inventories (Zhou et al., 2012).
Photochemical age values are zero when the toluene to benzene ratio is equal to that at the point of emission. Toluene and benzene mixing ratios (Figure S7) during the campaign are shown in the supplementary information.

Photochemical age values ranges between 13.9 and 38.1 hours. Table 1 shows the average photochemical age was $26.7 \pm 5.3$ hours. The photochemical age range is similar but slightly higher than values calculated by Cottrell et al. (2008) at Thompson Farm in semi-rural New England, which is slightly further from a major metropolitan area, Hayes et al. (2013) in Pasadena, CA, and Hu et al. (2013) in Changdao Island, China.

Figure 6a shows the time series of OA/$\Delta$CO colored as a function of photochemical age with respect to the toluene to benzene (predominantly anthropogenic hydrocarbons) ratio. While a decrease in OA/$\Delta$CO ratio is observed between June 17 and 21, after June 21, a more pronounced positive relation is observed (Figure 6a). As illustrated in Figure 6b, the positive correlation between OA/$\Delta$CO and the photochemical age is valid only up to approximately 30 hours, after which OA/$\Delta$CO decreases with age. This could indicate dilution by fresh airmasses high in CO. It also could mark a point where further aging leads to a decrease in OA, as has been suggested by Murphy et al. (2012) and observed in an aging of emissions within a tunnel (Tkacik et al., 2014). Their hypothesis is that fragmentation (as opposed to functionalization) of organic molecules will lead to their repartitioning to the gas phase. Rapid enhancement of OA over excess CO on the time scale of one day and a slower OA enhancement after a one-day period have been observed in other studies such as the New England Air Quality Study in 2002 (de Gouw et al., 2005) and the MILAGRO field campaign in Mexico City in 2006 (DeCarlo et al., 2010). However, those studies did not indicate the peak in the OA/$\Delta$CO ratio-photochemical age relationship observed here.
Figure 6. a.) OA/∆CO (µg m\(^{-3}\) ppmv\(^{-1}\)) ratios color coded by photochemical age (hr) b.) OA/∆CO (µg m\(^{-3}\) ppmv\(^{-1}\)) vs. photochemical age (hr). The measured ratios OA/∆CO are averaged into 10 bins according to photochemical age. Error bars show the range of data.

4. Conclusions

The average aerosol composition in DFW was dominated by OA and sulfate. A detailed analysis of OA concentrations shows a tight correlation with CO. Elemental analysis indicates the probable importance of carboxylic acid in OOA, but the wide range of OS\(c\) values observed suggests HOA also is important. The time series for pSOA, O\(_3\), and O\(_x\) track each other well and
suggest photochemical SOA formation. Overall, a positive correlation can be observed between
OA/ΔCO values and -log (NOx/NOy). More rapid OA enhancement is observed with lower
values (between 0 and 0.3) of -log (NOx/NOy), signifying OA processing and formation are more
rapid in fresher airmasses. Increasing OA/ΔCO with photochemical age is valid only up to
approximately 30 hours, after which OA/ΔCO decreases with age as a result of dilution or
reactions that decrease OA. These aging-OA/ΔCO relationships warrant further investigation
and highlight that caution must be used when describing an airmass as “aged.”

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to the particle-into-liquid sampler (PILS) for ground and airborne measurements of water


Supplemental Information

Figure S1. Time series of organic matter (green), $\text{SO}_4^{2-}$ (red), $\text{NH}_4^+$ (orange), and $\text{NO}_3^-$ (blue) mass concentrations ($\mu$g m$^{-3}$). Chloride is not included due to its very small concentrations.

Figure S2. Time series of $\text{SO}_2$ mixing ratios (gray, ppbv) and $\text{SO}_4^{2-}$ mass concentrations (red, $\mu$g m$^{-3}$).
Figure S3. Scatter plot of $2\times [\text{SO}_4^{2-}]$ (µmol m$^{-3}$) versus $[\text{NH}_4^+]$ (µmol m$^{-3}$) color coded by NH$_3$ (ppb).

Figure S4. Van Krevelen diagram of elemental ratios (O:C vs. H:C) estimated from HR-ToF-AMS measurements of OA.
Figure S5. Diurnal profile of OSc, with formatting as described in Figure 1.

Uncertainty Analysis

The upper-lower bound method was used to estimate the maximum uncertainties in OA/ΔCO and age metrics. Analytical uncertainties of relevant measurements and estimated maximum uncertainties of OA/ΔCO, SO$_4^{2-}$/ (SO$_4^{2-}$+SO$_2$), -log (NO$_x$/NO$_y$) and photochemical age are summarized in Table S1. Differences in diurnal profiles and in the comparisons shown in Figures 4b, 5b, and 6b were evaluated using a student’s t-test; results supported statistical differences from hour to hour in diurnal profile and in the relationships shown in Figures 5b and 6b.
Table S1. Analytical uncertainties in relevant measurements and estimated uncertainties in OA/ΔCO, SO₄²⁻/(SO₄²⁻+SO₂), -log (NOₓ/NOᵧ) and photochemical age.

<table>
<thead>
<tr>
<th>Measurements</th>
<th>Analytical Uncertainty</th>
<th>OA/ΔCO and Age Metrics</th>
<th>Estimated Uncertainty</th>
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<tr>
<td>OA</td>
<td>10%</td>
<td>OA/ΔCO</td>
<td>15%</td>
</tr>
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<td>CO</td>
<td>5%</td>
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<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>4%</td>
<td>SO₄²⁻/(SO₄²⁻+SO₂)</td>
<td>6%</td>
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<td>SO₄²⁻</td>
<td>8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>5%</td>
<td>-log (NOₓ/NOᵧ)</td>
<td>24%</td>
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<tr>
<td>NO₂</td>
<td>7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOᵧ</td>
<td>5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>15%</td>
<td>Photochemical Age</td>
<td>26%</td>
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<tr>
<td>Benzene</td>
<td>(Kim et al., 2015)</td>
<td></td>
<td></td>
</tr>
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</table>
Figure S6. Time series of NO\textsubscript{x} (gray) and NO\textsubscript{y} (black) mixing ratios (ppbv).

Figure S7. Time series of toluene (gray) and benzene (black) mixing ratios (ppbv).
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