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

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17 **Highlights**

- 18 • OA/ Δ CO and aging metrics for hydrocarbons and NO_x are correlated
- 19 • OA/ Δ CO is not correlated to a sulfur aging metric
- 20 • More rapid OA enhancement is observed with lower values of the NO_x aging metric
- 21 • Increasing OA/ Δ CO with photochemical age is valid only up to approximately 30 hours

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Abstract

The composition, concentration, and size of submicron particulate matter (PM_{10}) 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_{10} mass concentration ranged between 1.1 and $16.5 \mu g m^{-3}$, with a mean of 4.4 ± 2.6 (one s.d.) $\mu g m^{-3}$. Significant variability is observed in the time series of total PM_{10} and of four individual HR-ToF-AMS species, particularly between June 21 and 25. The average PM_{10} composition was dominated by OA ($55.0 \pm 14.8\%$) and sulfate ($30.7 \pm 12.3\%$). 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/ Δ CO 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/ Δ CO and nitrogen aging metrics indicate consistent aging. However, the relationship between photochemical age and OA/ Δ CO 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 air mass 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 measureable 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- μ m 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 OOAI 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 1/4" stainless steel tube from which instruments subsampled. The VOC inlet required 1/4" 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 (NO_y) 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, NO_y, O₃, SO₂, and VOCs, respectively. Meteorological data including planetary boundary layer height, temperature, wind speed, and wind direction were tracked with a Vaisala DigiCORA tethered sonde 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 ($55.0 \pm 14.8\%$) and sulfate ($30.7 \pm 12.3\%$), followed by smaller contributions from ammonium ($10.7 \pm 3.8\%$), and nitrate ($3.1 \pm 1.5\%$). 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.

Figure 1. Diurnal profile plots of OA ($\mu\text{g m}^{-3}$), CO (ppbv), and OA/ Δ CO ($\mu\text{g m}^{-3} \text{ ppmv}^{-1}$). 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 O_3 and the quantity O_x ($\text{O}_x = \text{O}_3 + \text{NO}_2$) are driven photochemically. However, O_x is a better tracer than O_3 because the reaction between NO and O_3 forms NO_2 , the photolysis of which

eventually reproduces O_3 . Previous studies have reported correlation between O_3 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 O_x and pSOA also has been reported in air masses affected on relatively short timescales (less than eight hours) and with no significant local NO_2 sources (Herndon *et al.*, 2008; Wood *et al.*, 2010).

The times series for pSOA, O_3 , and O_x track each other well for the DFW campaign. Correlation coefficients (R) are 0.64 and 0.71 for O_3 and O_x , respectively, with pSOA (Figure 2). The correlation of pSOA with O_3 and O_x confirms photochemically driven SOA formation.

Figure 2. a. pSOA mass concentration ($\mu g m^{-3}$) versus mixing ratio of O_x (ppb). **b.** Time series of pSOA mass concentration (black, $\mu g m^{-3}$), mixing ratio of O_x (dashed, ppbv), and mixing ratio of O_3 (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 ± 0.1 and reaches a value up to 0.9; the average value of H:C is 1.3 ± 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 ($OS_c = 2 \times O:C - H:C$) describes the extent of OA processing and usually ranges between -2 to +1 for observed OA (Kroll *et al.*, 2011). Lower OS_c represents HOA (between -1.7 to -1.6), while OOA typically has an OS_c between -0.5 to +0.9 (Kroll *et al.*, 2011). In this dataset most of the OS_c 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 OS_c values. OS_c 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/ Δ 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 Δ CO (measured CO minus background CO) can be used as an indicator of SOA formation.

To calculate the OA/ Δ CO ($\mu\text{g m}^{-3} \text{ppmv}^{-1}$) 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/ Δ 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/ Δ 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/ Δ CO in the DFW region was $113.9 \pm 60.8 \mu\text{g m}^{-3} \text{ppmv}^{-1}$, with a range of 23.9 and $346.9 \mu\text{g m}^{-3} \text{ppmv}^{-1}$ (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

228 1830 CST. However, values remain relatively consistent overnight. If the premise of this
 229 approach regarding co-location of CO and POA emissions is correct, this consistency at night
 230 potentially can be explained by OA formation at night to counter particle deposition and
 231 enhancement of CO in the shallower nocturnal boundary layer. An increase of OOA/ Δ CO at
 232 night was observed during a field campaign in Houston in 2006 (Cleveland *et al.*, 2012). The CO
 233 diurnal profile shows its first peak during morning rush hour between 0530 CST and 0930 CST,
 234 starts increasing at 1430 CST, keeps increasing until midnight, and then remains low.

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237 **Figure 3.** Time series of OA/ Δ CO (gray, $\mu\text{g m}^{-3} \text{ppmv}^{-1}$), mass concentrations of OA (black, $\mu\text{g m}^{-3}$), and the mixing
 238 ratio of CO (ppbv).

239 **Table 1.** Statistics of OA/ Δ CO and other aging metrics.

	OA/ Δ CO ($\mu\text{g m}^{-3}\text{ppmv}^{-1}$)	$-\log(\text{NO}_x/\text{NO}_y)$	$\text{SO}_4^{2-} / (\text{SO}_2 + \text{SO}_4^{2-})$	Photochemical Age (hr)
Mean	113.9	0.3	0.6	26.7
Median	99.9	0.3	0.7	26.9
Std Dev	60.8	0.2	0.1	5.3
Std Error	1.1	0.0	0.0	0.2
Min	23.9	0.0	0.4	13.9
Max	346.9	0.8	0.8	38.1

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241 3.4 Airmass Aging Metrics

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

250 3.4.1 Sulfur

251 The processing of the observed airmasses with respect to SO_2 is calculated by the ratio of
 252 sulfate from the HR-ToF-AMS to total sulfur (assuming sulfate and SO_2 constitute total sulfur),
 253 $\text{SO}_4^{2-} / (\text{SO}_4^{2-} + \text{SO}_2)$, because over time emitted SO_2 is oxidized to sulfuric acid which then forms
 254 SO_4^{2-} (Quinn *et al.*, 2005). The photochemical age is expected to increase with the increase in the
 255 ratio of $\text{SO}_4^{2-} / (\text{SO}_4^{2-} + \text{SO}_2)$. Because sulfur is predominantly emitted from coal-burning power
 256 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 ± 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 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/ΔCO ($\mu g m^{-3} ppmv^{-1}$) ratios color coded by $SO_4^{2-} / (SO_2 + SO_4^{2-})$ **b.)** OA/ΔCO ($\mu g m^{-3} ppmv^{-1}$) vs. $(SO_4^{2-} / (SO_2 + SO_4^{2-}))$. The OA/ΔCO ratios are averaged into 10 bins according to $SO_4^{2-} / (SO_2 + SO_4^{2-})$. 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_x/NO_y

The processing of the airmass with respect to NO_x is approximated with the value of $-\log(NO_x/NO_y)$. Nitrogen oxides, which are emitted mostly by fossil fuel combustion, are oxidized to species such as nitric acid, nitrous acid, nitrate radical, dinitrogen pentoxide, peroxyacetylnitrate, and peroxyacetylnitrate (and its analogs) as the air is processed photochemically. Because NO_y includes both NO_x and all of its oxidation products, photochemical age increases with the increase of $-\log(NO_x/NO_y)$ ratio, and smaller values represent fresh emissions (Kleinman *et al.*, 2007; DeCarlo *et al.*, 2008; Slowik *et al.*, 2011). For fresh emissions, $-\log(NO_x/NO_y) = 0$, and when NO_x is 10% of NO_y, $-\log(NO_x/NO_y) = 1$ (Kleinman *et al.*, 2008). This metric represents aging with respect to a combustion source.

The $-\log(NO_x/NO_y)$ ranged between 0.0 and 0.8 and showed a significant diurnal profile (not shown). The aging metric starts to increase at 0630 CST, peaks around 1530 CST, and keeps

decreasing overnight. The average metric value was 0.3 ± 0.2 (Table 1). The observed $-\log(\text{NO}_x/\text{NO}_y)$ 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 NO_x and NO_y (Figure S6) are included as supplementary information.

Figure 5a shows the same $\text{OA}/\Delta\text{CO}$ time series but colored by the aging metric with respect to NO_x . As illustrated in Figure 5a, values smaller than 0.2 are more likely when low $\text{OA}/\Delta\text{CO}$ ratios are observed; accordingly, values higher than 0.4 mostly correspond to higher $\text{OA}/\Delta\text{CO}$ values. This is intuitive as one would expect less OA enhancement in fresher airmasses. A significant positive correlation exists between $-\log(\text{NO}_x/\text{NO}_y)$ and $\text{OA}/\Delta\text{CO}$ (Figure 5b), but the slope of this relationship changes when $-\log(\text{NO}_x/\text{NO}_y)$ 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 NO_x aging metric is more likely to reflect local processes. Kleinman *et al.* (2007, 2008) observed similar trends in New England and Mexico City.

Figure 5. a.) $\text{OA}/\Delta\text{CO}$ ($\mu\text{g m}^{-3} \text{ppmv}^{-1}$) ratios color coded by $-\log(\text{NO}_x/\text{NO}_y)$ **b.)** $\text{OA}/\Delta\text{CO}$ ($\mu\text{g m}^{-3} \text{ppmv}^{-1}$) vs. $-\log(\text{NO}_x/\text{NO}_y)$. The measured ratios $\text{OA}/\Delta\text{CO}$ are averaged into 10 bins according to $-\log(\text{NO}_x/\text{NO}_y)$. Error bars show the range of data.

3.4.3 Photochemical Age

Photochemical age, Δt , with respect to hydrocarbons (toluene and benzene) is estimated as (Roberts *et al.*, 1984).

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

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 3×10^6 molecules cm^{-3}) and k_t and k_b are the rate coefficients (not temperature-corrected) for the reaction of OH with toluene ($5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and benzene ($1.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), 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 ± 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/ Δ CO colored as a function of photochemical age with respect to the toluene to benzene (predominantly anthropogenic hydrocarbons) ratio. While a decrease in OA/ Δ 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/ Δ CO and the photochemical age is valid only up to approximately 30 hours, after which OA/ Δ 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/ Δ CO ratio-photochemical age relationship observed here.

Figure 6. a.) $OA/\Delta CO$ ($\mu g m^{-3} ppmv^{-1}$) ratios color coded by photochemical age (hr) **b.)** $OA/\Delta CO$ ($\mu g m^{-3} ppmv^{-1}$) vs. photochemical age (hr). The measured ratios $OA/\Delta CO$ 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 OSc 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/ Δ CO values and $-\log(\text{NO}_x/\text{NO}_y)$. More rapid OA enhancement is observed with lower values (between 0 and 0.3) of $-\log(\text{NO}_x/\text{NO}_y)$, signifying OA processing and formation are more rapid in fresher airmasses. Increasing OA/ Δ CO with photochemical age is valid only up to approximately 30 hours, after which OA/ Δ CO decreases with age as a result of dilution or reactions that decrease OA. These aging-OA/ Δ CO relationships warrant further investigation and highlight that caution must be used when describing an airmass as “aged.”

Acknowledgements

This study was supported by the TCEQ Air Quality Research Program. The authors would like to thank Melanie Calzada, Caroline Gutierrez, and Kabindra Shakya for help in data collection, the Texas National Guard for providing access to the site, Dr. Wei Zhou for provision of the Texas emission information, and Dr. Loren Raun for helpful discussions.

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575 **Supplemental Information**

576
577 **Figure S1.** Time series of organic matter (green), SO_4^{2-} (red), NH_4^+ (orange), and NO_3^- (blue)
578 mass concentrations ($\mu\text{g m}^{-3}$). Chloride is not included due to its very small concentrations.

580
581 **Figure S2.** Time series of SO_2 mixing ratios (gray, ppbv) and SO_4^{2-} mass concentrations (red, μg
582 m^{-3}).

Figure S3. Scatter plot of $2 \times [\text{SO}_4^{2-}]$ ($\mu\text{mol m}^{-3}$) versus $[\text{NH}_4^+]$ ($\mu\text{mol m}^{-3}$) 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/ Δ CO and age metrics. Analytical uncertainties of relevant measurements and estimated maximum uncertainties of OA/ Δ CO, $\text{SO}_4^{2-}/(\text{SO}_4^{2-}+\text{SO}_2)$, $-\log(\text{NO}_x/\text{NO}_y)$ 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.

603 **Table S1.** Analytical uncertainties in relevant measurements and estimated uncertainties
 604 in OA/ Δ CO, $\text{SO}_4^{2-}/(\text{SO}_4^{2-}+\text{SO}_2)$, $-\log(\text{NO}_x/\text{NO}_y)$ and photochemical age.

Measurements	Analytical Uncertainty	OA/ Δ CO and Age Metrics	Estimated Uncertainty
OA	10%	OA/ Δ CO	15%
CO	5%		
SO ₂	4%	$\text{SO}_4^{2-}/(\text{SO}_4^{2-}+\text{SO}_2)$	6%
SO_4^{2-}	8%		
NO	5%	$-\log(\text{NO}_x/\text{NO}_y)$	24%
NO ₂	7%		
NO _y	5%		
Toluene	15%	Photochemical Age	26%
Benzene	(Kim <i>et al.</i> , 2015)

Figure S6. Time series of NO_x (gray) and NO_y (black) mixing ratios (ppbv).

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

609 Kim, S., Guenther, A., Lefer, B., Flynn, J., Griffin, R., Rutter, A.P., Gong, L. & Cevik, B.K.
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