



Chemical oxidative potential of secondary organic aerosol (SOA) generated from the photooxidation of biogenic and anthropogenic volatile organic compounds

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Abstract. Particulate matter (PM), of which a significant fraction is comprised of secondary organic aerosols (SOA), has received considerable attention due to its health implications. In this study, the water-soluble oxidative potential (OP^{WS}) of SOA generated from the photooxidation of biogenic and anthropogenic hydrocarbon precursors (isoprene, α -pinene, β -caryophyllene, pentadecane, *m*-xylene, and naphthalene) under different reaction conditions (“RO₂+HO₂” vs. “RO₂+NO” dominant, dry vs. humid) was characterized using dithiothreitol (DTT) consumption. The measured intrinsic OP^{WS-DTT} values ranged from 9 to 205 pmol min⁻¹ μ g⁻¹ and were highly dependent on the specific hydrocarbon precursor, with naphthalene and isoprene SOA generating the highest and lowest OP^{WS-DTT} values, respectively. Humidity and RO₂ fate affected OP^{WS-DTT} in a hydrocarbon-specific manner, with naphthalene SOA exhibiting the most pronounced effects, likely due to the formation of nitroaromatics. Together, these results suggest that precursor identity may be more influential than reaction condition in determining SOA oxidative potential, demonstrating the importance of sources, such as incomplete combustion, to aerosol toxicity. In the context of other PM sources, all SOA systems, with the exception of naphthalene SOA, were less DTT active than ambient sources related to incomplete combustion, including diesel and gasoline combustion as well as biomass burning. Finally, naphthalene SOA was as DTT active as biomass burning aerosol, which was found to be the most DTT-active OA source in a previous ambient

study. These results highlight a need to consider SOA contributions (particularly from anthropogenic hydrocarbons) to health effects in the context of hydrocarbon emissions, SOA yields, and other PM sources.

1 Introduction

Numerous epidemiological studies have found associations between elevated particulate matter (PM) concentrations and increased incidences of cardiopulmonary disease, including increases in lung cancer, asthma, chronic obstructive pulmonary disease, arrhythmia, and ischemic heart disease (Li et al., 2008; Pope III and Dockery, 2006; Brunekreef and Holgate, 2002; Dockery et al., 1993; Hoek et al., 2013; Anderson et al., 2011; Pope et al., 2002). Furthermore, ambient PM pollution ranked among the top 10 global risk factors in the 2010 Global Burden of Disease Study, with significant contributions from cardiopulmonary diseases and lower respiratory infections (Lim et al., 2012). Recent epidemiological studies have also found an association between particle oxidative potential and various cardiopulmonary health endpoints (Bates et al., 2015; Fang et al., 2016; Yang et al., 2016; Weichenthal et al., 2016). Furthermore, results from toxicology studies suggest that PM-induced oxidant production, including reactive oxygen and nitrogen species (ROS/RNS), is a possible mechanism by which PM exposure results in adverse health effects (Li et al., 2003a; Tao et al., 2003; Castro and Freeman,

2001; Gurgueira et al., 2002). These species can initiate inflammatory cascades, which may ultimately lead to oxidative stress and cellular damage (Wiseman and Halliwell, 1996; Hensley et al., 2000). Prolonged stimulation of inflammatory cascades may also lead to chronic inflammation, for which there is a well-established link between chronic inflammation and cancer (Philip et al., 2004). Collectively, these findings suggest a possible link between PM exposure and epidemiologically associated health endpoints since PM can contain ROS/RNS and generate ROS/RNS via redox reactions and by inducing cellular pathways that produce ROS/RNS.

Chemical assays in which an antioxidant is used to simulate redox reactions that would occur in biological systems have been developed to study the oxidative potential of PM samples (Kumagai et al., 2002; Cho et al., 2005). In these assays, redox-active species in PM samples catalyze electron transfer from the antioxidant (dithiothreitol, DTT; ascorbic acid, AA; etc.) to oxygen, and antioxidant decay provides a measure of the concentration of redox-active species in the sample (Fang et al., 2015b). These assays have been utilized extensively to characterize ambient PM samples, and source apportionment regressions have been applied to DTT activity results to identify PM sources that may be detrimental to health (Bates et al., 2015; Fang et al., 2015a; Verma et al., 2014, 2015a). Results from these regressions, as well as inhalation and exposure studies, suggest that organic carbon constituents may play a significant role in PM-induced health effects (Li et al., 2003b; Kleinman et al., 2005; Hamad et al., 2015; Verma et al., 2015b). In particular, humic-like substances (HULIS) and oxygenated polyaromatic hydrocarbons (PAHs) have been shown to contribute significantly to the redox activity of water-soluble PM samples (Verma et al., 2012, 2015a, b; Dou et al., 2015; Lin and Yu, 2011). Recently, Tuet et al. (2016) also showed that there is a significant correlation between intracellular ROS/RNS production and organic species (water-soluble organic carbon and brown carbon) for summer ambient samples, which suggests that photochemically driven secondary organic aerosols (SOA) may be important in PM-induced oxidative stress.

Many prior studies have focused on the health effects of primary emissions, such as PM directly emitted from diesel and gasoline engines (Bai et al., 2001; Kumagai et al., 2002; McWhinney et al., 2013a; Turner et al., 2015). Conversely, few studies have explored the potential health implications of SOA, which are formed from the oxidation of volatile organic compounds (VOCs; McWhinney et al., 2013b; Rattanavaraha et al., 2011; Kramer et al., 2016; Lund et al., 2013; McDonald et al., 2010, 2012; Baltensperger et al., 2008; Arashiro et al., 2016; Platt et al., 2014), even though field studies have shown that SOA often dominate over primary aerosols even in urban environments (Zhang et al., 2007; Jimenez et al., 2009; Ng et al., 2010). The few studies that exist focus on SOA generated from a single class of hydrocarbon precursor or on SOA formed in a simulated urban background (Kramer et al., 2016; McWhinney et al., 2013b;

Rattanavaraha et al., 2011; Arashiro et al., 2016; McDonald et al., 2012). While studies on oxidative potential have shown that SOA is indeed redox active, the combined range of oxidative potentials observed for individual SOA systems is quite large and remains unexplored (McWhinney et al., 2013b; Kramer et al., 2016). Furthermore, results from cellular exposure studies are inconclusive, with some studies finding significant response from SOA exposure and others finding little to no response. The exposure dose also differed from study to study, which may result in inconclusive results. This also highlights a need to consider dose–response relationships as demonstrated recently in Tuet et al. (2016). Comparisons between the observed cellular endpoints from exposure to SOA formed from individual precursors are also lacking (Baltensperger et al., 2008; Lund et al., 2013; McDonald et al., 2010, 2012; Arashiro et al., 2016). As such, there is a lack of perspective in terms of different individual SOA systems and their contributions to PM-induced health effects, making it unclear whether certain responses are indeed toxic for a range of sources and subtypes of PM. However, as cellular assays and animal inhalation experiments are more complex, a systematic study on the oxidative potential of individual SOA systems may be warranted first.

In the present study, the water-soluble oxidative potential of SOA generated from various precursors under different reaction conditions was measured using the DTT assay (henceforth referred to as OP^{WS-DTT}). While numerous cell-free assays have been developed to measure oxidative potential, the DTT assay is well-suited for the purposes of this study due to its proven sensitivity to organic carbon constituents and its correlation with organic carbon (Janssen et al., 2014; Visentin et al., 2016). Furthermore, there are many previous studies reporting the DTT activities of laboratory-generated SOA and ambient samples for comparison purposes (Kramer et al., 2016; Bates et al., 2015; McWhinney et al., 2013a, b; Verma et al., 2015a; Xu et al., 2015a, b; Fang et al., 2015b; Lu et al., 2014). VOCs were chosen to represent the major classes of compounds known to produce SOA upon oxidation by atmospheric oxidants and to include precursors of both anthropogenic and biogenic origins (Table S1 in the Supplement). Biogenic precursors include isoprene, α -pinene, and β -caryophyllene, while anthropogenic precursors include pentadecane, *m*-xylene, and naphthalene. Isoprene was chosen since it is the most abundant non-methane hydrocarbon, with estimated global emissions around 500 Tg yr^{-1} (Guenther et al., 2006). α -pinene and β -caryophyllene were chosen as representative, well-studied monoterpenes and sesquiterpenes, respectively. Both classes of compounds contribute significantly to ambient aerosol (Eddingsaas et al., 2012; Hoffmann et al., 1997; Tasoglou and Pandis, 2015; Goldstein and Galbally, 2007). α -pinene emissions ($\sim 50 \text{ Tg yr}^{-1}$) are also on the same order of global anthropogenic emissions ($\sim 110 \text{ Tg yr}^{-1}$; Guenther et al., 1993; Piccot et al., 1992). Similarly, anthropogenic precursors were chosen to include a long-chain alkane (pentadecane), a single-ring aromatic (*m*-

Table 1. Experimental conditions.

Experiment	Compound	OH precursor	Relative humidity (%)	[HC] ₀ (ppb)	[SOA] ^c (μg m ⁻³)
1 ^a	isoprene	H ₂ O ₂	< 5 %	97	5.73
2 ^a	α-pinene	H ₂ O ₂	< 5 %	191	119
3 ^a	β-caryophyllene	H ₂ O ₂	< 5 %	36	221
4 ^a	pentadecane	H ₂ O ₂	< 5 %	106	9.71
5 ^a	<i>m</i> -xylene	H ₂ O ₂	< 5 %	450	89.3
6 ^a	naphthalene	H ₂ O ₂	< 5 %	178	128
7	isoprene	H ₂ O ₂	< 5 % ^b	97	17.1
8	α-pinene	H ₂ O ₂	40 %	334	154
9	β-caryophyllene	H ₂ O ₂	42 %	63	230
10	pentadecane	H ₂ O ₂	45 %	106	23.5
11	<i>m</i> -xylene	H ₂ O ₂	45 %	450	13.9
12	naphthalene	H ₂ O ₂	44 %	431	132
13	isoprene	HONO	< 5 %	970	148
14	α-pinene	HONO	< 5 %	174	166
15	β-caryophyllene	HONO	< 5 %	21	80.8
16	pentadecane	HONO	< 5 %	74	35.7
17	<i>m</i> -xylene	HONO	< 5 %	431	153
18	naphthalene	HONO	< 5 %	145	142

^a These experiments were repeated to establish reproducibility. ^b Acidic seed (8 mM MgSO₄ and 16 mM H₂SO₄) was used instead of 8 mM (NH₄)₂SO₄. ^c Average SOA concentration in the chamber during filter collection.

xylene), and a poly-aromatic (naphthalene). These classes of compounds are emitted as products of incomplete combustion (Robinson et al., 2007; Jia and Batterman, 2010; Bruns et al., 2016) and have been shown to have considerable SOA yields (e.g., Chan et al., 2009; Ng et al., 2007b; Lambe et al., 2011). In addition to precursor identity, the effects of humidity (dry vs. humid) and NO_x (differing peroxy radical (RO₂) fates, RO₂+HO₂ vs. RO₂+NO) on OP^{WS-DTT} were investigated because these conditions have been shown to affect the chemical composition and mass loading of formed SOA (Chhabra et al., 2010, 2011; Eddingsaas et al., 2012; Ng et al., 2007a, b; Loza et al., 2014; Chan et al., 2009; Boyd et al., 2015). Finally, intrinsic OP^{WS-DTT} was compared with bulk aerosol composition, specifically elemental ratios, to investigate whether there is a link between OP^{WS-DTT} and aerosol composition.

2 Methods

2.1 Chamber experiments

SOA from the photooxidation of biogenic and anthropogenic VOCs were generated in the Georgia Tech Environmental Chamber (GTEC) facility. Details of the facility are described elsewhere (Boyd et al., 2015). Briefly, the facility consists of two 12 m³ Teflon chambers suspended inside a 6.4 m × 3.7 m (21 ft × 12 ft) temperature-controlled enclosure surrounded by black lights (Sylvania 24922) and natural sunlight fluorescent lamps (Sylvania 24477). Multiple sam-

pling ports from each chamber allow for gas- and aerosol-phase measurements as well as introduction of reagents. Gas-phase measurements include O₃, NO₂, and NO_x concentrations as measured by an O₃ analyzer (Teledyne T400), a cavity-attenuated phase shift (CAPS) NO₂ monitor (Aerodyne), and a chemiluminescence NO_x monitor (Teledyne 200EU), respectively. Additionally, a gas chromatography-flame ionization detector (GC-FID, Agilent 7890A) was used to monitor hydrocarbon decay and estimate hydroxyl radical (OH) concentration. In terms of aerosol-phase measurements, aerosol volume concentrations and distributions were measured using a scanning mobility particle sizer (SMPS, TSI), while bulk aerosol composition was determined using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne; henceforth referred to as the AMS) (DeCarlo et al., 2006). AMS data were analyzed using the data analysis toolkits SQUIRREL (v. 1.57) and PIKA (v. 1.16). Elemental ratios (O : C, H : C, and N : C) were obtained using the method outlined by Canagaratna et al. (2015) and were used to calculate the average carbon oxidation state ($\overline{\text{OS}}_c$) (Kroll et al., 2011). Temperature and relative humidity (RH) were monitored using a hydro-thermometer (Vaisala HMP110).

Experimental conditions, given in Table 1, were designed to probe the effects of humidity, RO₂ fate, and precursor hydrocarbon on OP^{WS-DTT}. All experiments were performed at ~ 25 °C under dry (RH < 5 %) or humid (RH ~ 45 %) conditions. Prior to each experiment, the chambers were flushed with pure air for ~ 24 h. For humid experiments, the cham-

bers were also humidified by means of a bubbler filled with deionized (DI) water during this time. Seed aerosol was then injected by atomizing a 15 mM $(\text{NH}_4)_2\text{SO}_4$ seed solution (Sigma Aldrich) until the seed concentration was approximately $20 \mu\text{g m}^{-3}$. It is noted that for experiment 7 (isoprene SOA under $\text{RO}_2 + \text{HO}_2$ -dominant, “humid” conditions), experimental conditions deviated due to extremely low SOA mass yields. For this experiment, an acidic seed solution (8 mM MgSO_4 and 16 mM H_2SO_4) was used under dry conditions to promote SOA formation via the IEPOX (isoprene epoxydiols) uptake pathway, which has a higher SOA mass yield compared to the IEPOX + OH pathway and contributes significantly to ambient OA (Surratt et al., 2010; Lin et al., 2012).

Once the seed concentration stabilized, hydrocarbon was added by injecting a known volume of hydrocarbon solution (isoprene, 99%; α -pinene, $\geq 99\%$; β -caryophyllene, $>98.5\%$; pentadecane, $\geq 99\%$; *m*-xylene, $\geq 99\%$; naphthalene, 99% (Sigma Aldrich)) into a glass bulb and passing zero air at 5 L min^{-1} over the solution until fully evaporated (~ 10 min). For pentadecane and β -caryophyllene, the glass bulb was gently heated to ensure full evaporation (Tasoglou and Pandis, 2015). Naphthalene was injected by passing pure air over the solid, as outlined in previous studies (Chan et al., 2009). After hydrocarbon injection, OH precursor was added to the chamber. Experiments were conducted under various NO_x conditions where different RO_2 reaction pathways prevailed. For $\text{RO}_2 + \text{HO}_2$ experiments, hydrogen peroxide (H_2O_2) was used as the OH precursor. H_2O_2 (50% aqueous solution, Sigma Aldrich) was injected using the method described for hydrocarbon injection to achieve an H_2O_2 concentration of 3 ppm, which yielded OH concentrations on the order of $10^6 \text{ molec cm}^{-3}$. For $\text{RO}_2 + \text{NO}$ experiments, nitrous acid (HONO) was used as the OH precursor. HONO was prepared by adding 10 mL of 1% wt aqueous NaNO_2 (VWR International) dropwise into 20 mL of 10% wt H_2SO_4 (VWR International) in a glass bulb. Zero air was then passed over the solution to introduce HONO into the chamber (Chan et al., 2009; Kroll et al., 2005). Photolysis of HONO yielded OH concentrations on the order of $10^7 \text{ molec cm}^{-3}$. NO and NO_2 were also formed as byproducts of HONO synthesis. Once all the H_2O_2 evaporated ($\text{RO}_2 + \text{HO}_2$ experiments) or NO_x concentrations stabilized ($\text{RO}_2 + \text{NO}$ experiments), the UV lights were turned on to initiate photooxidation.

2.2 Aerosol collection and extraction

Aerosol samples were collected onto 47 mm Teflon™ filters (0.45 μm pore size, Pall Laboratory) for approximately 1.5 h at a flow rate of 28 L min^{-1} . For each experiment, two filters (front filter and backing filter) were loaded in series to account for possible sampling artifacts (Conny and Slater, 2002). Total mass collected was determined by integrating the SMPS volume concentration as a function of time over the filter collection period and using the total volume of air

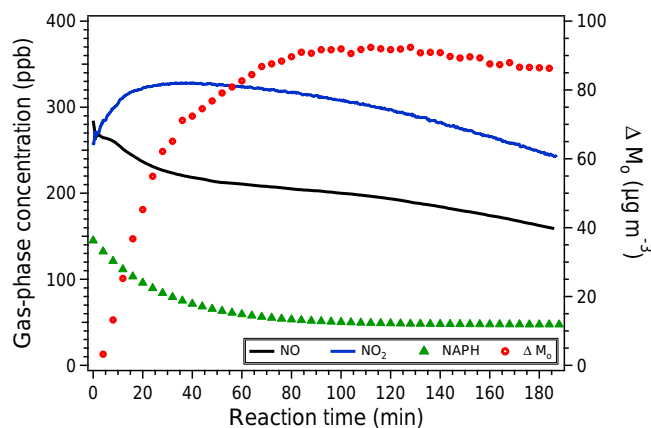


Figure 1. Typical reaction profile for a chamber experiment under $\text{RO}_2 + \text{NO}$ -dominant conditions. NO and NO_2 concentrations were monitored by CAPS NO_2 and chemiluminescence NO_x monitors, respectively. Hydrocarbon decay was monitored using GC-FID, while initial hydrocarbon (naphthalene) concentrations were determined using the chamber volume and mass of hydrocarbon injected. Aerosol mass concentrations were determined using volume concentrations obtained from SMPS and assuming an aerosol density of 1 g cm^{-3} . While typical SOA density is about 1.4 g cm^{-3} , it varies with hydrocarbon precursor identity and reaction conditions, and a density between ~ 1.0 and 1.6 g cm^{-3} has been reported in previous studies (Ng et al., 2006, 2007a, b; Chan et al., 2009; Tasoglou and Pandis, 2015; Bahreini et al., 2005). The use of a density of 1 g cm^{-3} is to facilitate easier comparisons with past and future studies. Results from future studies can be scaled accordingly for comparison with the current work. Mass concentrations have been corrected for particle wall loss (Nah et al., 2016).

collected. Volume concentrations were integrated using time-dependent data. Background filters containing seed and an OH precursor (H_2O_2 or HONO) only at experimental conditions were also collected to account for potential H_2O_2 or HONO uptake, which may influence oxidative potential. Collected filter samples were placed in sterile petri dishes, sealed with Parafilm M®, and stored at -20°C until extraction and analysis (Fang et al., 2015b). Prior to determining $\text{OP}^{\text{WS-DTT}}$, collected particles were extracted in DI water by submerging the filter and sonicating for 1 hr using an Ultrasonic Cleanser (VWR International; Fang et al., 2015a). Sonication steps were performed in 30 min intervals with water replacement after each interval to reduce bath temperature. After sonication, extracts were filtered using 0.45 μm PTFE (polytetrafluoroethylene) syringe filters (Fisherbrand™) to remove insoluble material (Fang et al., 2015b). All filter samples were extracted within 1–2 days of collection and analyzed immediately following extraction.

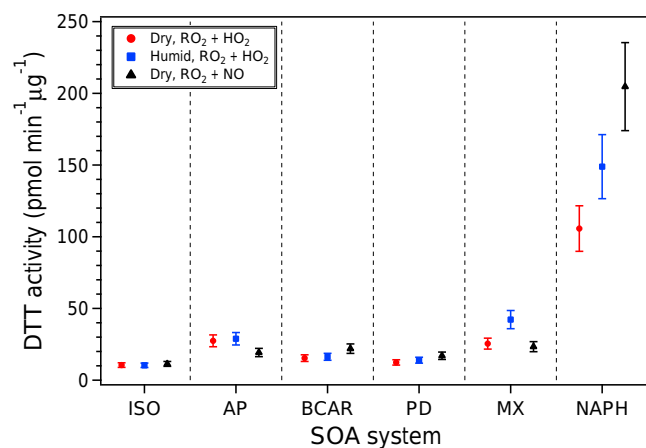


Figure 2. Intrinsic DTT activities for SOA generated from various hydrocarbon precursors (ISO: isoprene, AP: α -pinene, BCAR: β -caryophyllene, PD: pentadecane, MX: *m*-xylene, and NAPH: naphthalene) under various conditions (red circles: dry, RO₂ + HO₂; blue squares: humid, RO₂ + HO₂; and black triangles: dry, RO₂ + NO). Dry RO₂ + HO₂ experiments were repeated to ensure reproducibility in SOA generation and collection. Error bars represent a 15% coefficient of variation (Fang et al., 2015b).

2.3 Oxidative potential

The decay of DTT, a chemical species that reacts with redox-active species in a sample via electron transfer reactions, was used as a measure of oxidative potential (Cho et al., 2005; Kumagai et al., 2002). The intrinsic OP^{WS-DTT} of aerosol samples, as well as method blanks and positive controls (9,10-phenanthraquinone), was determined using a semiautomated DTT system. Specifics of the high-throughput system are detailed in Fang et al. (2015b). Briefly, the method consisted of three main steps: (1) oxidation of DTT by redox-active species in the sample, (2) reaction of residual DTT with DTNB (5,5'-dithiobis(2-nitrobenzoic acid)) to form 2-nitro-5-mercaptobenzoic acid (TNB), repeated at specific time intervals, and (3) measurement of TNB to determine DTT consumption. After each time interval and between samples, the system was flushed with DI water.

3 Results and discussion

3.1 Laboratory-generated aerosol

Over the course of each experiment, gas and aerosol composition was continuously monitored. A typical time series for NO, NO₂, gas-phase hydrocarbon concentration, and aerosol mass concentration is shown in Fig. 1 for naphthalene photooxidation under RO₂ + NO-dominant reaction conditions. Hydrocarbon decay was monitored using GC-FID, while initial gas-phase hydrocarbon concentrations were determined using the chamber volume and mass of hydrocarbon in-

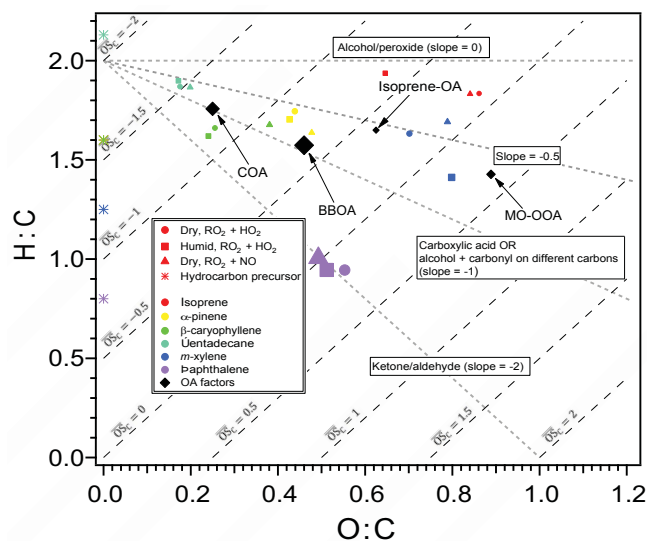


Figure 3. Van Krevelen plot for various SOA systems. Data points are colored by SOA system (red: isoprene, yellow: α -pinene, green: β -caryophyllene, light blue: pentadecane, blue: *m*-xylene, and purple: naphthalene), shaped according to reaction conditions (circle: dry, RO₂ + HO₂; square: humid, RO₂ + HO₂; and triangle: dry, RO₂ + NO), and sized by intrinsic DTT activity. OA factors resolved from PMF analysis of ambient AMS data are shown as black markers, also sized by intrinsic DTT activity. Hydrocarbon precursors are shown as stars, colored by SOA system. Specifics on site locations and factor resolution methods are described elsewhere. COA: cooking OA, BBOA: biomass burning OA, Isoprene-OA: isoprene-derived OA, MO-OOA: more-oxidized oxygenated OA (Verma et al., 2015a; Xu et al., 2015a, b).

jected. Following irradiation, NO decreased due to reaction with RO₂ from hydrocarbon oxidations. Nevertheless, ozone formation was suppressed owing to the high NO concentration throughout the experiment. Aerosol growth is observed shortly after initiation of photooxidation (i.e., turning on the lights) due to the efficient photolysis of HONO, which produced a high OH concentration on the order of 10⁷ molec cm⁻³. Once HONO was completely consumed, no further decay in the parent hydrocarbon and growth in aerosol mass were observed.

For each experiment, aerosol chemical composition was also monitored using the AMS. The average AMS mass spectra (Fig. S1 in the Supplement) for all VOC systems were consistent with those reported in previous studies (Chhabra et al., 2010, 2011). For RO₂ + NO-dominant experiments, the NO⁺ : NO₂⁺ ratio has been used extensively in previous studies to differentiate between organic and inorganic nitrates (Farmer et al., 2010; Fry et al., 2009; Boyd et al., 2015; Xu et al., 2015b). The observed NO⁺ : NO₂⁺ ratio for all RO₂ + NO-dominant experiments (4.2–6.1) was higher than that observed for inorganic (ammonium) nitrates (~2.3), which indicates that these peaks are likely from organic nitrates rather than inorganic nitrates. The observed range is

also consistent with values measured in previous organic nitrate studies for similar VOC systems and ambient studies (Bruns et al., 2010; Sato et al., 2010; Xu et al., 2015b). Elemental ratios (O : C, H : C, and N : C) were also obtained for each SOA system using the AMS. The aerosol systems investigated span a wide range of O : C ratios, as observed in previous laboratory and field studies (Chhabra et al., 2011; Lambe et al., 2011; Jimenez et al., 2009; Ng et al., 2010).

3.2 Effect of hydrocarbon precursor and reaction condition on oxidative potential

To investigate whether different types of SOA differ in toxicity, the OP^{WS-DTT} , a measure of the concentration of redox-active species present in a sample, was measured for SOA generated from six VOCs under three conditions (see Table 1 for specifics). The blank-corrected OP^{WS-DTT} values, represented on a per mass (μg) basis, are shown in Fig. 2. Uncertainties associated with OP^{WS-DTT} determination were approximated using a 15 % coefficient of variation, in accordance with previous studies using the same semiautomated system (Fang et al., 2015b). The OP^{WS-DTT} values of all backing filters and background filters were also measured and found to be within the uncertainty for blank Teflon filters, which indicates that there were no observable sampling artifacts, gaseous absorption onto Teflon filters, or H_2O_2 or HONO uptake onto seed particles.

Overall, it is clear that the hydrocarbon precursor identity influenced OP^{WS-DTT} , with naphthalene having the highest intrinsic DTT activity (Fig. 2). All other hydrocarbon precursors investigated produced SOA with relatively low intrinsic OP^{WS-DTT} ($\sim 9\text{--}45 \text{ pmol min}^{-1} \mu\text{g}^{-1}$). For isoprene, the SOA in this study was generated through different reaction pathways, including isoprene photooxidation under different RO_2 fates and IEPOX reactive uptake to acidic seed particles. Although these different conditions produced different products and SOA compositions (Xu et al., 2014; Surratt et al., 2010; Chan et al., 2010), the OP^{WS-DTT} is very similar. It is important to note that the intrinsic OP^{WS-DTT} values for SOA generated under all conditions in this study are in agreement with the isoprene-derived OA factor resolved from positive matrix factorization (PMF) analysis of ambient AMS data (Fig. 4; Xu et al., 2015a, b; Verma et al., 2015a). The isoprene-derived OA from ambient measurements is largely attributed to IEPOX uptake, but it possibly contains some contribution from other isoprene oxidation pathways (Xu et al., 2015a, b). The similarity between laboratory-generated and ambient isoprene SOA suggests that isoprene SOA may have low OP^{WS-DTT} regardless of reaction conditions. A previous laboratory chamber study by Kramer et al. (2016) also measured the DTT activity of isoprene SOA produced via different pathways, including SOA formed from direct photooxidation of isoprene. It was found that isoprene SOA formed under “high- NO_x ” conditions was more DTT active than that formed under “low- NO_x ” conditions. These re-

sults are in contrast with those obtained in this study, where the OP^{WS-DTT} of isoprene SOA was similar regardless of reaction condition. However, we caution that (1) the SOA measured in Kramer et al. (2016) was formed under different experimental conditions, and (2) they utilized a different method for measuring DTT consumption (i.e., different extraction solvent, different initial DTT concentration, different method for quantifying DTT activity); therefore, the results from their study and ours may not be directly comparable. For instance, for isoprene photooxidation experiments, the low- NO_x conditions in Kramer et al. (2016) corresponded to “5 ppm isoprene and 200 ppb NO ”, where the reaction regime was largely defined by the VOC / NO_x ratio. It has been shown previously that SOA formed under the same VOC / NO_x conditions can be drastically different and the use of this metric might not necessarily reflect the actual peroxy radical fate (Ng et al., 2007b; Kroll and Seinfeld, 2008; Wennberg, 2013). In our study, the low- NO_x experimental condition is defined by the fate of peroxy radicals directly, i.e., no NO_x added, but with the presence of H_2O_2 to enhance the $\text{RO}_2 + \text{HO}_2$ reaction pathway, which is dominant in ambient environments when NO_x levels are low.

α -pinene, β -caryophyllene, and pentadecane produced low OP^{WS-DTT} across all conditions explored in this study (Fig. 2). Specifically, the SOA formed under different reaction conditions do not appear to have significantly different OP^{WS-DTT} , even though different NO_x conditions have been shown to affect SOA loading and composition due to competing RO_2 chemistry (Chan et al., 2009; Eddingsaas et al., 2012; Loza et al., 2014; Ng et al., 2007a). For instance, under conditions that favor $\text{RO}_2 + \text{NO}$, organic nitrates are formed, whereas under conditions that favor $\text{RO}_2 + \text{HO}_2$, organic peroxides are the predominant products. In this study, the formation of organic nitrates is evident in the $\text{RO}_2 + \text{NO}$ experiments with the relatively higher $\text{NO}^+ : \text{NO}_2^+$ ratio in the AMS mass spectra. It is possible that neither the organic peroxides or organic nitrates formed from the oxidation of these precursors are highly redox active, such that the overall OP^{WS-DTT} is similar even though the products differ. Further studies are required to establish this.

Similarly, the OP^{WS-DTT} of SOA formed from *m*-xylene under conditions that favor different RO_2 fates were not significantly different. Since OP^{WS-DTT} is intended as a measure of redox activity, the reaction products' ability to participate in electron transfer may explain this lack of difference (e.g., lack of conjugated systems and associated pi bonds with unbound electrons). Under both $\text{RO}_2 + \text{HO}_2$ and $\text{RO}_2 + \text{NO}$ pathways, a large number of *m*-xylene oxidation products do not retain the aromatic ring (Vivanco and Santiago, 2010; Jenkin et al., 2003). Therefore, these products may have similar OP^{WS-DTT} as reaction products of α -pinene, β -caryophyllene, and pentadecane, which also do not contain an aromatic ring. Under humid conditions, aerosols formed from the oxidation of *m*-xylene were more DTT active than those formed under dry conditions. The AMS mass

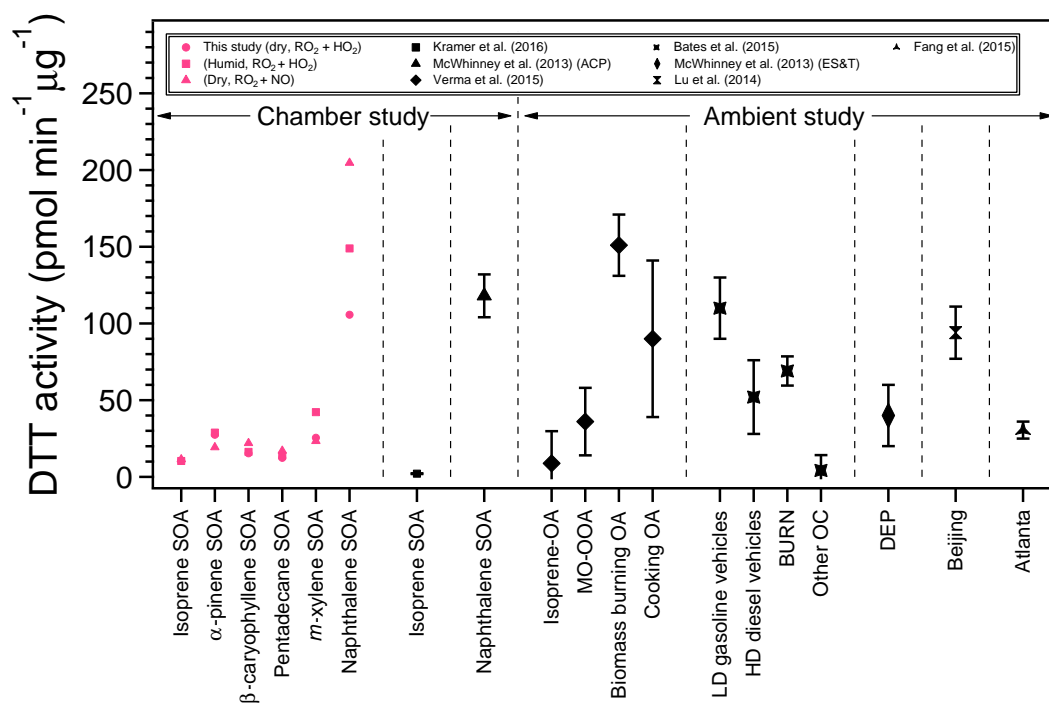


Figure 4. Intrinsic DTT activities for chamber SOA, various PM subtypes resolved from ambient data, and diesel exhaust particles. It should be noted that the DTT activity for isoprene SOA in Kramer et al. (2016) was determined using a different DTT method and may not be directly comparable. All other studies shown used the method outlined in Cho et al. (2005). DTT activities obtained in this study are shaped by reaction condition (circle: dry, $\text{RO}_2 + \text{HO}_2$; square: humid, $\text{RO}_2 + \text{HO}_2$; triangle: dry, $\text{RO}_2 + \text{NO}$). Specifics on site locations and factor resolution methods are described elsewhere. DTT activities for Beijing and Atlanta are averages obtained across multiple seasons. Isoprene-OA: isoprene-derived OA, MO-OOA: more-oxidized oxygenated OA, BBOA: biomass burning OA, COA: cooking OA, LDGV: light-duty gasoline vehicles, HDDV: heavy-duty diesel vehicles, BURN: biomass burning, DEP: diesel exhaust particles (Kramer et al., 2016; McWhinney et al., 2013b; Verma et al., 2015a; Bates et al., 2015; McWhinney et al., 2013a; Xu et al., 2015a, b; Lu et al., 2014; Fang et al., 2015b).

spectra for aerosol formed under humid conditions also differs notably for several characteristic fragments (Fig. S2), which may explain the difference observed in $\text{OP}^{\text{WS-DTT}}$. More specifically, m/z 44, which serves as an indication of oxidation (O : C ratio) (Ng et al., 2010), is very different for this experiment (dry signal: 0.098 vs. humid signal: 0.15). It is possible that the degree of oxidation may be an important factor for SOA formed from the same hydrocarbon, and systematic chamber studies investigating changes in O : C for SOA formed from a single hydrocarbon precursor would be valuable. Previous studies involving the effect of humidity on SOA composition also yield mixed results, with some finding significant changes in SOA composition and yields (Nguyen et al., 2011; Wong et al., 2015; Healy et al., 2009; Stirnweis et al., 2016) and others reporting little difference (Boyd et al., 2015; Edney et al., 2000; Cocker et al., 2001). Humidity effects are therefore highly hydrocarbon-dependent. Further study into the specific oxidation mechanisms and products in the photooxidation of aromatic hydrocarbon under dry and humid conditions may be warranted to understand the difference in DTT activity.

For naphthalene, the $\text{OP}^{\text{WS-DTT}}$ measured for SOA generated under dry, $\text{RO}_2 + \text{HO}_2$ -dominant conditions is in agreement with that measured by McWhinney et al. (2013b) (Fig. 4), which generated naphthalene SOA under similar chamber conditions using the same OH radical precursor. These values should be directly comparable since the same standard method described by Cho et al. (2005) was used to obtain the oxidative potentials in both McWhinney et al. (2013b) and this study. The $\text{OP}^{\text{WS-DTT}}$ of naphthalene aerosol also appears to be strongly influenced by humidity and RO_2 fate (Fig. 2), with higher toxicities observed for aerosol formed under both humid and $\text{RO}_2 + \text{NO}$ -dominant conditions. The effect of RO_2 fate may be explained by the different products known to form from $\text{RO}_2 + \text{HO}_2$ and $\text{RO}_2 + \text{NO}$ reaction pathways. Many of the same products, including naphthoquinones and all of the ring-opening derivatives of 2-formylcinnamaldehyde, are formed under both reaction conditions (Kautzman et al., 2010). Naphthoquinones are also known to be DTT active and have been shown to account for approximately 21 % of the DTT activity observed for naphthalene SOA (Charrier and Anastasio, 2012; McWhinney et al., 2013b). In addition to these products, ni-

troaromatics including nitronaphthols and nitronaphthalenes are formed under $\text{RO}_2 + \text{NO}$ conditions (Kautzman et al., 2010). The nitrite group next to the aromatic ring in these products may further promote electron transfer between nitroaromatics and DTT, resulting in more DTT consumption and a higher $\text{OP}^{\text{WS-DTT}}$. This effect was not observed for *m*-xylene SOA due to the formation of predominantly ring-opening products (Vivanco and Santiago, 2010; Jenkin et al., 2003). The presence of an aromatic ring in SOA products may therefore be important for determining oxidative potentials, and polyaromatic precursors may yield products of substantial toxicity. This is further supported by the observation that the AMS mass spectra for highly DTT-active naphthalene SOA contain peaks at m/z 77 and m/z 91, which are indicative of aromatic phenyl and benzyl ions (Chhabra et al., 2010; McLafferty and Tureček, 1993). Additionally, peaks indicative of aromatic compounds greater than m/z 120 were observed with similar mass spectral features as those reported for aerosol generated from naphthalene oxidation by OH radicals in previous studies (Riva et al., 2015). Aromatic species are also exclusive to HULIS (Sannigrahi et al., 2006), and ambient data have shown that HULIS are a significant aerosol component contributing to $\text{OP}^{\text{WS-DTT}}$ (Verma et al., 2012, 2015b; Dou et al., 2015; Lin and Yu, 2011).

Bulk aerosol elemental ratios (O : C, H : C, and N : C) were also determined for each SOA system since different types of aerosol are known to span a wide range of O : C (Chhabra et al., 2011; Lambe et al., 2011). All elemental ratios were stable during the filter collection period and could thus be represented by a single value. To visualize these differences in oxidation, the van Krevelen diagram was utilized (Fig. 3) because changes in the slope of data points within the van Krevelen space can provide information on SOA functionalization (Heald et al., 2010; Van Krevelen, 1950; Ng et al., 2011). Starting from the precursor hydrocarbon, a slope of 0 indicates addition of alcohol groups, a slope of -1 indicates addition of carbonyl and alcohol groups on separate carbons or addition of carboxylic acids, and a slope of -2 indicates addition of ketones or aldehydes. Previous studies show that both laboratory-generated and ambient OA occupy a narrow van Krevelen space with a slope of ~ -1 to -0.5 (Heald et al., 2010; Ng et al., 2011). Ambient data included in Fig. 3 are for different organic aerosol subtypes resolved from PMF analysis of AMS data collected in the southeastern US (Verma et al., 2015a; Xu et al., 2015a, b).

The laboratory-generated aerosols span the range of H : C and O : C observed in the ambient. As seen in Fig. 3 (data points sized by intrinsic $\text{OP}^{\text{WS-DTT}}$), while different reaction conditions produced aerosol of differing composition (i.e., different O : C and H : C), the intrinsic $\text{OP}^{\text{WS-DTT}}$ does not appear to be affected by these differences. On the other hand, the hydrocarbon precursor identity influences $\text{OP}^{\text{WS-DTT}}$ substantially. It has been shown that ambient OA from different sources can become increasingly oxidized (increasing O : C ratio) with atmospheric aging (Jimenez et al.,

2009; Ng et al., 2011). Based on the results shown in Fig. 3, it appears that a higher O : C ratio did not correspond to a higher $\text{OP}^{\text{WS-DTT}}$. This is true for both the laboratory-generated SOA in this study and the different OA subtypes resolved from ambient data (Verma et al., 2015a; Xu et al., 2015a, b). Nevertheless, the O : C ratios for individual systems (i.e., SOA formed from the same hydrocarbon precursor) may affect the intrinsic $\text{OP}^{\text{WS-DTT}}$. Indeed, for several SOA systems (β -caryophyllene, pentadecane, and *m*-xylene), SOA with higher O : C ratios also had a higher intrinsic $\text{OP}^{\text{WS-DTT}}$ (Figs. 2, 3). For SOA systems formed under $\text{RO}_2 + \text{NO}$ -dominant conditions, N : C ratios were also determined to investigate if there is a link between N : C and intrinsic DTT activity (Fig. S3). Again, with the exception of naphthalene SOA, the intrinsic $\text{OP}^{\text{WS-DTT}}$ does not appear to be affected by N : C ratio even though the systems explored span a wide range of N : C. This is consistent with the results observed in the van Krevelen diagram and further emphasizes the importance of hydrocarbon identity in determining oxidative potentials.

3.3 Comparison to other types of PM

In order to evaluate how the oxidative potential of individual SOA systems compares to other sources and subtypes of PM, the intrinsic $\text{OP}^{\text{WS-DTT}}$ values from this study are compared to values reported in the literature (Fig. 4). Comparatively, SOA formed from the photooxidation of isoprene, α -pinene, β -caryophyllene, pentadecane, and *m*-xylene were not very DTT active and produced low intrinsic $\text{OP}^{\text{WS-DTT}}$. The $\text{OP}^{\text{WS-DTT}}$ values of these aerosol systems were also within the range of various OA subtypes resolved from ambient data. The method for determining intrinsic $\text{OP}^{\text{WS-DTT}}$ for various OA subtypes is provided in the Supplement. As noted earlier, the $\text{OP}^{\text{WS-DTT}}$ for isoprene SOA generated in this study is similar to the isoprene-derived OA factor from ambient data. The other ambient OA factors include a highly oxidized MO-OOA (more-oxidized oxygenated OA) factor resolved from PMF analysis of ambient OA data, as well as an oxidized organic aerosol factor containing contributions from biogenic SOA (other OC) resolved using the chemical mass balance (CMB) method with ensemble-averaged source impact profiles (Bates et al., 2015; Xu et al., 2015a, b; Verma et al., 2014). While sources of MO-OOA have not been identified, studies have shown that the aerosol mass spectra for various sources of OA approach those of MO-OOA as it ages (Ng et al., 2010), and it has been speculated that MO-OOA may contain aerosol from multiple aged sources (Xu et al., 2015b). Furthermore, MO-OOA has been shown to have widespread contributions across urban and rural sites, as well as different seasons (Xu et al., 2015a, b). Conversely, naphthalene SOA was highly DTT active with an $\text{OP}^{\text{WS-DTT}}$ on the order of biomass burning OA (BBOA (Verma et al., 2015a), BURN (Bates et al., 2015)). The BBOA and BURN factors were resolved using different source apportionment

methods and as such, the range for comparison is large. Here, we focus on BBOA since Verma et al. (2015a) previously showed that BBOA had the highest intrinsic DTT activity among all OA subtypes resolved from PMF analysis of ambient AMS data collected in the southeastern US (see Fig. 4 for comparison). Because naphthalene aerosols formed under $\text{RO}_2 + \text{NO}$ -dominant conditions may be even more redox active than BBOA and anthropogenic emissions are more abundant in urban environments with higher NO_x , this system warrants further systematic studies. It should however be noted that comparisons of intrinsic DTT activities between SOA from a pure VOC and an ambient source are difficult. BBOA is a source that contains many compounds, some of which may not be redox active. Thus, although it may contain highly DTT-active components with high intrinsic activities, the overall intrinsic activity will be much lower. As a result, a direct comparison with pure naphthalene SOA on a per mass basis is tenuous. However, naphthalene SOA formed under urban conditions ($\text{RO}_2 + \text{NO}$) also produces nitroaromatics, which may induce DNA breaks and other mutagenic effects (Baird et al., 2005; Helmig et al., 1992). As such, aerosols formed from photooxidation of PAHs may be a particularly important OA source in terms of PM health effects.

Other common sources of PM are those related to traffic. Previous studies have determined that products of incomplete combustion include quinones capable of participating in redox reactions, including the oxidation of DTT (Kumagai et al., 2002; McWhinney et al., 2013a). The SOA systems investigated, including isoprene, α -pinene, β -caryophyllene, pentadecane, and *m*-xylene produced SOA that were less DTT active than diesel exhaust particles (DEPs) collected from light-duty diesel vehicle (LDDV) engines operated under various conditions (McWhinney et al., 2013a) and resolved for heavy-duty diesel vehicles (HDDVs) from ambient data (Bates et al., 2015). It should be noted that the DTT activity reported for DEPs includes both water-soluble and water-insoluble fractions (total DTT activity), whereas the DTT activity measured for SOA is water-soluble. However, there should be very little contribution from water-insoluble species to SOA (McWhinney et al., 2013a). Conversely, the intrinsic $\text{OP}^{\text{WS-DTT}}$ of naphthalene SOA was on par with that of light-duty gasoline vehicles (LDGVs) and higher than that of HDDVs and DEPs (Verma et al., 2014; Bates et al., 2015). Since naphthalene may also be emitted from gasoline and diesel combustion (Jia and Batterman, 2010), traffic-related controls may be extremely important to control these highly DTT-active sources. Furthermore, since SOA often dominate over POA (primary organic aerosols) even in urban centers (Zhang et al., 2007; Ng et al., 2011), even SOA that is only slightly DTT active may contribute significantly to PM-induced health effects.

3.4 Implications

The water-soluble oxidative potential, as measured by DTT consumption, was determined for SOA generated from six different hydrocarbon precursors under three conditions of varying humidity and RO_2 fate. Results from this study demonstrate that hydrocarbon precursor identity influenced intrinsic SOA oxidative potential substantially. The biogenic and anthropogenic precursors investigated yielded SOA with $\text{OP}^{\text{WS-DTT}}$ values ranging from 9 to 205 $\text{pmol min}^{-1} \mu\text{g}^{-1}$, with isoprene SOA and naphthalene SOA having the lowest and highest intrinsic $\text{OP}^{\text{WS-DTT}}$, respectively. In general, $\text{OP}^{\text{WS-DTT}}$ values for biogenic SOA were lower than those for anthropogenic SOA. Therefore, to evaluate overall oxidative potentials of ambient SOA, hydrocarbon precursor emissions and their corresponding SOA formation potential must be considered. Moreover, it may be possible to roughly estimate regional oxidative potentials using individual intrinsic $\text{OP}^{\text{WS-DTT}}$ of different types of SOA in conjunction with VOC emissions and SOA loadings in models. For instance, DTT activities of aerosols collected in Beijing, China (77–111 $\text{pmol min}^{-1} \mu\text{g}^{-1}$; Lu et al., 2014), where anthropogenic emissions dominate, more closely resemble the $\text{OP}^{\text{WS-DTT}}$ of naphthalene SOA. Conversely, ambient aerosols collected in the southeastern US have DTT activities (25–36 $\text{pmol min}^{-1} \mu\text{g}^{-1}$; Fang et al., 2015b) that more closely resemble those of biogenic SOA. It may therefore be informative to investigate whether concentration addition can be applied to DTT consumption by exploring well-characterized PM mixtures.

Chamber reaction conditions, including relative humidity and specific RO_2 fate, influenced SOA elemental composition substantially and affected $\text{OP}^{\text{WS-DTT}}$ in a hydrocarbon-specific manner, although hydrocarbon identity was by far the most influential in determining $\text{OP}^{\text{WS-DTT}}$. For several VOCs (isoprene, α -pinene, β -caryophyllene, and pentadecane), the reaction conditions had a negligible effect on $\text{OP}^{\text{WS-DTT}}$, which suggests that the organic peroxides and organic nitrates formed from the oxidation of these precursors may have similarly low redox activity. An investigation into the redox activity of individual known photooxidation products, including organic peroxides and organic nitrates, may elucidate further information on the lack of reaction condition effect. Similarly, nitroaromatics may explain the difference observed between naphthalene aerosol formed under different RO_2 reaction pathways since the nitrite group may promote electron transfer and result in a higher $\text{OP}^{\text{WS-DTT}}$. This effect was not observed for *m*-xylene SOA due to the formation of predominantly ring-opening products. The loss of the aromatic ring may also explain the differences in intrinsic $\text{OP}^{\text{WS-DTT}}$. For instance, naphthalene SOA, which contains many aromatic ring-retaining products, is as redox active as BBOA, one of the most DTT-active aerosol subtypes found in ambient studies. Conversely, *m*-xylene SOA with predominantly aromatic ring-breaking products

is much less redox active and the measured OP^{WS-DTT} is lower than that of traffic-related sources and several OA subtypes (BBOA and cooking OA, COA). This further supports earlier findings (Verma et al., 2015b) that the polyaromatic ring structure may be an important consideration for understanding SOA redox activity, which may have implications for cellular redox imbalance (Tuet et al., 2016). Furthermore, nitroaromatics and polyaromatics may also have significant health effects beyond redox imbalance, including various mutagenic effects (Baird et al., 2005; Helmig et al., 1992). As such, hydrocarbon precursors forming aromatic ring-retaining products may be the most important to consider in PM-induced health effects in terms of oxidative potential. This is consistent with many studies using DTT to show oxidative potential associated with sources related to incomplete combustion (Bates et al., 2015; Verma et al., 2014; McWhinney et al., 2013b) and the identification of HULIS (Verma et al., 2015b; Dou et al., 2015; Lin and Yu, 2011), and more specifically, quinones as key components contributing to oxidative potential (Verma et al., 2014). Finally, redox-active metals are also emitted by traffic through mechanical processes, such as brake and tire wear (Charrier and Anastasio, 2012; Fang et al., 2015a). These species were not considered in the chamber experiments explored in this study. Inclusion of redox-active metals in future SOA experiments may be valuable to further understand the roles of SOA and metal species in overall redox activity.

Abbreviations

PM: particulate matter, SOA: secondary organic aerosol, ROS/RNS: reactive oxygen and nitrogen species, DTT: dithiothreitol, OP^{WS} : oxidative potential of water-soluble species.

4 Data availability

Data are available upon request to the corresponding author (ng@chbe.gatech.edu).

The Supplement related to this article is available online at doi:10.5194/acp-17-839-2017-supplement.

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