1 **Chemical oxidative potential of secondary organic aerosol (SOA) generated from the**

2 **photooxidation of biogenic and anthropogenic volatile organic compounds**

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11   Abstract

12   Particulate matter (PM), of which a significant fraction is comprised of secondary organic

13   aerosols (SOA), has received considerable attention due to their health implications. In this study,

14   the water-soluble oxidative potential (OP^{WS}) of SOA generated from the photooxidation of

15   biogenic and anthropogenic hydrocarbon precursors (isoprene, α-pinene, β-caryophyllene,

16   pentadecane, *m*-xylene, and naphthalene) under different reaction conditions ("$RO_2 + HO_2$"/"RO_2

17   + NO" dominant, dry/humid) was characterized using dithiothreitol (DTT) consumption. The

18   measured intrinsic $OP^{WS\text{-}DTT}$ ranged from 9–205 pmol min^{-1} µg^{-1} and were highly dependent on

19   the specific hydrocarbon precursor, with naphthalene and isoprene SOA generating the highest

20   and lowest $OP^{WS\text{-}DTT}$, respectively. Humidity and RO_2 fate affected $OP^{WS\text{-}DTT}$ in a hydrocarbon-

21   specific manner, with naphthalene SOA exhibiting the most pronounced effects, likely due to the

22   formation of nitroaromatics. Together, these results suggest that precursor identity may be more

23   influential than reaction condition in determining SOA oxidative potential, demonstrating the

24   importance of sources, such as incomplete combustion, to aerosol toxicity. In the context of other

25   PM sources, all SOA systems with the exception of naphthalene SOA were less DTT active than

26   ambient sources related to incomplete combustion, including diesel and gasoline combustion as

27   well as biomass burning. Finally, naphthalene SOA was as DTT active as biomass burning aerosol,

28   which was found to be the most DTT active OA source in a previous ambient study. These results

29   highlight a need to consider SOA contributions (particularly from anthropogenic hydrocarbons) to

30   health effects in the context of hydrocarbon emissions, SOA yields, and other PM sources.

31   Introduction

32   Numerous epidemiological studies have found associations between elevated particulate

33   matter (PM) concentrations and increased incidences of cardiopulmonary disease, including

34   increases in lung cancer, asthma, chronic obstructive pulmonary disease, arrhythmia, and ischemic

35   heart disease (Li et al., 2008; Pope III and Dockery, 2006; Brunekreef and Holgate, 2002; Dockery

36   et al., 1993; Hoek et al., 2013; Anderson et al., 2011; Pope et al., 2002). Furthermore, ambient PM

37   pollution ranked among the top 10 global risk factors in the 2010 Global Burden of Disease Study,

38   with significant contributions from cardiopulmonary diseases and lower respiratory infections

39   (Lim et al., 2012). Recent epidemiological studies have also found an association between particle

40   oxidative potential and various cardiopulmonary health endpoints (Bates et al., 2015; Fang et al.,

41   2016; Yang et al., 2016; Weichenthal et al., 2016), and results from toxicology studies suggest that

42   PM-induced oxidant production, including reactive oxygen and nitrogen species (ROS/RNS), is a

43   possible mechanism by which PM exposure results in adverse health effects (Li et al., 2003a; Tao

44   et al., 2003; Castro and Freeman, 2001; Gurgueira et al., 2002). These species can initiate

45   inflammatory cascades, which may ultimately lead to oxidative stress and cellular damage

46   (Wiseman and Halliwell, 1996; Hensley et al., 2000). Prolonged stimulation of inflammatory

47   cascades may also lead to chronic inflammation, for which there is a well-established link between

48   chronic inflammation and cancer (Philip et al., 2004). Collectively, these findings suggest a

49   possible link between PM exposure and epidemiologically associated health endpoints as PM can

50   contain ROS/RNS and generate ROS/RNS via redox reactions and by inducing cellular pathways

51   that produce ROS/RNS.

52   Chemical assays in which an anti-oxidant is used to simulate redox reactions that would

53   occur in biological systems have been developed to study the oxidative potential of PM samples

54   (Kumagai et al., 2002; Cho et al., 2005). In these assays, redox-active species in PM samples

55   catalyze electron transfer from the anti-oxidant (e.g., dithiothreitol, DTT; ascorbic acid, AA; etc.)

56   to oxygen, and anti-oxidant decay provides a measure of the concentration of redox-active species

57   in the sample (Fang et al., 2015b). These assays have been utilized extensively to characterize

58   ambient PM samples and source apportionment regressions have been applied to DTT activity

59   results to identity PM sources that may be detrimental to health (Bates et al., 2015; Fang et al.,

60   2015a; Verma et al., 2015a; Verma et al., 2014). Results from these regressions, as well as

61   inhalation and exposure studies, suggest that organic carbon constituents may play a significant

62   role in PM-induced health effects (Li et al., 2003b; Kleinman et al., 2005; Hamad et al., 2015;

63   Verma et al., 2015b). In particular, humic-like substances (HULIS) and oxygenated polyaromatic

64   hydrocarbons (PAH) have been shown to contribute significantly to the redox activity of water-

65   soluble PM samples (Verma et al., 2012; Verma et al., 2015a; Dou et al., 2015; Verma et al.,

66   2015b; Lin and Yu, 2011). Recently, Tuet et al. (2016) also showed that there is a significant

67   correlation between intracellular ROS/RNS production and organic species (water-soluble organic

68   carbon and brown carbon) for summer ambient samples, which suggests that photochemically-

69   driven secondary organic aerosols (SOA) may be important in PM-induced oxidative stress.

70   Many prior studies have focused on the health effects of primary emissions, such as PM

71   directly emitted from diesel and gasoline engines (Bai et al., 2001; Kumagai et al., 2002;

72   McWhinney et al., 2013a; Turner et al., 2015). Conversely, few studies have explored the potential

73   health implications of SOA, which are formed from the oxidation of volatile organic compounds

74   (VOCs) (McWhinney et al., 2013b; Rattanavaraha et al., 2011; Kramer et al., 2016; Lund et al.,

75   2013; McDonald et al., 2010; McDonald et al., 2012; Baltensperger et al., 2008; Arashiro et al.,

76   2016; Platt et al., 2014), even though field studies have shown that SOA often dominate over

77 primary aerosols even in urban environments (Zhang et al., 2007; Jimenez et al., 2009; Ng et al.,

78 2010). The few studies that exist focus on SOA generated from a single class of hydrocarbon

79 precursor or on SOA formed in a simulated urban background (Kramer et al., 2016; McWhinney

80 et al., 2013b; Rattanavaraha et al., 2011; Arashiro et al., 2016; McDonald et al., 2012). While

81 studies on oxidative potential have shown that SOA is indeed redox active, the combined range of

82 oxidative potentials observed for individual SOA systems is quite large and remains unexplored

83 (McWhinney et al., 2013b; Kramer et al., 2016). Furthermore, results from cellular exposure

84 studies are inconclusive, with some studies finding significant response from SOA exposure and

85 others finding little to no response. The exposure dose also differed from study to study, which

86 may result in inconclusive results. This also highlights a need to consider dose-response

87 relationships as demonstrated recently in Tuet et al. (2016). Comparisons between the observed

88 cellular endpoints from exposure to SOA formed from individual precursors are also lacking

89 (Baltensperger et al., 2008; Lund et al., 2013; McDonald et al., 2010; McDonald et al., 2012;

90 Arashiro et al., 2016). As such, there is a lack of perspective in terms of different individual SOA

91 systems and their contributions to PM-induced health effects, making it unclear whether certain

92 responses are indeed toxic for a range of sources and subtypes of PM. However, as cellular assays

93 and animal inhalation experiments are more complex, a systematic study on the oxidative potential

94 of individual SOA systems may be warranted first.

95   In the present study, the water-soluble oxidative potential of SOA generated from various

96 precursors under different reaction conditions was measured using the DTT assay (henceforth

97 referred to as OP^{WS-DTT}). While numerous cell-free assays have been developed to measure

98 oxidative potential, the DTT assay is well-suited for the purposes of this study due to its proven

99 sensitivity to organic carbon constituents and correlation with organic carbon (Janssen et al., 2014;

100   Visentin et al., 2016). Furthermore, there are many previous studies reporting the DTT activities

101   of laboratory-generated SOA and ambient samples for comparison purposes (Kramer et al., 2016;

102   Bates et al., 2015; McWhinney et al., 2013a; McWhinney et al., 2013b; Verma et al., 2015a; Xu

103   et al., 2015a; Xu et al., 2015b; Fang et al., 2015b; Lu et al., 2014). VOCs were chosen to represent

104   the major classes of compounds known to produce SOA upon oxidation by atmospheric oxidants

105   and to include precursors of both anthropogenic and biogenic origins (Table S1). Biogenic

106   precursors include isoprene, α-pinene, and β-caryophyllene, while anthropogenic precursors

107   include pentadecane, *m*-xylene, and naphthalene. Isoprene was chosen as it is the most abundant

108   non-methane hydrocarbon, with estimated global emissions around 500 Tg yr^{-1} (Guenther et al.,

109   2006). α-pinene and β-caryophyllene were chosen as representative, well-studied monoterpenes

110   and sesquiterpenes, respectively. Both classes of compounds contribute significantly to ambient

111   aerosol (Eddingsaas et al., 2012; Hoffmann et al., 1997; Tasoglou and Pandis, 2015; Goldstein and

112   Galbally, 2007). α-pinene emissions (~50 Tg yr^{-1}) are also on the same order of global

113   anthropogenic emissions (~110 Tg yr^{-1}) (Guenther et al., 1993; Piccot et al., 1992). Similarly,

114   anthropogenic precursors were chosen to include a long-chain alkane (pentadecane), a single-ring

115   aromatic (*m*-xylene), and a poly-aromatic (naphthalene). These classes of compounds are emitted

116   as products of incomplete combustion (Robinson et al., 2007; Jia and Batterman, 2010; Bruns et

117   al., 2016) and have been shown to have considerable SOA yields (e.g., Chan et al., 2009; Ng et

118   al., 2007b; Lambe et al., 2011). In addition to precursor identity, the effects of humidity (dry vs.

119   humid) and NO$_x$ (differing peroxy radical (RO$_2$) fates, RO$_2$ + HO$_2$ vs. RO$_2$ + NO) on OP^{WS-DTT}

120   were investigated, as these conditions have been shown to affect the chemical composition and

121   mass loading of SOA formed (Chhabra et al., 2010; Chhabra et al., 2011; Eddingsaas et al., 2012;

122   Ng et al., 2007b; Loza et al., 2014; Ng et al., 2007a; Chan et al., 2009; Boyd et al., 2015). Finally,

123   intrinsic OP$^{\text{WS-DTT}}$ was compared with bulk aerosol composition, specifically elemental ratios, to

124   investigate whether there is a link between OP$^{\text{WS-DTT}}$ and aerosol composition.

125   Methods

126   **Chamber experiments.** SOA from the photooxidation of biogenic and anthropogenic

127   VOCs were generated in the Georgia Tech Environmental Chamber (GTEC) facility. Details of

128   the facility are described elsewhere (Boyd et al., 2015). Briefly, the facility consists of two 12 m^3

129   Teflon chambers suspended inside a 6.4 m x 3.7 m (21 ft x 12 ft) temperature-controlled enclosure,

130   surrounded by black lights (Sylvania 24922) and natural sunlight fluorescent lamps (Sylvania

131   24477). Multiple sampling ports from each chamber allow for gas- and aerosol-phase

132   measurements, as well as introduction of reagents. Gas-phase measurements include O_3, NO_2, and

133   NO_x concentrations as measured by an O_3 analyzer (Teledyne T400), a cavity attenuated phase

134   shift (CAPS) NO_2 monitor (Aerodyne), and a chemiluminescence NO_x monitor (Teledyne 200EU)

135   respectively. Additionally, a gas chromatography-flame ionization detector (GC-FID, Agilent

136   7890A) was used to monitor hydrocarbon decay and estimate hydroxyl radical (OH) concentration.

137   In terms of aerosol-phase measurements, aerosol volume concentrations and distributions were

138   measured using a Scanning Mobility Particle Sizer (SMPS, TSI), while bulk aerosol composition

139   was determined using a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-

140   AMS, Aerodyne; henceforth referred to as the AMS) (DeCarlo et al., 2006). HR-ToF-AMS data

141   was analyzed using the data analysis toolkit SQUIRREL (v. 1.57) and PIKA (v. 1.16G). Elemental

142   ratios (O:C, H:C, and N:C) were obtained using the method outlined by Canagaratna et al. (2015),

143   and used to calculate the average carbon oxidation state ($\overline{\text{OS}}_{\text{c}}$) (Kroll et al., 2011). Temperature

144   and relative humidity (RH) were monitored using a hydro-thermometer (Vaisala HMP110).

145   Experimental conditions, given in Table 1, were designed to probe the effects of humidity,

146   RO_2 fate, and precursor hydrocarbon on OP^{WS-DTT}. All experiments were performed at ~25 °C

147   under dry (RH < 5%) or humid (RH ~ 45%) conditions. Prior to each experiment, the chambers

148   were flushed with pure air for ~24 hrs. For humid experiments, the chambers were also humidified

149   by means of a bubbler filled with deionized (DI) water during this time. Seed aerosol was then

150   injected by atomizing a 15 mM $(NH_4)_2SO_4$ seed solution (Sigma Aldrich) until the seed

151   concentration was approximately 20 µg m^{-3}. It is noted that for experiment 7 (isoprene SOA under

152   RO_2 + HO_2 dominant, "humid" conditions), experimental conditions deviated due to extremely

153   low SOA mass yields. For this experiment, an acidic seed solution (8 mM $MgSO_4$ and 16 mM

154   H_2SO_4) was used under dry conditions to promote SOA formation via the IEPOX uptake pathway,

155   which has a higher SOA mass yield compared to the IEPOX + OH pathway and contributes

156   significantly to ambient OA (Surratt et al., 2010; Lin et al., 2012).

157   Once the seed concentration stabilized, hydrocarbon was added by injecting a known

158   volume of hydrocarbon solution [isoprene, 99%; α-pinene, ≥ 99%; β-caryophyllene, > 98.5%;

159   pentadecane, ≥ 99%; *m*-xylene, ≥ 99%; naphthalene, 99% (Sigma Aldrich)] into a glass bulb and

160   passing zero air at 5 L min^{-1} over the solution until fully evaporated (~10 min). For pentadecane

161   and β-caryophyllene, the glass bulb was gently heated to ensure full evaporation (Tasoglou and

162   Pandis, 2015). Naphthalene was injected by passing pure air over the solid, as outlined in previous

163   studies (Chan et al., 2009). After hydrocarbon injection, OH precursor was added to the chamber.

164   Experiments were conducted under various NO_x conditions where different RO_2 reaction pathways

165   prevailed. For RO_2 + HO_2 experiments, hydrogen peroxide (H_2O_2) was used as the OH precursor.

166   H_2O_2 (50% aqueous solution, Sigma Aldrich) was injected using the method described for

167   hydrocarbon injection to achieve an H_2O_2 concentration of 3 ppm, which yielded OH

168   concentrations on the order of 10^6 molec cm^{-3}. For $RO_2 + NO$ experiments, nitrous acid (HONO),

169   was used as the OH precursor. HONO was prepared by adding 10 mL of 1%wt aqueous $NaNO_2$

170   (VWR International) dropwise into 20 mL of 10%wt H_2SO_4 (VWR International) in a glass bulb.

171   Zero air was then passed over the solution to introduce HONO into the chamber (Chan et al., 2009;

172   Kroll et al., 2005). Photolysis of HONO yielded OH concentrations on the order of 10^7 molec cm$^-$

173   ^{3}. NO and NO_2 were also formed as byproducts of HONO synthesis. Once all the H_2O_2 evaporated

174   ($RO_2 + HO_2$ experiments) or NO_x concentrations stabilized ($RO_2 + NO$ experiments), the UV lights

175   were turned on to initiate photooxidation.

176   **Aerosol collection and extraction.** Aerosol samples were collected onto 47 mm Teflon^{TM}

177   filters (0.45 μm pore size, Pall Laboratory) for approximately 1.5 hrs at a flow rate of 28 L min^{-1}.

178   For each experiment, two filters (front filter and backing filter) were loaded in series to account

179   for possible sampling artifacts (Conny and Slater, 2002). Total mass collected was determined by

180   integrating the SMPS volume concentration as a function of time over the filter collection period

181   and using the total volume of air collected. Volume concentrations were integrated using time-

182   dependent data. Background filters containing seed and OH precursor (H_2O_2 or HONO) only at

183   experimental conditions were also collected to account for potential H_2O_2 or HONO uptake, which

184   may influence oxidative potential. Collected filter samples were placed in sterile petri dishes,

185   sealed with Parafilm M$^®$, and stored at -20 °C until extraction and analysis (Fang et al., 2015b).

186   Prior to determining OP^{WS-DTT}, collected particles were extracted in DI water by submerging the

187   filter and sonicating for 1 hr using an Ultrasonic Cleanser (VWR International) (Fang et al., 2015a).

188   Sonication steps were performed in 30 min intervals with water replacement after each interval to

189   reduce bath temperature. After sonication, extracts were filtered using 0.45 μm PTFE syringe

190   filters (Fisherbrand™) to remove insoluble material (Fang et al., 2015b). All filter samples were

191   extracted within 1-2 days of collection and analyzed immediately following extraction.

192   **Oxidative potential.** The decay of DTT, a chemical species that reacts with redox-active

193   species in a sample via electron transfer reactions, was used as a measure of oxidative potential

194   (Cho et al., 2005; Kumagai et al., 2002). The intrinsic OP^{WS-DTT} of aerosol samples, as well as

195   method blanks and positive controls (9,10-phenanthraquinone), was determined using a semi-

196   automated DTT system. Specifics of the high-throughput system are detailed in Fang et al. (2015b)

197   Briefly, the method consisted of three main steps: (1) oxidation of DTT by redox-active species in

198   the sample, (2) reaction of residual DTT with DTNB to form 2-nitro-5-mercaptobenzoic acid

199   (TNB), repeated at specific time intervals, and (3) measurement of TNB to determine DTT

200   consumption. After each time interval and between samples, the system was flushed with DI water.

201   Results and Discussion

202   **Laboratory-generated aerosol.** Over the course of each experiment, gas and aerosol

203   composition was continuously monitored. A typical time series for NO, NO_2, gas-phase

204   hydrocarbon concentration, and aerosol mass concentration is shown in Fig. 1 for naphthalene

205   photooxidation under $RO_2 + NO$ dominant reaction conditions. Hydrocarbon decay was monitored

206   using GC-FID, while initial gas-phase hydrocarbon concentrations were determined using the

207   chamber volume and mass of hydrocarbon injected. Following irradiation, NO decreased due to

208   reaction with RO_2 from hydrocarbon oxidations. Nevertheless, ozone formation was suppressed

209   owing to the high NO concentration throughout the experiment. Aerosol growth is observed

210   shortly after initiation of photooxidation (i.e., turning on the lights) due to the efficient photolysis

211   of HONO, which produced a high OH concentration on the order of 10^7 molec cm^{-3}. Once HONO

212   was completely consumed, no further decay in the parent hydrocarbon and growth in aerosol mass

213   were observed.

214   For each experiment, aerosol chemical composition was also monitored using the AMS.

215   The average AMS mass spectra (Fig. S1) for all VOC systems were consistent with those reported

216   in previous studies (Chhabra et al., 2010; Chhabra et al., 2011). For RO_2 + NO dominant

217   experiments, the $NO^+:NO_2^+$ ratio has been used extensively in previous studies to differentiate

218   between organic and inorganic nitrates (Farmer et al., 2010; Fry et al., 2009; Boyd et al., 2015; Xu

219   et al., 2015b). The observed $NO^+:NO_2^+$ ratio for all RO_2 + NO dominant experiments (4.2–6.1)

220   was higher than that observed for inorganic (ammonium) nitrates (~2.3), which indicates that these

221   peaks are likely from organic nitrates rather than inorganic nitrates. The observed range is also

222   consistent with values measured in previous organic nitrate studies for similar VOC systems and

223   ambient studies (Bruns et al., 2010; Sato et al., 2010; Xu et al., 2015b). Elemental ratios (O:C,

224   H:C, and N:C) were also obtained for each SOA system using the AMS. The aerosol systems

225   investigated span a wide range of O:C ratios, as observed in previous laboratory and field studies

226   (Chhabra et al., 2011; Lambe et al., 2011; Jimenez et al., 2009; Ng et al., 2010).

227   **Effect of hydrocarbon precursor and reaction condition on oxidative potential.** To

228   investigate whether different types of SOA differ in toxicity, the $OP^{WS\text{-}DTT}$, a measure of the

229   concentration of redox-active species present in a sample, was measured for SOA generated from

230   six VOCs under three conditions (see Table 1 for specifics). The blank-corrected $OP^{WS\text{-}DTT}$,

231   represented on a per mass (μg) basis, are shown in Fig. 2. Uncertainties associated with $OP^{WS\text{-}DTT}$

232   determination were approximated using a 15% coefficient of variation, in accordance with

233   previous studies using the same semi-automated system (Fang et al., 2015b). The $OP^{WS\text{-}DTT}$ of all

234   backing filters and background filters were also measured and found to be within the uncertainty

235   for blank Teflon filters, which indicates that there were no observable sampling artifacts, gaseous

236   absorption onto Teflon filters, or H_2O_2/HONO uptake onto seed particles.

237   Overall, it is clear that the hydrocarbon precursor identity influenced OP^{WS-DTT}, with

238   naphthalene having the highest intrinsic DTT activity (Fig. 2). All other hydrocarbon precursors

239   investigated produced SOA with relatively low intrinsic OP^{WS-DTT} (~9 – 45 pmol min^{-1} µg^{-1}). For

240   isoprene, the SOA in this study was generated through different reaction pathways, including

241   isoprene photooxidation under different RO_2 fates and IEPOX reactive uptake to acidic seed

242   particles. Although these different conditions produced different products and SOA compositions

243   (Xu et al., 2014; Surratt et al., 2010; Chan et al., 2010), the OP^{WS-DTT} is very similar. It is important

244   to note that the intrinsic OP^{WS-DTT} for SOA generated under all conditions in this study are in

245   agreement with the isoprene-derived OA factor resolved from positive matrix factorization (PMF)

246   analysis of ambient AMS data (Fig. 4) (Xu et al., 2015a; Xu et al., 2015b; Verma et al., 2015a).

247   The isoprene-derived OA from ambient measurements is largely attributed to IEPOX uptake, but

248   possibly contains some contribution from other isoprene oxidation pathways (Xu et al., 2015a; Xu

249   et al., 2015b). The similarity between laboratory-generated and ambient isoprene SOA suggests

250   that isoprene SOA may have low OP^{WS-DTT} regardless of reaction conditions. A previous

251   laboratory chamber study by Kramer et al. (2016) also measured the DTT activity of isoprene SOA

252   produced via different pathways, including SOA formed from direct photooxidation of isoprene.

253   It was found that isoprene SOA formed under "high-NO_x" conditions was more DTT active than

254   that formed under "low-NO_x" conditions. These results are in contrast with those obtained in this

255   study, where the OP^{WS-DTT} of isoprene SOA was similar regardless of reaction condition. However,

256   we caution that 1) the SOA measured in Kramer et al. (2016) was formed under different

257   experimental conditions, and 2) they utilized a different method for measuring DTT consumption

258   (i.e., different extraction solvent, different initial DTT concentration, different method for

259   quantifying DTT activity), therefore the results from their study and ours may not be directly

260   comparable. For instance, for isoprene photooxidation experiments, the "low-NO_x" conditions in

261   Kramer et al. (2016) corresponded to "5 ppm isoprene and 200 ppb NO", where the reaction regime

262   was largely defined by the VOC/NO_x ratio. It has been shown previously that SOA formed under

263   the same VOC/NO_x conditions can be drastically different and the use of this metric might not

264   necessarily reflect the actual peroxy radical fate (Ng et al., 2007b; Kroll and Seinfeld, 2008;

265   Wennberg, 2013). In our study, the "low-NO_x" experimental condition is defined by the fate of

266   peroxy radicals directly, i.e., no NO_x added, but with the presence of H_2O_2 to enhance the $RO_2 +$

267   HO_2 reaction pathway, which is dominant in ambient environments when NO_x levels are low.

268   α-pinene, β-caryophyllene, and pentadecane produced low $OP^{WS\text{-}DTT}$ across all conditions

269   explored in this study (Fig. 2). Specifically, the SOA formed under different reaction conditions

270   do not appear to have significantly different $OP^{WS\text{-}DTT}$, even though different NO_x conditions have

271   been shown to affect SOA loading and composition due to competing RO_2 chemistry (Chan et al.,

272   2009; Eddingsaas et al., 2012; Loza et al., 2014; Ng et al., 2007a). For instance, under conditions

273   that favor $RO_2 + NO$, organic nitrates are formed, whereas under conditions that favor $RO_2 + HO_2$,

274   organic peroxides are the predominant products. In this study, the formation of organic nitrates is

275   evident in the $RO_2 + NO$ experiments with the relatively higher $NO^+:NO_2^+$ ratio in the AMS mass

276   spectra. It is possible that the organic peroxides and organic nitrates formed from the oxidation of

277   these precursors are both not highly redox active, such that the overall $OP^{WS\text{-}DTT}$ is similar even

278   though the products differ. Further studies are required to establish this.

279   Similarly, the $OP^{WS\text{-}DTT}$ of SOA formed from *m*-xylene under conditions that favor

280   different RO_2 fates were not significantly different. Since $OP^{WS\text{-}DTT}$ is intended as a measure of

281   redox activity, the reaction products' ability to participate in electron transfer may explain this lack

282   of difference (e.g., lack of conjugated systems and associated pi bonds with unbound electrons).

283   Under both $RO_2 + HO_2$ and $RO_2 + NO$ pathways, a large portion of m-xylene oxidation products

284   do not retain the aromatic ring (Vivanco and Santiago, 2010; Jenkin et al., 2003). Therefore, these

285   products may have similar OP^{WS-DTT} as reaction products of α-pinene, β-caryophyllene, and

286   pentadecane, which also do not contain an aromatic ring. Under humid conditions, aerosol formed

287   from the oxidation of m-xylene were more DTT active than those formed under dry conditions.

288   The AMS mass spectra for aerosol formed under humid conditions also differs notably for several

289   characteristic fragments (Fig. S2), which may explain the difference observed in OP^{WS-DTT}. More

290   specifically, m/z 44, which serves as an indication of oxidation (O:C ratio) (Ng et al., 2010), is

291   very different for this experiment (dry signal: 0.098 vs. humid signal: 0.15). It is possible that the

292   degree of oxidation may be an important factor for SOA formed from the same hydrocarbon, and

293   systematic chamber studies investigating changes in O:C for SOA formed from a single

294   hydrocarbon precursor would be valuable. Previous studies involving the effect of humidity on

295   SOA composition also yield mixed results, with some finding significant changes in SOA

296   composition and yields (Nguyen et al., 2011; Wong et al., 2015; Healy et al., 2009; Stirnweis et

297   al., 2016) and others reporting little difference (Boyd et al., 2015; Edney et al., 2000; Cocker III

298   et al., 2001). Humidity effects are therefore highly hydrocarbon-dependent. Further study into the

299   specific oxidation mechanisms and products in the photooxidation of aromatic hydrocarbon under

300   dry and humid conditions may be warranted to understand the difference in DTT activity.

301   For naphthalene, the OP^{WS-DTT} measured for SOA generated under dry, $RO_2 + HO_2$

302   dominant conditions is in agreement with that measured by McWhinney et al. (2013b) (Fig. 4),

303   which generated naphthalene SOA under similar chamber conditions using the same OH radical

304   precursor. These values should be directly comparable as the same standard method described by

305   Cho et al. (2005) was used to obtain the oxidative potentials in both McWhinney et al. (2013b)

306   and this study. The OP^{WS-DTT} of naphthalene aerosol also appears to be strongly influenced by

307   humidity and RO_2 fate (Fig. 2), with higher toxicities observed for aerosol formed under both

308   humid and $RO_2 + NO$ dominant conditions. The effect of RO_2 fate may be explained by the

309   different products known to form from $RO_2 + HO_2$ and $RO_2 + NO$ reaction pathways. Many of the

310   same products, including naphthoquinones and all of the ring-opening derivatives of 2-

311   formylcinnamaldehyde, are formed under both reaction conditions (Kautzman et al., 2010).

312   Naphthoquinones are also known to be DTT active and have been shown to account for

313   approximately 21% of the DTT activity observed for naphthalene SOA (Charrier and Anastasio,

314   2012; McWhinney et al., 2013b). In addition to these products, nitroaromatics including

315   nitronaphthols and nitronaphthalenes are formed under $RO_2 + NO$ conditions (Kautzman et al.,

316   2010). The nitrite group next to the aromatic ring in these products may further promote electron

317   transfer between nitroaromatics and DTT, resulting in more DTT consumption and a higher OP^{WS-DTT}.

318   This effect was not observed for m-xylene SOA due to the formation of predominantly ring-

319   opening products (Vivanco and Santiago, 2010; Jenkin et al., 2003). The presence of an aromatic

320   ring in SOA products may therefore be important for determining oxidative potentials and

321   polyaromatic precursors may yield products of substantial toxicity. This is further supported by

322   the observation that the AMS mass spectra for highly DTT active naphthalene SOA contains peaks

323   at m/z 77 and m/z 91, which are indicative of aromatic phenyl and benzyl ions (Chhabra et al.,

324   2010; McLafferty and Tureček, 1993). Additionally, peaks indicative of aromatic compounds

325   greater than m/z 120 were observed with similar mass spectral features as those reported for aerosol

326   generated from naphthalene oxidation by OH radicals in previous studies (Riva et al., 2015).

327   Aromatic species are also exclusive to HULIS (Sannigrahi et al., 2006), and ambient data have

328   shown that HULIS is a significant aerosol component contributing to OP^{WS-DTT} (Verma et al.,

329   2015b; Verma et al., 2012; Dou et al., 2015; Lin and Yu, 2011).

330   Bulk aerosol elemental ratios (O:C, H:C, and N:C) were also determined for each SOA

331   system as different types of aerosol are known to span a wide range of O:C (Chhabra et al., 2011;

332   Lambe et al., 2011). All elemental ratios were stable during the filter collection period and could

333   thus be represented by a single value. To visualize these differences in oxidation, the van Krevelen

334   diagram was utilized (Fig. 3), as changes in the slope of data points within the van Krevelen space

335   can provide information on SOA functionalization (Heald et al., 2010; Van Krevelen, 1950; Ng et

336   al., 2011). Starting from the precursor hydrocarbon, a slope of 0 indicates addition of alcohol

337   groups, a slope of -1 indicates addition of carbonyl and alcohol groups on separate carbons or

338   addition of carboxylic acids, and a slope of -2 indicates addition of ketones or aldehydes. Previous

339   studies show that both laboratory-generated and ambient OA occupy a narrow van Krevelen space

340   with a slope of ~-1 – -0.5 (Heald et al., 2010; Ng et al., 2011). Ambient data included in Fig. 3 are

341   for different organic aerosol subtypes resolved from PMF analysis of AMS data collected in the

342   southeastern U.S. (Verma et al., 2015a; Xu et al., 2015a; Xu et al., 2015b).

343   The laboratory-generated aerosols span the range of H:C and O:C observed in the ambient.

344   As seen in Fig. 3 (data points sized by intrinsic OP^{WS-DTT}), while different reaction conditions

345   produced aerosol of differing composition (i.e., different O:C and H:C), the intrinsic OP^{WS-DTT}

346   does not appear to be affected by these differences. On the other hand, the hydrocarbon precursor

347   identity influences OP^{WS-DTT} substantially. It has been shown that ambient OA from different

348   sources can become increasingly oxidized (increasing O:C ratio) with atmospheric aging (Jimenez

349   et al., 2009; Ng et al., 2011). Based on the results shown in Fig. 3, it appears that a higher O:C

350 ratio did not correspond to a higher $OP^{WS\text{-}DTT}$. This is true for both the laboratory-generated SOA

351 in this study and the different OA subtypes resolved from ambient data (Verma et al., 2015a; Xu

352 et al., 2015a; Xu et al., 2015b). Nevertheless, the O:C ratios for individual systems (i.e. SOA

353 formed from the same hydrocarbon precursor) may affect the intrinsic $OP^{WS\text{-}DTT}$. Indeed, for

354 several SOA systems (β-caryophyllene, pentadecane, and *m*-xylene), SOA with higher O:C ratios

355 also had a higher intrinsic $OP^{WS\text{-}DTT}$ (Fig. 2, 3). For SOA systems formed under RO_2 + NO

356 dominant conditions, N:C ratios were also determined to investigate if there is a link between N:C

357 and intrinsic DTT activity (Fig. S3). Again, with the exception of naphthalene SOA, the intrinsic

358 $OP^{WS\text{-}DTT}$ does not appear to be affected by N:C ratio even though the systems explored span a

359 wide range of N:C. This is consistent with that observed in the van Krevelen diagram and further

360 emphasizes the importance of hydrocarbon identity in determining oxidative potentials.

361 **Comparison to other types of PM.** In order to evaluate how the oxidative potential of

362 individual SOA systems compares to other sources and subtypes of PM, the intrinsic $OP^{WS\text{-}DTT}$

363 from this study are compared to values reported in the literature (Fig. 4). Comparatively, SOA

364 formed from the photooxidation of isoprene, α-pinene, β-caryophyllene, pentadecane, and *m*-

365 xylene were not very DTT active and produced low intrinsic $OP^{WS\text{-}DTT}$. The $OP^{WS\text{-}DTT}$ of these

366 aerosol systems were also within the range of various OA subtypes resolved from ambient data.

367 The method for determining intrinsic $OP^{WS\text{-}DTT}$ for various OA subtypes is provided in the

368 Supplement. As noted earlier, the $OP^{WS\text{-}DTT}$ for isoprene SOA generated in this study is similar to

369 the isoprene-derived OA factor from ambient data. The other ambient OA factors include a highly

370 oxidized MO-OOA (more-oxidized oxygenated OA) factor resolved from PMF analysis of

371 ambient OA data, as well as an oxidized organic aerosol factor containing contributions from

372 biogenic SOA (other OC) resolved using the chemical mass balance (CMB) method with

373 ensemble-averaged source impact profiles (Bates et al., 2015; Xu et al., 2015a; Xu et al., 2015b;

374 Verma et al., 2014). While sources of MO-OOA have not been identified, studies have shown that

375 the aerosol mass spectra for various sources of OA approach that of MO-OOA as it ages (Ng et

376 al., 2010) and it has been speculated that MO-OOA may contain aerosol from multiple aged

377 sources (Xu et al., 2015b). Furthermore, MO-OOA has been shown to have widespread

378 contributions across urban and rural sites, as well as different seasons (Xu et al., 2015a; Xu et al.,

379 2015b). On the other hand, naphthalene SOA was highly DTT active with an OP^{WS-DTT} on the

380 order of biomass burning OA [BBOA (Verma et al., 2015a), BURN (Bates et al., 2015)]. The

381 BBOA and BURN factors were resolved using different source apportionment methods and as

382 such, the range for comparison is large. Here, we focus on BBOA as Verma et al. (2015a)

383 previously showed that BBOA had the highest intrinsic DTT activity among all OA subtypes

384 resolved from PMF analysis of ambient AMS data collected in the southeastern U.S. (see Fig. 4

385 for comparison). Because naphthalene aerosol formed under $RO_2 + NO$ dominant conditions may

386 be even more redox active than BBOA and anthropogenic emissions are more abundant in urban

387 environments with higher NO_x, this system warrants further systematic studies. It should however

388 be noted that comparisons of intrinsic DTT activities between SOA from a pure VOC and an

389 ambient source is difficult. BBOA is a source that contains many compounds, some of which may

390 not be redox active. Thus, although it may contain highly DTT-active components with high

391 intrinsic activities, the overall intrinsic activity will be much lower. As a result, a direct comparison

392 with pure naphthalene SOA on a per mass basis is tenuous. However, naphthalene SOA formed

393 under urban conditions ($RO_2 + NO$) also produces nitroaromatics, which may induce DNA breaks

394 and induce other mutagenic effects (Baird et al., 2005; Helmig et al., 1992). As such, aerosols

395   formed from photooxidation of PAHs may be a particularly important OA source in terms of PM

396   health effects.

397   Other common sources of PM are those related to traffic. Previous studies have determined

398   that products of incomplete combustion include quinones capable of participating in redox

399   reactions, including the oxidation of DTT (Kumagai et al., 2002; McWhinney et al., 2013a). The

400   SOA systems investigated, including isoprene, α-pinene, β-caryophyllene, pentadecane, and *m*-

401   xylene produced SOA that were less DTT active than diesel exhaust particles (DEP) collected from

402   light-duty diesel vehicle (LDDV) engines operated under various conditions (McWhinney et al.,

403   2013a) and resolved for heavy-duty diesel vehicles (HDDV) from ambient data (Bates et al., 2015).

404   It should be noted that the DTT activity reported for DEP includes both water-soluble and water-

405   insoluble fractions (total DTT activity), whereas the DTT activity measured for SOA is water-

406   soluble. However, there should be very little contribution from water-insoluble species to SOA

407   (McWhinney et al., 2013a). Conversely, the intrinsic $OP^{WS\text{-}DTT}$ of naphthalene SOA was on par

408   with that of light-duty gasoline vehicles (LDGV) and higher than that of HDDV and DEP (Verma

409   et al., 2014; Bates et al., 2015). Since naphthalene may also be emitted from gasoline and diesel

410   combustion (Jia and Batterman, 2010), traffic-related controls may be extremely important to

411   control these highly DTT active sources. Furthermore, since SOA often dominate over POA even

412   in urban centers (Zhang et al., 2007; Ng et al., 2011), even SOA that is only slightly DTT active

413   may contribute significantly to PM-induced health effects.

414   **Implications.** The water-soluble oxidative potential, as measured by DTT consumption,

415   was determined for SOA generated from six different hydrocarbon precursors under three

416   conditions of varying humidity and RO_2 fate. Results from this study demonstrate that hydrocarbon

417   precursor identity influenced intrinsic SOA oxidative potential substantially. The biogenic and

418 anthropogenic precursors investigated yielded SOA with $OP^{WS\text{-}DTT}$ ranging from 9–205 pmol min^{-}

419 ^{1} µg^{-1}, with isoprene SOA and naphthalene SOA having the lowest and highest intrinsic $OP^{WS\text{-}DTT}$

420 respectively. In general, $OP^{WS\text{-}DTT}$ for biogenic SOA were lower than those for anthropogenic

421 SOA. Therefore, to evaluate overall oxidative potentials of ambient SOA, hydrocarbon precursor

422 emissions and their corresponding SOA formation potential must be considered. Moreover, it may

423 be possible to roughly estimate regional oxidative potentials using individual intrinsic $OP^{WS\text{-}DTT}$

424 of different types of SOA in conjunction with VOC emissions and SOA loadings in models. For

425 instance, DTT activities of aerosols collected in Beijing, China (77–111 pmol min^{-1} µg^{-1}) (Lu et

426 al., 2014), where anthropogenic emissions dominate, more closely resemble the $OP^{WS\text{-}DTT}$ of

427 naphthalene SOA, whereas ambient aerosols collected in the southeastern U.S. have DTT activities

428 (25–36 pmol min^{-1} µg^{-1}) (Fang et al., 2015b) that more closely resemble those of biogenic SOA.

429 It may therefore be informative to investigate whether concentration addition can be applied to

430 DTT consumption by exploring well-characterized PM mixtures.

431 Chamber reaction conditions, including relative humidity and specific RO_2 fate, influenced

432 SOA elemental composition substantially and affected $OP^{WS\text{-}DTT}$ in a hydrocarbon-specific

433 manner, although hydrocarbon identity was by far the most influential in determining $OP^{WS\text{-}DTT}$.

434 For several VOCs (isoprene, α-pinene, β-caryophyllene, and pentadecane), the reaction conditions

435 had a negligible effect on $OP^{WS\text{-}DTT}$, which suggests that the organic peroxides and organic nitrates

436 formed from the oxidation of these precursors may have similarly low redox activity. An

437 investigation on the redox activity of individual known photooxidation products, including organic

438 peroxides and organic nitrates, may elucidate further information on the lack of reaction condition

439 effect. Similarly, nitroaromatics may explain the difference observed between naphthalene aerosol

440 formed under different RO_2 reaction pathways as the nitrite group may promote electron transfer

441 and result in a higher $OP^{WS\text{-}DTT}$. This effect was not observed for *m*-xylene SOA, due to the

442 formation of predominantly ring-opening products. The loss of the aromatic ring may also explain

443 the differences in intrinsic $OP^{WS\text{-}DTT}$. For instance, naphthalene SOA, which contains many

444 aromatic ring-retaining products, is as redox active as BBOA, one of the most DTT active aerosol

445 subtypes found in ambient studies. On the other hand, *m*-xylene SOA with predominantly aromatic

446 ring-breaking products is much less redox active and the measured $OP^{WS\text{-}DTT}$ is lower than that of

447 traffic-related sources and several OA subtypes (BBOA and cooking OA, COA). This further

448 supports earlier findings (Verma et al., 2015b) that the poly-aromatic ring structure may be an

449 important consideration for understanding SOA redox activity, which may have implications for

450 cellular redox imbalance (Tuet et al., 2016). Furthermore, nitroaromatics and polyaromatics may

451 also have significant health effects beyond redox imbalance, including various mutagenic effects

452 (Baird et al., 2005; Helmig et al., 1992). As such, hydrocarbon precursors forming aromatic ring-

453 retaining products may be the most important to consider in PM-induced health effects, in terms

454 of oxidative potential. This is consistent with many studies using DTT to show oxidative potential

455 associated with sources related to incomplete combustion (Bates et al., 2015; Verma et al., 2014;

456 McWhinney et al., 2013b) and the identification of HULIS (Verma et al., 2015b; Dou et al., 2015;

457 Lin and Yu, 2011), and more specifically, quinones as key components contributing to oxidative

458 potential (Verma et al., 2014). Finally, redox-active metals are also emitted by traffic through

459 mechanical processes, such as brake and tire wear (Charrier and Anastasio, 2012; Fang et al.,

460 2015a). These species have not be considered in the chamber experiments explored in this study.

461 Inclusion of redox-active metals in future SOA experiments may be valuable to further understand

462 the roles of SOA and metal species in overall redox activity.

463

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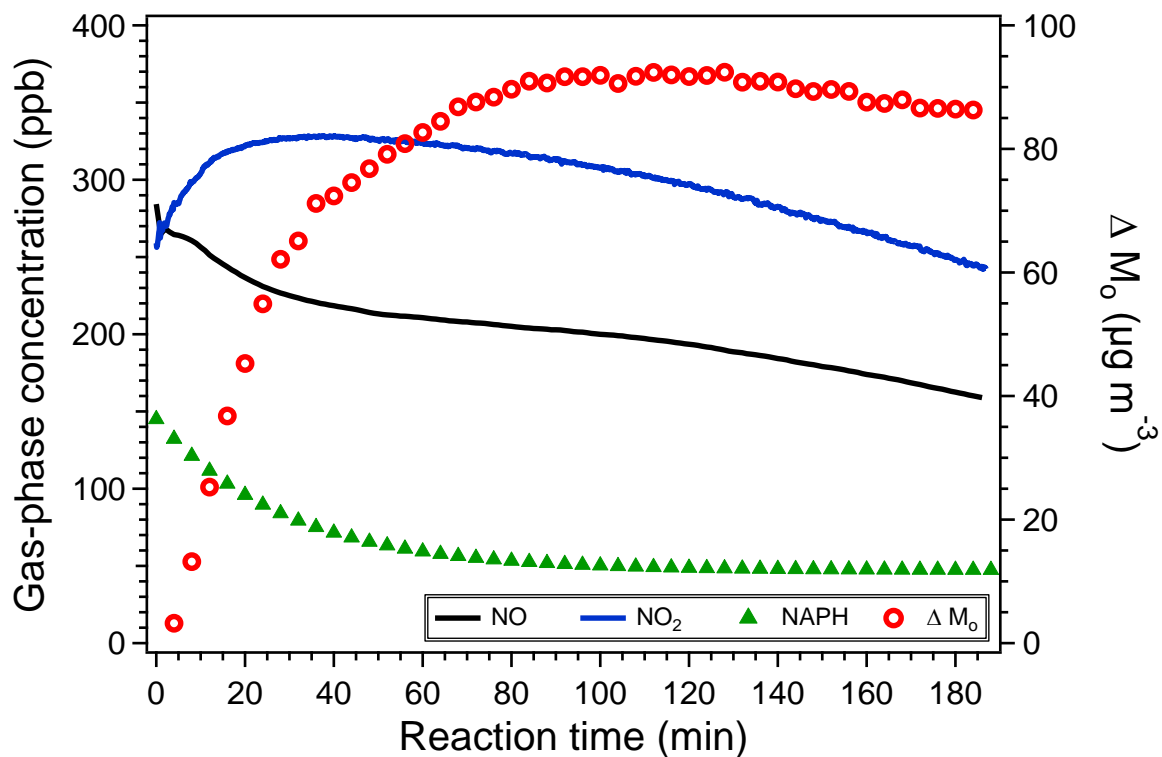
Figure 1. Typical reaction profile for a chamber experiment under $RO_2 + NO$ dominant conditions.

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NO and NO_2 concentrations were monitored by CAPS NO_2 and chemiluminescence NO_x monitors,

466

respectively. Hydrocarbon decay was monitored using GC-FID, while initial hydrocarbon

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(naphthalene) concentrations were determined using the chamber volume and mass of hydrocarbon

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injected. Aerosol mass concentrations were determined using volume concentrations obtained

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from SMPS and assuming an aerosol density of 1 g cm^{-3}. While typical SOA density is about 1.4

470

g cm^{-3}, it varies with hydrocarbon precursor identity and reaction conditions, and a density between

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~1.0–1.6 g cm^{-3} has been reported in previous studies (Ng et al., 2007a; Ng et al., 2007b; Chan et

472

al., 2009; Tasoglou and Pandis, 2015; Bahreini et al., 2005; Ng et al., 2006). The use of a density

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of 1 g cm^{-3} is to facilitate easier comparisons with past and future studies. Results from future

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studies can be scaled accordingly for comparison with the current work. Mass concentrations have

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been corrected for particle wall loss (Nah et al., 2016).

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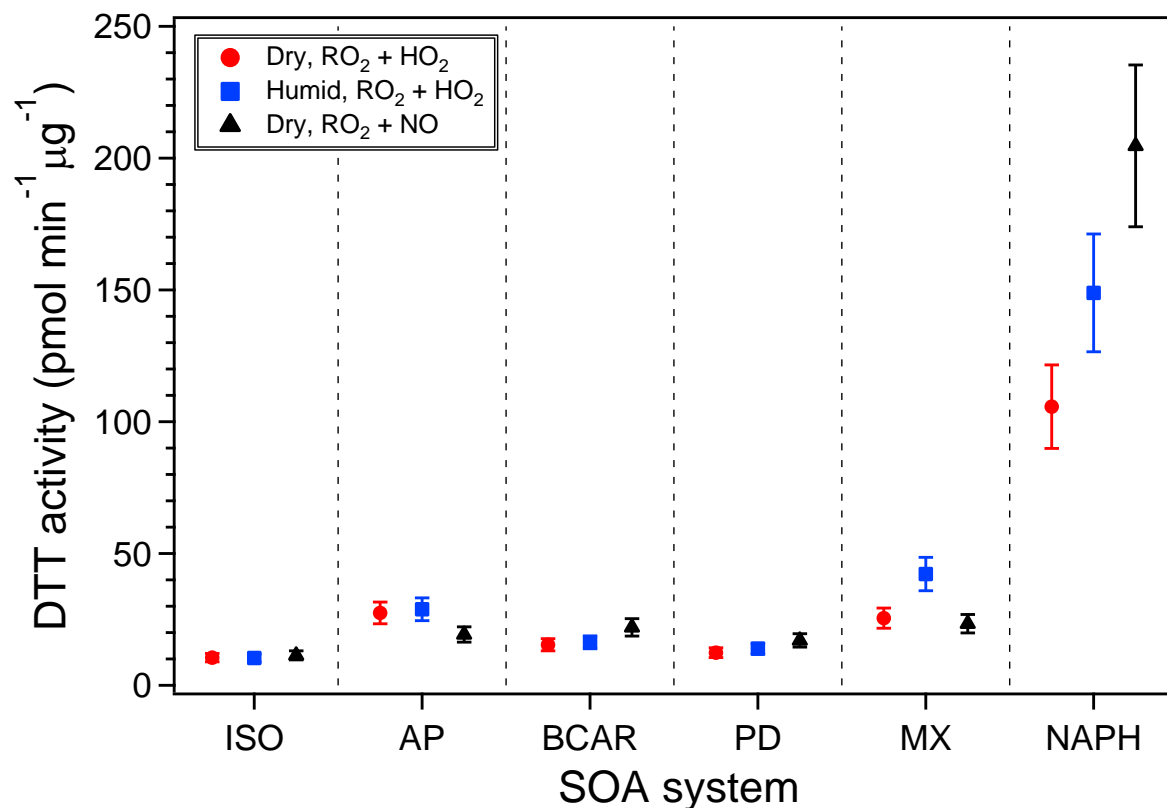
Figure 2. Intrinsic DTT activities for SOA generated from various hydrocarbon precursors (ISO:

isoprene, AP: α-pinene, BCAR: β-caryophyllene, PD: pentadecane, MX: *m*-xylene, and NAPH:

naphthalene) under various conditions (**red circles**: dry, $RO_2 + HO_2$; **blue squares**: humid, RO_2

$+ HO_2$; and **black triangles**: dry, $RO_2 + NO$). Dry, $RO_2 + HO_2$ experiments were repeated to

ensure reproducibility in SOA generation and collection. Error bars represent a 15% coefficient

of variation (Fang et al., 2015b).

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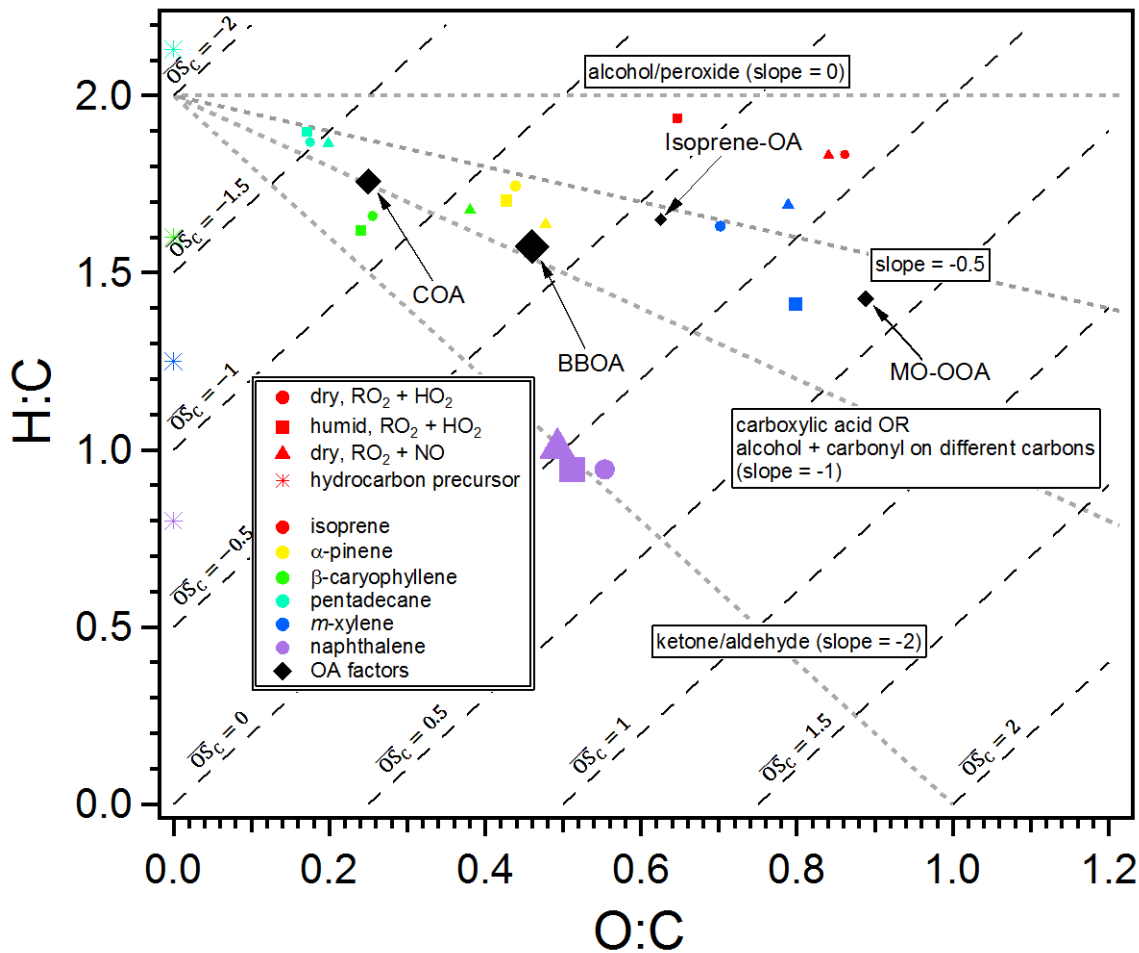
Figure 3. van Krevelen plot for various SOA systems. Data points are colored by SOA system (red: isoprene, yellow: α-pinene, green: β-caryophyllene, light blue: pentadecane, blue: *m*-xylene, and purple: naphthalene), shaped according to reaction conditions (circle: dry, $RO_2 + HO_2$; square: humid, $RO_2 + HO_2$; and triangle: dry, $RO_2 + NO$), 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; Xu et al., 2015b).
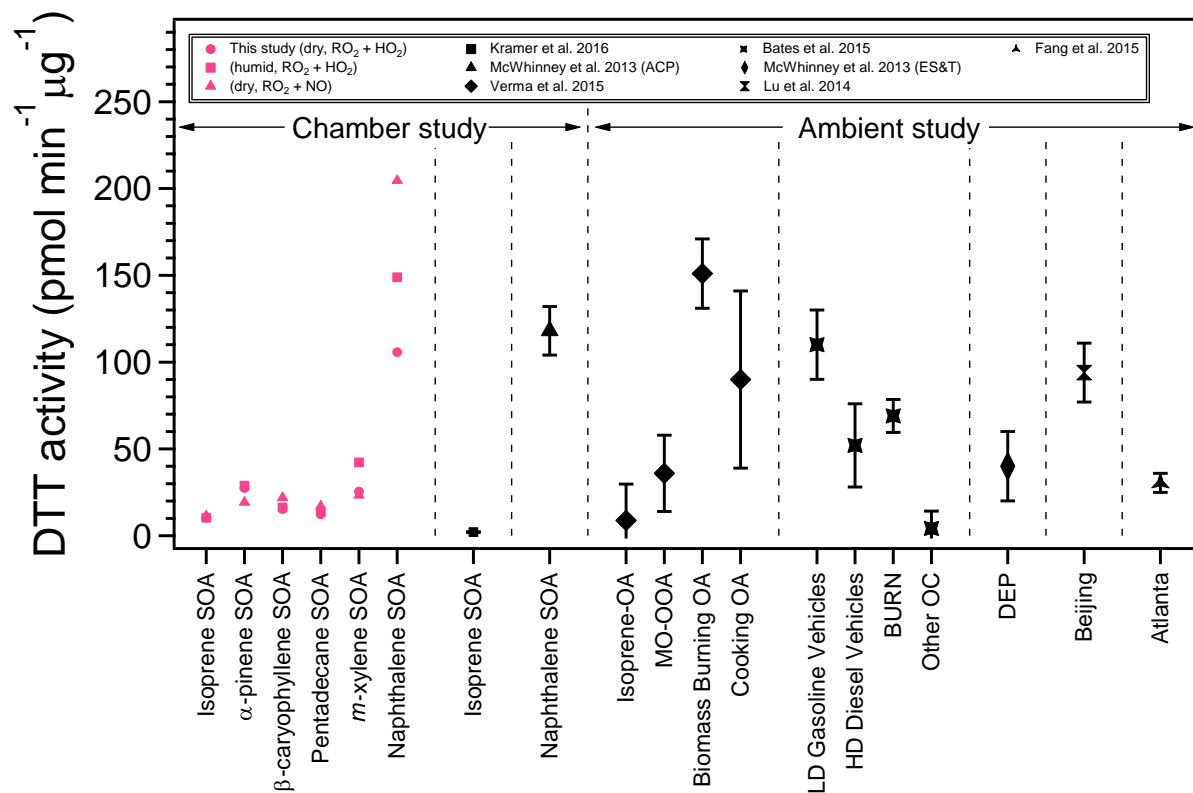
Figure 4. Intrinsic DTT activities for chamber SOA, various PM subtypes resolved from

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, $RO_2 + HO_2$; square:

humid, $RO_2 + HO_2$; triangle: dry, $RO_2 + NO$). 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

505   particles (Kramer et al., 2016; McWhinney et al., 2013b; Verma et al., 2015a; Bates et al., 2015;

506   McWhinney et al., 2013a; Xu et al., 2015a; Xu et al., 2015b; Lu et al., 2014; Fang et al., 2015b).

507 **Table 1.** Experimental conditions.

Experiment	Compound	OH precursor	Relative humidity (%)	$[HC]_0$ (ppb)	$[SOA]^c$ ($\mu g\ m^{-3}$)
1[a]	isoprene	H_2O_2	<5%	97	5.73
2[a]	α-pinene	H_2O_2	<5%	191	119
3[a]	β-caryophyllene	H_2O_2	<5%	36	221
4[a]	pentadecane	H_2O_2	<5%	106	9.71
5[a]	*m*-xylene	H_2O_2	<5%	450	89.3
6[a]	naphthalene	H_2O_2	<5%	178	128
7	isoprene	H_2O_2	<5%[b]	97	17.1
8	α-pinene	H_2O_2	40%	334	154
9	β-caryophyllene	H_2O_2	42%	63	230
10	pentadecane	H_2O_2	45%	106	23.5
11	*m*-xylene	H_2O_2	45%	450	13.9
12	naphthalene	H_2O_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	*m*-xylene	HONO	<5%	431	153
18	naphthalene	HONO	<5%	145	142

508 [a] These experiments were repeated to establish reproducibility; [b] Acidic seed (8 mM $MgSO_4$ and

509 16 mM H_2SO_4) was used instead of 8 mM $(NH_4)_2SO_4$; [c] Average SOA concentration in the

510 chamber during filter collection

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515 ABBREVIATIONS

516 PM: particulate matter; SOA: secondary organic aerosol; ROS/RNS: reactive oxygen and

517 nitrogen species; DTT: dithiothreitol; OP^{WS}: oxidative potential of water-soluble species

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