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 health effects, 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   generate ROS/RNS via redox reactions and by inducing cellular pathways that produce ROS/RNS.

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

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

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

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

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

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

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

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

59 2015a; Verma et al., 2015a; Verma et al., 2014). Results from these regressions, as well as

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

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

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

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

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

65 2015b; Lin and Yu, 2011). Recently, Tuet et al. (2016) also showed that there is a significant

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

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

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

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

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

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

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

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

74 2013; McDonald et al., 2010; McDonald et al., 2012; Baltensperger et al., 2008; Arashiro et al.,

75 2016; Platt et al., 2014), even though field studies have shown that SOA often dominate over

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

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77   2010). The few studies that exist focus on SOA generated from a single class of hydrocarbon

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

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

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

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

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

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

84   others finding little to no response. Comparisons between the observed cellular endpoints from

85   exposure to SOA formed from individual precursors are also lacking (Baltensperger et al., 2008;

86   Lund et al., 2013; McDonald et al., 2010; McDonald et al., 2012; Arashiro et al., 2016). As such,

87   there is a lack of perspective in terms of different individual SOA systems and their contributions

88   to PM-induced health effects, making it unclear whether certain responses are indeed toxic for a

89   range of sources and subtypes of PM. However, as cellular assays and animal inhalation

90   experiments are more complex, a systematic study on the oxidative potential of individual SOA

91   systems may be warranted first.

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

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

94   referred to as $OP^{WS\text{-}DTT}$). VOCs were chosen to represent the major classes of compounds known

95   to produce SOA upon oxidation by atmospheric oxidants and to include precursors of both

96   anthropogenic and biogenic origins (Table S1). Biogenic precursors include isoprene, α-pinene,

97   and β-caryophyllene, while anthropogenic precursors include pentadecane, m-xylene, and

98   naphthalene. Isoprene was chosen as it is the most abundant non-methane hydrocarbon, with

99   estimated global emissions around 500 Tg yr^{-1} (Guenther et al., 2006). α-pinene and β-

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100   caryophyllene were chosen as representative, well-studied monoterpenes and sesquiterpenes,

101   respectively. Both classes of compounds contribute significantly to ambient aerosol (Eddingsaas

102   et al., 2012; Hoffmann et al., 1997; Tasoglou and Pandis, 2015; Goldstein and Galbally, 2007). α-

103   pinene emissions (~50 Tg yr^{-1}) are also on the same order of global anthropogenic emissions (~110

104   Tg yr^{-1}) (Guenther et al., 1993; Piccot et al., 1992). Similarly, anthropogenic precursors were

105   chosen to include a long-chain alkane (pentadecane), a single-ring aromatic (*m*-xylene), and a

106   poly-aromatic (naphthalene). These classes of compounds are emitted as products of incomplete

107   combustion (Robinson et al., 2007; Jia and Batterman, 2010; Bruns et al., 2016) and have been

108   shown to have considerable SOA yields (e.g., Chan et al., 2009; Ng et al., 2007b; Lambe et al.,

109   2011). In addition to precursor identity, the effects of humidity (dry vs. humid) and NO_x (differing

110   peroxy radical (RO_2) fates, $RO_2 + HO_2$ vs. $RO_2 + NO$) on OP^{WS-DTT} were investigated, as these

111   conditions have been shown to affect the chemical composition and mass loading of SOA formed

112   (Chhabra et al., 2010; Chhabra et al., 2011; Eddingsaas et al., 2012; Ng et al., 2007b; Loza et al.,

113   2014; Ng et al., 2007a; Chan et al., 2009; Boyd et al., 2015). Finally, intrinsic OP^{WS-DTT} was

114   compared with bulk aerosol composition, specifically elemental ratios, to investigate whether there

115   is a link between OP^{WS-DTT} and aerosol composition.

116   Methods

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

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

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

120   Teflon chambers suspended inside a 21 ft x 12 ft temperature-controlled enclosure, surrounded by

121   black lights and natural sunlight fluorescent lamps. Multiple sampling ports from each chamber

122   allow for gas- and aerosol-phase measurements, as well as introduction of reagents. Gas-phase

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123   measurements include O_3, NO_2, and NO_x concentrations as measured by an O_3 analyzer (Teledyne

124   T400), a cavity attenuated phase shift (CAPS) NO_2 monitor (Aerodyne), and a chemiluminescence

125   NO_x monitor (Teledyne 200EU) respectively. Additionally, a gas chromatography-flame

126   ionization detector (GC-FID, Agilent 7890A) was used to monitor hydrocarbon decay and estimate

127   hydroxyl radical (OH) concentration. In terms of aerosol-phase measurements, aerosol volume

128   concentrations and distributions were measured using a Scanning Mobility Particle Sizer (SMPS,

129   TSI), while bulk aerosol composition was determined using a High Resolution Time-of-Flight

130   Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne; henceforth referred to as the AMS)

131   (DeCarlo et al., 2006). HR-ToF-AMS data was analyzed using the data analysis toolkit

132   SQUIRREL (v. 1.57) and PIKA (v. 1.16G). Elemental ratios (O:C, H:C, and N:C) were obtained

133   using the method outlined by Canagaratna et al. (2015), and used to calculate the average carbon

134   oxidation state ($\overline{OS_c}$) (Kroll et al., 2011). Temperature and relative humidity (RH) were monitored

135   using a hydro-thermometer (Vaisala HMP110).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

151   passing zero air over the solution until fully evaporated (~10 min). For pentadecane and β-

152   caryophyllene, the glass bulb was gently heated to ensure full evaporation (Tasoglou and Pandis,

153   2015). Naphthalene was injected by passing pure air over the solid, as outlined in previous studies

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

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

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

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

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

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

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

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

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

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

164   ^{3}. NO and NO_2 were also formed as byproducts of HONO synthesis. Once all the H_2O_2 evaporated

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

166   were turned on to initiate photooxidation.

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

168   filters (0.45 μm pore size, Pall Laboratory). For each experiment, two filters (front filter and

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169   backing filter) were loaded in series to account for possible sampling artifacts (Conny and Slater,

170   2002). Total mass collected was determined by integrating the SMPS volume concentration as a

171   function of time over the filter collection period and using the total volume of air collected. Volume

172   concentrations were integrated using time-dependent data. Background filters containing seed and

173   OH precursor (H_2O_2 or HONO) only at experimental conditions were also collected to account for

174   potential H_2O_2 or HONO uptake, which may influence oxidative potential. Collected filter samples

175   were placed in sterile petri dishes, sealed with Parafilm M®, and stored at -20 °C until extraction

176   and analysis (Fang et al., 2015b). Prior to determining OP^{WS-DTT}, collected particles were extracted

177   in DI water by submerging the filter and sonicating for 1 hr using an Ultrasonic Cleanser (VWR

178   International) (Fang et al., 2015a). Sonication steps were performed in 30 min intervals with water

179   replacement after each interval to reduce bath temperature. After sonication, extracts were filtered

180   using 0.45 µm PTFE syringe filters (Fisherbrand™) to remove insoluble material (Fang et al.,

181   2015b). All filter samples were analyzed within 1-2 days of collection.

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

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

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

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

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

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

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

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

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

191   <u>Results and Discussion</u>

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

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

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

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

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

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

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

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

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

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

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

203   were observed.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

248 therefore the results from their study and ours may not be directly comparable. For instance, for

249 isoprene photooxidation experiments, the "low-NO_x" conditions in Kramer et al. (2016)

250 corresponded to "5 ppm isoprene and 200 ppb NO", where the reaction regime was largely defined

251 by the VOC/NO_x ratio. It has been shown previously that SOA formed under the same VOC/NO_x

252 conditions can be drastically different and the use of this metric might not necessarily reflect the

253 actual peroxy radical fate (Ng et al., 2007b; Kroll and Seinfeld, 2008; Wennberg, 2013). In our

254 study, the "low-NO_x" experimental condition is defined by the fate of peroxy radicals directly, i.e.,

255 no NO_x added, but with the presence of H_2O_2 to enhance the $RO_2 + HO_2$ reaction pathway, which

256 is dominant in ambient environments when NO_x levels are low.

257   α-pinene, β-caryophyllene, and pentadecane produced low OP^{WS-DTT} across all conditions

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

259 do not appear to have significantly different OP^{WS-DTT}, even though different NO_x conditions have

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

261   2009; Eddingsaas et al., 2012; Loza et al., 2014; Ng et al., 2007a). For instance, under conditions

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

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

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

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

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

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

268   Similarly, the OP^{WS-DTT} of SOA formed from m-xylene under conditions that favor

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

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

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

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

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

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

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

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

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

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

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

280   very different for this experiment. It is possible that the degree of oxidation may be an important

281   factor for SOA formed from the same hydrocarbon, and systematic chamber studies investigating

282   changes in O:C for SOA formed from a single hydrocarbon precursor would be valuable. Previous

283   studies involving the effect of humidity on SOA composition also yield mixed results, with some

284   finding significant changes in SOA composition and yields (Nguyen et al., 2011; Wong et al.,

285   2015; Healy et al., 2009; Stirnweis et al., 2016) and others reporting little difference (Boyd et al.,

286   2015; Edney et al., 2000; Cocker III et al., 2001). Humidity effects are therefore highly

287   hydrocarbon-dependent. Further study into the specific oxidation mechanisms and products in the

288   photooxidation of aromatic hydrocarbon under dry and humid conditions may be warranted to

289   understand the difference in DTT activity.

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

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

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

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

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

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

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

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

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

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

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

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

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

303   2012; McWhinney et al., 2013b). In addition to these products, nitroaromatics including

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

305   2010). The nitrite group next to the aromatic ring in these products may further promote electron

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

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307   ^{DTT}. This effect was not observed for *m*-xylene SOA due to the formation of predominantly ring-

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

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

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

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

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

313   2010; McLafferty and Tureček, 1993). Aromatic species are also exclusive to HULIS (Sannigrahi

314   et al., 2006), and ambient data have shown that HULIS is a significant aerosol component

315   contributing to $OP^{WS\text{-}DTT}$ (Verma et al., 2015b; Verma et al., 2012; Dou et al., 2015; Lin and Yu,

316   2011). Nitroaromatics are also known to have mutagenic properties and polyaromatics may further

317   induce toxicity via DNA adduct formation (Baird et al., 2005; Helmig et al., 1992). As such,

318   polyaromatic precursors may have significant health implications beyond redox imbalance.

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

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

321   Lambe et al., 2011). To visualize these differences in oxidation, the van Krevelen diagram was

322   utilized (Fig. 3), as changes in the slope of data points within the van Krevelen space can provide

323   information on SOA functionalization (Heald et al., 2010; Van Krevelen, 1950; Ng et al., 2011).

324   Starting from the precursor hydrocarbon, a slope of 0 indicates addition of alcohol groups, a slope

325   of -1 indicates addition of carbonyl and alcohol groups on separate carbons or addition of

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

327   show that both laboratory-generated and ambient OA occupy a narrow van Krevelen space with a

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

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

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

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

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

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

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

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

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

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

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

339   in this study and the different OA subtypes resolved from ambient data. Nevertheless, the O:C

340   ratios for individual systems (i.e. SOA formed from the same hydrocarbon precursor) may affect

341   the intrinsic OP^{WS-DTT}. Indeed, for several SOA systems (β-caryophyllene, pentadecane, and *m*-

342   xylene), SOA with higher O:C ratios also had a higher intrinsic OP^{WS-DTT} (Fig. 3). For SOA

343   systems formed under RO_2 + NO dominant conditions, N:C ratios were also determined to

344   investigate if there is a link between N:C and intrinsic DTT activity (Fig. S3). Again, with the

345   exception of naphthalene SOA, the intrinsic OP^{WS-DTT} does not appear to be affected by N:C ratio

346   even though the systems explored span a wide range of N:C. This is consistent with that observed

347   in the van Krevelen diagram and further emphasizes the importance of hydrocarbon identity in

348   determining oxidative potentials.

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

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

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

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

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

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

355   The method for determining intrinsic OP^{WS-DTT} for various OA subtypes is provided in the

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

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

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

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

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

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

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

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

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

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

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

367   2015b). On the other hand, naphthalene SOA was highly DTT active with an OP^{WS-DTT} on the

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

383   formed from photooxidation of PAHs may be a particularly important OA source in terms of health

384   effects.

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

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

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

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

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

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

391   2013a) and resolved for heavy-duty diesel vehicles (HDDV) from ambient data (Bates et al., 2015).

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

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

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

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

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

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

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

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

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

401 may contribute significantly to PM-induced health effects.

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

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

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

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

406 anthropogenic precursors investigated yielded SOA with OP^{WS-DTT} ranging from 9–205 pmol min^{-1}

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

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

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

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

411 be possible to roughly estimate regional oxidative potentials using individual intrinsic OP^{WS-DTT}

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

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

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

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

416 (25–36 pmol min^{-1} μg^{-1}) (Fang et al., 2015b) that more closely resemble those of biogenic SOA.

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

418 DTT consumption by exploring well-characterized PM mixtures.

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

420 SOA elemental composition substantially and affected OP^{WS-DTT} in a hydrocarbon-specific

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

442   of oxidative potential. This is consistent with many studies showing oxidative potential associated

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

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444   et al., 2013b) and the identification of HULIS (Verma et al., 2015b; Dou et al., 2015; Lin and Yu,

445   2011), and more specifically, quinones as key components contributing to oxidative potential

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

447   processes, such as brake and tire wear (Charrier and Anastasio, 2012; Fang et al., 2015a). These

448   species have not be considered in the chamber experiments explored in this study. Inclusion of

449   redox-active metals in future SOA experiments may be valuable to further understand the roles of

450   SOA and metal species in overall redox activity.

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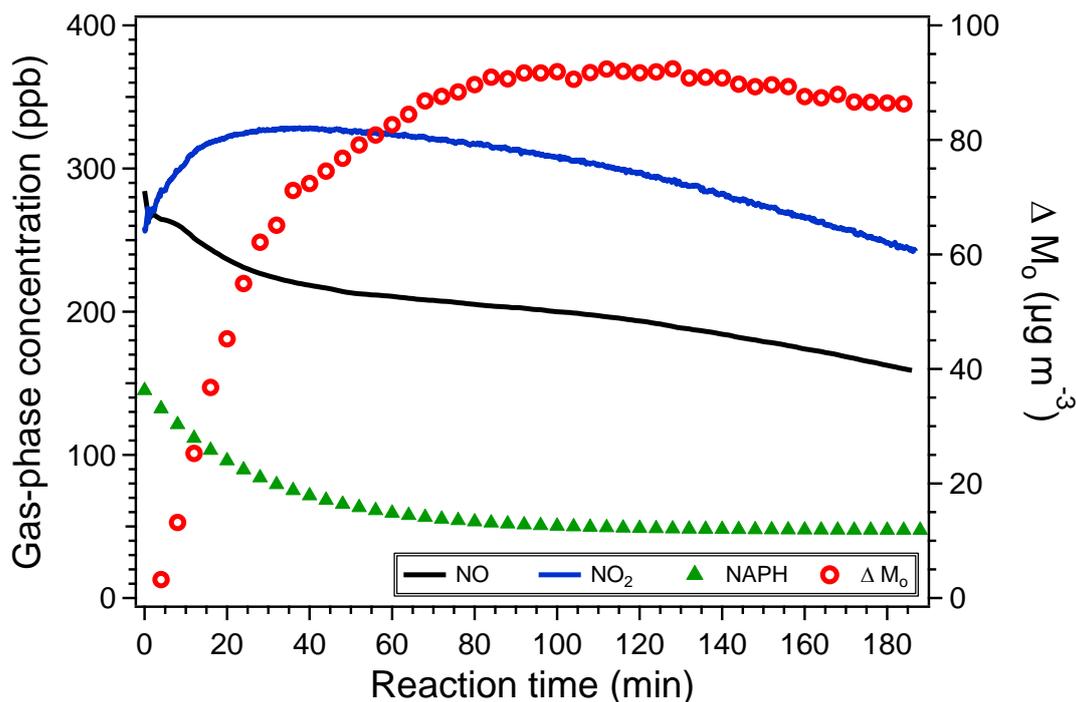
452

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

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

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

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

457 injected. Aerosol mass concentrations were determined using volume concentrations obtained

458 from SMPS and assuming an aerosol density of 1 g cm^{-3}. Mass concentrations have been corrected

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

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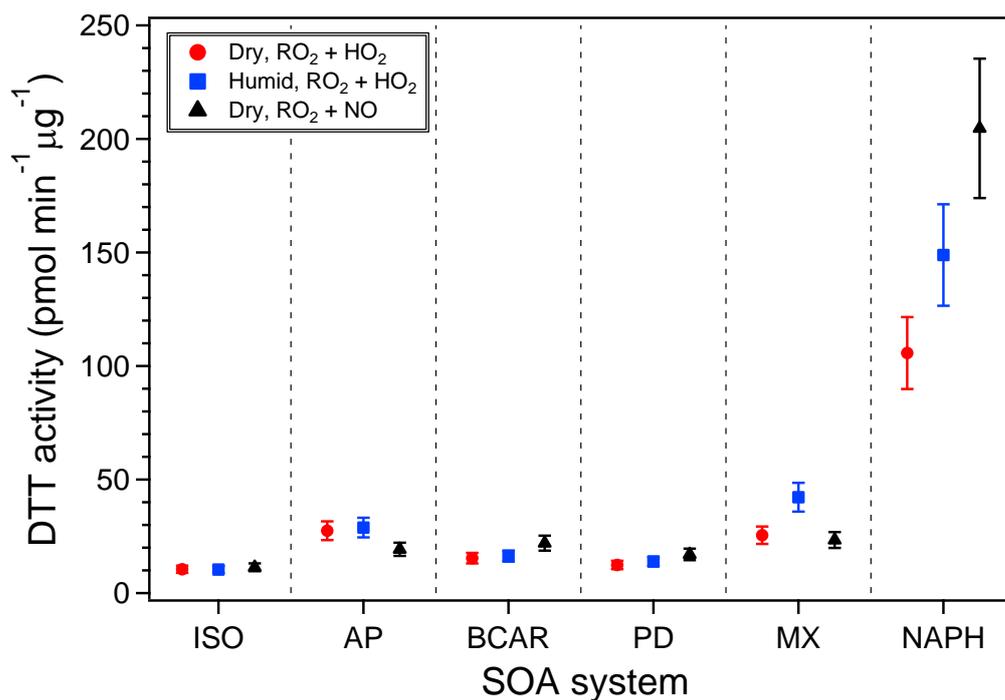
Figure 2. Intrinsic DTT activities for SOA generated from various hydrocarbon precursors (ISO:

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).
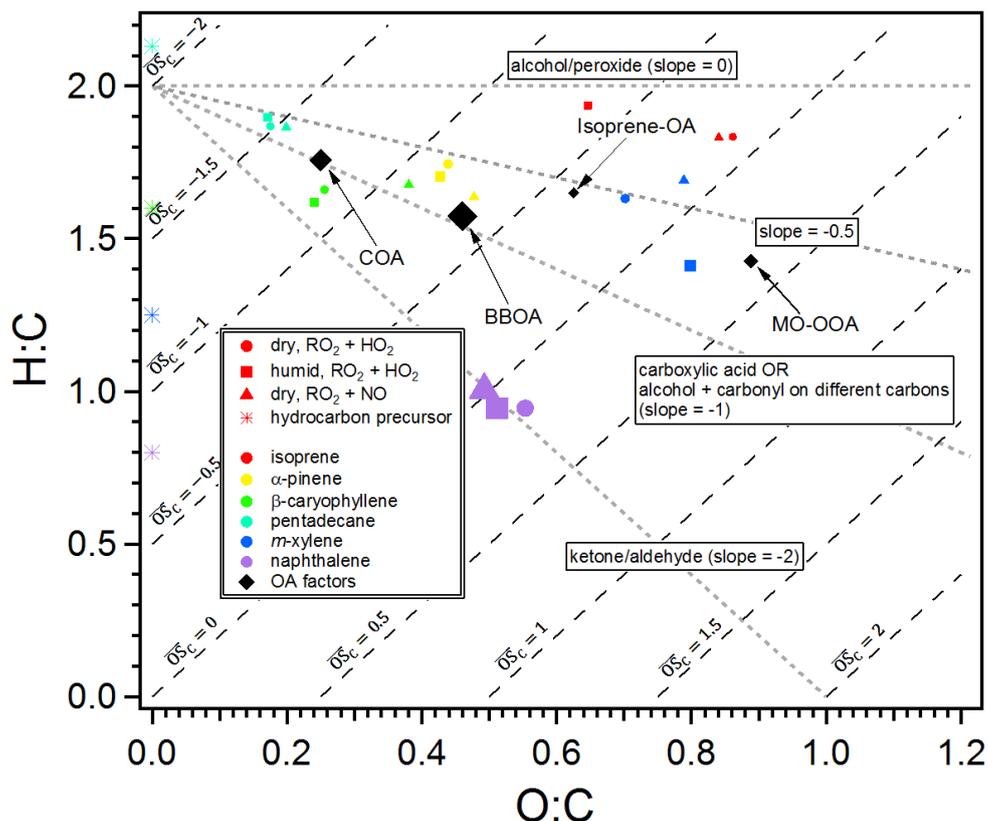
Figure 3. van Krevelen plot for various SOA systems. Data points are colored by SOA system (red: isoprene, yellow: α-pinene, green: β-caryophyllene, light blue: pentadecane, blue: *m*-xylene, and purple: naphthalene), shaped according to reaction conditions (circle: dry, $RO_2 + HO_2$; square: humid, $RO_2 + HO_2$; 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).

477
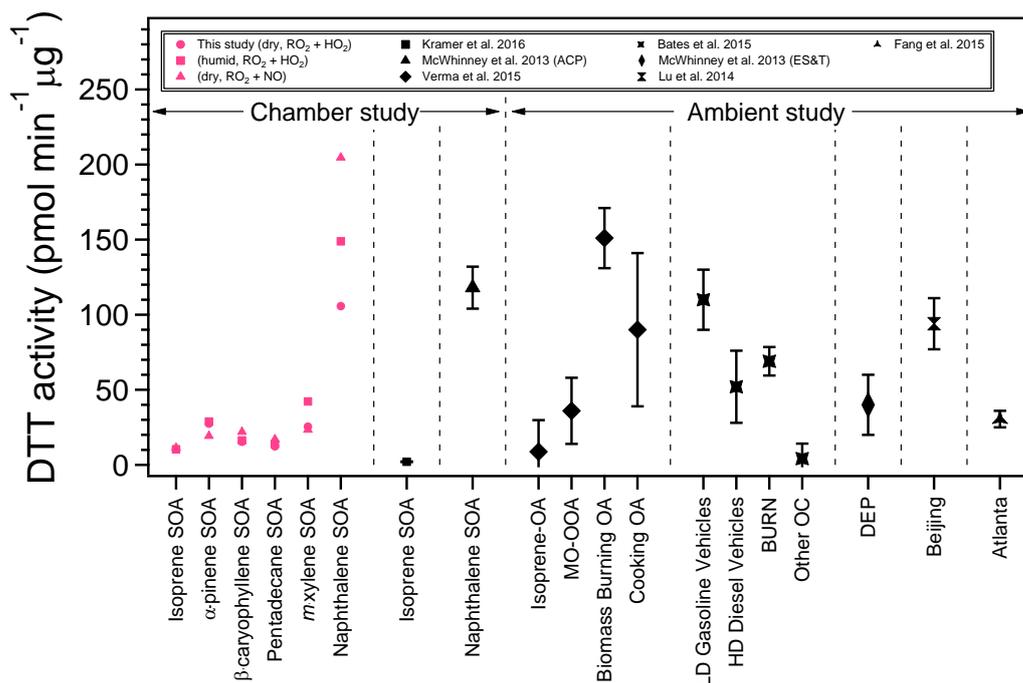
Figure 4. Intrinsic DTT activities for chamber SOA, various PM subtypes resolved from

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

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

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

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490 **Table 1.** Experimental conditions.

Experiment	Compound	OH precursor	Relative humidity (%)	[HC]$_0$ (ppb)	[SOA][c] (µg 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

491 [a] These experiments were repeated to establish reproducibility; [b] Acidic seed (8 mM MgSO$_4$ and

492 16 mM H_2SO_4) was used instead of 8 mM $(NH_4)_2SO_4$; [c] Average SOA concentration in the

493 chamber during filter collection

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498   ABBREVIATIONS

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

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

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