



Optical Properties and Aging of Light Absorbing Secondary Organic Aerosol

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17 Abstract

18 The light-absorbing organic aerosol (OA), commonly referred to as “brown carbon (BrC)”, has attracted
19 considerable attention in recent years because of its potential to affect atmospheric radiation balance,
20 especially in the ultraviolet region and thus impact photochemical processes. A growing amount of data
21 has indicated that BrC is prevalent in the atmosphere, which has motivated numerous laboratory and
22 field studies; however, our understanding of the relationship between the chemical composition and
23 optical properties of BrC remains limited. We conducted chamber experiments to investigate the effect
24 of various VOC precursors, NO_x concentrations, photolysis time and relative humidity (RH) on the light
25 absorption of selected secondary organic aerosols (SOA). Light absorption of chamber generated SOA
26 samples, especially aromatic SOA, was found to increase with NO_x concentration, at moderate RH, and
27 for the shortest photolysis aging times. The highest mass absorption coefficients (MAC) value is
28 observed from toluene SOA products formed under high NO_x conditions at moderate RH, in which
29 nitro-aromatics were previously identified as the major light absorbing compounds. BrC light
30 absorption is observed to decrease with photolysis time, correlated with a decline of the organonitrate
31 fraction of SOA. SOA formed from mixtures of aromatics and isoprene absorb less visible and UV light
32 than SOA formed from aromatic precursors alone on a mass basis. However, the mixed-SOA absorption
33 was underestimated when optical properties were predicted using a two-product SOA formation model,
34 as done in many current climate models. Further investigation, including analysis on detailed
35 mechanisms, are required to explain the discrepancy.

36



37 1. Introduction

38 Climate forcing by various atmospheric components has been intensely investigated over the last few
39 decades but significant uncertainties still exist (IPCC, 2013). One of the largest uncertainties comes
40 from the role of carbonaceous aerosols, including black carbon (BC) and organic carbon (OC). Black
41 carbon is formally defined as an ideally light-absorbing substance composed of carbon (Petzold et al.,
42 2013) with strong absorption across a wide spectrum of visible wavelengths, which is caused by a
43 significant, wavelength-independent imaginary part k (i.e., ~ 0.79 (Bond et al., 2013)) of the refractive
44 index. BC has long been known as the strongest light-absorbing aerosol in the visible wavelengths (e.g.,
45 Bond et al., 2013). On the other hand, OC has been treated as a scattering species, and only a few recent
46 global modeling studies have focused on the radiative forcing by absorbing OC (Lin et al., 2014a; Feng
47 et al., 2013; Chung et al., 2012). Light absorbing OA are collectively called brown carbon (BrC) (Laskin
48 et al., 2015; Moise et al., 2015; Andreae and Gelencsér, 2006). In contrast to BC, the imaginary
49 refractive index of BrC has stronger wavelength dependence ($\lambda^{-2}-\lambda^{-6}$) that increases towards shorter
50 visible and ultraviolet (UV) wavelengths. This broad absorption band in the blue/violet region of the
51 spectrum gives BrC its eponymous yellow or brown color (Alexander et al., 2008; Andreae and
52 Gelencsér, 2006; Lukács et al., 2007). BrC has been widely observed in many environments, including
53 urban environments largely impacted by anthropogenic emissions (Zhang et al., 2013; Du et al., 2014),
54 biomass burning plumes (Lack et al., 2013; Lack et al., 2012; Forrister et al., 2015), over the
55 ocean (Bikkina and Sarin, 2013), rainwater (Kieber et al., 2006) and in the troposphere (Liu et al.,
56 2014; Alexander et al., 2008).

57



58 A variety of studies have investigated sources of BrC in both the laboratory and in the field. Incomplete
59 and smoldering combustion of hydrocarbons, especially those associated with biomass burning, is
60 known to directly produce particulate BrC (Hoffer et al., 2006;Hecobian et al., 2010;Lack et al.,
61 2013;Desyaterik et al., 2013;Chakrabarty et al., 2010;Kirchstetter and Thatcher, 2012;Mohr et al., 2013).
62 There is also evidence based on ambient studies of a secondary BrC source (Duarte et al., 2005) and
63 laboratory studies show formation of chromophores (components of molecules that absorb light)
64 through a variety of mechanisms, including photooxidation of aromatics (Lambe et al., 2013;Liu et al.,
65 2015b), ozonolysis of terpenes subsequently aged in the presence of ammonium ions and humidity
66 (Bones et al., 2010;Nguyen et al., 2013;Laskin et al., 2014;Updyke et al., 2012), and a variety of
67 additional aqueous phase reactions, such as lignin (Hoffer et al., 2006) and isoprene oxidation (Limbeck
68 et al., 2003), reactions of carbonyls (e.g., glyoxal, methyglyoxal) in acidic solutions(Sareen et al., 2010),
69 with amino acids (De Haan et al., 2009), amines (De Haan et al., 2009;Powelson et al., 2014;Zarzana et
70 al., 2012), or ammonium salts (Sareen et al., 2010;Lin et al., 2015a;Galloway et al., 2009;Kampf et al.,
71 2012;Shapiro et al., 2009). Among those studies, it is suggested that the chemical and optical properties
72 of laboratory generated SOA might be influenced by a variety of factors, including the composition of
73 the volatile organic carbon (VOC) precursor, oxidation chemistry, relative humidity (RH), and
74 potentially “aging” at longer time scales (i.e., in-particle reactions and photobleaching). Particularly,
75 SOA aged in the presence of dissolved ammonium has been shown to produce BrC efficiently, which
76 may contribute to aerosol optical density in regions with elevated concentrations of ammonium salts
77 (i.e., Updyke et al., 2012).

78



79 This study focuses on measuring light absorption by laboratory-generated SOA that simulate both urban
80 and remote environments. Four VOCs representative of biogenic and anthropogenic emission are
81 chosen as SOA precursors in this study. Biogenic VOCs selected include isoprene and α -pinene, of
82 which isoprene is the most abundant biogenic non-methane hydrocarbon emitted into the atmosphere
83 (Guenther et al., 2006), while α -pinene accounts for approximately 40% of global monoterpene ($C_{10}H_{16}$)
84 emissions (Guenther et al., 2012). For anthropogenic VOCs, we selected trimethylbenzene (TMB) and
85 toluene, the photooxidation of which in the presence of NO_x is a major source of anthropogenic SOA
86 (Ng et al., 2007; Kleindienst et al., 2004; Henze et al., 2008). Four different types of experiments were
87 conducted to investigate the effects of (1) NO_x levels, (2) VOC precursors, (3) photolysis time, and (4)
88 RH on SOA light absorption. We compare the light absorption of formed SOA by ultraviolet/visible
89 (UV/Vis) absorption measured from aerosol samples extracted in water and methanol.

90

91 2. Experimental methods

92 Experiments were performed in the indoor 10.6 m^3 Teflon chamber at the Pacific Northwest National
93 Laboratory (PNNL) operating in batch mode where a discrete quantity of a VOC is introduced into the
94 chamber and allowed to react with the gas-phase oxidants (Liu et al., 2012). The Teflon chamber was
95 flushed continuously with dry purified air until particle concentrations were less than 5 cm^{-3} prior to all
96 experiments. For each experiment, a measured amount of VOC was injected into a glass bulb with a
97 syringe, evaporated with gentle heating, and transferred to the chamber in a flow of purified air. After
98 the VOC injection, 0.5 mL of H_2O_2 solution (Sigma-Aldrich, 50 wt% in H_2O) was injected into the
99 chamber in the same manner. Humidity was controlled by passing pure air at a variable flow rate



100 through pure water (18.2 MΩ cm, <5ppbv TOC) with a HEPA filter downstream of the bubbler to
101 remove any contaminant particles. In experiments in which NO_x were present, NO was injected from a
102 gas cylinder containing a known NO concentration (500 ppm, Matheson Tri-Gas®) with flows regulated
103 by mass flow controllers. After all components were injected and well-mixed in the chamber, UV lights
104 were turned on to initiate photooxidation. The UV flux in the chamber, averaged $J_{NO_2}=0.16 \text{ min}^{-1}$, was
105 measured continuously by a radiometer that is calibrated to an equivalent photolysis rate of NO₂ and
106 suspended in the center of the chamber. Measurements of J_{NO_2} using the photostationary state method
107 were in agreement with the radiometer measurements (Leighton, 1961).

108

109 During the experiments, a suite of online instruments were used to characterize the gas- and particle-
110 phase composition. The mixing ratios of the hydrocarbons were continuously monitored with an
111 Ionicon proton-transfer-reaction mass spectrometry (PTR-MS). The mass loading of the aerosol
112 particles was measured using an Aerodyne high-resolution time of flight mass spectrometer (HR-ToF-
113 AMS) (DeCarlo et al., 2006), while the number and volume concentrations were measured with a TSI
114 scanning mobility particle sizer (SMPS). An NO/NO₂/NO_x analyzer (Thermo Environmental
115 Instruments model 42c) was used to measure the concentration of NO and NO_x. A UV absorption O₃
116 analyzer (Thermo Environmental Instruments model 49C) allowed for the measurement of O₃
117 concentration.

118

119 SOA samples were collected on filters to measure their light absorption. Photooxidation products were
120 collected onto PTFE filters (Pall Life Sciences, 47 mm, 1 μm pore size) at a flow rate of 9 L min⁻¹ for a



121 collection period of 60-120 minutes. Typically at least 20 μg of organic mass is required for accurate
122 measurement of light absorption. As described in previous studies (Hecobian et al., 2010;Zhang et al.,
123 2011), filters were extracted in high purity water ($> 18.2 \text{ M}\Omega \text{ cm}$), filtered through a 25mm diameter
124 0.45 μm pore syringe filter (Fisher Scientific, FisherbrandTM Syringe Filters) and transferred into a long-
125 path (100 cm pathlength) UV-Visible spectrometer (Ocean Optics) to determine the light-absorption
126 spectra. After water extraction, filters were also sonicated in methanol (VWR International, A.C.S.
127 Grade) to extract non-water soluble mass (Liu et al., 2013;Liu et al., 2015a). Total absorption due to
128 BrC ($\text{Abs}(\lambda)$) is determined as the sum of water-soluble and methanol-extracted absorption from the
129 sequential extraction processes. An extraction efficiency test was performed with 6 filters, in which
130 filters were cut in halves, one half extracted with methanol only and the other half processed with the
131 sequential extraction. Results show that the sum of light absorption from the sequential extraction is
132 comparable to methanol extraction alone, with a slope within 8% of 1 (Figure S1). Studies have shown
133 that the extraction efficiency of organic mass is $>90\%$ using methanol as the solvent (Chen and Bond,
134 2010;Updyke et al., 2012). Thus, it is reasonable to assume that total light absorption determined from
135 the sequential extraction procedure closely approximates the “true” optical properties of the SOA
136 samples. The limit of detection (LOD) was 0.081 Mm^{-1} in the 300-700 nm wavelength range with an
137 estimated uncertainty of 21%. The mass absorption coefficient (MAC) was then estimated using
138 equation 1:

$$139 \quad \text{MAC}(\lambda) = \frac{\text{Abs}(\lambda)}{\text{OM}} \quad (1)$$

140 in which $\text{Abs}(\lambda)$ is the light absorption from filter-collected aerosol samples at a wavelength λ , and OM
141 is the SOA mass concentrations on the filter estimated from AMS measurements and the sampled air



142 volume. Wall-loss corrections were not applied to either measured SOA mass concentrations or light
143 absorption determined from filter-collected aerosol samples for consistency. Based on lowest SOA mass
144 concentrations during all experiments, the LOD of the MAC is estimated as $0.004 \text{ m}^2 \text{ g}^{-1}$.

145

146 **2.1 Description of the SOA two-product model**

147 Ambient studies have shown that SOA produced from urban emissions in isoprene-rich environments
148 tend to have much lower BrC absorption compared to that in anthropogenic emission dominant
149 environments (Zhang et al., 2011). In our study, two mixed precursor experiments were conducted to
150 investigate the changes in aromatic BrC due to addition of isoprene reaction products. We employ a
151 two-product model to describe the partitioning of organic mass between aromatic- and isoprene-derived
152 SOA (Pankow, 1994; Odum et al., 1996). SOA yield parameters for pure compounds are determined by
153 fitting real-time batch mode data as described in the literature (Presto and Donahue, 2006). In the mixed
154 precursor experiments, the PTR-MS data is used to determine the amount of each precursor reacted
155 during the filter collection periods. Then, the pure compound yield parameterizations are used to
156 calculate the relative fractions of the isoprene- and aromatic-derived SOA collected on the filter. The
157 calculation assumes that all SOA components are mutually miscible and reproduced the measured SOA
158 mass with the difference less than 10% (Table S1). These fractions are then used along with the optical
159 properties of the single-precursor SOA to predict the optical properties of the mixed aerosol.

160

161 **3. Results and Discussion**

162 3.1 Effects of VOC types and NO_x levels



163 The wavelength-dependent MAC values for SOA derived from four selected precursor VOCs are
164 plotted in Figure 1. In general, the shapes of the spectra are characteristic of typical atmospheric BrC
165 materials, with relatively higher absorption in the UV range (i.e., Hecobian et al., 2010; Chen and Bond,
166 2010). Figure 2 shows a comparison of the MAC at 365 nm among four different SOA samples
167 (isoprene, α -pinene, TMB and toluene) produced under NO_x -free and high- NO_x conditions.

168

169 The MAC values of isoprene SOA are close to the LOD in the 300-700 nm wavelength range and there
170 is no significant difference in the UV-Vis spectra of isoprene SOA formed under NO_x -free and high-
171 NO_x conditions. Quantum mechanical calculations suggest that electrons must be delocalized over the
172 equivalent of 7-8 bond lengths before an absorption will occur at 360 nm (Kuhn, 1949). Therefore our
173 results suggest SOA produced from isoprene photochemical oxidation does not contain products that
174 have extended carbon conjugated chains, consistent with current understanding that isoprene
175 photochemical oxidation products consist of carbonyls, hydroxycarbonyls, diols and organic peroxides
176 (e.g., Nguyen et al., 2011). On the other hand, Lin et al. (2014) has suggested that acidic seeds may
177 promote formation of oligomers through reactive uptake of IEPOX and produced light-absorbing
178 organic aerosols under certain conditions (Lin et al., 2014b). In our experiments, neither acidic seeds
179 nor excess ammonia are present, which likely explains the difference between our observations and
180 those of Lin et al. (2014).

181

182 SOA formed from photochemical oxidation of α -pinene also showed very limited light absorption.
183 However, we observe a slight increase in the MAC values at wavelengths below 450 nm for the α -



184 pinene SOA formed under high-NO_x conditions relative to that formed in the absence of NO_x. These
185 observations are consistent with other studies that have found minimal light absorption for α-pinene
186 SOA, again indicating that the compounds partitioning to the condensed phase do not have extended
187 conjugation (Henry and Donahue, 2012; Nakayama et al., 2010; Laskin et al., 2014).

188

189 In contrast to the SOA produced from the terpene precursors, aromatic precursors representative of
190 anthropogenic VOCs produce SOA that significantly absorbs light, particularly in the UV wavelength
191 range. Overall, the MAC values of the SOA produced from both TMB and toluene are much higher than
192 biogenic SOA, for both NO_x-free and high-NO_x conditions (Figure 2). Lambe et al. (2013) has
193 suggested that the conjugated double bonds retained in oxidation products of aromatic precursors are
194 likely to contribute to absorption in the ultraviolet to near visible range (Lambe et al., 2013). SOA
195 formed from non-aromatic precursors, on the other hand, did not show strong light absorption in the
196 ultraviolet/visible range due to lack of extended conjugated double bond networks.

197

198 For both toluene and TMB SOA, high NO_x products show substantially higher light absorption than low
199 NO_x. Shown in figures 1 and 2, aromatic SOA formed under high NO_x conditions have much higher
200 MAC values, both in the UV and in the visible. Several studies, based upon both chamber and field
201 observations, have suggested that nitrogen-containing molecules are strong light absorbers (i.e.,
202 Nakayama et al., 2013; Liu et al., 2015b; Zhang et al., 2011; Lin et al., 2015b). In a companion study, we
203 reported detailed characterization of the most prominent BrC chromophores in toluene-SOA formed
204 under both NO_x-free and high-NO_x conditions by deploying liquid chromatography combined with a



205 UV/vis detector and high-resolution mass spectrometry (LC-UV/Vis-ESI/HRMS) (Lin et al., 2015b).
206 Samples of toluene-SOA produced under high-NO_x and NO_x-free conditions have substantially different
207 chemical compositions. In high-NO_x SOA, we identified 15 nitro-aromatic compounds, including
208 nitrocatechol, dinitrocatechol and nitrophenol, the total absorbance of which accounts for 60% and 41%
209 of the overall absorbance in the wavelength ranges of 300-400nm and 400-500nm, respectively (Lin et
210 al., 2015b). In contrast, photooxidation products observed in NO_x-free SOA are dominated by non-
211 aromatic compounds with high degree of saturation, which did not show substantial light absorption in
212 the UV/Vis range. Similar to toluene SOA, TMB SOA produced under high-NO_x conditions contains
213 nitrogen-containing compounds in contrast to NO_x-free SOA, which explains the difference in light-
214 absorbing properties (Liu et al., 2012).

215

216 For similar reaction conditions, the TMB-derived SOA are less absorptive than the toluene SOA. The
217 difference in the light absorption properties between toluene SOA and TMB SOA may be explained by
218 the difference in the production of nitrophenols. Sato et al. (2012) showed that nitrophenols were not
219 detected in the TMB SOA, possibly due to the fact that NO₂ addition to the phenoxy radical formed in
220 reaction of TMB with OH is inhibited (Sato et al., 2012). Our measurement is consistent with this
221 hypothesis and infers that nitro-aromatics such as nitrophenols are the main sources of light absorption
222 for the aromatic SOA.

223

224 The MAC values of SOA produced from aromatic VOCs are comparable to those of other light-
225 absorbing material relevant to atmospheric aerosol particles, such as fulvic acid. Shown in Figure 3a,



226 the blue shaded area represents the measured MAC range of SOA produced in the toluene+NO_x
227 experiments, with the MAC of Suwannee River fulvic acid as a reference. Over the wavelength range
228 380-480 nm, toluene SOA has higher MAC values than fulvic acid. Since fulvic acid is often cited as a
229 surrogate of atmospheric BrC, this comparison shows that light absorption by BrC produced from
230 anthropogenic VOCs can be significant under certain photochemical condition.

231

232 3.2 Mixed precursor experiments

233 Results from laboratory studies have shown that the addition of isoprene reduced the BrC absorption of
234 aerosols formed from toluene+ α -pinene mixtures (Jaoui et al., 2008). The lower absorption was
235 attributed to decreased organic aerosol yields (e.g., lower amounts of light-absorbing SOA were formed)
236 (Jaoui et al., 2008). From ambient observations, Zhang et al. (2011) reported contrasting light
237 absorption properties in two urban environments. Fresh SOA in LA displayed much higher light-
238 absorption presumably because of the anthropogenic-dominated environment, while Atlanta aerosols
239 formed from a mix of anthropogenic and biogenic (isoprene) VOC precursors had a 4-6 times lower
240 MAC value (Zhang et al., 2011). Hecobian et al. (2010) measured the light absorption of water-soluble
241 organic carbon (WSOC) in Atlanta in different seasons and found that the winter WSOC has a ~3 times
242 higher MAC than summer, due to biomass burning influence in winter (Hecobian et al., 2010). Using
243 summer-time samples collected in Atlanta, Liu et al. (2013) reported a significantly higher BrC MAC
244 value that was associated with primary anthropogenic emissions, compared to the lower MAC value
245 observed at sites with local anthropogenic emissions on top of regional biogenic-dominant emissions
246 (Liu et al., 2013). To investigate whether isoprene photooxidation products enhance or inhibit



247 absorption of aromatic SOA, we conducted two mixed-precursor experiments. Figure 4 shows the
248 comparison of MAC values at 365 nm of SOA formed from single precursor and from mixed isoprene
249 and aromatic VOCs, under high-NO_x conditions. In both isoprene/toluene and isoprene/TMB
250 experiments, the SOA formed has lower MAC values than those formed from the pure aromatics alone.
251 Qualitatively, this is the behavior that one would expect, since non-absorbing isoprene SOA will “dilute”
252 the chromophores from the aromatic-derived SOA. To determine whether the total aerosol absorption
253 can be described quantitatively, we first estimate the mass of aromatic- and isoprene-derived SOA
254 (Table S1) using a partitioning model described in section 2.1. We then calculate predicted aerosol
255 MAC values as the mass-weighted average of the MAC values measured for the pure isoprene- and
256 aromatic- derived SOA species. Figure 4 shows a comparison of the measured and predicted mixed-
257 precursor SOA optical properties. The predicted MAC values are 31%-55% lower than the
258 measurements, a difference that is likely outside of the measurement uncertainty. There are several
259 potential explanations for the difference between the predicted and observed MAC values. First, it is
260 possible that SOA formation is not well-described by partitioning theory. One potential source of error
261 in our calculation is that we assume isoprene and aromatic SOA are fully miscible in one another;
262 however, we note that the total predicted SOA mass is within 10% of the observed SOA mass and hence
263 the underprediction of the MAC values cannot be explained by this error. A second possibility is that
264 the partitioning model underestimates the mass of aromatic SOA that has condensed into the mixed-
265 phase particles. Studies have shown that gas-phase wall loss of toluene reaction products can be
266 significant under certain conditions in batch-mode experiments (Zhang et al., 2014). The SOA yield
267 parameterizations are based on data collected in the absence of seed particles, in which case gas-phase



268 wall loss could be significant. However, isoprene reacts much more quickly than toluene (Figure S2);
269 therefore isoprene SOA should form first and provide surface area which should mitigate gas-phase
270 wall loss of the toluene reaction products. Because no seed particles were present in the pure toluene
271 experiments, we would expect those yield values to be biased low relative to the toluene yield in the
272 mixed precursor experiments, thus potentially explain the underprediction of MAC values. A third
273 possibility is that reactions between organic peroxide and alcohol functionalities known to be the
274 dominant component of isoprene SOA (Krechmer et al., 2015) react with toluene SOA components to
275 produce oligomers capable of absorbing in the UV/VIS. Examination of the AMS spectra in the mixed
276 experiments and comparison to the spectra of the pure aromatic- and isoprene- SOA were inconclusive
277 in providing evidence of this hypothesis. Samples were not collected for detailed analysis by LC-
278 UV/Vis-ESI/HRMS. Therefore, at this time we can't conclusively explain the apparent absorption
279 enhancements we observe.

280

281 3.3 Effect of Relative Humidity on Light Absorption by aromatic SOA

282 In order to investigate the effect of RH on SOA light absorption, both toluene and TMB photo-oxidation
283 experiments were conducted at fixed VOC and NO_x values but variable RH levels (Table 1). Figure 5
284 illustrates the light absorption spectra of toluene- and TMB-derived SOA as a function of experimental
285 RH. The data shown here were from samples collected at a photolysis time of 200 minutes which
286 corresponds to the time when light absorption reached its highest value. In both TMB and toluene
287 experiments, SOA generated under dry conditions (RH <5%) displayed significantly lower MACs than
288 SOA formed at RH>30%. SOA formed at 30, 50 and 80% RH have similar light absorption to one



289 another. Thus moderate RH enhances the MAC values by a factor of 1.33 at 365 nm and further
290 increases in RH have no effect. An overview of toluene-SOA molecular compositions was analyzed by
291 nano-DESI/HRMS(Lin et al., 2015b), and showed that a large number of nitrogen containing
292 compounds (CHON) were produced under moderate RH condition (Figure S3). The difference in
293 molecular compositions suggest that low RH inhibited the formation of nitrogen-containing compounds,
294 which have been shown to be major light absorbers in toluene-SOA formed in the presence of
295 NO_x(Nakayama et al., 2013;Liu et al., 2015b;Zhang et al., 2011;Lin et al., 2015b).

296

297 We are unable to identify any gas-phase reactions in the toluene photolysis mechanism directly
298 involving water vapor. Thus, we conclude that RH must be affecting particle-phase reactions that
299 enhance chromophore formation. Several studies have investigated the effect of RH on various particle-
300 phase SOA chemistry and optical properties. Song et al. (2013) found that SOA produced from α -
301 pinene+NO_x+O₃ in the presence of acidic seed aerosols at elevated RH was less light-absorbing than
302 SOA formed under dry conditions (Song et al., 2013) , which is opposite of our observations. They
303 suggested that the change in light-absorbing properties might be triggered by evaporation of water,
304 which may have enhanced the acidity of aerosol seeds (Nguyen et al., 2012), thereby promoting
305 oligomerization reactions. Zhong et al. (2014) investigated the light absorption of BrC formed from
306 wood burning and observed a faster decay of chromophores at higher RH, which they attributed to the
307 decomposition of chromophores by H₂O₂ that is produced by aqueous-phase photooxidation in the
308 presence of elevated water content level (Zhong and Jang, 2014). Moderate to high RH may promote
309 heterogeneous reactions, which aids in the reactive uptake of volatile compounds into aerosols. Cao and



310 Jang (2010) decoupled SOA mass into partitioning and heterogeneous aerosol production in a toluene-
311 NO_x system, and suggested that moderate RH results in a higher fraction of SOA formed via
312 heterogeneous reactions than low RH conditions (Cao and Jang, 2010). Similar effects might be also
313 pertinent to the toluene SOA. Another possible explanation is that SOA formed under low RH
314 conditions may exist in a viscous, semi-solid, or glassy state due to particle-phase oligomerization
315 reactions (Saukko et al., 2012; Shiraiwa et al., 2013) while SOA formed at moderate/high RH would be
316 less viscous. Since only one experiment was conducted under dry condition for each compound it is
317 difficult to draw conclusions, but further investigations are warranted.

318

319 3.4 Effect of photochemical aging on light absorption of aromatic SOA

320 Atmospheric aerosols have a wide range of lifetimes, ranging from hours to days (i.e., Wagstrom and
321 Pandis, 2009). Previous studies have observed a decrease in aerosol absorption with aging in BrC from
322 various sources including biomass burning and SOA formed from aromatics (Forrister et al.,
323 2015; Zhong and Jang, 2011; Lee et al., 2014). We therefore performed several experiments to study the
324 effect of aging on BrC absorption. Figure 6 shows the MAC values at 365 nm as a function of
325 photolysis time for toluene and TMB SOA produced in the presence of NO_x at 30% RH. We observe a
326 clear decrease in aerosol absorption with aging with MAC values decreasing by ~35% after 400 minutes
327 and >50% after 800 minutes.

328

329 Laboratory studies have suggested that photo-bleaching was due to degradation of BrC chromophores
330 (Lee et al., 2014; Zhong and Jang, 2011; Zhong and Jang, 2014). In our observations, the decrease of



331 MAC with aging is accompanied by a decreasing ON-to-OM ratio, shown in Figure 6. Here we define
332 the term ON as the sum of NO, NO₂ and C_xH_yO_zN_w families measured by AMS, to represent organic
333 nitrates formed during the experiments. NO and NO₂ come exclusively from organic nitrates in these
334 experiments. Ammonium is below the instrument detection limit, and the ratio of m/z 30:46 (around 5-6)
335 is indicative of organic nitrate, thus ruling out formation of ammonium nitrate (Farmer et al., 2010).
336 Therefore, the decrease in the aerosol ON:OM with time indicates the loss of ON groups (Figure 6). ON
337 groups have been identified as the strong light absorbers in aromatic SOA formed under high-NO_x
338 conditions, thus the relative decrease in ON fraction relative to OM is consistent with the observed
339 evolution in OA light absorption.

340

341 This observed loss of ON could be caused by photolysis and/or hydrolysis of ON groups. Lee et al.
342 (2014) has observed a substantial decline in the double bond equivalent (DBE) values upon photolysis
343 of aromatic SOA, and suggested that the decrease in SOA light absorption and chemical composition
344 was due to photolysis (Lee et al., 2014). On the other hand, Liu et al. (2012) suggested that particle-
345 phase hydrolysis could substantially reduce ON group concentration, which they also related to a
346 decrease in BrC light absorption (Liu et al., 2012). To distinguish between the effects from photolysis
347 and hydrolysis, SOA was allowed to age in the chamber with UV lights off but at elevated RH in
348 several experiments. Shown in figure 7, the MAC values of toluene and TMB SOA are approximately
349 constant with aging despite the elevated RH. Therefore, we conclude that decrease in MAC values are
350 driven primarily by photolysis (i.e., photobleaching), which is correlated with loss of ON groups that
351 have been shown in many studies, including our sister study, to be BrC chromophores (Lin et al.,



2015b;Liu et al., 2015b;Zhang et al., 2013). The effect of RH is less clear, with the dark experiments suggesting the net effect of water-related processes, such as hydrolysis and oligomerization, is either negligible or tends to slightly enhance BrC light absorption, while comparison of experiments with and without RH (section 3.3) suggesting moderate RH enhances the SOA MAC values.

3.5 Imaginary refractive indices

So far, our discussion focused on mass-normalized absorption based on solution measurements, which is not directly relatable to light absorption by aerosol particles. Therefore, we derive the imaginary refractive index, k , from spectroscopic data, which can be incorporated into climate models. The k value is derived using equation 2:

$$k = \frac{\rho_p \lambda \cdot Abs(\lambda)}{4\pi \cdot OM} = \frac{\rho_p \lambda}{4\pi} MAC(\lambda) \quad (2)$$

where $Abs(\lambda)$ is the solution absorption at a given wavelength, OM is the organic mass extracted in solution, and ρ_p is the density of organic aerosols. The density of organic aerosols was calculated by comparing the volume-weighted mobility size measured by SMPS and the mass-weighted aerodynamic size distribution measured by AMS (DeCarlo et al., 2004). A density of $1.25 \pm 0.3 \text{ g cm}^{-3}$ was obtained for SOA produced under NO_x -free conditions, while a density of $1.41 \pm 0.2 \text{ g cm}^{-3}$ was estimated for SOA produced in high- NO_x experiments. Those density values were employed in equation 2 to estimate k values at 365 nm for various types of SOA, which are summarized in Table 2 (k values for the 300-700 nm range are listed in Table S2).



372 Although α -pinene and isoprene have large contribution to the global SOA budget, they were shown to
373 produce SOA with very small light absorption coefficients, which agrees with literature data (i.e.,
374 Nakayama et al., 2010;Lang-Yona et al., 2010). The SOA compounds produced are dominated by
375 carbonyl, carboxyl, and hydroxyl functional groups, which do not have strong electronic transitions in
376 the UV/Vis range. As a result, those biogenic SOA particles are expected to have a mostly cooling
377 effect on global radiative balance. However, studies have shown that biogenic SOA can be converted
378 into BrC via reactions with dissolved ammonia (Updyke et al., 2012;Laskin et al., 2014). Furthermore,
379 it has been demonstrated that reactive uptake of IEPOX into acidic aerosols produce BrC (Lin et al.,
380 2014b), which may have substantial impacts on specific regions with elevated ammonia levels and/or
381 active IEPOX chemistry.

382

383 In the present study, the SOA generated from the photooxidation of aromatic VOC precursors,
384 particularly toluene, were found to have significant absorption in the UV/Vis range when formed in the
385 presence of NO_x . Toluene-SOA formed under high- NO_x conditions has a k value ranged from 0.019 to
386 0.047 at 365 nm, and 0.011-0.033 at 405 nm. Shown in Figure 3b, the k values are in good agreement
387 with the measurement by Nakayama et al. (2010), where reported k values were 0.047 at 355 nm and
388 0.007 at 532 nm(Nakayama et al., 2010). The k values reported by Zhong and Jang (2011) and Liu et al.
389 (2015) are close to the lower limit from this work, the former reported a k value of 0.0214 at 350 nm,
390 and the latter reported a range of 0.022-0.033 at 320 nm(Zhong and Jang, 2014;Liu et al., 2015b).
391 However, the k values derived in this work are substantially higher than those in Nakayama et al. (2013),
392 which reported k values ranging from 0.0018 to 0.0072 at 405 nm. A possible explanation is the



393 difference in NO_x levels among the experiments; Zhong and Jang (2011) and Nakayama et al. (2013)
394 studies were conducted at NO_x levels lower than 1 ppmv (Zhong and Jang, 2014; Nakayama et al., 2013),
395 which are lower than employed in our study. Nakayama et al. (2013) has reported that light absorption
396 of SOA has a dependence on NO_x , that MAC increases with NO_x (Nakayama et al., 2013), which likely
397 also explains the higher k values reported by earlier work from the same group (Nakayama et al., 2010).
398 Another potentially important difference among the experiments is the RH, with Nakayama 2013 and
399 the Liu studies conducted under dry conditions (Nakayama et al., 2013; Liu et al., 2015b). From what we
400 have observed, moderate RH could enhance the light absorption of BrC.

401

402 **4. Conclusions and Atmospheric Implications**

403 Among ambient studies reporting BrC light absorption, high MAC values are almost exclusively
404 reported for aerosols attributed to biomass burning (Kirchstetter et al., 2004; Hoffer et al.,
405 2006; Alexander et al., 2008; Dinar et al., 2008; Chakrabarty et al., 2010; Lack et al., 2013), and the
406 limited number of models that include BrC generally use biomass burning aerosol optical properties as
407 high-absorption references (Lin et al., 2014a; Feng et al., 2013). Our results suggest that organic aerosols
408 formed from certain anthropogenic VOC precursors also display efficient light absorption. Specifically,
409 the MAC values obtained from the toluene+high- NO_x experiment were comparable to that of fulvic acid,
410 which has been used as model compounds for biomass burning HULIS (Dinar et al., 2006; Brooks et al.,
411 2004; Chan and Chan, 2003; Fuzzi et al., 2001; Samburova et al., 2005). The results suggest that in
412 addition to BrC from biomass burning, the photooxidation of anthropogenic precursors can also have
413 significant impacts on light absorption at wavelengths that drive photochemical reactions.



414

415 BrC observed in urban environments has large variations in reported MAC values, and our mixed-
416 precursor experiments may provide some explanations for the observed variation. From our
417 measurements, SOA formed from mixtures of isoprene+aromatic VOC have lower MAC values than
418 those formed from the pure aromatics, suggesting that isoprene photooxidation products dilute light-
419 absorbing compounds. Therefore, it is possible that some of the variance in BrC properties between
420 urban sites can be explained by the presence or absence of biogenic emissions. In addition, our results
421 suggested that NO_x concentration, RH level, and photolysis time have considerable influences on the
422 formation and decay of light-absorbing compounds. The result suggests that we should revisit how SOA
423 is treated in climate models, especially in urban areas. Several current regional and global models
424 include NO_x-dependent SOA yield (Lane et al., 2008; Farina et al., 2010; Ahmadov et al., 2012);
425 accurately parameterizing BrC formation from SOA will require a similar strategy.

426

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696 under natural sunlight, *Atmos. Chem. Phys.*, 14, 1517-1525, 10.5194/acp-14-1517-2014, 2014.



698 Table 1. Summary of experiments and experimental conditions described in this work.

Experiment	Experiment type	VOC	Initial VOC concentration (ppb)	Initial NO (ppb)	RH (%)
1	1	isoprene	359.37	<1	30
2	1	α -pinene	22.73	<1	30
3	1	TMB	316.30	<1	30
4	1	toluene	339.92	<1	30
5	2	isoprene	311.45	1754.67	30
6	2	α -pinene	45.45	466.09	30
7	2	TMB	289.94	1589.6	30
8	2	toluene	317.26	1800	30
9	2	Isoprene+TMB	178.51+123.71	1800	30
10	2	Isoprene+toluene	158.09+106.43	1800	30
11	3	TMB	263.58	1500	30
12	3	toluene	339.92	1900	30
13	4	TMB	263.58	1800	<5
14	4	TMB	263.58	1800	50
15	4	TMB	263.58	1800	80
16	4	Toluene	396	1800	<5
17	4	Toluene	300	1800	50
18	4	Toluene	339.92	1800	80

699

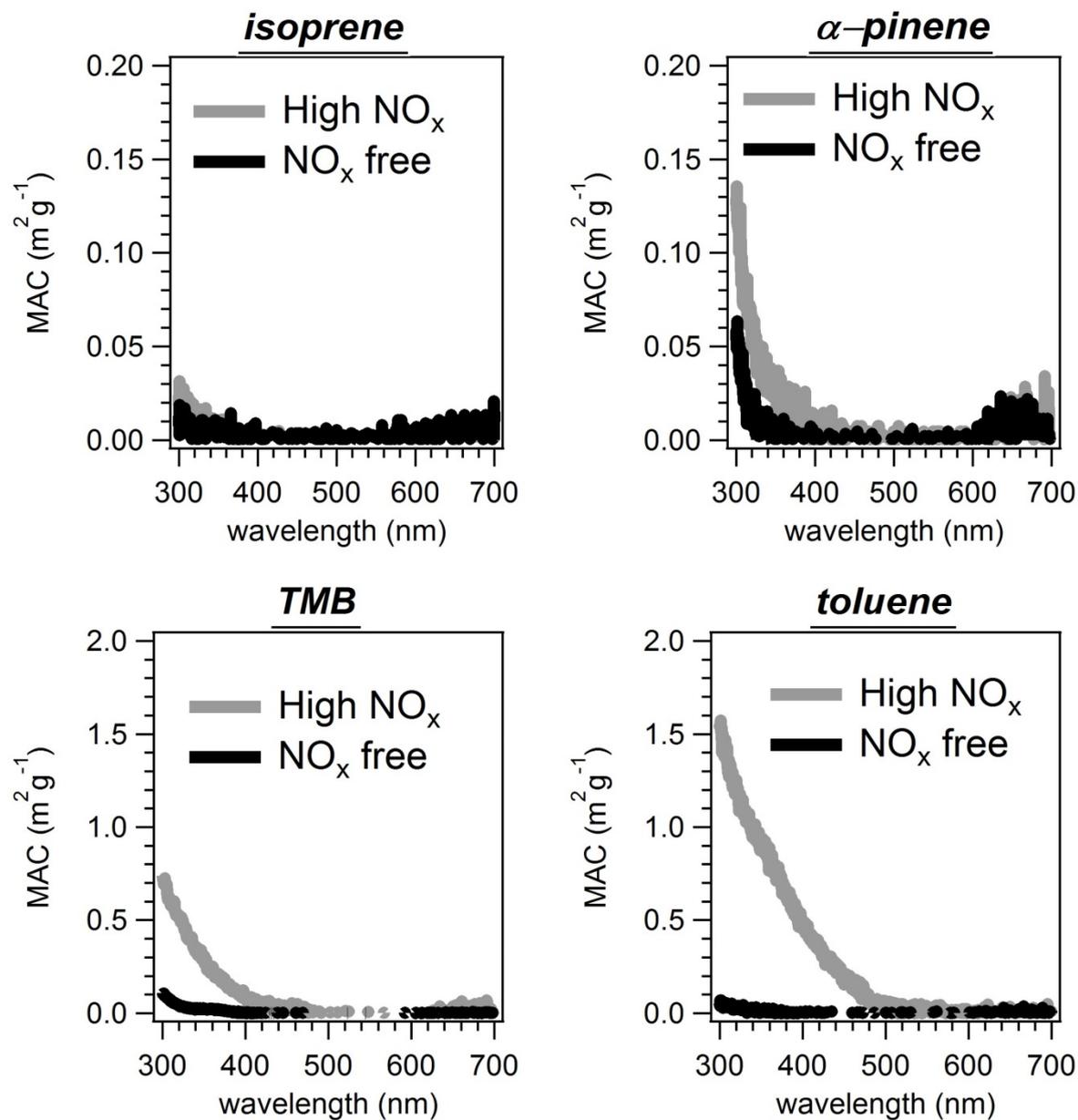
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701 Table 2. Derived imaginary part of refractive index (k) of brown carbon formed from various VOC
702 precursors at 365 nm. Tabulated values are $k \times 10^3$.

	NO _x -free	High-NO _x
Isoprene	0.029	0.196
α-pinene	0	1.15
TMB	0.967	6.028-9.899
toluene	0.461	19.48-46.87

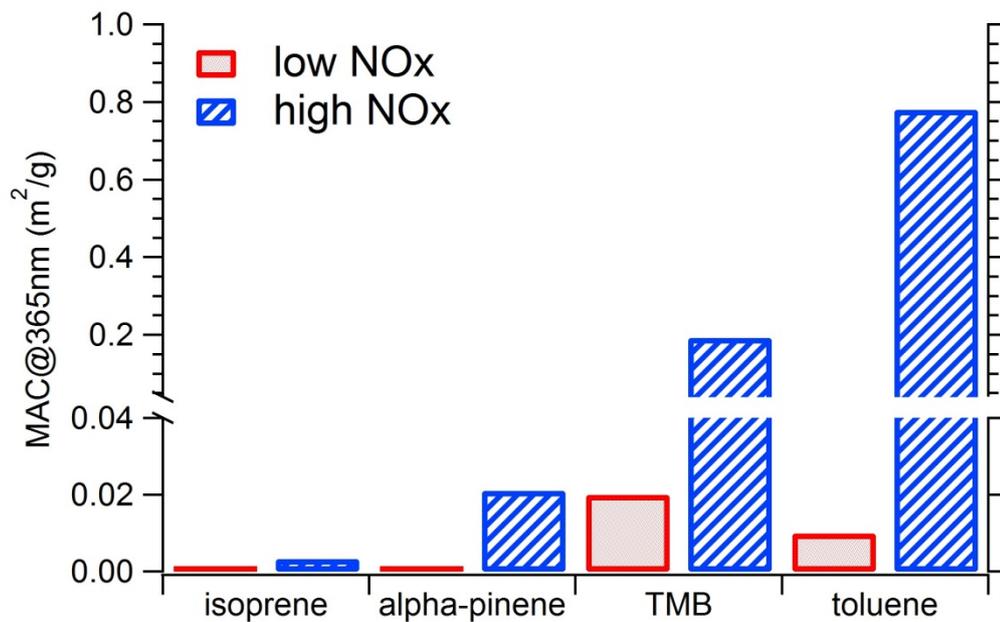
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704

705 Figure 1. MAC values for SOA formed under NO_x -free and high- NO_x conditions, from isoprene, α -
706 pinene, TMB, and toluene. Note the 10 \times difference in scale between the terpene and aromatic
707 precursors.

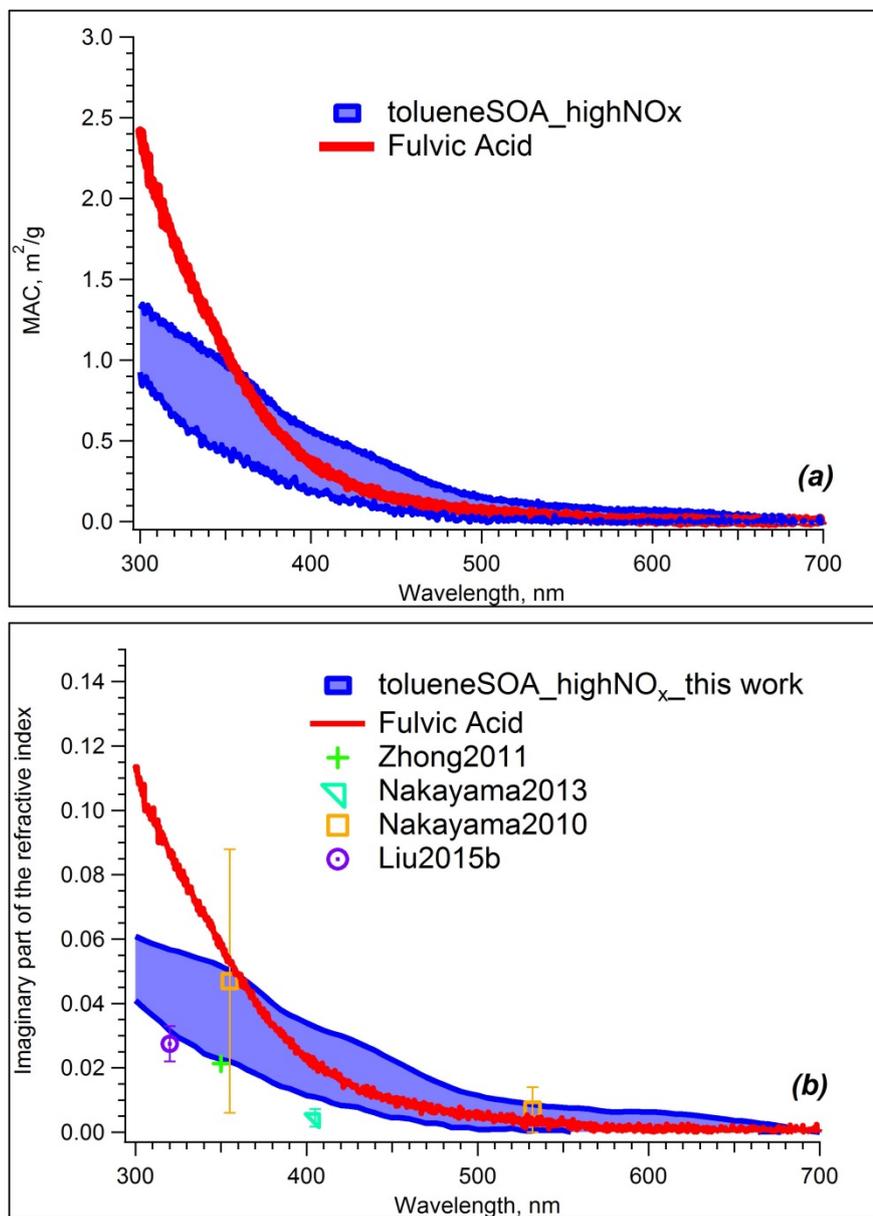
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710 Figure 2. Comparison of MAC from various types of SOA, at a wavelength of 365 nm.

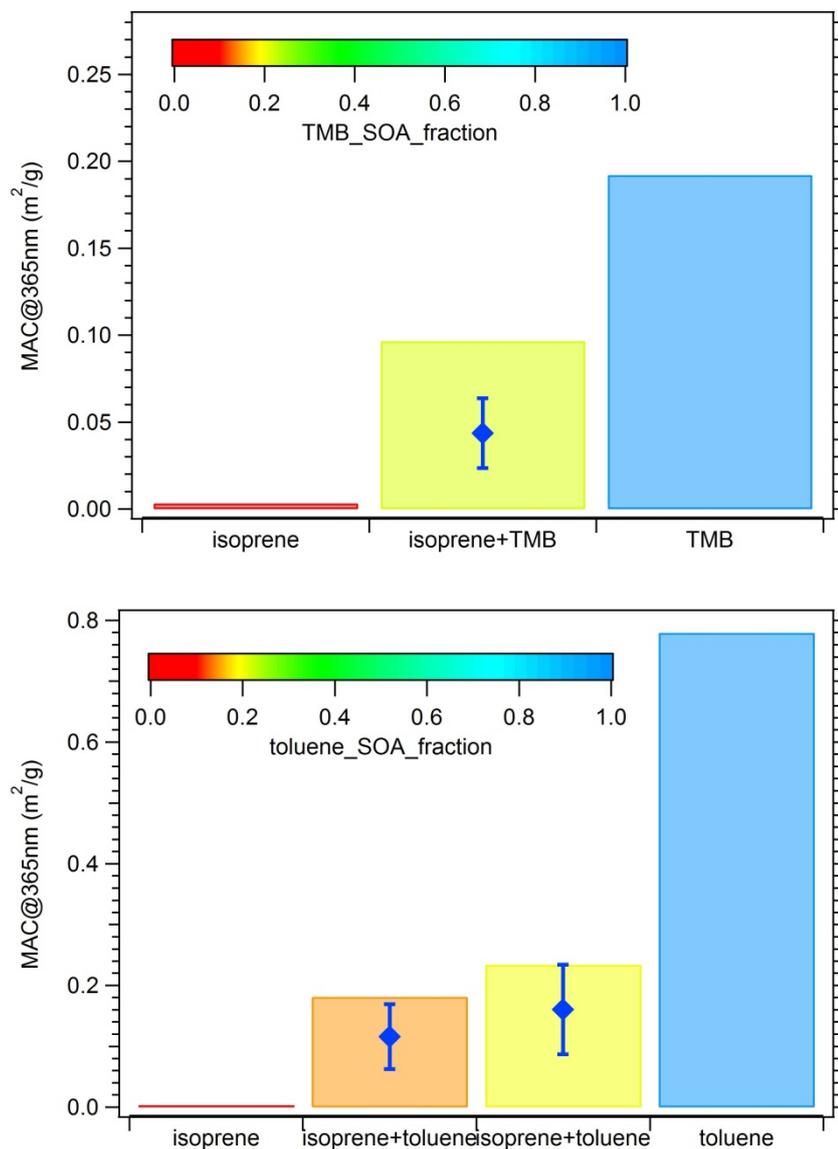
711



712

713 Figure 3. (a) MAC values of Suwanee River fulvic acid (SRFA), and toluene-SOA formed at different
714 high- NO_x conditions. (b) Imaginary part of the refractive index, k , derived from toluene high- NO_x SOA
715 measurements through the 300-700 nm range, with SRFA and literature data as references (Nakayama
716 et al., 2010; Nakayama et al., 2013; Liu et al., 2015b; Zhong and Jang, 2011). SRFA k values were
717 estimated assuming a density of 1.47 g cm^{-3} (Dinar et al., 2006).

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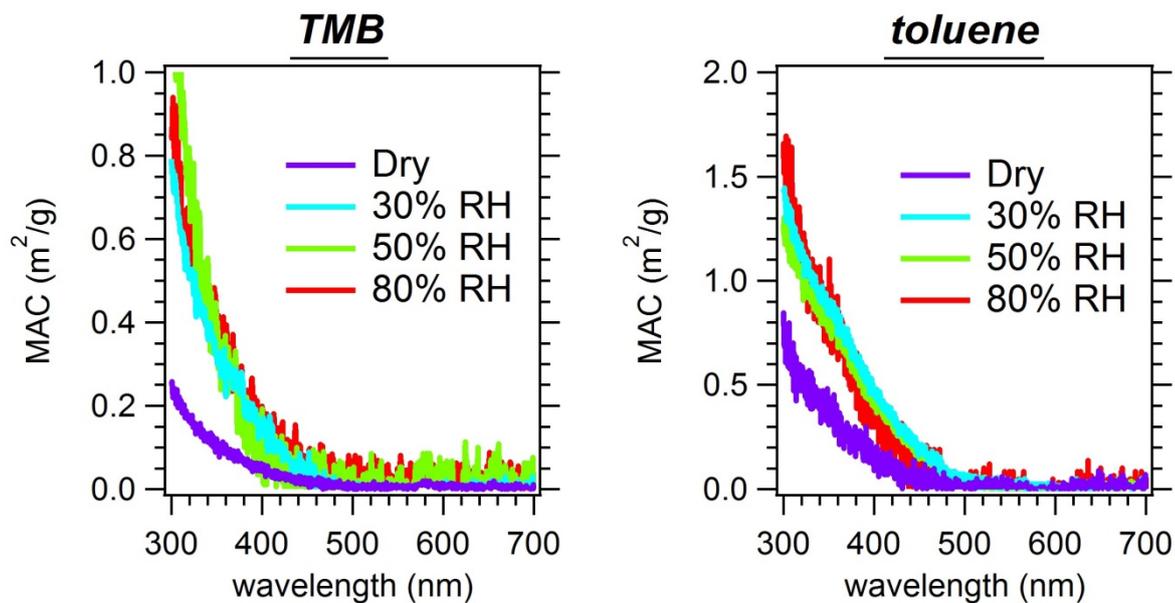
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720 Figure 4. Comparison of MAC values from single-precursor and mixed precursor experiments. Bars
721 represent the MAC values at 365 nm from measurements, and are color-coded by the mass fraction of
722 aromatic SOA. The blue diamonds represent the predicted MAC values based on the modeled fraction
723 of isoprene SOA and aromatic SOA, with error bars indicating the uncertainty.

724



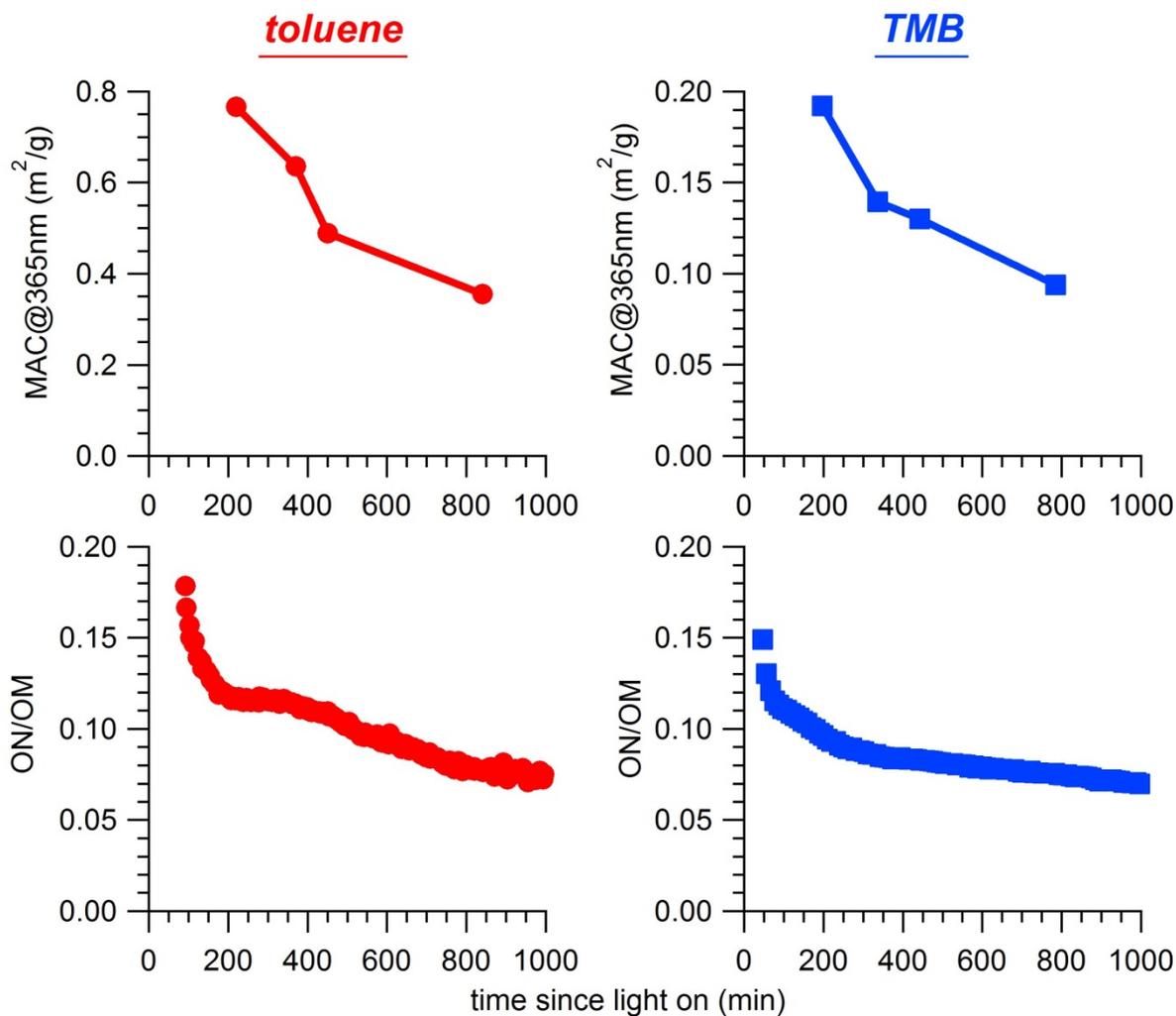
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727 Figure 5. MAC spectra of TMB and toluene SOA formed at <5%, 30%, 50% and 80% RH.

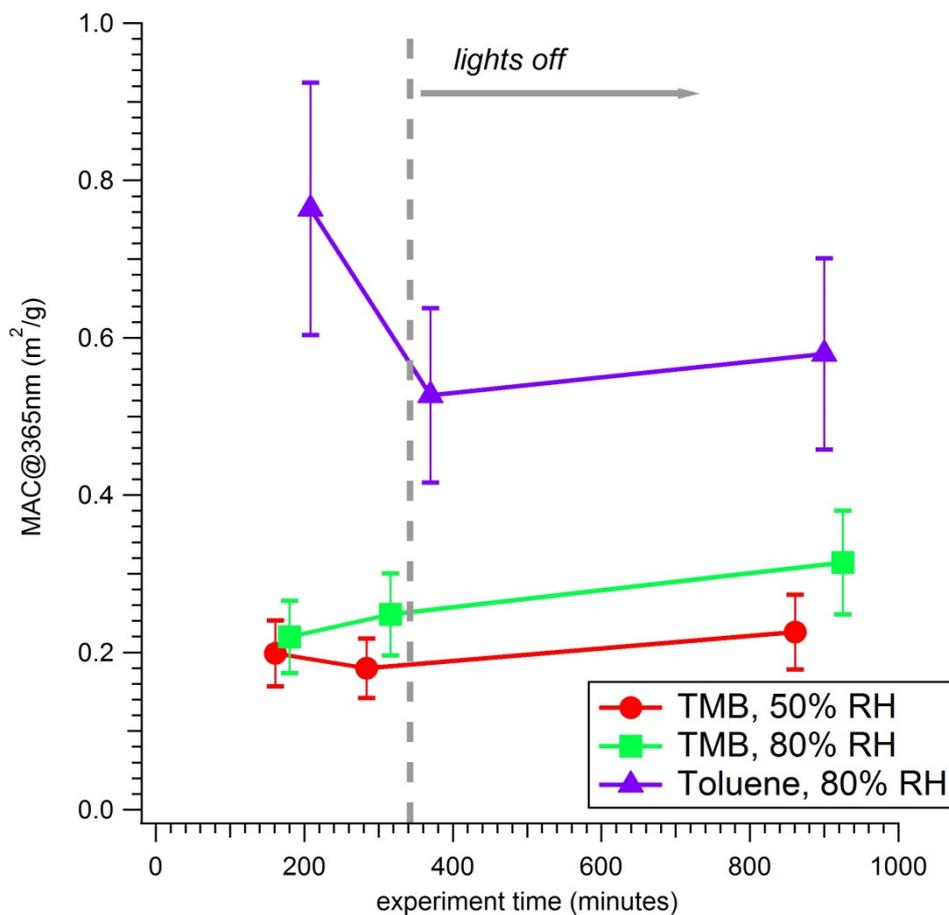
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729

730 Figure 6. Measurements of the MAC values (at 365 nm) of toluene and TMB SOA formed at 30% RH in
731 the presence of NO_x as a function of photochemical age (top panels). The bottom panels show the
732 AMS-measured ON-to-OM ratio.

733



734

735 Figure 7. MAC values of aromatic SOA formed under high NO_x conditions and aged in the chamber
736 with the lights off at different RH levels.

737