

**Ultraviolet and Visible Complex Refractive Indices of Secondary Organic Material
Produced by Photooxidation of the Aromatic Compounds Toluene and *m*-Xylene**

by

P. F. Liu (1), N. Abdelmalki (1), H.-M. Hung (1, 2), Y. Wang (1), W. H. Brune (3), and S. T.
Martin* (1, 4)

(1) School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA

(2) Department of Atmospheric Sciences, National Taiwan University, Taipei, Taiwan

(3) Department of Meteorology, Pennsylvania State University, University Park, PA, USA

(4) Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA

E-mail: scot_martin@harvard.edu

<http://www.seas.harvard.edu/environmental-chemistry>

Submitted: July 2014

Revised: November, 2014

Atmospheric Chemistry and Physics

*To Whom Correspondence Should be Addressed

1 **Abstract**

2 Secondary organic material (SOM) produced by the oxidation of anthropogenic volatile
3 organic compounds can be light-absorbing (i.e., brown carbon). Spectral data of the optical
4 properties, however, are scarce. The present study obtained the continuous spectra of the real and
5 imaginary refractive indices ($m = n - i k$) in the ultraviolet (UV)-to-visible region using
6 spectroscopic ellipsometry for n and UV-visible spectrometry for k . Several different types of
7 SOM were produced in an oxidation flow reactor by photooxidation of toluene and m -xylene for
8 variable concentrations of nitrogen oxides (NO_x). The results show that the k values of the
9 anthropogenically derived material were at least ten times greater than those of the biogenically
10 derived material. The presence of NO_x was associated with the production of organonitrogen
11 compounds, such as nitro-aromatics and organonitrates, which enhanced light absorption.
12 Compared with the SOM derived from m -xylene, the toluene-derived SOM had larger k values,
13 as well as a greater NO_x -induced enhancement, suggesting different brown-carbon-forming
14 potentials of different aromatic precursor compounds. The results imply that anthropogenic SOM
15 produced around urban environments can have an important influence on ultraviolet irradiance,
16 which might consequently influence photochemical cycles of urban pollution.

17 **1. Introduction**

18 Aerosol particles affect many atmospheric processes. Globally, aerosol particles
19 influence Earth's radiative balance both directly by scattering and absorbing solar radiation and
20 indirectly by acting as cloud nuclei. At the urban and regional scale, aerosol particles contribute
21 to the degradation of visibility (Chen et al., 2012) and adversely influence human health
22 (Dockery et al., 1993). A major fraction of the ambient particle population is secondary organic
23 material (SOM) produced by oxidation of anthropogenic and biogenic gaseous precursors
24 (Kanakidou et al., 2005;Hallquist et al., 2009). The magnitude and properties of SOM, however,
25 are still poorly represented in models (Heald et al., 2005;Volkamer et al., 2006).

26 Ultraviolet-absorbing components in atmospheric particles can significantly reduce
27 ultraviolet (UV) irradiation, thus affecting photochemistry in the atmospheric boundary layer
28 (Jacobson, 1999;Barnard et al., 2008). Modeling the optical properties and radiative effects,
29 however, requires spectral data of complex refractive indices ($m = n - i k$), including both the
30 refractory index n and the absorptive index k . Lack of this information, especially in the UV
31 region (300-400 nm), hampers an understanding of the photochemical effect of anthropogenic
32 SOM.

33 In highly polluted urban regions, anthropogenic aromatic compounds constitute up to
34 70% of the non-methane hydrocarbons (Ran et al., 2012). Among the anthropogenic aromatics,
35 toluene and xylenes are the most abundant compounds, and the yields for the production of SOM
36 from these compounds are high (Odum et al., 1996;Odum et al., 1997;Ng et al.,
37 2007;Hilderbrandt et al., 2009;Zhang et al., 2014). Quantitative estimates of the climate effects
38 of anthropogenic SOM, however, remain limited for several different reasons, including the
39 incomplete knowledge of chemical composition and optical properties.

40 The gas- and particle-phase chemistry of aromatic oxidation is complex, and a broad
41 spectrum of products is produced from the oxidation of a single precursor (Forstner et al.,
42 1997;Jang and Kamens, 2001a). The concentration of nitrogen oxides (NO_x) further influences
43 the product distribution (Sato et al., 2007). Some of the molecular products resulting from the
44 oxidation of aromatic precursors have been identified and quantified (Forstner et al.,
45 1997;Cocker III et al., 2001;Jang and Kamens, 2001a;Hamilton et al., 2005;Sato et al., 2007).
46 These products, however, typically constitute less than 50% of the reacted carbon (Forstner et al.,
47 1997;Hamilton et al., 2005;Sato et al., 2007). Particle-phase reactions have been proposed as an
48 important mechanism of SOM production from aromatic precursors, which may explain the
49 uncharacterized components of aromatic-derived SOM (Jang and Kamens, 2001a;Jang et al.,
50 2002;Kalberer et al., 2004).

51 The chemical complexity of SOM propagates into the optical properties. Recent studies
52 have shown that different types of SOM have varying light-absorbing properties in the ultraviolet
53 (UV) and visible regions of the electromagnetic spectrum (Nakayama et al., 2010;Lambe et al.,
54 2013;Liu et al., 2013). Some types of SOM absorb light significantly in the UV-visible region
55 and are then considered constituents of so-called “brown carbon” (Shapiro et al., 2009;Laskin et
56 al., 2010;Updyke et al., 2012;Zarzana et al., 2012). In particular, several studies have pointed out
57 that aromatic-derived SOM is an important class of UV absorbers. The investigated precursors
58 have included phenolic catechol and guaiacol (Ofner et al., 2011;Lambe et al., 2013;Liu et al.,
59 2013), polycyclic aromatic naphthalene (Lambe et al., 2013), and monocyclic toluene
60 (Nakayama et al., 2010;Zhong and Jang, 2011;Zhong et al., 2012;Nakayama et al., 2013;Li et al.,
61 2014).

62 In the present work, the spectroscopic complex refractive indices of several types of
63 aromatic-derived SOM are measured using spectroscopic ellipsometry for n (Liu et al., 2013)
64 and UV-visible spectroscopy for k . The SOMs were produced from the photooxidation of toluene
65 and *m*-xylene in an oxidation flow reactor, both in the absence of NO_x (hereafter "low NO_x "; <
66 70 ppt) and in the presence of NO_x at different levels (hereafter "high NO_x "). For the high- NO_x
67 experiments, the initial NO_x concentration varied from 2.5 to 10 ppm, corresponding to initial
68 hydrocarbon: NO_x ratios of 3.5 to 16 ppbC ppbN⁻¹. In complement to the optical measurements,
69 the chemical composition was characterized by the infrared spectroscopy. The paper concludes
70 with a case study of light-absorbing particles in an urban plume. Based on the calculations using
71 a Mie-theory-based optical model, possible radiative effects of brown carbon from
72 anthropogenically derived SOMs are discussed.

73 **2. Experimental**

74 **2.1 Production of Secondary Organic Material**

75 Toluene (EMD Chemicals, $\geq 99.8\%$) and *m*-xylene (Sigma Aldrich, $\geq 99\%$) were
76 continuously injected by a syringe pump (Chemyx, Fusion 200) into a glass round-bottom flask
77 (Ace glass, 100 mL). The flask was held at 310 K, and the organic liquids vaporized at the tip of
78 a syringe prior to the formation of a falling drop. The resulting gas-phase molecules were swept
79 in a flow of pure air (Aadco 737 Pure Air Generator; 1.0 L min⁻¹) into an oxidation flow reactor
80 (OFR). The injected precursor concentration was 5.0 ± 0.5 ppm, which was calculated from the
81 injection rate of the liquid into the flow rate of the reactor.

82 Aerosol particles composed of secondary organic material were produced in the oxidation
83 flow reactor (Kang et al., 2007; Lambe et al., 2011). Aromatic precursors were oxidized by
84 hydroxyl radicals (OH) (Figure 1), and some of the resulting low-volatility products contributed

85 to new particle production in the OFR. The experimental conditions are listed in Table 1. The
86 OFR was operated at a temperature of 293 ± 2 K, a flow rate of 7.0 ± 0.1 L min⁻¹, and a
87 residence time of 110 ± 2 s. Hydroxyl radicals were produced by photochemical reactions
88 involving ozone and water inside the OFR, as follows: (i) $O_3 + h\nu$ (254 nm) $\rightarrow O_2 + O(^1D)$
89 followed by (ii) $O(^1D) + H_2O \rightarrow 2 OH$. Ozone was generated outside the reactor by irradiating
90 pure air with the ultraviolet emissions of a mercury lamp ($\lambda = 185$ nm). The injected ozone
91 concentration was 13 ± 2 ppm. Water vapor was introduced by bubbling ultrapure water
92 (18.2 M Ω -cm) with air. The relative humidity inside the reactor was $13 \pm 3\%$.

93 The experiments were conducted for several different concentrations of NO_x. For “low
94 NO_x” experiments, no NO_x was added, and the nitric oxide (NO) concentration in the pure air
95 was below the detection limit of the NO_x analyzer (Eco Physics CLD 899 Y; <70 ppt NO_x). For
96 “high NO_x” experiments, NO of 2.5 to 10 ppm was injected using a mass flow controller (Table
97 1). In a control experiment to assess the possible importance of ozonolysis, in the dark the
98 produced particle mass concentration was 0.1% of that obtained when the ultraviolet lamps were
99 illuminated, indicating that photooxidation was the major pathway of SOM production.

100 **2.2 Spectroscopic Ellipsometry**

101 Spectroscopic ellipsometry of SOM films followed the procedures introduced in Liu et al.
102 (2013). Thin, continuous, mirror-like films of SOM were synthesized by electrostatic deposition
103 of aerosol particles onto silicon substrates. Information about film preparation and
104 characterization was provided in Liu et al. (2013). Spectroscopic ellipsometry was carried out
105 across 280 to 1200 nm at different incident angles using a variable-angle spectroscopic
106 ellipsometer (J.A. Woollam VASE). From the data sets, film thickness, film non-uniformity, and
107 wavelength-dependent real refractive indices n were retrieved using the WVASE32 software

108 package (J.A. Woollam VASE). Individual film thickness ranged from 100 to 350 nm. The non-
109 uniformity in film thickness was 5 to 10% over the ellipsometric sampling spot. An absence of
110 systematic error in retrieved refractive indices, as related to film thickness or film non-uniformity,
111 was confirmed previously (Liu et al., 2013).

112 For each thin film sample, duplicate measurements were conducted at two or more
113 different spots. The retrieved n values agreed with each other within an absolute difference of
114 0.015. An overall uncertainty of n , taking both the reproducibility and the fitting error into
115 account, was within ± 0.015 (10 and 90% confidence interval) across the studied wavelength
116 range from 280 to 1200 nm. As a confirmation of the overall approach, the n values retrieved for
117 squalane, a non-absorbing standard, and nigrosin dye, a light-absorbing standard, were consistent
118 with literature values (cf. supporting information in Liu et al., 2013).

119 **2.3 Ultraviolet-Visible Spectroscopy**

120 Particles were collected onto Teflon filters (Millipore FGLP, 0.2 μm pore size). The
121 collected SOM mass was determined by weighing the filter before and after sample collection
122 using an analytical balance (Sartorius, LA120S; 2.0 to 10.0 mg, with an uncertainty of 0.1 mg).
123 The filters were extracted in methanol (40.0 to 100.0 mL) while ultrasonicing (Branson 2510;
124 20 min). The concentration c was calculated from the measured SOM mass and the volume of
125 solvent. An extraction efficiency of 100% was assumed (Updyke et al., 2012). The extract was
126 pipetted into a quartz cuvette having an optical length of 10 mm. Absorbance spectra were
127 recording using an ultraviolet-visible spectrometer (Agilent Model 8453). The spectrum of neat
128 methanol was used as baseline. Analysis of blank filters showed no absorbance across the
129 studied region of 240 to 800 nm.

130 The imaginary refractive indices k were calculated from the data sets, as follows (Sun et
131 al., 2007):

$$132 \quad k = \frac{\ln(10)}{4\pi} \frac{\rho\lambda}{cL} A(\lambda) \quad (1)$$

133 for an absorbance A , an optical path length L (m), a material density ρ (kg m^{-3}), and a
134 concentration c (kg m^{-3}). A material density of $(1.4 \pm 0.1) \times 10^3 \text{ kg m}^{-3}$ was used in the analysis
135 for toluene- and *m*-xylene-derived SOMs (Ng et al., 2007). For Suwannee river fulvic acid, a
136 material density of $(1.47 \pm 0.02) \times 10^3 \text{ kg m}^{-3}$ was used (Dinar et al., 2006). For the k values
137 derived from UV-visible spectroscopy, propagation of uncertainties in ρ , c , and $A(\lambda)$ leads to an
138 overall uncertainty of $\pm 15\%$ (10 and 90% confidence interval) for $\lambda < 420 \text{ nm}$.

139 In an alternative to the UV-visible spectroscopy, the k values are also retrieved by
140 ellipsometry (Liu et al., 2013). A comparison of k values derived from UV-visible spectroscopy
141 and to those from ellipsometry is provided in the supporting information (cf. Fig. S1). Overall
142 agreement is good. For the smallest k values (< 0.005), the ellipsometry retrievals have
143 uncertainties approaching $> 50\%$. The uncertainties for UV-visible spectroscopy are considerably
144 smaller ($< 15\%$). Even so, this method requires sample extraction, and artifacts associated with
145 extraction efficiency, material density, and solvent effect can be introduced. All factors
146 considered, the k values derived from UV-visible spectroscopy were adopted in this study for
147 further analysis.

148 **2.4 Infrared Spectroscopy**

149 Aerosol particles were collected on Teflon filters (Sartorius Stem, $0.2 \mu\text{m}$) at a flow rate
150 of 2 L min^{-1} for up to 24 h. The collected mass on the filters ranged from 0.8 to 2.0 mg. The
151 Teflon filter was cut to the shape of the germanium element of an Attenuated Total Reflectance
152 (ATR) accessory (Pike Technologies). The assembly was then screw-pressed to the crystal

153 surface, the holder was opened, and the filter was peeled off. A thin layer of secondary organic
154 material remained on the surface of the crystal (Hung et al., 2012). An experiment using a blank
155 filter showed no residual signal from the Teflon filter after peeling. This preparation method
156 avoided interference from Teflon filters across 900-1250 cm^{-1} (Russell et al., 2009b; Russell et al.,
157 2011; Takahama et al., 2012), which otherwise obscured the absorption bands of C–O stretching.

158 After preparation, the filter samples were taken for spectroscopy analysis. Infrared
159 spectra were recorded using the ATR accessory in a Fourier Transform Infrared Spectrometer
160 (FTIR, Nicolet 670). The spectral resolution was 0.5 cm^{-1} . The number of scans was 16.
161 Additional information about the ATR-FTIR protocols is provided in Hung et al. (2012). A band
162 fitting algorithm, implemented in MATLAB, was used to analyze the infrared spectra. The
163 algorithm was adopted from Russell et al. (2009a) and Takahama et al. (2012). The absorption
164 bands of alkanes (C–H), carboxylic hydroxyls (O–H), alcoholic hydroxyls (O–H), and carbonyls
165 (C=O) were identified using the literature-described algorithm. The algorithm was further
166 developed in the present study to characterize nitrate ($-\text{ONO}_2$), nitro ($-\text{NO}_2$), and ether (C–O–C)
167 groups.

168 **3. Results and Discussion**

169 **3.1 Optical Properties of Aromatic-derived SOMs and the Effect of NO_x**

170 The wavelength-dependent absorptive component k of the refractive index is plotted in
171 Fig. 2a for toluene- and *m*-xylene-derived SOMs prepared at several different initial NO
172 concentrations (cf. Table S1 for tabulated data). The k values increase with increasing initial NO
173 concentration. For toluene-derived SOMs, the k values at 405 nm range from 0.0017 to 0.0153.
174 These values compare to a range of 0.0018 to 0.0072 reported by Nakayama et al. (2013) for
175 SOMs produced by toluene photooxidation in an environmental chamber.

176 The increase of k for high NO_x can in part be explained by the production of light-
177 absorptive organonitrogen compounds, mostly nitro-aromatic compounds, such as nitrophenols,
178 nitrocatechols, and dinitrophenols (cf. Section 3.2). These compounds have been identified as
179 products from toluene photooxidation under high- NO_x conditions (Forstner et al., 1997;Jang and
180 Kamens, 2001b;Sato et al., 2007;Zhong et al., 2012;Nakayama et al., 2013). Nitro-aromatic
181 compounds have also been identified in brown carbon sampled in urban plumes dominated by
182 anthropogenic SOM (Zhang et al., 2011;Zhang et al., 2013). The spectra for several methyl-
183 nitrophenol isomers were measured (cf. Section S1), and the results confirm that these
184 compounds are strong UV absorbers. In particular, the aromatic compounds having hydroxyl and
185 nitro groups in *para* substitution, such as 2-methyl-4-nitrophenol (a major product of aromatic
186 photooxidation), have a strong absorption band at 320 nm. Compounds having this configuration
187 are good candidates for contribution to the main peak in the difference spectra Δk (i.e., $\Delta k = k -$
188 $k_{\text{NO}_0=0}$) (Fig. 2b).

189 For similar reaction conditions, the *m*-xylene-derived SOMs are less absorptive than the
190 toluene-derived SOMs (Fig. 3a; Table 1). The filter samples of toluene-derived SOMs have a
191 yellowish to light brownish color, even for samples collected in low- NO_x experiments. For
192 comparison, *m*-xylene samples have a light yellowish color only for high- NO_x experiments and
193 are visually white otherwise.

194 The k values of the aromatic-derived SOMs can be compared to those of other light-
195 absorbing material relevant to atmospheric aerosol particles (Fig. 4). The k values decrease for
196 increasing wavelength for the aromatic-derived SOMs. Similar wavelength-dependent behavior
197 is observed for light-absorbing carbonaceous materials referred to as “brown carbon” in literature
198 (Kirchstetter et al., 2004;Andreae and Gelencser, 2006;Hoffer et al., 2006;Alexander et al.,

199 2008;Dinar et al., 2008;Chakrabarty et al., 2010;Cappa et al., 2012;Lack et al., 2013). In
200 contradistinction, the value of k for black carbon is independent of wavelength (Kirchstetter et al.,
201 2004). Compared to the k values of SOMs derived from examples of biogenic precursors (B-
202 SOM), such as α -pinene and limonene SOM (Liu et al., 2013), the k values of the studied
203 anthropogenic SOMs (A-SOM) are one order of magnitude more absorptive in the UV-visible
204 region, even for those produced at low NO_x . These higher values suggest that conjugated double
205 bonds are retained in some oxidation products, which have absorption transitions in the
206 ultraviolet to near visible (Lambe et al., 2013). Even so, the k values in the low- NO_x experiments
207 are smaller than those of a reference compound like Suwannee river fulvic acid, which is often
208 cited as a surrogate of atmospheric humic-like substances (HULIS) (Gelencsér et al., 2003). In
209 the high- NO_x experiments, however, the k values are within the range of atmospheric brown
210 carbon (cf. shaded region in Fig. 4).

211 The real refractive indices n of toluene- and m -xylene- derived SOMs are shown in Fig. 5
212 for several different initial NO concentrations. The n values decrease for increasing wavelength.
213 The curves can be parameterized by the three-term form of Cauchy's equation (cf. Table S2).
214 The Cauchy-form of the curves for the studied anthropogenic SOMs also holds for the biogenic
215 SOMs reported previously (Liu et al., 2013).

216 The refractive indices n shift +0.02 for both toluene- and m -xylene-derived SOMs for an
217 increase of the initial NO concentration from 0 to 10 ppm (Fig. 5). This upward shift of n for
218 increasing initial NO concentration is possibly attributed to an increasing abundance of nitrogen
219 in the SOM produced at higher initial NO concentrations. Nitrogen has a higher atomic
220 polarizability (1.03 \AA^3) than both oxygen (0.57 \AA^3) and hydrogen (0.17 \AA^3) (Bosque and Sales,
221 2002). The n value of a material is related to its polarizability by the Lorentz-Lorenz equation

222 (Bosque and Sales, 2002). Within the tolerance of the measurement uncertainty, the n values do
223 not differ between SOMs derived from the two different aromatic precursors at the same initial
224 NO_x concentration. The implication could be that the n values of SOMs are mainly determined
225 by bulk chemical properties, such as the elemental ratios or functional groups (cf. Section 3.2
226 and 3.3). Detailed chemical properties, such as the molecular structure, might play a minor role
227 in determining the value of n . In this case, upscaling of the laboratory parameterizations to large-
228 scale models of the effects of different types of SOMs on radiative forcing and climate is
229 simplified (Lambe et al., 2013; Flores et al., 2014; Kim et al., 2014). As a caveat, the SOMs of
230 this study were produced at mass concentrations much higher than typical atmospheric
231 concentrations. Both elemental composition and refractive index can depend on mass
232 concentration (Shilling et al., 2009; Kim et al., 2012; Kim and Paulson, 2013), and further
233 investigations are needed to quantify this possible effect.

234 **3.2 Production of Organonitrogen Compounds and Light Absorption**

235 The infrared spectra in the presence and absence of NO_x are similar, except for
236 organonitrogen groups, such as $-\text{NO}_2$ and $-\text{ONO}_2$ (Fig. 6). This similarity suggests that the
237 oxygen-containing functional groups, excluding nitrogen-containing groups, are substantially
238 similar for SOMs produced at the different NO_x concentrations. SOMs derived from toluene and
239 *m*-xylene also have similar overall compositions.

240 Organonitrogen compounds are detected in SOM collected in high- NO_x experiments. The
241 bands at 846, 1281, and 1647 cm^{-1} , corresponding to organonitrate groups ($-\text{ONO}_2$), are present
242 in both toluene- and *m*-xylene-derived SOMs (Roberts, 1990; Liu et al., 2012). The area of the $-\text{ONO}_2$
243 band from 1610 to 1690 cm^{-1} , when normalized by the alkane C–H bands from 2790 to
244 2980 cm^{-1} to account for different masses on the filters, increases for greater initial NO

245 concentrations (Fig. 3c). Comparison of the spectrum of the toluene-derived SOM to that of *m*-
246 xylene-derived SOM for fixed initial NO_x concentration shows that the –ONO₂ fractions are
247 approximately equal for both types of SOMs produced. The dominant mechanism for –ONO₂
248 production, which is the reaction of peroxy radicals (RO₂) with NO (Roberts, 1990), can explain
249 why the fraction of –ONO₂ increases for greater NO concentrations.

250 In the high-NO_x experiments, –NO₂ groups are produced. For the toluene-derived SOM,
251 the production of –NO₂ groups is indicated by a strong band at 1558 cm⁻¹ and a weak band at
252 1342 cm⁻¹ (Fig. 6a). For *m*-xylene-derived SOM, only the strong band at 1558 cm⁻¹ is observed
253 (Fig. 6b). Based on an analysis of area ratios, the mole fraction of –NO₂ groups in the *m*-xylene-
254 derived SOM is 35 to 50% lower than that in the toluene-derived SOM for fixed initial NO_x
255 concentration (Fig. 3c). The production mechanism of –NO₂ group has been proposed as the
256 adduction of –NO₂ to phenoxy radicals to produce nitrophenols (Forstner et al., 1997;Jang and
257 Kamens, 2001b;Nakayama et al., 2013). Compared to toluene, the alkyl substitution at a *meta*
258 site of *m*-xylene can inhibit the production of stable –NO₂ adducts of phenoxy radicals
259 (Nakayama et al., 2013), which can explain the lower –NO₂ fraction observed for *m*-xylene-
260 derived SOM.

261 The difference in –NO₂ fraction explains in part but not entirely the differences in *k*
262 values for toluene- compared to *m*-xylene-derived SOMs (cf. Section 3.1). When normalized by
263 –NO₂ fractions and for similar reaction conditions, Δ*k* at 320 nm for toluene-derived SOM is 50%
264 higher than that of *m*-xylene-derived SOM. The implication is that the compounds in toluene-
265 derived SOM are more UV-absorptive than those in *m*-xylene-derived SOM. Differences in the
266 extent of conjugation of the oxygenated products can be important. The *k* values in the UV
267 region at low NO_x (*k*_{NO₀=0}) provide a baseline to quantify this influence. When normalized by

268 both $k_{\text{NO}_0=0}$ and $-\text{NO}_2$ fraction, the two types of SOM are similarly absorptive (Fig. 3d).
269 Organonitrogen groups attached to a conjugated chain can have increased light absorption as
270 well as shifts in absorption to longer wavelengths.

271 3.3 Oxygenated Groups and the Importance of Particle-Phase Reactions

272 The infrared spectra show that several different types of oxygenated functional groups are
273 present in the SOMs (Fig. 6). The groups include alcoholic hydroxyls (O–H) at 3100-3700 cm^{-1} ,
274 carboxylic hydroxyls (O–H) at 2400-3300 cm^{-1} , carboxylic carbonyls (C=O), and mixed
275 ketones/aldehydes (C=O) at 1640-1850 cm^{-1} . The spectra of aromatic-derived SOMs are similar
276 to those reported in the literature for related SOMs (Jang and Kamens, 2001a; Liu et al., 2012).
277 The new finding of the present study is the presence of a strong C–O stretch at 1000-1260 cm^{-1}
278 (cf. Table S3). This band was obscured in previous studies by ammonium sulfate or Teflon filter.
279 As explained for Figure 7, this C–O band cannot be explained by alcohols, phenols, cyclic
280 anhydrides, carboxylic acids, or other carbonyls that have been identified as major products from
281 oxidation reactions of aromatic precursors.

282 Figure 7 shows a ternary diagram representing the relative areas of O–H, C–O, and C=O
283 bands for toluene- and *m*-xylene-derived SOMs (cf. Section S2). Reference compounds having
284 different types of oxygenated functional group are also plotted. The ternary diagram groups
285 different types of oxygenated compounds into clusters. The individual products from
286 photooxidation of toluene identified by gas chromatography/mass spectrometry (GC/MS) are
287 plotted for comparison (Forstner et al., 1997). The cluster representing the toluene- and *m*-
288 xylene-derived SOMs is uniquely situated and differentiated from the reference compounds
289 because of the C–O stretch at 1000-1260 cm^{-1} .

290 This absorption band at 1000-1260 cm^{-1} is plausibly contributed by an ether group (C–O–
291 C) of acetals and hemiacetals produced via particle-phase reactions (Jang et al., 2002;Kroll and
292 Seinfeld, 2008;Lim et al., 2010). These reactions tend to drive product distribution toward the C–
293 O vertex of the composition diagram (cf. arrow in Fig. 7). The gas-phase oxidation of aromatic
294 precursors produces dialdehydes in high yields, including glyoxal and methylglyoxal. These
295 dialdehydes readily oligomerize along hemiacetal and acetal pathways, with associated changes
296 in the C–O/C=O stretch band ratio (Loeffler et al., 2006). Hemiacetal/acetal production reactions
297 leading to oligomerization can occur in SOM produced by photooxidation of trimethylbenzene
298 (TMB), even in the absence of catalysis by sulfuric acid (Kalberer et al., 2004).

299 The mole fraction of each functional group is estimated using the absorptivity of Russell
300 et al. (2009b) and Takahama et al. (2012), along with the area ratios of ether (C–O–C) to alkane
301 (C–H) bands for 19 ether and acetal compounds appearing in the NIST database. The analysis
302 concludes that ether groups constitute up to 50% of the SOM mass. This result agrees with a
303 modeling study suggesting that 20-80% of the SOM derived from toluene is produced by
304 particle-phase reactions (Cao and Jang, 2009). These particle-phase reactions can produce
305 oligomers having conjugated structures that contribute to the light absorption even in the absence
306 of nitrogen moieties (Zhong et al., 2012).

307 **3.4 Atmospheric Implications**

308 For the obtained spectral data sets of n and k (Section 3.1), the optical effects of brown
309 carbon (BrC) from anthropogenic SOM can be assessed. A model case study is formulated to
310 represent light-absorbing particles in a fresh urban plume close to the anthropogenic sources.
311 Parameters defining the case study are listed in Table 2. The case study considers a population of
312 brown carbon particles produced by photooxidation of anthropogenic aromatic precursors in the

313 presence of NO_x . This population is compared with populations of black carbon (BC) particles
314 (representing emissions from fossil fuel combustion) and externally mixed at variable ratios with
315 ammonium sulfate particles (representing the regional background atmospheric aerosol). The
316 number-diameter distributions of the BrC and sulfate particle populations are representative of
317 polluted urban regions (Wu et al., 2008). The BC particle population having a relatively smaller
318 mode diameter is typical for fresh soot particles emitted from motor vehicles (Kleeman et al.,
319 2000). The investigated ratios of BC and ammonium sulfate are representative of Asian outflows
320 (Ramana et al., 2010). The external mixing assumption is consistent with the small absorption
321 enhancement of BC in urban regions (Cappa et al., 2012). The single-scattering albedo ω ,
322 defined as the ratio of scattering to total extinction, is calculated for each population and their
323 mixtures using a Mie-theory-based optical model (Bohren and Huffman, 1983; Liu et al., 2013)
324 (Fig. 8a). The relative contribution of BrC absorption to total light absorption (i.e., $\text{BrC}/(\text{BrC} +$
325 $\text{BC})$) is calculated as a function of the mass ratio of organic matter to BC. The calculated results
326 for $\lambda = 320, 405, \text{ and } 550 \text{ nm}$ are plotted in Fig. 8b. These three wavelengths are selected
327 because solar radiation in these bands respectively regulates O_3 photolysis, NO_2 photolysis, and
328 energy balance (cf. Fig. 8a).

329 Results of the case study have several implications for climate and atmospheric chemistry
330 modeling. The ω values of the BrC particle populations are close to unity for $\lambda > 500 \text{ nm}$ (Fig.
331 8a). When externally mixed with BC, the studied BrC has a negligible contribution to light
332 absorption at 550 nm (Fig. 8b). These results indicate that these BrC populations have a net
333 cooling effect. The ω values, however, decrease below unity for $\lambda < 400 \text{ nm}$, meaning that the
334 particle population becomes absorptive in the UV region. Although the solar irradiance in the
335 UV region contributes only 10% of the total solar irradiation, meaning a small heating effect by

336 brown carbon for the conditions of the case study, the effect can still be important because UV
337 irradiance determines the photolysis rates of many chemical species (Fig. 8a). For example,
338 reduced UV irradiance for $\lambda < 320$ nm slows ozone photolysis, thus suppressing the production of
339 OH radicals (Martin et al., 2003;Tie et al., 2003). The case study suggests that BrC populations
340 can have a substantial contribution for light absorption in this band (Fig. 8b). For a mass ratio of
341 organic matter to BC in a range of 2 to 20, which is typical for urban atmosphere (Turpin et al.,
342 1991), BrC accounts for 15-80% of the UV absorption at 320 nm. The photolysis of NO₂ is
343 similarly suppressed by reduced UV irradiance for $\lambda < 405$ nm, thus inhibiting the production of
344 ozone (Dickerson et al., 1997;Martin et al., 2003). The implication is that, as an effective UV
345 absorber, BrC influences the production of O₃ and OH by reducing UV irradiance and
346 consequently affects the oxidation capacity of the regional atmosphere.

347 In conclusion, photooxidation of toluene and *m*-xylene in the presence of NO_x can
348 produce SOMs having *k* values similar to those reported for brown carbon in biomass burning
349 and urban plumes (Kirchstetter et al., 2004;Hoffer et al., 2006;Alexander et al., 2008;Dinar et al.,
350 2008;Chakrabarty et al., 2010;Cappa et al., 2012;Lack et al., 2013). The implication is that the
351 photooxidation of anthropogenic precursors can be a significant source of atmospheric brown
352 carbon. These findings are consistent with atmospheric observations in urban regions, such as the
353 Los Angeles basin (Zhang et al., 2011;Cappa et al., 2012;Zhang et al., 2013), Mexico city
354 (Barnard et al., 2008), and Beijing (Cheng et al., 2011). The case studies considered in the
355 present study suggest that anthropogenic brown carbon, along with brown carbon from biomass
356 burning, can have a major influence on light absorption at wavelengths that drive photochemical
357 reactions. This effect needs to be evaluated in the future modeling studies of atmospheric
358 chemistry.

Acknowledgments

This study was funded under NASA grant #NNX12AG95G through the Radiation Science Program and NSF grant #AGS-1244995. This work was performed in part at the Harvard Center for Nanoscale Systems (CNS), a member of the NSF National Nanotechnology Infrastructure Network (NNIN). Pengfei Liu acknowledges support from the NASA Earth and Space Science Fellowship Program. We thank the Vecitis Lab from Harvard University for providing a sample of the Suwannee river fulvic acid.

References

- Alexander, D. T. L., Crozier, P. A., and Anderson, J. R.: Brown carbon spheres in East Asian outflow and their optical properties, *Science*, 321, 833-836, 10.1126/science.1155296, 2008.
- Andreae, M. O., and Gelencser, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, *Atmos. Chem. Phys.*, 6, 3131-3148, 10.5194/acp-6-3131-2006, 2006.
- Barnard, J. C., Volkamer, R., and Kassianov, E. I.: Estimation of the mass absorption cross section of the organic carbon component of aerosols in the Mexico City Metropolitan Area, *Atmos. Chem. Phys.*, 8, 6665-6679, 10.5194/acp-8-6665-2008, 2008.
- Bohren, C. F., and Huffman, D. R.: *Absorption and scattering of light by small particles*, Wiley, New York, 530 pp., 1983.
- Bond, T. C., and Bergstrom, R. W.: Light absorption by carbonaceous particles: an investigative review, *Aerosol Sci. Technol.*, 40, 27-67, 10.1080/02786820500421521, 2006.
- Bosque, R., and Sales, J.: Polarizabilities of solvents from the chemical composition, *J. Chem. Inf. Comput. Sci.*, 42, 1154-1163, 10.1021/ci025528x, 2002.
- Cao, G., and Jang, M.: An SOA model for toluene oxidation in the presence of inorganic aerosols, *Environ. Sci. Technol.*, 44, 727-733, 10.1021/es901682r, 2009.
- Cappa, C. D., Onasch, T. B., Massoli, P., Worsnop, D. R., Bates, T. S., Cross, E. S., Davidovits, P., Hakala, J., Hayden, K. L., Jobson, B. T., Kolesar, K. R., Lack, D. A., Lerner, B. M., Li, S.-M., Mellon, D., Nuaaman, I., Olfert, J. S., Petäjä, T., Quinn, P. K., Song, C., Subramanian, R., Williams, E. J., and Zaveri, R. A.: Radiative absorption enhancements due to the mixing state of atmospheric black carbon, *Science*, 337, 1078-1081, 10.1126/science.1223447, 2012.
- Chakrabarty, R. K., Moosmüller, H., Chen, L. W. A., Lewis, K., Arnott, W. P., Mazzoleni, C., Dubey, M. K., Wold, C. E., Hao, W. M., and Kreidenweis, S. M.: Brown carbon in tar balls from smoldering biomass combustion, *Atmos. Chem. Phys.*, 10, 6363-6370, 10.5194/acp-10-6363-2010, 2010.
- Chen, J., Zhao, C. S., Ma, N., Liu, P. F., Göbel, T., Hallbauer, E., Deng, Z. Z., Ran, L., Xu, W. Y., Liang, Z., Liu, H. J., Yan, P., Zhou, X. J., and Wiedensohler, A.: A parameterization of low visibilities for hazy days in the North China Plain, *Atmos. Chem. Phys.*, 12, 4935-4950, 10.5194/acp-12-4935-2012, 2012.
- Cheng, Y., He, K. B., Zheng, M., Duan, F. K., Du, Z. Y., Ma, Y. L., Tan, J. H., Yang, F. M., Liu, J. M., Zhang, X. L., Weber, R. J., Bergin, M. H., and Russell, A. G.: Mass absorption efficiency of elemental carbon and water-soluble organic carbon in Beijing, China, *Atmos. Chem. Phys.*, 11, 11497-11510, 10.5194/acp-11-11497-2011, 2011.
- Cocker III, D. R., Mader, B. T., Kalberer, M., Flagan, R. C., and Seinfeld, J. H.: The effect of water on gas-particle partitioning of secondary organic aerosol: II. m-xylene and 1,3,5-trimethylbenzene photooxidation systems, *Atmos. Environ.*, 35, 6073-6085, 10.1016/S1352-2310(01)00405-8, 2001.
- Dickerson, R. R., Kondragunta, S., Stenchikov, G., Civerolo, K. L., Doddridge, B. G., and Holben, B. N.: The impact of aerosols on solar ultraviolet radiation and photochemical smog, *Science*, 278, 827-830, 10.1126/science.278.5339.827, 1997.
- Dinar, E., Mentel, T. F., and Rudich, Y.: The density of humic acids and humic like substances (HULIS) from fresh and aged wood burning and pollution aerosol particles, *Atmos. Chem. Phys.*, 6, 5213-5224, 10.5194/acp-6-5213-2006, 2006.

- Dinar, E., Abo Riziq, A., Spindler, C., Erlick, C., Kiss, G., and Rudich, Y.: The complex refractive index of atmospheric and model humic-like substances (HULIS) retrieved by a cavity ring down aerosol spectrometer (CRD-AS), *Faraday Discuss.*, 137, 279-295, 10.1039/b703111d, 2008.
- Dockery, D. W., Pope, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris, B. G., and Speizer, F. E.: An association between air pollution and mortality in six U.S. cities, *N. Engl. J. Med.*, 329, 1753-1759, doi:10.1056/NEJM199312093292401, 1993.
- Flores, J. M., Zhao, D. F., Segev, L., Schlag, P., Kiendler-Scharr, A., Fuchs, H., Watne, Å. K., Bluvshstein, N., Mentel, T. F., Hallquist, M., and Rudich, Y.: Evolution of the complex refractive index in the UV spectral region in ageing secondary organic aerosol, *Atmos. Chem. Phys.*, 14, 5793-5806, 10.5194/acp-14-5793-2014, 2014.
- Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol from the photooxidation of aromatic hydrocarbons: molecular composition, *Environ. Sci. Technol.*, 31, 1345-1358, 10.1021/es9605376, 1997.
- Gelencsér, A., Hoffer, A., Kiss, G., Tombácz, E., Kurdi, R., and Bencze, L.: In-situ formation of light-absorbing organic matter in cloud water, *J. Atmos. Chem.*, 45, 25-33, 10.1023/a:1024060428172, 2003.
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155-5236, 10.5194/acp-9-5155-2009, 2009.
- Hamilton, J. F., Webb, P. J., Lewis, A. C., and Reviejo, M. M.: Quantifying small molecules in secondary organic aerosol formed during the photo-oxidation of toluene with hydroxyl radicals, *Atmos. Environ.*, 39, 7263-7275, 2005.
- Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H., and Weber, R. J.: A large organic aerosol source in the free troposphere missing from current models, *Geophys. Res. Lett.*, 32, L18809, 10.1029/2005GL023831, 2005.
- Hildebrandt, L., Donahue, N. M., and Pandis, S. N.: High formation of secondary organic aerosol from the photo-oxidation of toluene, *Atmos. Chem. Phys.*, 9, 2973-2986, 10.5194/acp-9-2973-2009, 2009.
- Hoffer, A., Gelencsér, A., Guyon, P., Kiss, G., Schmid, O., Frank, G. P., Artaxo, P., and Andreae, M. O.: Optical properties of humic-like substances (HULIS) in biomass-burning aerosols, *Atmos. Chem. Phys.*, 6, 3563-3570, 10.5194/acp-6-3563-2006, 2006.
- Hung, H.-M., Chen, Y.-Q., and Martin, S. T.: Reactive aging of films of secondary organic material studied by infrared spectroscopy, *J. Phys. Chem. A*, 117, 108-116, 10.1021/jp309470z, 2012.
- Jacobson, M. Z.: Isolating nitrated and aromatic aerosols and nitrated aromatic gases as sources of ultraviolet light absorption, *J. Geophys. Res.*, 104, 3527-3542, 10.1029/1998JD100054, 1999.
- Jang, M. S., and Kamens, R. M.: Characterization of secondary aerosol from the photooxidation of toluene in the presence of NO_x and 1-propene, *Environ. Sci. Technol.*, 35, 3626-3639, 10.1021/es010676+, 2001a.

- Jang, M. S., and Kamens, R. M.: Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst, *Environ. Sci. Technol.*, 35, 4758-4766, 10.1021/es010790s, 2001b.
- Jang, M. S., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, *Science*, 298, 814-817, 10.1126/science.1075798, 2002.
- Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A. S. H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., and Baltensperger, U.: Identification of polymers as major components of atmospheric organic aerosols, *Science*, 303, 1659-1662, 10.1126/science.1092185, 2004.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5, 1053-1123, 10.5194/acp-5-1053-2005, 2005.
- Kang, E., Root, M. J., Toohey, D. W., and Brune, W. H.: Introducing the concept of Potential Aerosol Mass (PAM), *Atmos. Chem. Phys.*, 7, 5727-5744, 10.5194/acp-7-5727-2007, 2007.
- Kim, H., Barkey, B., and Paulson, S. E.: Real refractive indices and formation yields of secondary organic aerosol generated from photooxidation of limonene and α -pinene: the effect of the HC/NO_x ratio, *J. Phys. Chem. A*, 116, 6059-6067, 10.1021/jp301302z, 2012.
- Kim, H., and Paulson, S. E.: Real refractive indices and volatility of secondary organic aerosol generated from photooxidation and ozonolysis of limonene, α -pinene and toluene, *Atmos. Chem. Phys.*, 13, 7711-7723, 10.5194/acp-13-7711-2013, 2013.
- Kim, H., Liu, S., Russell, L. M., and Paulson, S. E.: Dependence of real refractive indices on O:C, H:C and mass fragments of secondary organic aerosol generated from ozonolysis and photooxidation of limonene and α -pinene, *Aerosol Sci. Technol.*, 48, 498-507, 10.1080/02786826.2014.893278, 2014.
- Kirchstetter, T. W., Novakov, T., and Hobbs, P. V.: Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon, *J. Geophys. Res.*, 109, D21208, 10.1029/2004jd004999, 2004.
- Kleeman, M. J., Schauer, J. J., and Cass, G. R.: Size and composition distribution of fine particulate matter emitted from motor vehicles, *Environ. Sci. Technol.*, 34, 1132-1142, 10.1021/es981276y, 2000.
- Kroll, J. H., and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, *Atmos. Environ.*, 42, 3593-3624, 10.1016/j.atmosenv.2008.01.003, 2008.
- Lack, D. A., Bahreini, R., Langridge, J. M., Gilman, J. B., and Middlebrook, A. M.: Brown carbon absorption linked to organic mass tracers in biomass burning particles, *Atmos. Chem. Phys.*, 13, 2415-2422, 10.5194/acp-13-2415-2013, 2013.
- Lambe, A.T., A.T. Ahern, L.R. Williams, J.G. Slowik, J.P.S. Wong, J.P.D. Abbatt, W.H. Brune, N.L. Ng, J.P. Wright, D.R. Croasdale, D.R. Worsnop, P. Davidovits, T.B. Onasch, Characterization of aerosol photooxidation flow reactors: heterogeneous oxidation, secondary organic aerosol formation and cloud condensation nuclei activity measurements, *Atmos. Meas. Tech.*, 4, 445-461, 10.5194/amt-4-445-2011, 2011.
- Lambe, A. T., Cappa, C. D., Massoli, P., Onasch, T. B., Forestieri, S. D., Martin, A. T., Cummings, M. J., Croasdale, D. R., Brune, W. H., Worsnop, D. R., and Davidovits, P.:

- Relationship between oxidation level and optical properties of secondary organic aerosol, *Environ. Sci. Technol.*, 47, 6349-6357, 10.1021/es401043j, 2013.
- Laskin, J., Laskin, A., Roach, P. J., Slysz, G. W., Anderson, G. A., Nizkorodov, S. A., Bones, D. L., and Nguyen, L. Q.: High-resolution desorption electrospray ionization mass spectrometry for chemical characterization of organic aerosols, *Anal. Chem.*, 82, 2048-2058, 10.1021/ac902801f, 2010.
- Li, K., Wang, W., Ge, M., Li, J., and Wang, D.: Optical properties of secondary organic aerosols generated by photooxidation of aromatic hydrocarbons, *Sci. Rep.*, 4, 10.1038/srep04922, 2014.
- Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, *Atmos. Chem. Phys.*, 10, 10521-10539, 10.5194/acp-10-10521-2010, 2010.
- Liu, P. F., Zhang, Y., and Martin, S. T.: Complex refractive indices of thin films of secondary organic materials by spectroscopic ellipsometry from 220 to 1200 nm, *Environ. Sci. Technol.*, 47, 13594-13601, 10.1021/es403411e, 2013.
- Liu, S., Shilling, J. E., Song, C., Hiranuma, N., Zaveri, R. A., and Russell, L. M.: Hydrolysis of organonitrate functional groups in aerosol particles, *Aerosol Sci. Technol.*, 46, 1359-1369, 10.1080/02786826.2012.716175, 2012.
- Loeffler, K. W., Koehler, C. A., Paul, N. M., and De Haan, D. O.: Oligomer formation in evaporating aqueous glyoxal and methyl glyoxal solutions, *Environ. Sci. Technol.*, 40, 6318-6323, 10.1021/es060810w, 2006.
- Martin, R. V., Jacob, D. J., Yantosca, R. M., Chin, M., and Ginoux, P.: Global and regional decreases in tropospheric oxidants from photochemical effects of aerosols, *J. Geophys. Res.- Atmos.*, 108, 4097, 10.1029/2002jd002622, 2003.
- Nakayama, T., Matsumi, Y., Sato, K., Imamura, T., Yamazaki, A., and Uchiyama, A.: Laboratory studies on optical properties of secondary organic aerosols generated during the photooxidation of toluene and the ozonolysis of alpha-pinene, *J. Geophys. Res.*, 115, D24204, 10.1029/2010jd014387, 2010.
- Nakayama, T., Sato, K., Matsumi, Y., Imamura, T., Yamazaki, A., and Uchiyama, A.: Wavelength and NO_x dependent complex refractive index of SOAs generated from the photooxidation of toluene, *Atmos. Chem. Phys.*, 13, 531-545, 10.5194/acp-13-531-2013, 2013.
- Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, *Atmos. Chem. Phys.*, 7, 3909-3922, 10.5194/acp-7-3909-2007, 2007.
- Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H.: Gas/particle partitioning and secondary organic aerosol yields, *Environ. Sci. Technol.*, 30, 2580-2585, 10.1021/es950943+, 1996.
- Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Flagan, R. C., and Seinfeld, J. H.: The atmospheric aerosol-forming potential of whole gasoline vapor, *Science*, 276, 96-99, 10.1126/science.276.5309.96, 1997.
- Ofner, J., Kruger, H. U., Grothe, H., Schmitt-Kopplin, P., Whitmore, K., and Zetzsch, C.: Physico-chemical characterization of SOA derived from catechol and guaiacol - a model substance for the aromatic fraction of atmospheric HULIS, *Atmos. Chem. Phys.*, 11, 1-15, 10.5194/acp-11-1-2011, 2011.

- Ramana, M. V., Ramanathan, V., Feng, Y., Yoon, S. C., Kim, S. W., Carmichael, G. R., and Schauer, J. J.: Warming influenced by the ratio of black carbon to sulphate and the black-carbon source, *Nature Geosci.*, 3, 542-545, doi:10.1038/ngeo918, 2010.
- Ran, L., Zhao, C. S., Xu, W. Y., Han, M., Lu, X. Q., Han, S. Q., Lin, W. L., Xu, X. B., Gao, W., Yu, Q., Geng, F. H., Ma, N., Deng, Z. Z., and Chen, J.: Ozone production in summer in the megacities of Tianjin and Shanghai, China: a comparative study, *Atmos. Chem. Phys.*, 12, 7531-7542, 10.5194/acp-12-7531-2012, 2012.
- Roberts, J. M.: The atmospheric chemistry of organic nitrates, *Atmos. Environ.*, 24, 243-287, 10.1016/0960-1686(90)90108-Y, 1990.
- Russell, L. M., Bahadur, R., Hawkins, L. N., Allan, J., Baumgardner, D., Quinn, P. K., and Bates, T. S.: Organic aerosol characterization by complementary measurements of chemical bonds and molecular fragments, *Atmos. Environ.*, 43, 6100-6105, 10.1016/j.atmosenv.2009.09.036, 2009a.
- Russell, L. M., Takahama, S., Liu, S., Hawkins, L. N., Covert, D. S., Quinn, P. K., and Bates, T. S.: Oxygenated fraction and mass of organic aerosol from direct emission and atmospheric processing measured on the R/V Ronald Brown during TEXAQS/GoMACCS 2006, *Journal of Geophysical Research: Atmospheres*, 114, D00F05, 10.1029/2008jd011275, 2009b.
- Russell, L. M., Bahadur, R., and Ziemann, P. J.: Identifying organic aerosol sources by comparing functional group composition in chamber and atmospheric particles, *Proc. Natl. Acad. Sci. U. S. A.*, 108, 3516-3521, 10.1073/pnas.1006461108, 2011.
- Sato, K., Hatakeyama, S., and Imamura, T.: Secondary organic aerosol formation during the photooxidation of toluene: NO_x dependence of chemical composition, *J. Phys. Chem. A*, 111, 9796-9808, 10.1021/jp071419f, 2007.
- Shapiro, E. L., Szprengiel, J., Sareen, N., Jen, C. N., Giordano, M. R., and McNeill, V. F.: Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics, *Atmos. Chem. Phys.*, 9, 2289-2300, 2009.
- Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., DeCarlo, P. F., Aiken, A. C., Sueper, D., Jimenez, J. L., and Martin, S. T.: Loading-dependent elemental composition of alpha-pinene SOA particles, *Atmos. Chem. Phys.*, 9, 771-782, 2009.
- Sun, H., Biedermann, L., and Bond, T. C.: Color of brown carbon: A model for ultraviolet and visible light absorption by organic carbon aerosol, *Geophys. Res. Lett.*, 34, L17813, 10.1029/2007gl029797, 2007.
- Takahama, S., Johnson, A., and Russell, L. M.: Quantification of carboxylic and carbonyl functional groups in organic aerosol infrared absorbance spectra, *Aerosol Sci. Technol.*, 47, 310-325, 10.1080/02786826.2012.752065, 2012.
- Tie, X., Madronich, S., Walters, S., Zhang, R., Rasch, P., and Collins, W.: Effect of clouds on photolysis and oxidants in the troposphere, *J. Geophys. Res.*, 108, 4642, 10.1029/2003jd003659, 2003.
- Toon, O. B., Pollack, J. B., and Khare, B. N.: The optical constants of several atmospheric aerosol species: Ammonium sulfate, aluminum oxide, and sodium chloride, *J. Geophys. Res.*, 81, 5733-5748, 10.1029/JC081i033p05733, 1976.
- Turpin, B. J., Huntzicker, J. J., Larson, S. M., and Cass, G. R.: Los Angeles summer midday particulate carbon: primary and secondary aerosol, *Environ. Sci. Technol.*, 25, 1788-1793, 10.1021/es00022a017, 1991.

- Updyke, K. M., Nguyen, T. B., and Nizkorodov, S. A.: Formation of brown carbon via reactions of ammonia with secondary organic aerosols from biogenic and anthropogenic precursors, *Atmos. Environ.*, 63, 22-31, 10.1016/j.atmosenv.2012.09.012, 2012.
- Volkamer, R., Jimenez, J. L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L. T., Worsnop, D. R., and Molina, M. J.: Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, *Geophys. Res. Lett.*, 33, L17811, doi: 10.1029/2006GL026899, 2006.
- Wu, Z., Hu, M., Lin, P., Liu, S., Wehner, B., and Wiedensohler, A.: Particle number size distribution in the urban atmosphere of Beijing, China, *Atmos. Environ.*, 42, 7967-7980, 10.1016/j.atmosenv.2008.06.022, 2008.
- Zarzana, K. J., De Haan, D. O., Freedman, M. A., Hasenkopf, C. A., and Tolbert, M. A.: Optical properties of the products of α -dicarbonyl and amine reactions in simulated cloud droplets, *Environ. Sci. Technol.*, 46, 4845-4851, 10.1021/es2040152, 2012.
- Zhang, X., Lin, Y.-H., Surratt, J. D., Zotter, P., Prevot, A. S. H., and Weber, R. J.: Light-absorbing soluble organic aerosol in Los Angeles and Atlanta: A contrast in secondary organic aerosol, *Geophys. Res. Lett.*, 38, L21810, doi:21810.21029/22011GL049385, 2011.
- Zhang, X., Lin, Y.-H., Surratt, J. D., and Weber, R. J.: Sources, composition and absorption Ångström exponent of light-absorbing organic components in aerosol extracts from the Los Angeles basin, *Environ. Sci. Technol.*, 47, 3685-3693, 10.1021/es305047b, 2013.
- Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, *Proc. Natl. Acad. Sci. U. S. A.*, 111, 5802-5807, 10.1073/pnas.1404727111, 2014.
- Zhong, M., and Jang, M.: Light absorption coefficient measurement of SOA using a UV-Visible spectrometer connected with an integrating sphere, *Atmos. Environ.*, 45, 4263-4271, 10.1016/j.atmosenv.2011.04.082, 2011.
- Zhong, M., Jang, M., Oliferenko, A., Pillai, G. G., and Katritzky, A. R.: The SOA formation model combined with semiempirical quantum chemistry for predicting UV-Vis absorption of secondary organic aerosols, *Phys. Chem. Chem. Phys.*, 14, 9058-9066, 10.1039/c2cp23906j, 2012.

List of Figures

Figure 1. Schematic diagram of experimental apparatus. (i) Production of secondary organic material in aerosol form. (ii) Sampling of particles onto a Teflon filter and growth of a thin film by electrostatic precipitation of particles onto a silicon substrate. (iii) Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-VIS), and spectroscopic ellipsometry of collected secondary organic material.

Figure 2. Absorptive component k of the refractive indices of (column 1) toluene-derived SOMs and (column 2) *m*-xylene-derived SOMs for several different initial NO concentrations. Row 1 shows the k values, and row 2 shows Δk values (i.e., $\Delta k = k - k_{\text{NO}_0=0}$). The k values are derived from UV-Vis measurements (see main text). The shaded regions show confidence intervals of 10% to 90%, as calculated by propagation of individual uncertainties for the parameters of Eq. 1.

Figure 3. (a) Imaginary refractive indices k at 320 nm, (b) real refractive indices n at 320 and 550 nm, (c) the areas of nitro and nitrate absorption bands normalized by the area of alkane bands, all as a function of initial NO concentration. Shown in panel (d) is the ratio of $k/k_{\text{NO}_0=0}$ as a function of the normalized area of nitro band ($A_{\text{-NO}_2}/A_{\text{-C-H}}$), as drawn from panels *a* and *c*. See also note *b* for Table 1.

Figure 4. Comparison of wavelength-dependent k values for different types of atmospherically relevant light-absorbing materials. This study: anthropogenic SOMs (A-SOM)

derived from reacting toluene or *m*-xylene at low NO_x (NO₀ = 0 ppm) and high NO_x (NO₀ = 10 ppm; HC₀/NO₀ = 3.5 and 4.0 ppbC ppbN⁻¹ for toluene and *m*-xylene, respectively), and a brown carbon (BrC) surrogate (Suwannee river fulvic acid). Literature: α -pinene- and limonene-derived biogenic SOMs (B-SOM), various atmospheric BrC in both biomass burning (BB) and urban plumes, and black carbon (BC).

Figure 5. Real refractive indices n of (a) toluene-derived SOMs and (b) *m*-xylene-derived SOMs for several different initial NO concentrations. The shaded regions represent confidence intervals of 10% to 90% for the ellipsometry analysis.

Figure 6. Infrared spectra of (a) toluene-derived SOMs and (b) *m*-xylene-derived SOMs for several different initial NO concentrations. Individual curves are offset from each other so that differences can be seen. Spectra are normalized to the peak height at 1100 cm⁻¹, corresponding to a C–O stretch, to compensate for different masses on the filter samples.

Figure 7. Ternary diagram representing the relative areas of O–H, C–O, and C=O bands for aromatic-derived SOMs. Data for reference compounds in the NIST database, as well as of individual products reported in the literature for toluene-derived SOM, are also shown for comparison. The arrow illustrates the direction of particle-phase reactions. See Section S2 in Supporting Information for further explanation of this diagram.

Figure 8. (a) Calculated single-scattering albedo of light absorbing particles for a scenario of an urban plume. Cumulative distributions for solar irradiance (orange) and photolysis rate coefficients (light blue) are also shown. The k values of BrC were bounded by the cases for *m*-xylene + OH + NO_x (HC₀/NO₀ = 4.0 ppbC ppbN⁻¹) and the toluene + OH + NO_x (HC₀/NO₀ = 3.5 ppbC ppbN⁻¹), as shown in Fig. 4. The cases for “BC + sulfate” represent a BC population externally mixed with an ammonium sulfate population at variable mixing ratios representative of typical ambient values in a pollution plume (Ramana et al., 2010). Table 2 lists the physical parameters used for modeling the several different particle populations. The cumulative distributions were calculated for a standard solar spectrum of *Air Mass 1.5* (<http://rredc.nrel.gov/solar/spectra/am1.5/>). (b) Contribution of BrC absorption to total absorption, as a function of the mass ratio of organic matter to black carbon. The BrC cases were the same as those shown in panel (a). External mixing of BrC and BC populations was assumed in the calculation.

Table 1. Experimental conditions, infrared band areas of organonitrogen groups normalized by the area of alkane bands, and complex refractive indices of the studied SOMs

Precursor	HC ₀ (ppm)	NO ₀ (ppm)	HC ₀ /NO ₀ (ppbC ppbN ¹)	Particle Mass Concentration ($\mu\text{g m}^{-3}$) ^a	Infrared Band Area Ratio ^b		320 nm		405 nm	
					$A_{-\text{NO}_2}/A_{\text{C-H}}$	$A_{-\text{ONO}_2}/A_{\text{C-H}}$	<i>n</i>	<i>k</i> ($\times 10^3$)	<i>n</i>	<i>k</i> ($\times 10^3$)
A1 Toluene	5.0	0.0	n/a	$(2.08 \pm 0.17) \times 10^3$	0.00	0.00	1.567 ± 0.008	11 \pm 1	1.546 ± 0.004	1.7 \pm 0.2
A2 Toluene	5.0	2.5	14	$(1.84 \pm 0.16) \times 10^3$	0.46	0.79	1.570 ± 0.007	22 \pm 2	1.552 ± 0.004	4.1 \pm 0.5
A3 Toluene	5.0	5.0	7.0	$(1.37 \pm 0.15) \times 10^3$	0.94	2.11	1.585 ± 0.007	26 \pm 2	1.562 ± 0.005	6.6 \pm 0.6
A4 Toluene	5.0	10.0	3.5	$(0.77 \pm 0.13) \times 10^3$	1.47	2.68	1.591 ± 0.009	33 \pm 4	1.571 ± 0.005	15.3 \pm 1.6
B1 <i>m</i> -Xylene	5.0	0.0	n/a	$(2.75 \pm 0.10) \times 10^3$	0.00	0.00	1.554 ± 0.011	7 \pm 1	1.531 ± 0.006	0.8 \pm 0.1
B2 <i>m</i> -Xylene	5.0	2.5	16	$(2.81 \pm 0.13) \times 10^3$	0.22	0.78	1.558 ± 0.006	10 \pm 1	1.535 ± 0.004	1.2 \pm 0.3
B3 <i>m</i> -Xylene	5.0	5.0	8.0	$(1.67 \pm 0.10) \times 10^3$	0.46	1.65	1.578 ± 0.012	11 \pm 1	1.549 ± 0.006	1.6 \pm 0.2
B4 <i>m</i> -Xylene	5.0	10.0	4.0	$(0.84 \pm 0.10) \times 10^3$	0.94	2.66	1.589 ± 0.008	15 \pm 1	1.565 ± 0.007	3.0 \pm 0.3

^aValues are shown as (mean \pm one standard deviation) during the sampling periods.

^b $A_{-\text{NO}_2}$ represents the area of $-\text{NO}_2$ band at 1558 cm^{-1} ; $A_{-\text{ONO}_2}$ represents the area of $-\text{ONO}_2$ band at 1647 cm^{-1} ; and $A_{\text{C-H}}$ represents the area of C-H bands from 2790 to 2980 cm^{-1} .

Table 2. Parameters describing the different particle populations used in the case study of Section 3.4.

Type of particles	Particle number-diameter distribution ^a		Material density (kg m ⁻³)	Complex refractive indices
	<i>gmd</i> (nm)	<i>gsd</i>		
Brown carbon				
Toluene + OH + NO _x	100	1.8	1400	wavelength dependent (this study) ^b
<i>m</i> -Xylene + OH + NO _x	100	1.8	1400	wavelength dependent (this study) ^c
Black carbon	50	1.8	1800	1.85 – 0.71 <i>i</i> ^d
Sulfate	100	1.8	1770	1.53 – 0.00 <i>i</i> ^e

^aParameters describing a single-mode log-normal number-diameter distribution for the governing

equation:
$$\frac{dN}{d \log d_p} = N_T \frac{1}{\sqrt{2\pi} gsd} \exp\left[-\frac{(\log d_p - \log gmd)^2}{2gsd^2}\right].$$
 N_T represents the total number

concentration (m⁻³) and d_p represents the particle diameter (nm).

^bValues taken from Experiment A4 (cf. Table 1).

^cValues taken from Experiment B4 (cf. Table 1).

^dValue recommended by Bond and Bergstrom, 2006.

^eValue taken from Toon et al., 1976.