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Molecular Characterization of Brown Carbon (BrC) Chromophores in Secondary Organic Aerosol Generated From Photo-Oxidation of Toluene

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ABSTRACT

Atmospheric Brown carbon (BrC) is a significant contributor to light absorption and climate forcing. However, little is known about a fundamental relationship between the chemical composition of BrC and its optical properties. In this work, light-absorbing secondary organic aerosol (SOA) was generated in the PNNL chamber from toluene photo-oxidation in the presence of NO_x (Tol-SOA). Molecular structures of BrC components were examined using nanospray desorption electrospray ionization (nano-DESI) and liquid chromatography (LC) combined with UV/Vis spectroscopy and electrospray ionization (ESI) high-resolution mass spectrometry (HRMS). The chemical composition of BrC chromophores and the light absorption properties of toluene SOA (Tol-SOA) depend strongly on the initial NO_x concentration. Specifically, Tol-SOA generated under high-NOx conditions (defined here as initial NO_x/toluene of 5/1) appears yellow and mass absorption coefficient of the bulk sample (MAC_{bulk}@365nm = 0.78 m^2 g^{-1}) is nearly 80 fold higher than that measured for the Tol-SOA sample generated under low-NO_x conditions (NO_x/toluene < 1/300). Fifteen compounds, most of which are nitrophenols, are identified as major BrC chromophores responsible for the enhanced light absorption of Tol-SOA material produced in the presence of NO_x. The integrated absorbance of these fifteen chromophores accounts for 40-60% of the total light absorbance by Tol-SOA at wavelengths between 300 nm and 500 nm. The combination of tandem LC-UV/Vis-ESI/HRMS measurements provides an analytical platform for predictive understanding of light absorption properties by BrC and their relationship to the structure of individual chromophores. General trends in the UV/vis absorption by plausible isomers of the BrC chromophores were evaluated using theoretical chemistry calculations. The molecular-level understanding of BrC chemistry is helpful for better understanding the evolution and behavior of light absorbing aerosols in the atmosphere.

1   **INTRODUCTION**

2   Interactions between solar radiation and atmospheric aerosols have significant yet
3   poorly understood impact on the Earth's energy balance and climate forcing.[1] Understanding
4   the chemical composition of aerosols is essential to improve the accuracy of predicting their
5   effects in climate models.[2] Light-absorbing constituents of aerosols are of particular importance
6   due to their warming effect on climate. Optical properties of the strongest light-absorbing
7   atmospheric particles such as black carbon (BC) and mineral dust have been extensively studied
8   in the past and have been incorporated into climate models.[3, 4] However, there is still
9   substantial discrepancy between model predictions and observational data on aerosol
10   absorption and radiative forcing.[5] In part, this gap may be attributed to organic aerosol
11   components that strongly absorb solar radiation in the UV and short wavelengths of visible
12   region.[6] They are collectively referred to as atmospheric "brown carbon (BrC)"[6, 7] because of
13   their apparently yellow to brown color.

14   BrC is recognized as a significant contributor to light absorption and climate forcing.[8] In
15   certain geographic areas or urban environments, BrC may contribute substantially or even
16   dominate the total aerosol absorption at specific wavelengths.[5, 9, 10] Global models estimate
17   that light absorption by BrC in different regions of the world may be 27%-70% of BC light
18   absorption.[11] However, quantitative predictions of the BrC contribution to the overall light
19   absorption is still a challenging task because of its compositional complexity.[12, 13] Numerous
20   studies indicate that both the structure and concentration of BrC chromophores are highly
21   variable across sources and locations.[12, 13] Optical properties of organic compounds strongly
22   depend on their molecular structures. However, little is known about the fundamental
23   relationship between the chemical composition of BrC and its light absorbing properties, which
24   in turn results in high uncertainties in predicting and mitigating their climate effects.[9, 14, 15]

25   The sources of BrC are complex.[12, 13] BrC constituents can be present in primary aerosols
26   emitted from combustion sources,[16] or they also can be formed in secondary organic aerosols
27   (SOA) through various reaction pathways[12] including reactions of ammonia or amines with
28   carbonyl compounds in SOA or cloud droplets,[17, 18, 19, 20] dehydration of oligomers formed
29   through reactive uptake of isoprene epoxydiols,[21] and photooxidation of aromatic volatile
30   organic compounds (VOC).[22-24] Formation of light-absorbing nitro-aromatic compounds has
31   been demonstrated in photooxidation of various aromatic precursors including
32   benz[a]pyrene,[25] naphthalene,[22] catechol and guaiacol,[26, 27] and toluene in the presence of
33   NO$_x$.[28, 29] A theoretical study postulated that nitro- and nitrated aromatic compounds in the gas
34   and aerosol phase may contribute significantly to light absorption within the boundary layer in
35   the Los Angeles area.[30] Nitrophenols and nitrocatechols have been identified as dominant

36   light-absorbing compounds in cloud water samples and PM$_{2.5}$ particles impacted by biomass

37   burning.[31, 32]

38   Toluene is an abundant aromatic VOC and a potential source of anthropogenic SOA

39   formed in polluted urban air.[33, 34] Optical properties of SOA produced from photooxidation of

40   toluene (Tol-SOA) in the presence of NO$_x$ have been discussed in a number of recent papers.[28,

41   29, 35-37] All of these studies reported that the produced Tol-SOA exhibits substantial BrC

42   characteristics. Light absorption by Tol-SOA in the visible range increases dramatically with

43   increase in the initial NO$_x$ concentration in laboratory chamber experiments.[28, 29] Although the

44   chemical composition of Tol-SOA has been extensively studied in the last two decades,[38-41] the

45   direct correlation between light absorption and chemical composition of relevant BrC

46   chromophores has not been established.

47   In this work, we identify and characterize chemical and light-absorbing properties of the

48   most prominent BrC chromophores in Tol-SOA formed under high NO$_x$ conditions. We use

49   nanospray desorption electrospray ionization (nano-DESI) to identify potential BrC

50   chromophores. These species are subsequently analyzed using a combination of high

51   performance liquid chromatography (HPLC) for efficient separation of Tol-SOA constituents, a

52   UV/Vis photodiode array (PDA) detector for detection of light-absorbing molecules eluting from

53   the HPLC column, and an electrospray ionization high-resolution mass spectrometer (ESI/HRMS)

54   for identification of molecular formulas of individual chromophores in Tol-SOA. The LC-UV/Vis-

55   ESI/HRMS platform allows the separation of BrC mixtures into numerous fractions with

56   individual UV-Vis spectra (BrC chromophores) and assessment of their plausible molecular

57   compositions. Chromophores identified in this study are representative of BrC formed in urban

58   areas with strong anthropogenic emissions. Therefore, molecular identification of these

59   chromophores is an important prerequisite for improved understanding of sources and aging

60   chemistry of BrC in the atmosphere.

61   **METHODS**

62   **Generation and sampling of Toluene SOA.** Secondary organic aerosols were prepared in

63   the PNNL 10.6 m^3 Teflon chamber by photooxidation of toluene in the batch mode of operation.

64   Before each experiment, the chamber was flushed with purified air for several hours. Following

65   cleaning, the particle concentration in the chamber was lower than 1 cm^{-3}, and NO$_x$ was lower

66   than 2 ppbv. Toluene was injected into the chamber by passing pure air through a gently

67   heated glass bulb containing a measured volume of the pure compound (Sigma-Aldrich, 99.8%).

68   Initial concentrations of toluene in the chamber were 320 ppbv. H$_2$O$_2$ was used as OH radical

69   precursor, and was introduced into the chamber by passing pure air over 0.5 mL H$_2$O$_2$ (Sigma-

70   Aldrich, 50wt% in H$_2$O) solution. For toluene SOA samples formed under high-NO$_x$ conditions

71   (defined here as initial NO$_x$:toluene = 5:1), NO was injected into chamber from a gas cylinder

72   (Matheson, 500 ppm in N_2). Of note, the definitions of "high NO_x" and "low NO_x" that we use

73   here are rather arbitrarily in comparison with those used in other chamber studies focused on

74   the estimates of SOA yields.[42, 43] For example, in the study of Ng et al.,[43] the "high NO_x"

75   condition was reached by using NO_x:toluene ≈10:1, where the peroxy radicals (RO_2) reacted

76   only with NO. In our work here, the environmental chamber experiments were conducted to

77   generate two sets of the Tol-SOA samples with substantially different optical properties. Thus,

78   the terms of "high NOx" and "low NOx" used in this study are to distinguish these two different

79   samples, and emphasize effects of NO_x on the formation of BrC SOA during toluene photo-

80   oxidation.

81   During the experiment, a suite of online instruments were used to characterize both the

82   gas- and particle-phase composition. The evolution of toluene concentration was tracked by an

83   Ionicon proton-transfer-reaction mass spectrometry (PTR-MS). For aerosols formed in the

84   chamber, number and volume concentrations were measured with a scanning mobility particle

85   spectrometer (SMPS), and mass concentration and compositions was measured by an Aerodyne

86   high-resolution time of flight mass spectrometry (HR-ToF-AMS). A detailed description of the

87   experimental and instrument operation procedures will be presented elsewhere.[44]

88   Tol-SOA samples were collected onto Teflon filters (Pall life sciences, 37 mm, 1 µm pore

89   size) for light absorption measurements. Filters were sonicated in 10 mL of high purity water

90   (18.2 MΩ) to extract water-soluble brown carbon. The liquid extracts were then filtered via a

91   25mm-diameter 0.45 µm pore syringe filter (Fisher Scientific, Fisherbrand™ Syringe Filters) to

92   remove insoluble components, and transferred into a Liquid Waveguide Capillary Cell

93   spectrophotometer to quantify the water-soluble UV-Vis light absorption spectra.[45] The filter

94   was then dried and extracted in 10 mL acetonitrile (AcN hereafter) and transferred into

95   spectrophotometer again to determine the light absorbance by water-insoluble components.

96   The solution absorption due to BrC ($Abs(\lambda)$, Mm^{-1}) is determined as the sum of absorption from

97   both water and acetonitrile extracts, shown below,

98    $$Abs_{H_2O}(\lambda) = (A_{H_2O}(\lambda) - A_{H_2O}(700)) \frac{V_L}{V_a \cdot l} \cdot ln(10) \qquad (1)$$

99    $$Abs_{AcN}(\lambda) = (A_{AcN}(\lambda) - A_{AcN}(700)) \frac{V_L}{V_a \cdot l} \cdot ln(10) \qquad (2)$$

100   $$Abs(\lambda) = Abs_{H_2O}(\lambda) + Abs_{AcN}(\lambda) \qquad (3)$$

101   Measurements are referenced to absorption at 700nm, a region believed to be free of

102   absorption,[16, 46] to account for any signal drift. V_l is the liquid volume the filter is extracted into

103   (10 mL) and V_a the volume of air sampled during the filter collection period (9 L min^{-1} for 1-3

104   hours). l is the waveguide optical path length (1 m in this study) and ln(10) converts from base

105   10 (the form provided by the spectrophotometer) to natural logarithm. The limit of detection

106   (LOD) was 0.066 Mm^{-1}, and the uncertainty was estimated at 13%. Spectrophotometric
107   measurements of the solution light absorption at a given wavelength ($Abs(\lambda)$) were then used
108   to determine the bulk solution mass absorption coefficient (MAC_{bulk}, in units of m^2 g^{-1}) by,

109   $$MAC_{bulk}(\lambda) = \frac{Abs(\lambda)}{M/V_a} \qquad (4)$$

110   Where the aerosol loading on the filter, M, was estimated based on aerosol mass
111   concentration measured by the AMS, the flow rate, and the sample collection time.[44]

112   Size-segregated Tol-SOA samples for detailed chemical analysis were collected onto a
113   second set of Teflon substrates (Whatman, Inc.) using a ten-stage micro orifice uniform
114   deposition impactor (MOUDI, MSP Corp., Shoreview, MN, USA) operating at a flow rate of 30 L
115   min^{-1}. The Teflon filters were weighed using a microbalance before and after sampling to obtain
116   SOA mass loadings on each filter. MOUDI was used to collect bulk aerosol samples of SOA.
117   Samples from four stages with the highest mass loadings were used for detailed analysis.
118   Samples of high-NO$_x$ Tol-SOA were collected on the 6th and 7th stages of MOUDI (0.32μm < D$_p$ <
119   1.0 μm), where ~80% of the aerosol mass was deposited. In the low-NO$_x$ experiments the
120   particle size distribution of Tol-SOA was shifted to smaller sizes, and ~80% of the aerosol mass
121   was distributed over the 7th and 8th stages (0.18μm < Dp < 0.56 μm) which were used for
122   analysis, respectively. The total mass loadings collected on two stages in each of the
123   experiments were similar between low-NO$_x$ Tol-SOA (230 μg on stage 7 and 40μg on stage 8)
124   and high-NO$_x$ Tol-SOA (160 μg on stage 6 and 110μg on stage 7). Later, Tol-SOA materials
125   collected on two stages were combined together and extracted for HPLC analysis. Identical
126   solvents were used to extract Tol-SOA from filters for both the detailed chemical analysis and
127   for the optical measurements of MAC_{bulk}.

128   **Chemical Characterization.** Tol-SOA samples were first probed directly from the
129   substrate without any sample preparation, by using a high resolution LTQ-Orbitrap mass
130   spectrometer (Thermo Electron, Bremen, Germany) interfaced with a custom-built nanospray
131   desorption electrospray ionization (nano-DESI) source. Details about the experiment setup have
132   been described in our previous studies.[47, 48] Briefly, the sample was positioned on a computer-
133   controlled XYZ stage and brought in contact with the nano-DESI probe, which was assembled
134   using two fused silica capillaries (50 × 193 μm, ID × OD, Polymicro Technologies, L.L.C., Phoenix).
135   The solvent (50/50%, acetonitrile/water) was infused using a syringe pump at a flow rate of 0.3-
136   1μL/min that was matched to the self-aspiration rate of the nanospray capillary.[47] Typical
137   experimental conditions were: spray voltage of 3.5kV, 250 °C temperature of the heated
138   capillary, and the mass spectrometer was operated in the negative ion mode with a resolving
139   power of $\Delta m/m = 10^5$ at m/z 400. The instrument was regularly calibrated using a standard
140   calibration MSCAL 5 mixture (Sigma-Aldrich, Inc.).

141   For HPLC analysis, portions of the filter samples were extracted into 500 μL mixtures of
142   50/50% (v/v) acetonitrile and ultrapure water (LC-MS CHROMASOLV®, Sigma-Aldrich). Visual
143   inspection of the filters after solvent extraction indicated that all the material was efficiently
144   removed from the filter. The resulting solutions were first concentrated through evaporation
145   under slow N_2 flow to a volume of ~20 μL. Next, 100μL of ultrapure water was added to make
146   the solvent compatible to the initial setting of solvent gradient of HPLC analysis. The mass
147   concentration of Tol-SOA in the final solution was estimated to be approximately the same
148   0.56μg/μL for both high and low-NO_x Tol-SOA samples. The estimation was based on the
149   measured SOA mass loading on the Teflon substrates, assuming 100% efficiency of solvent
150   extraction.

151   Solutions containing Tol-SOA samples were subsequently analyzed using a HPLC-UV-Vis-
152   ESI/HRMS platform for identification and characterization of the BrC chromophores. The LC/MS
153   consists of a Surveyor Plus system (including LC pump, autosampler and PDA detector), a
154   standard IonMAX^{TM} electrospray ionization (ESI) source, and a high resolution LTQ-Orbitrap
155   mass spectrometer (all modules are from Thermo Electron, Inc). The separation was performed
156   on a reverse-phase column (Luna C18, 2×150mm, 100Å pores, 5μm particles, Phenomenex,
157   Inc.). Gradient elution was performed by H_2O/AcN at a flow rate of 200 μL min^{-1}: 0-3 min hold
158   at 10% of AcN, 3-43 min linear gradient to 90% AcN, 43-50 min hold this level, 50-51 min back
159   to 10% AcN, and hold until 70 min to recondition the column and make it ready for injection of
160   the next sample. UV/vis absorption was measured using PDA over the wavelength range of 200
161   to 700 nm. The ESI setting were: -3.5kV spray potential, 35 units of sheath gas flow, 10 units of
162   auxiliary gas flow, and 8 units of sweep gas flow.

163   Xcalibur (Thermo Scientific) was used to acquire raw data. Mass spectral features with a
164   minimum signal-to-noise ratio of 10 were extracted by using Decon2LS software[49] developed at
165   Pacific Northwest National Laboratory (PNNL) (http://ncrr.pnl.gov/software/). Data processing
166   was performed using a suite of Microsoft Excel macros developed in our group, including
167   background subtraction, first and second-order Kendrick mass defect analysis. Details about
168   these procedures have been described in our previous studies.[50, 51] Elemental formulas were
169   assigned to one peak in each group using MIDAS molecular formula calculator
170   (http://magnet.fsu.edu/~midas/). Formula assignments were performed using the following
171   constraints: C ≤ 50, H ≤ 100, N ≤ 5, and O ≤ 50. Neutral formulas were obtained by adding a
172   proton to the formulas of [M-H$^-$] ions. The double-bond equivalent (DBE) of the neutral
173   formulas was calculated using the equation: DBE = $c - h/2 + n/2 + 1$. Where c, h, and n
174   correspond to the number of carbon, hydrogen and nitrogen atoms in the neutral formula,
175   respectively.

176   **Chemical Structure and UV/vis Calculations.** The quantum chemical calculations of the

177   optimized structures and UV/vis absorption spectra where performed using the Gaussian

178   software package.[52] As a balance between accuracy and computational efficiency, the B3LYP/6-

179   311++G** level of theory and basis sets were employed for both geometry optimizations and

180   the TD-DFT UV/vis calculations of the first 20 excited singlet electronic states.[53] Solvent effects

181   were not included since we were looking for general trends in the behavior of the UV/vis

182   spectra on the location of the specific functional groups around the aromatic rings of the

183   spectral candidates relevant to BrC. The suitability of the selected quantum chemistry method

184   was tested by performing a series of calculations for selected aromatic compounds of

185   increasing complexity to ensure the calculated UV/vis trends were correct. The series included

186   naphthalene, anthracene, and tetracene. The computed trends of maximum absorption (λ_{max})

187   between these compounds matched well their corresponding literature values.[54] Specifically,

188   the calculated (literature) values were: naphthalene = 285nm (301nm), anthracene = 383nm

189   (376nm), and tetracene = 500nm (474nm). Thus, the level of theory and the basis sets selected

190   for our study were sufficient to reproduce trends quite well.

191

192   **RESULTS AND DISCUSSIONS**

193   Samples of Tol-SOA produced under high and low NO_x conditions have substantially

194   different light absorbing properties as inferred from both visual observations and MAC_{bulk}

195   measurements. Figure 1 shows photographs of the high- and low-NOx Tol-SOA samples along

196   with a plot indicating differences in their MAC_{bulk} values. It is observed that the sample of high-

197   NO_x Tol-SOA appears yellow in color and exhibits significant light absorption at near UV and

198   short visible wavelength with MAC_{bulk}@365nm = 0.78 m^2 g^{-1}. In contrast, Tol-SOA produced

199   under low-NO_x conditions is colorless, and its MAC_{bulk}@365nm value of 0.01 m^2 g^{-1} is almost

200   two orders of magnitudes lower than that of the high-NO_x Tol-SOA. These two samples were

201   further analyzed to obtain detailed information on the chemical composition and the light

202   absorption properties of the individual molecular components.

203   **Compositional differences between Tol-SOA generated under high- and low-NO_x**

204   **conditions.** The Tol-SOA samples were first analyzed by nano-DESI/HRMS to obtain an overview

205   of their molecular composition. Figure 2 shows mass spectra of Tol-SOA generated at high-NO_x

206   and low-NO_x conditions. The chemical composition of Tol-SOA generated under high-NO_x

207   conditions is remarkably different from that formed under low-NO_x conditions. A large number

208   of nitrogen containing compounds (CHON) were produced under high-NO_x conditions, and

209   accounted for ~68% of the assigned elemental formulas. A majority of the CHON molecules

210   (~90%) have O/N ratios higher than 2, consistent with the assumption that those products

211   contain at least one nitro group (-NO_2). The candidates for these CHON compounds include

212   nitro-phenol analogues, organic nitrates, acylperoxyl nitrates, and unsaturated hydroxyl nitro
213   acids, which can overall account for > 60% of aerosol mass in tol-SOA, as predicted by the
214   kinetic mechanism of photochemical oxidation of toluene.[55] In contrast, photooxidation
215   products observed in Tol-SOA produced under low-NO_x conditions are dominated by
216   compounds composed of carbon, hydrogen and oxygen atoms (CHO). Although some of the
217   CHON compounds were also detected in low-NO_x Tol-SOA, they were only observed as ions
218   with very low intensities (signal/noise ratio < 80). Those compounds are likely products of SOA
219   carbonyl compounds reacting with NH_3 during exposure of samples to an ambient air at the
220   time of sample handling and data acquisition.[17, 47]

221   The compositional diversity of Tol-SOA components and their dependence on the initial
222   concentration of NO_x reflects differences in mechanisms of toluene oxidation by mixed OH/NO_x
223   oxidants. Oxidation of toluene initiated by reactions with OH radical has been studied by
224   several groups.[38-41, 55-57] For instance, Forstner et al.[38] reported that about 90% of products
225   were formed through OH radical addition resulting in formation of methyl hydroxyl
226   cyclohexadieny radicals, which may further react with O_2 (k ≈ 5×10^{-16} cm^3 molecule^{-1} s^{-1}) or NO_2
227   (k ≈ 3×10^{-11} cm^3 molecule^{-1} s^{-1}).[57, 58] It is reported that the reaction with O_2 leads to a series of
228   fragmentation, rearrangement, and radical propagation products with CHO composition such as
229   reactive aldehydes, carboxylic acids, quinoid and furanoid compounds.[39, 56] Under common
230   tropospheric conditions, the O_2 pathway typically dominates.[57] However, when NOx
231   concentrations are high, a fraction of the cyclohexadienyl radicals noted above react by
232   addition of NO_2[41] to the aromatic ring leading to formation of nitro aromatic compounds.[39]
233   Though this pathway likely represents a small subset of all reactions, it does not lead to
234   fragmentation and therefore may contribute substantially to SOA mass.

235   Additionally, about 10% of toluene oxidation products are formed through H-atom
236   abstraction of the methyl group and results in formation of benzaldehydes, which can further
237   oxidize to lower volatility benzoic acid[38] that partitions into particle phase. In the condensed
238   phase, benzoic acids and benzaldehydes may participate in oligomerization reactions yielding
239   higher molecular weight (high-MW) products.[59] In contrast, at high-NO_x conditions, reaction
240   products are shifted towards formation of nitrophenols[39] that have lower tendency for
241   fragmentation and oligomerization.

242   A variety of organic radicals are produced through radical propagation reactions during
243   toluene oxidation. These organic radicals may also react with NO_2 and lead to nitrogen
244   containing products. For instance, it was estimated that the effective yield of the reaction
245   between methyl phenoxy radicals and NO_2 increased from 0.34 to 0.69 as the effective NO_2
246   concentration increased from 13 to 97 ppbv,[28] demonstrating the overwhelming reaction with

247 NO_2 rather than with other oxidants. The reactions of organic radicals with NO_x regulate the
248 amount of nitrogen containing compounds formed in Tol-SOA as illustrated by Figure 2.

249   Figure 2 indicates that Tol-SOA produced under low-NO_x conditions contain a larger
250 fraction of high-MW products in comparison with Tol-SOA formed under high-NO_x. These high-
251 MW species are mainly CHO compounds. As we mentioned before, the O_2 pathway leads to a
252 series of radical propagation reactions and results in a variety of aldehydes and organic peroxy
253 radicals (RO_2). High-MW compounds are formed from these reactive aldehydes through
254 hemiacetal/acetal oligomerization and/or aldol condensation.[59, 60] Under high-NO_x conditions,
255 the addition of NO_2 to organic radicals terminate radical propagation, which result in more ring-
256 retaining products and less aldehydes that may not favor oligomerization. Under low NO_x
257 conditions, RO_2 radicals react with hydroperoxyl radical (HO_2), forming organic hydroperoxides
258 (ROOH) that may further react with aldehyde species to produce low volatile peroxy
259 hemiacetals, which play an important role in SOA formation.[61] In contrast, under high NO_x
260 conditions, RO_2 radicals react with NO_x to produce species which are less likely to undergo
261 particle-phase oligomerization reactions that contribute to the formation of high-MW products.
262 In summary, comparison of nano-DESI spectra of Tol-SOA produced under low-NO_x and high-
263 NO_x conditions suggests that nitrogen-containing species abundant in the high-NO_x Tol-SOA
264 may contribute to the observed light absorption while oligomeric products abundant in the
265 low-NO_x Tol-SOA do not absorb visible light to a significant extent.

266   UV/Vis absorption spectra of organic molecules vary dramatically with their structural
267 features. The extent of the double bond conjugation that can be indirectly inferred from a
268 number of double bonds and rings in the molecule expressed as DBE is an important parameter
269 that determines molecular optical properties.[62] Figure 3 shows the DBE values for compounds
270 observed in the high-NO_x and low-NO_x Tol-SOA plotted as a function of a number of carbon
271 atoms. The upper compositional boundary for naturally occurring hydrocarbons in fossil resources[63] is
272 shown by the blue line. The extent of unsaturation and conjugation in each identified product
273 can be inferred from this plot. Specifically, oxidation products observed in Tol-SOA generated
274 under high- NO_x conditions have higher extent of unsaturation in comparison to compounds
275 observed in Tol-SOA generated under low-NO_x conditions. This is consistent with previous work
276 by Birdsall et al[64] showing that a larger fraction of aromatic products are present in high-NO_x
277 Tol-SOA, while under low-NO_x conditions, the addition of O_2 initiates a series of radical
278 propagation reactions leading to a variety of ring cleavage products. Higher degree of
279 conjugation tends to reduce the energy gap for $\pi \rightarrow \pi^*$ transitions, leading to light absorption at
280 longer wavelengths. In addition, light absorption by organic molecules is also affected by
281 functional groups. For example, it is well-established that absorption of visible light is often
282 enhanced in the presence of nitro/nitrate groups in the molecule.[65] As discussed earlier,
283 nitroaromatic compounds have been identified as the dominant light-absorbing species in field-

284   collected aerosol samples.[31, 32] However, detailed speciation of the light-absorbing molecules in
285   Tol-SOA has not been previously reported. In the following section we describe chemical
286   characterization of the individual BrC chromophores in Tol-SOA using HPLC-UV/Vis-ESI/HRMS.

287   **Identification of BrC chromophores.** Figure 4 shows UV/Vis chromatograms integrated
288   over the 300-500nm region and MS total ion count (TIC) chromatograms obtained by HPLC
289   analysis of both high-NO_x and low-NO_x Tol-SOA samples. The results demonstrate that the high-
290   NO_x Tol-SOA sample contains a number of well-separated molecular fractions that efficiently
291   absorb light in the 300-500nm region. In contrast, a very different UV/Vis chromatogram was
292   obtained for the low-NO_x Tol-SOA sample with only several small features observed above the
293   background. Similarly, the TIC chromatogram obtained for the high-NO_x sample exhibits distinct
294   features in comparison to that of the low-NO_x sample (Figure 4). After correcting for the shift in
295   retention times (RT) between the signals recorded by MS and UV/Vis detectors, the major
296   absorption peaks in the UV/Vis chromatogram were found to correlate well with the major
297   peaks observed in the TIC chromatogram, suggesting that ions contributing to the MS signal are
298   also responsible for signals detected by the PDA detector.

299   The mass spectrum of each chromatographic peak usually contains a number of ions
300   corresponding to the analyte of interest as well as to the solvent background and species that
301   were not separated by HPLC. We used comparative analysis of MS spectra recorded at the
302   beginning, maximum, and end of the chromatographic feature to identify ion signals strongly
303   correlated with the UV/Vis chromatographic peaks. Details of the data analysis methodology
304   are elaborated in the SI file (see Figure S1 and the associated text).

305   Figure 5 shows extracted ion chromatograms (EIC) of selected abundant ions that
306   correlate with the features in the UV/Vis chromatogram of the high-NO_x Tol-SOA sample. A
307   majority of these compounds contain 6-7 carbon atoms with DBE values ranging from 5 to 7,
308   indicative of the preserved aromatic ring. In addition, there are also 1-3 nitrogen atoms and 3-7
309   oxygen atoms in each molecule, making O/N ratio greater than 2 in all of the identified species.
310   These observations suggest that these compounds most likely contain nitro group, an
311   assumption that explains DBE values in excess of 4 (characteristic for a single aromatic ring).

312   A summary of the most prominent BrC chromophores, their UV/Vis spectra and
313   corresponding retention times (RT) is listed in Table 1. Overall, 15 major BrC features along with
314   their elemental composition were identified and their plausible molecular structures were
315   suggested. Several commercially available compounds such as picnic acid and 3,5-
316   dinitrosalicylic acid were analyzed using the same experimental conditions. This allowed a
317   direct comparison of their UV/Vis spectra and retention times with the features observed in the
318   high-NO_x Tol-SOA sample. In addition, we were able to identify several compounds by
319   comparing their elemental composition with the composition of toluene photooxidation

320   products identified in previous studies and their UV/Vis spectra with UV/Vis spectra of
321   individual compounds reported in literature. For example, the UV/Vis spectrum of the peak that
322   eluted at 16.5min is characterized by maximum absorption (λ_{max}) at 347nm and a shoulder
323   around 310nm. Based on the HRMS data, the compound eluted at this time was assigned with
324   neutral elemental formula $C_6H_5NO_4$, which is most likely nitrocatechol. The UV/Vis spectrum of
325   4-nitrocatechol was reported with λ_{max} at 345nm and a shoulder at 309nm.[66] In contrast,
326   another isomer, 3-nitrocatechol was reported with λ_{max} at 296nm.[67] Based on this comparison
327   we identified the chromophore eluting at 16.5 min as 4-nitrocatechol.

328   We note that in some cases, the observed UV-Vis spectrum may be a combination of the
329   UV/vis spectra of several compounds. For example, absorbance at RT = 24.3 min correlates well
330   with the elution time of two molecules with elemental formula of $C_7H_7NO_3$ and $C_6H_4N_2O_5$,
331   respectively. Nitrocresols ($C_7H_7NO_3$) have been identified in Tol-SOA produced in the presence
332   of NO_x.[39] One of its isomers, 4-nitro-o-cresol, has peak absorption wavelength (λ_p) at 319nm,[30]
333   which is close to λ_p (325nm) of the spectrum observed at RT = 24.3min (Table 1). The minor red-
334   shift of the observed absorption may be caused by co-eluted $C_6H_4N_2O_5$, probably dinitrophenol.
335   Some of its isomers, e.g., 2,6-dinitrophenol and 2,3-dinitrophenol, absorb light at longer
336   wavelengths of 350 and 329 nm, respectively[30] and could contribute to the observed
337   absorption.

338   There are two elemental formulas corresponding to the compounds eluted at RT =
339   21.7min: $C_7H_7NO_4$ and $C_6H_4N_2O_6$, which are likely methyl-nitrocatechol[40] and dinitrocatechol,[68]
340   respectively. The PDA spectrum at this RT appeared to be similar to that eluted at 16.5min,
341   which was mainly contributed by nitrocatechol. Moreover, for each identified formula, multiple
342   structural isomers are possible. In order to assess the effect of methyl-substitution and
343   functional groups' positions on the UV/Vis spectra of aromatic compounds, the spectroscopic
344   properties of several model compounds were evaluated by quantum chemistry calculations of
345   their electronic structures.[53] Figure S2 shows the chemical structures of the 14 model
346   compounds and their absorption spectra obtained from quantum calculations. Table 1 includes
347   several conclusions that were drawn from these results. First, the substitution of methyl group
348   and its position on the aromatic ring doesn't change substantially the UV/Vis spectra of
349   aromatic compounds, as demonstrated by comparing the structures 1 – 3 of Figure S2. Second,
350   the UV/Vis spectra of structures 4-7 suggest that the relative positions of –OH and –NO_2 groups
351   on the aromatic ring significantly affect the absorbance of nitrocatechol. Similar effects were
352   also found for the isomers of dinitrocatechol (structures 8-14). The calculated results indicate
353   that molecular structures with -NO_2 groups in *para* positions have the longest wavelength of
354   light absorbance, followed by *ortho* and *meta* isomers. The position of –OH groups have
355   additional but less pronounced influence. In the end, we should point out that all the
356   theoretical calculations used here are applied for single molecule only, without taking into

357 account the solute-solvent interactions, which were suggested to have a direct and significant
358 influence on the UV/Vis spectra.[66] This makes it difficult to directly compare the spectra
359 measured by PDA with those calculated by quantum methods. However, the quantum chemical
360 calculations do provide important trends as to the effect of different locations of the functional
361 groups around the aromatic rings on the UV/vis spectra. The key result of these calculations
362 indicate that when the nitro groups are farthest apart, i.e., on opposite sides of the aromatic
363 ring, the HOMO-LUMO gap is reduced yielding absorption wavelengths that are red-shifted
364 with respect to compounds with adjacent nitro groups. This can be easily understood via the
365 well-known quantum particle in a box – larger boxes allow for absorption at longer wavelengths.

366   Figure 6 illustrates analysis results in two cases where identification of BrC features was
367 assisted by comparison with commercially available standards. Specifically, the compound with
368 assigned elemental formula $C_6H_3N_3O_7$ was identified as the most abundant ion eluted at RT =
369 39.1 min, while the signals of other ions with the same chromatographic record were
370 substantially lower. The EIC of these ions correlate well with the UV/Vis signal (Figure 6a). In
371 ESI-MS, the intensity of ion signal is determined by both concentration and ionization efficiency
372 of the analyte molecule. Therefore, it is hard to unambiguously conclude whether the signal
373 intensities of these compounds, as shown in Figure 6a, represent their relative concentrations
374 in the mixture and relative contribution to UV/Vis absorbance. However, in this case it was
375 possible to compare the UV/Vis spectrum of this BrC feature with a commercially available
376 standard of picric acid ($C_6H_3N_3O_7$). As shown in Figure 6c, the corresponding two spectra match
377 very well with each other. The result implies that picric acid is most likely the dominant BrC
378 chromophore responsible for light absorption at RT = 39.1 min.

379   Figure 6b shows another example of BrC chromophore eluting at RT = 36.9min, where
380 two major ions (with neutral formulas $C_7H_4N_2O_7$ and $C_6H_4N_2O_5$) along with several low-
381 abundance species were detected. The UV/Vis spectrum of this BrC feature was found to
382 match well with the spectrum of 3, 5-dinitrosalicylic acid ($C_7H_4N_2O_7$) (Figure 6d). The latter was
383 also analyzed with LC-MS using the same experimental conditions and was found to elute at
384 similar retention time. The mass spectrum of 3, 5-dinitrosalicylic acid also contained both
385 $C_7H_4N_2O_7$ and $C_6H_4N_2O_5$ suggesting that $C_6H_4N_2O_5$ is a fragment of $C_7H_4N_2O_7$ formed in the ESI
386 process or through in-source fragmentation. It follows that 3, 5-dinitrosalicylic acid is the
387 characteristic BrC chromophore responsible for light absorption at RT = 36.9 min.

388   The results shown in Figures 5 and 6 indicate that the most abundant ions observed in
389 MS determined the light absorption observed by UV/Vis. The absorption spectra of 15
390 identified peaks from Table 1 were summed together to evaluate their contributions to the
391 total absorption measured by PDA detector as shown in Figure 7. The total absorbance of these
392 15 peaks accounts for 60% and 41% of the overall absorbance in the wavelength ranges of 300-

393   400nm and 400-500nm, respectively. The rest of the absorption is mainly due to the rising
394   baseline or a broad "hump" observed in the UV/vis chromatogram at 15-30min (Figure 4, blue
395   line). This chromatographic feature is similar to those frequently observed in gas
396   chromatography (GC) data of atmospheric aerosols[69, 70] or other complex organic mixtures,
397   where a term unresolved complex mixtures (UCM) was introduced.[71] The mass spectra of LC
398   fractions eluted within this period were averaged and processed following the same
399   methodology described in Figure S1 of the SI file. The resulting mass spectrum consisted of over
400   100 ions, including 11 of the identified chromophores from Table 1 as the most abundant ions
401   (see Figure S2 of the SI file). The intensities of other ions were substantially smaller than the
402   intensities of the identified ions, indicating either their low individual concentrations or poor
403   ionization efficiency. It is also possible that some chromophores detected by PDA are not
404   ionized by ESI. Further identification of chromophores in the UCM fraction is still challenging
405   and may require two-dimensional chromatographic technology,[72] which is beyond our current
406   instrumental capability.

407   Figure 7 also illustrates that among 15 identified chromophores, light absorption above
408   350 nm is dominated by 10 peaks eluting between 14-40 min. As shown in Table 1,
409   chromophores eluting during this period are mainly nitro-phenolic compounds. It is interesting
410   to note that the UCM fraction also elutes at the same time (i.e., 15-30min). This observation
411   suggests that compounds in the UCM fraction have similar physiochemical properties as the
412   abundant chromophores identified in this study, which may explain the substantial light
413   absorption by UCM. We assigned molecular formulas to the observed ions in the UCM fraction
414   as described in the experimental section. Overall, 98 ions were successfully assigned with
415   reasonable formulas within the constraints used in this study ($C \leq 50$, $H \leq 100$, $N \leq 5$, and $O \leq$
416   50). Unambiguous formula assignment of other peaks was not possible either due to the
417   reduced mass accuracy for low- intensity peaks or because of the presence of other elements
418   not considered in our assignment. 78 of the 98 identified formulas are CHON compounds with
419   O/N ratio greater than 2, and 92 compounds contain at least six carbon atoms and have DBE/C >
420   0.5, suggesting the presence of nitro/nitrate groups and aromatic structures. It follows that
421   chromophores in the UCM fraction are also predominately nitro-aromatic and/or organonitrate
422   compounds.

423   **Atmospheric implications.** The combination of HPLC with UV/Vis spectroscopy and
424   ESI/HRMS is shown to be an effective analytical platform for the identification of BrC
425   chromophores and characterization of their light-absorption properties. Tol-SOA, selected as
426   one of the best characterized secondary BrC aerosols, were examined in this study. The results
427   provide direct evidence that nitro-phenols are significant BrC chromophores responsible for the
428   enhanced BrC characteristics of Tol-SOA generated under high-NO$_x$ conditions. Considering that
429   both aromatic hydrocarbons and NO$_x$ are substantial anthropogenic air pollutants in urban

430   regions,[73] nitro-phenolic compounds produced from the photo-oxidation of aromatic
431   hydrocarbons could be an important source of BrC in urban atmosphere.

432   In this study, BrC SOA was produced in a smog chamber simulating the daytime
433   troposphere photochemistry, and nitro-phenols were identified as significant BrC
434   chromophores. It should be pointed out that, besides daytime gas-phase chemistry, there are
435   also other atmospheric processes or emission sources that can produce nitro-phenols. Such
436   processes/sources include nighttime $^\bullet NO_3$-mediated nitration of phenols in the gas phase,[74]
437   hydroxylation and nitration of aqueous benzene in the presence of nitrite under UV-
438   irradiation,[75] combustion processes of motor vehicles,[76] and biomass burning.[31, 32, 77] A recent
439   study of Liu et al. reported that the imaginary part (k) of refractive indices ($m = n - ik$) of the
440   aromatic SOA produced from photooxidation of toluene and m-xylene in the presence of NOx is
441   similar to those reported for BrC in urban and biomass burning plumes.[29] The conclusions of
442   these studies expand the significance of nitro-phenolic compounds as BrC chromophores in the
443   atmosphere.

444   It is important to point out that most of these nitro-phenolic compounds are acidic in
445   nature and deprotonation of the neutral BrC chromophores may have significant effect on their
446   absorption spectra.[78] Table 2 lists several nitro-phenolic compounds with known acid
447   dissociation constants (pKa) and their longest peak UV/Vis absorption wavelength (λ_p). It is
448   shown that the deprotonated forms of these compounds usually absorb at considerably longer
449   wavelength than their neutral counterparts. Molar (or mass) absorption coefficients also vary
450   greatly for deprotonated and protonated forms of molecules. Deprotonation of an acidic
451   compound depends on its pKa and the pH of the solution.[79] The pH of cloud and fog droplets
452   was measured in a wide range of 2.3-7.6.[80, 81] Aerosol in-situ pH cannot be directly measured
453   due to its low liquid water content (LWC), but can be estimated by thermodynamic models.[82, 83]
454   In urban area, the in-situ pH of ambient aerosols is generally acidic (pH < 4.0),[84, 85] regulated by
455   the molar ratio of major inorganic components and LWC.[86] Since the pKa values of nitro-
456   phenolic compounds are close to or within the range of atmospheric pH, their light absorption
457   spectra may be significantly affected by changes in the acidity of aerosol population.

458   Despite the acidic nature of SOA produced from gas- and aqueous-phase oxidation
459   processes in urban atmosphere, another class of light absorbing aerosol, mineral dust, is mainly
460   composed of alkaline components. Mineral dust aerosols can transport over thousands
461   kilometers from their source regions and account for a larger fraction of aerosol flux on global
462   scale. The alkaline components of mineral dust have shown great capacity to buffer the acidity
463   of rain water.[87, 88] The acidity of SOA may be neutralized in the same way when they mixed with
464   mineral dust or marine aerosols.[89-91] As a result, the light absorption properties of BrC SOA may
465   also be modified. In the case of tol-SOA, its BrC characteristics are enhanced during this process.

466 We propose that the pH dependence of light absorption characteristics may be an important
467 property of BrC aerosols that need to be systematically investigated in future studies.

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478   References:

479   1.   IPCC, *Fourth Assessment Record: Climate Change 2007*, Cambridge University Press, New York,
480   2007.
481   2.   J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate*
482   *Change*, Wiley-Interscience; 2 edition, 2006.
483   3.   T. C. Bond, C. Zarzycki, M. G. Flanner and D. M. Koch, *Atmos Chem Phys*, 2011, **11**, 1505-1525.
484   4.   X. Ma, F. Yu and G. Luo, *Atmos Chem Phys*, 2012, **12**, 5563-5581.
485   5.   C. E. Chung, V. Ramanathan and D. Decremer, *P Natl Acad Sci USA*, 2012, **109**, 11624-11629.
486   6.   M. O. Andreae and A. Gelencser, *Atmos Chem Phys*, 2006, **6**, 3131-3148.
487   7.   P. Formenti, W. Elbert, W. Maenhaut, J. Haywood, S. Osborne and M. O. Andreae, *J Geophys*
488   *Res-Atmos*, 2003, **108**, 8488.
489   8.   Y. Feng, V. Ramanathan and V. R. Kotamarthi, *Atmos Chem Phys*, 2013, **13**, 8607-8621.
490   9.   R. Bahadur, P. S. Praveen, Y. Y. Xu and V. Ramanathan, *P Natl Acad Sci USA*, 2012, **109**, 17366-
491   17371.
492   10.   V. Ramanathan, F. Li, M. V. Ramana, P. S. Praveen, D. Kim, C. E. Corrigan, H. Nguyen, E. A. Stone,
493   J. J. Schauer, G. R. Carmichael, B. Adhikary and S. C. Yoon, *J Geophys Res-Atmos*, 2007, **112**,
494   D22S21.
495   11.   G. X. Lin, J. E. Penner, M. G. Flanner, S. Sillman, L. Xu and C. Zhou, *J Geophys Res-Atmos*, 2014,
496   **119**, 7453-7476.
497   12.   T. Moise, J. Michel Flores and Y. Rudich, *chemical reviews*, 2015, **115**, 4400-4439.
498   13.   A. Laskin, J. Laskin and S. A. Nizkorodov, *Chemical Reviews*, 2015, **115**, 4335-4382.
499   14.   D. T. L. Alexander, P. A. Crozier and J. R. Anderson, *Science*, 2008, **321**, 833-836.
500   15.   T. C. Bond and R. W. Bergstrom, *Aerosol Sci Tech*, 2006, **40**, 27-67.
501   16.   Y. Chen and T. C. Bond, *Atmos Chem Phys*, 2010, **10**, 1773-1787.
502   17.   J. Laskin, A. Laskin, P. J. Roach, G. W. Slysz, G. A. Anderson, S. A. Nizkorodov, D. L. Bones and L. Q.
503   Nguyen, *Anal Chem*, 2010, **82**, 2048-2058.
504   18.   K. M. Updyke, T. B. Nguyen and S. A. Nizkorodov, *Atmos Environ*, 2012, **63**, 22-31.
505   19.   A. K. Y. Lee, R. Zhao, R. Li, J. Liggio, S. M. Li and J. P. D. Abbatt, *Environ Sci Technol*, 2013, **47**,
506   12819-12826.
507   20.   M. H. Powelson, B. M. Espelien, L. N. Hawkins, M. M. Galloway and D. O. De Haan, *Environ Sci*
508   *Technol*, 2014, **48**, 985-993.
509   21.   Y. H. Lin, H. Budisulistiorini, K. Chu, R. A. Siejack, H. F. Zhang, M. Riva, Z. F. Zhang, A. Gold, K. E.
510   Kautzman and J. D. Surratt, *Environ Sci Technol*, 2014, **48**, 12012-12021.
511   22.   A. T. Lambe, C. D. Cappa, P. Massoli, T. B. Onasch, S. D. Forestieri, A. T. Martin, M. J. Cummings,
512   D. R. Croasdale, W. H. Brune, D. R. Worsnop and P. Davidovits, *Environ Sci Technol*, 2013, **47**,
513   6349-6357.
514   23.   H. J. Lee, P. K. Aiona, A. Laskin, J. Laskin and S. A. Nizkorodov, *Environ Sci Technol*, 2014, **48**,
515   10217-10226.
516   24.   S. Liu, J. E. Shilling, C. Song, N. Hiranuma, R. A. Zaveri and L. M. Russell, *Aerosol Sci Tech*, 2012,
517   **46**, 1359-1369.
518   25.   J. W. Lu, J. M. Flores, A. Lavi, A. Abo-Riziq and Y. Rudich, *Phys Chem Chem Phys*, 2011, **13**, 6484-
519   6492.
520   26.   Z. Kitanovski, A. Cusak, I. Grgic and M. Claeys, *Atmos Meas Tech*, 2014, **7**, 2457-2470.
521   27.   J. Ofner, H. U. Kruger, H. Grothe, P. Schmitt-Kopplin, K. Whitmore and C. Zetzsch, *Atmos Chem*
522   *Phys*, 2011, **11**, 1-15.
523   28.   T. Nakayama, K. Sato, Y. Matsumi, T. Imamura, A. Yamazaki and A. Uchiyama, *Atmos Chem Phys*,
524   2013, **13**, 531-545.

525 29.   P. F. Liu, N. Abdelmalki, H.-M. Hung, Y. Wang, W. H. Brune and A. T. Martin, *Atmos. Chem. Phys.*,
526   2015, **15**, 1435-1436.
527 30.   M. Z. Jacobson, *J Geophys Res-Atmos*, 1999, **104**, 3527-3542.
528 31.   M. Claeys, R. Vermeylen, F. Yasmeen, Y. Gomez-Gonzalez, X. G. Chi, W. Maenhaut, T. Meszaros
529   and I. Salma, *Environ Chem*, 2012, **9**, 273-284.
530 32.   Y. Desyaterik, Y. Sun, X. H. Shen, T. Y. Lee, X. F. Wang, T. Wang and J. L. Collett, *J Geophys Res-*
531   *Atmos*, 2013, **118**, 7389-7399.
532 33.   S. D. Piccot, J. J. Watson and J. W. Jones, *J Geophys Res-Atmos*, 1992, **97**, 9897-9912.
533 34.   Jack G. Calvert, Roger Atkinson, Karl H. Becker, Richard M. Kamens, John H. Seinfeld, Timonthy H.
534   Wallington and G. Yarwood, *The Mechanisms of Atmospheric Oxidation of the Aromatic*
535   *Hydrocarbons*, Oxford University Press, New York, 2002.
536 35.   H. Kim and S. E. Paulson, *Atmos Chem Phys*, 2013, **13**, 7711-7723.
537 36.   K. Li, W. Wang, M. Ge, J. Li and D. Wang, *Sci. Rep.*, 2014, **4**, 4922.
538 37.   M. Zhong and M. Jang, *Atmos Environ*, 2011, **45**, 4263-4271.
539 38.   H. J. L. Forstner, R. C. Flagan and J. H. Seinfeld, *Environ Sci Technol*, 1997, **31**, 1345-1358.
540 39.   M. S. Jang and R. M. Kamens, *Environ Sci Technol*, 2001, **35**, 3626-3639.
541 40.   J. L. Kelly, D. V. Michelangeli, P. A. Makar, D. R. Hastie, M. Mozurkewich and J. Auld, *Atmos*
542   *Environ*, 2010, **44**, 361-369.
543 41.   K. Sato, S. Hatakeyama and T. Imamura, *J Phys Chem A*, 2007, **111**, 9796-9808.
544 42.   J. H. Kroll, N. L. Ng, S. M. Murphy, R. C. Flagan and J. H. Seinfeld, *Geophys Res Lett*, 2005, **32**,
545   L18808.
546 43.   N. L. Ng, J. H. Kroll, A. W. H. Chan, P. S. Chhabra, R. C. Flagan and J. H. Seinfeld, *Atmos Chem Phys*,
547   2007, **7**, 3909-3922.
548 44.   J. Liu, P. Lin, J. Laskin, A. Laskin and J. E. Shilling, *to be submitted to Atmospheric Chemistry and*
549   *Physics*, 2015.
550 45.   A. Hecobian, X. Zhang, M. Zheng, N. Frank, E. S. Edgerton and R. J. Weber, *Atmos Chem Phys*,
551   2010, **10**, 5965-5977.
552 46.   J. Liu, M. Bergin, H. Guo, L. King, N. Kotra, E. Edgerton and R. J. Weber, *Atmos Chem Phys*, 2013,
553   **13**, 12389-12404.
554 47.   P. J. Roach, J. Laskin and A. Laskin, *Analyst*, 2010, **135**, 2233-2236.
555 48.   P. J. Roach, J. Laskin and A. Laskin, *Anal Chem*, 2010, **82**, 7979-7986.
556 49.   N. Jaitly, A. Mayampurath, K. Littlefield, J. N. Adkins, G. A. Anderson and R. D. Smith, *Bmc*
557   *Bioinformatics*, 2009, **10**, 87.
558 50.   P. A. Eckert, P. J. Roach, A. Laskin and J. Laskin, *Anal Chem*, 2012, **84**, 1517-1525.
559 51.   P. J. Roach, J. Laskin and A. Laskin, *Anal Chem*, 2011, **83**, 4924-4929.
560 52.   M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G.
561   Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D.
562   Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B.
563   Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K.
564   Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B.
565   Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I.
566   Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A.
567   Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C.
568   Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98* (2002) Gaussian, Inc.,
569   Pittsburgh, PA.
570 53.   R. Bauernschmitt and R. Ahlrichs, *Chem Phys Lett*, 1996, **256**, 454-464.
571 54.   K. Hirayama, *Handbook of Ultraviolet and Visible Absorption Spectra of Organic Compounds*,
572   Plenum Press Data Division, New York, 1967.

573 55. D. Hu, M. Tolocka, Q. Li and R. M. Kamens, *Atmos Environ*, 2007, **41**, 6478-6496.

574 56. J. F. Hamilton, P. J. Webb, A. C. Lewis and M. M. Reviejo, *Atmos Environ*, 2005, **39**, 7263-7275.

575 57. R. Koch, R. Knispel, M. Elend, M. Siese and C. Zetzsch, *Atmos Chem Phys*, 2007, **7**, 2057-2071.

576 58. R. Knispel, R. Koch, M. Siese and C. Zetzsch, *Ber Bunsen Phys Chem*, 1990, **94**, 1375-1379.

577 59. M. Kalberer, D. Paulsen, M. Sax, M. Steinbacher, J. Dommen, A. S. H. Prevot, R. Fisseha, E.
578   Weingartner, V. Frankevich, R. Zenobi and U. Baltensperger, *Science*, 2004, **303**, 1659-1662.

579 60. M. S. Jang, N. M. Czoschke, S. Lee and R. M. Kamens, *Science*, 2002, **298**, 814-817.

580 61. D. Johnson, M. E. Jenkin, K. Wirtz and M. Martin-Reviejo, *Environ Chem*, 2004, **1**, 150-165.

581 62. H.-H. Perkampus, *UV-Vis Atlas of Organic Compounds*, Weinheim, New York, 1992.

582 63. V. V. Lobodin, A. G. Marshall and C. S. Hsu, *Anal Chem*, 2012, **84**, 3410-3416.

583 64. A. W. Birdsall, J. F. Andreoni and M. J. Elrod, *J Phys Chem A*, 2010, **114**, 10655-10663.

584 65. J. A. Dean, *Lange's Handbook of Chemistry,*, McGraw-Hill, New York, 1992.

585 66. J. P. Cornard, Rasmiwetti and J. C. Merlin, *Chem Phys*, 2005, **309**, 239-249.

586 67. D. Prakash, J. Pandey, B. N. Tiwary and R. K. Jain, *Bmc Biotechnol*, 2010, **10**, 49.

587 68. K. Sato, A. Takami, Y. Kato, T. Seta, Y. Fujitani, T. Hikida, A. Shimono and T. Imamura, *Atmos
588   Chem Phys*, 2012, **12**, 4667-4682.

589 69. A. W. H. Chan, G. Isaacman, K. R. Wilson, D. R. Worton, C. R. Ruehl, T. Nah, D. R. Gentner, T. R.
590   Dallmann, T. W. Kirchstetter, R. A. Harley, J. B. Gilman, W. C. Kuster, J. A. deGouw, J. H.
591   Offenberg, T. E. Kleindienst, Y. H. Lin, C. L. Rubitschun, J. D. Surratt, P. L. Hayes, J. L. Jimenez and
592   A. H. Goldstein, *J Geophys Res-Atmos*, 2013, **118**, 6783-6796.

593 70. J. J. Schauer, M. J. Kleeman, G. R. Cass and B. R. T. Simoneit, *Environ Sci Technol*, 1999, **33**, 1578-
594   1587.

595 71. M. A. Gough and S. J. Rowland, *Nature*, 1990, **344**, 648-650.

596 72. D. R. Stoll, X. P. Li, X. O. Wang, P. W. Carr, S. E. G. Porter and S. C. Rutan, *J Chromatogr A*, 2007,
597   **1168**, 3-43.

598 73. L. Ran, C. S. Zhao, W. Y. Xu, M. Han, X. Q. Lu, S. Q. Han, W. L. Lin, X. B. Xu, W. Gao, Q. Yu, F. H.
599   Geng, N. Ma, Z. Z. Deng and J. Chen, *Atmos Chem Phys*, 2012, **12**, 7531-7542.

600 74. E. Bolzacchini, M. Bruschi, J. Hjorth, S. Meinardi, M. Orlandi, B. Rindone and E. Rosenbohm,
601   *Environ Sci Technol*, 2001, **35**, 1791-1797.

602 75. D. Vione, V. Maurino, C. Minero, M. Lucchiari and E. Pelizzetti, *Chemosphere*, 2004, **56**, 1049-
603   1059.

604 76. J. Tremp, P. Mattrel, S. Fingler and W. Giger, *Water Air Soil Poll*, 1993, **68**, 113-123.

605 77. Y. Iinuma, O. Boge, R. Grafe and H. Herrmann, *Environ Sci Technol*, 2010, **44**, 8453-8459.

606 78. J. Ehlerova, L. Trevani, J. Sedlbauer and P. Tremaine, *J Solution Chem*, 2008, **37**, 857-874.

607 79. M. Roses, F. Rived and E. Bosch, *J Chromatogr A*, 2000, **867**, 45-56.

608 80. K. B. Budhavant, P. S. P. Rao, P. D. Safai, L. Granat and H. Rodhe, *Atmos Environ*, 2014, **88**, 59-65.

609 81. Y. Wang, J. Guo, T. Wang, A. J. Ding, J. A. Gao, Y. Zhou, J. L. Collett and W. X. Wang, *Atmos Res*,
610   2011, **99**, 434-442.

611 82. S. L. Clegg, P. Brimblecombe and A. S. Wexler, *J Phys Chem A*, 1998, **102**, 2137-2154.

612 83. A. Nenes, S. N. Pandis and C. Pilinis, *Aquat Geochem*, 1998, **4**, 123-152.

613 84. K. He, Q. Zhao, Y. Ma, F. Duan, F. Yang, Z. Shi and G. Chen, *Atmos Chem Phys*, 2012, **12**, 1377-
614   1395.

615 85. Z. Y. Meng, J. H. Seinfeld, P. Saxena and Y. P. Kim, *Aerosol Sci Tech*, 1995, **22**, 111-123.

616 86. J. Xue, A. K. H. Lau and J. Z. Yu, *Atmos Environ*, 2011, **45**, 7081-7088.

617 87. S. Fujita, A. Takahashi, J. H. Weng, L. F. Huang, H. K. Kim, C. K. Li, F. T. C. Huang and F. T. Jeng,
618   *Atmos Environ*, 2000, **34**, 525-537.

619 88. A. H. Tang, G. S. Zhuang, Y. Wang, H. Yuan and Y. L. Sun, *Atmos Environ*, 2005, **39**, 3397-3406.

620 89. S. Ghorai, B. B. Wang, A. Tivanski and A. Laskin, *Environ Sci Technol*, 2014, **48**, 2234-2241.

621   90.   A. Laskin, R. C. Moffet, M. K. Gilles, J. D. Fast, R. A. Zaveri, B. B. Wang, P. Nigge and J.
622   Shutthanandan, *J Geophys Res-Atmos*, 2012, **117**, D15302.
623   91.   B. B. Wang and A. Laskin, *J Geophys Res-Atmos*, 2014, **119**, 3335-3351.

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Tables and Figures

Figure 1:
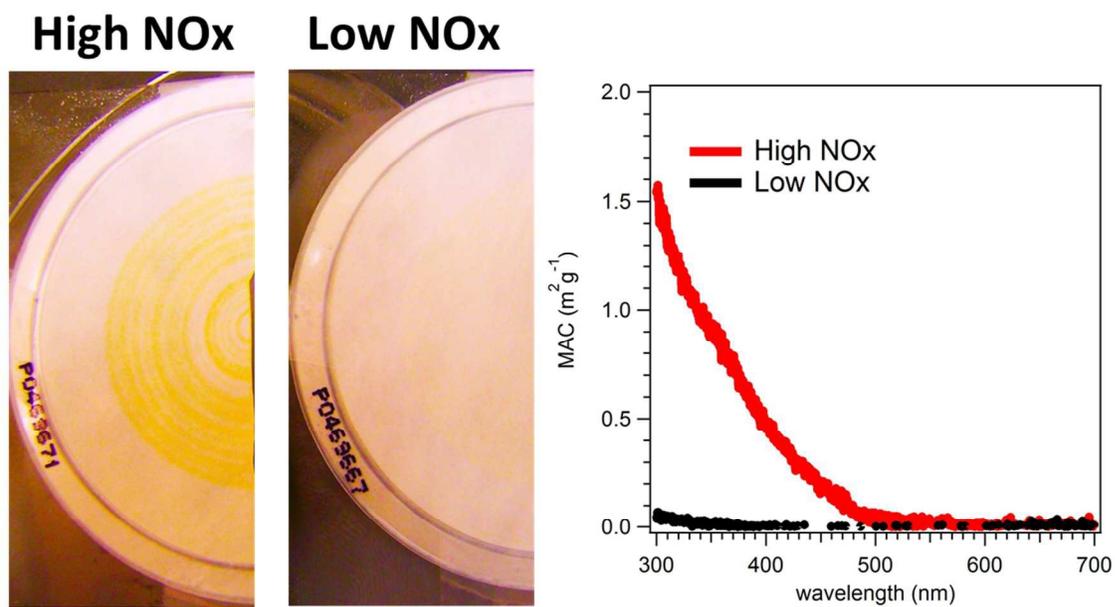
Figure 1. Photographs of the Tol-SOA samples collected in toluene photooxidation experiments performed under high-NOx and low-NOx conditions, indicating distinct optical properties of Tol-SOA produced under different initial NOx concentrations. The plot on the right compares their mass absorption coefficients (MAC$_{bulk}$) in wavelength range 300-700 nm.

Figure 2:
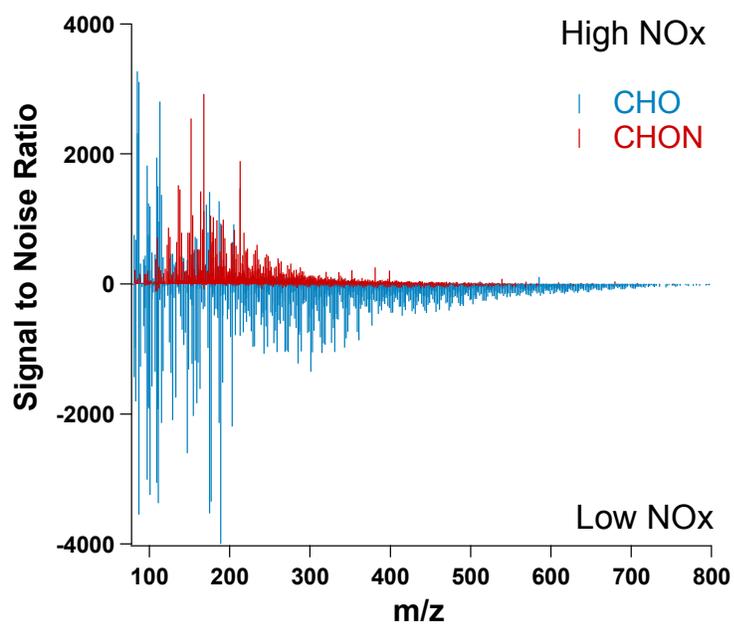
Figure 2. Negative mode nano-DESI/HRMS spectra of Tol-SOA samples generated under high-NOx (positive intensities) and low-NOx conditions (negative intensities). Formulas are grouped based on their elemental composition (see text for details).

Figure 3:
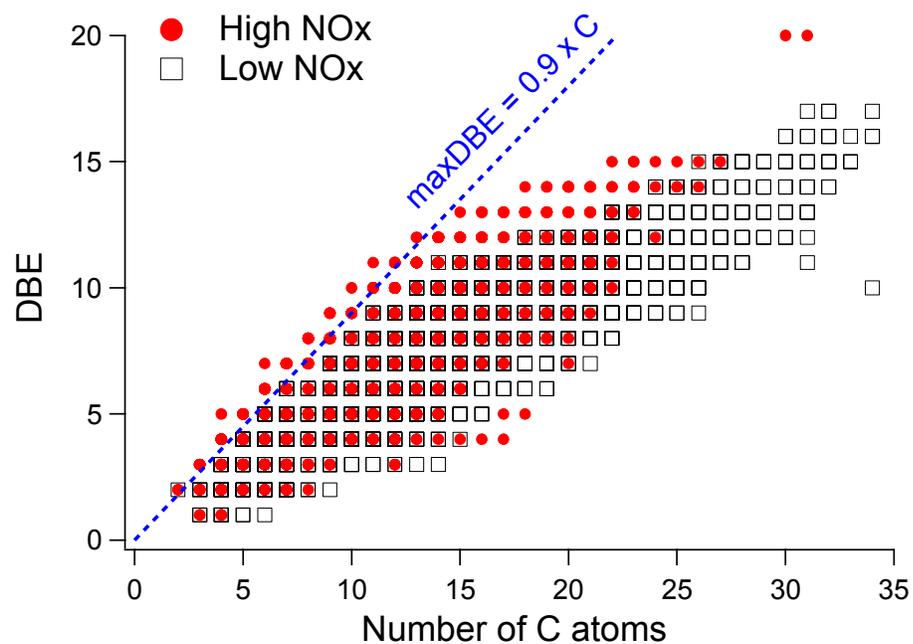
Figure 3. Plot of double bond equivalent (DBE) values as a function of the number of carbon atoms for molecules identified in Tol-SOA produced under high NOx (red dots) and low-NOx conditions (black squares). The blue dashed line indicates the upper compositional boundary for naturally occurring hydrocarbons in fossil resources.[63]
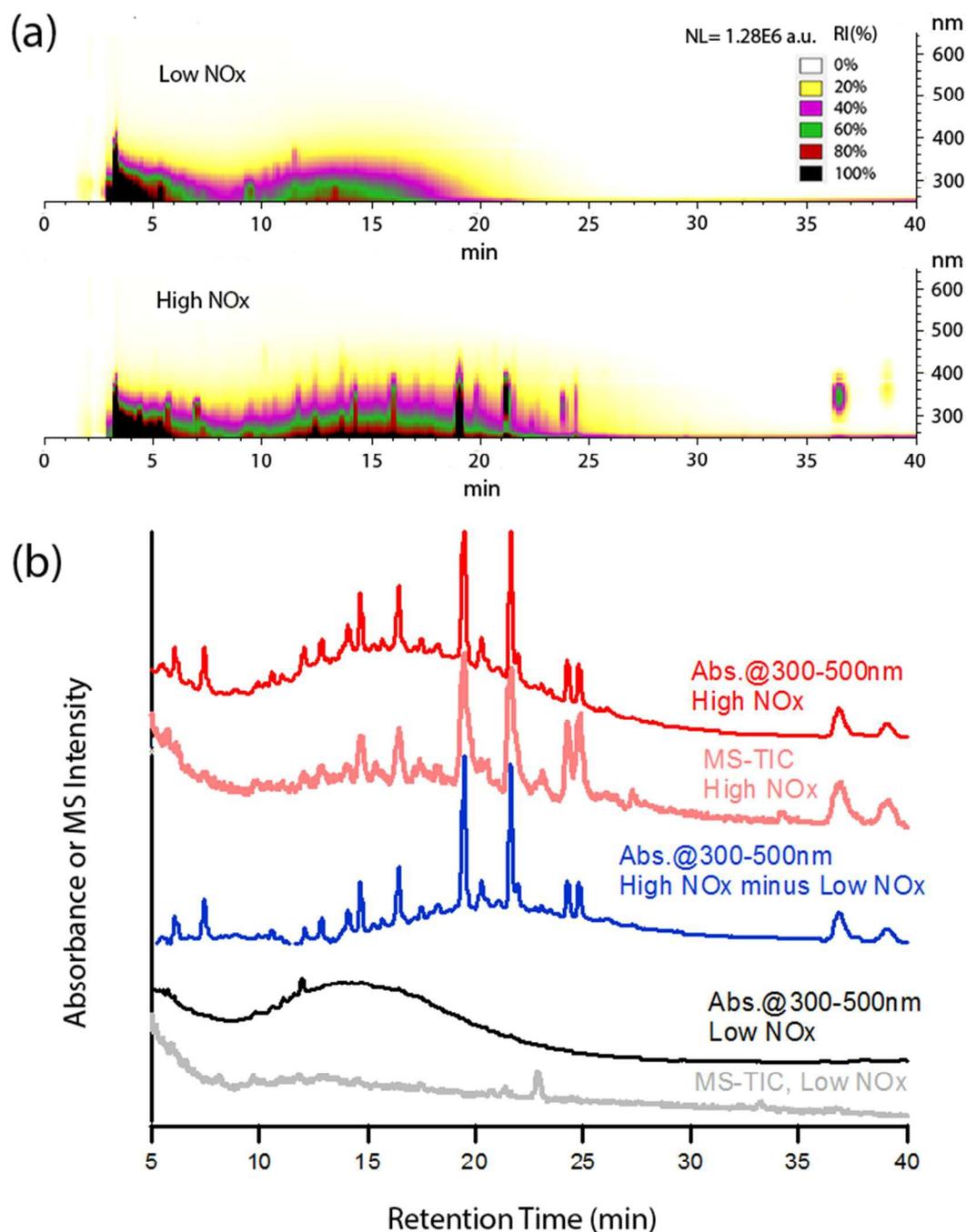
Figure 4. (a) The plot of PDA signals as a function of retention time (min) and light wavelength (nm) for the Tol-SOA sample produced under low-NO_x and high-NO_x conditions, respectively. (b) UV/Vis photodiode array (PDA) detector chromatogram and MS total ion count (TIC) chromatogram of Tol-SOA samples generated under high-NO_x and low-NO_x conditions. The absorbance signals were integrated over wavelengths of 300-500nm. The blue plot shows the difference of the PDA chromatograms between high-NO_x (red) and low-NO_x (black) chromatograms. The intensities are offset along y-axis to facilitate comparison.

Figure 5:
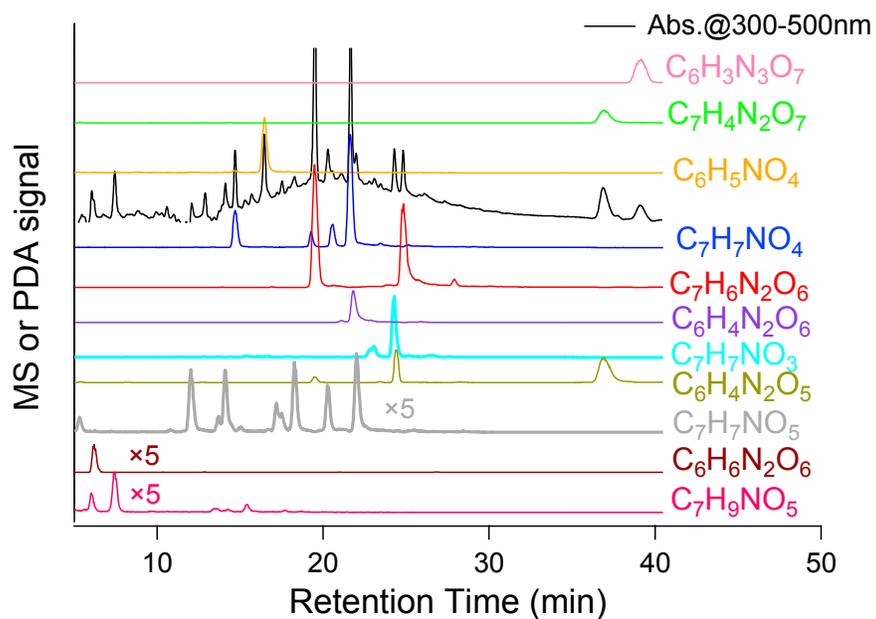
Figure 5. A UV/Vis (PDA) chromatogram integrated over 300-500nm (black trace) and MS extracted ion chromatograms (EIC) of major BrC chromophores observed in the sample of high-NOx Tol-SOA.

Figure 6:
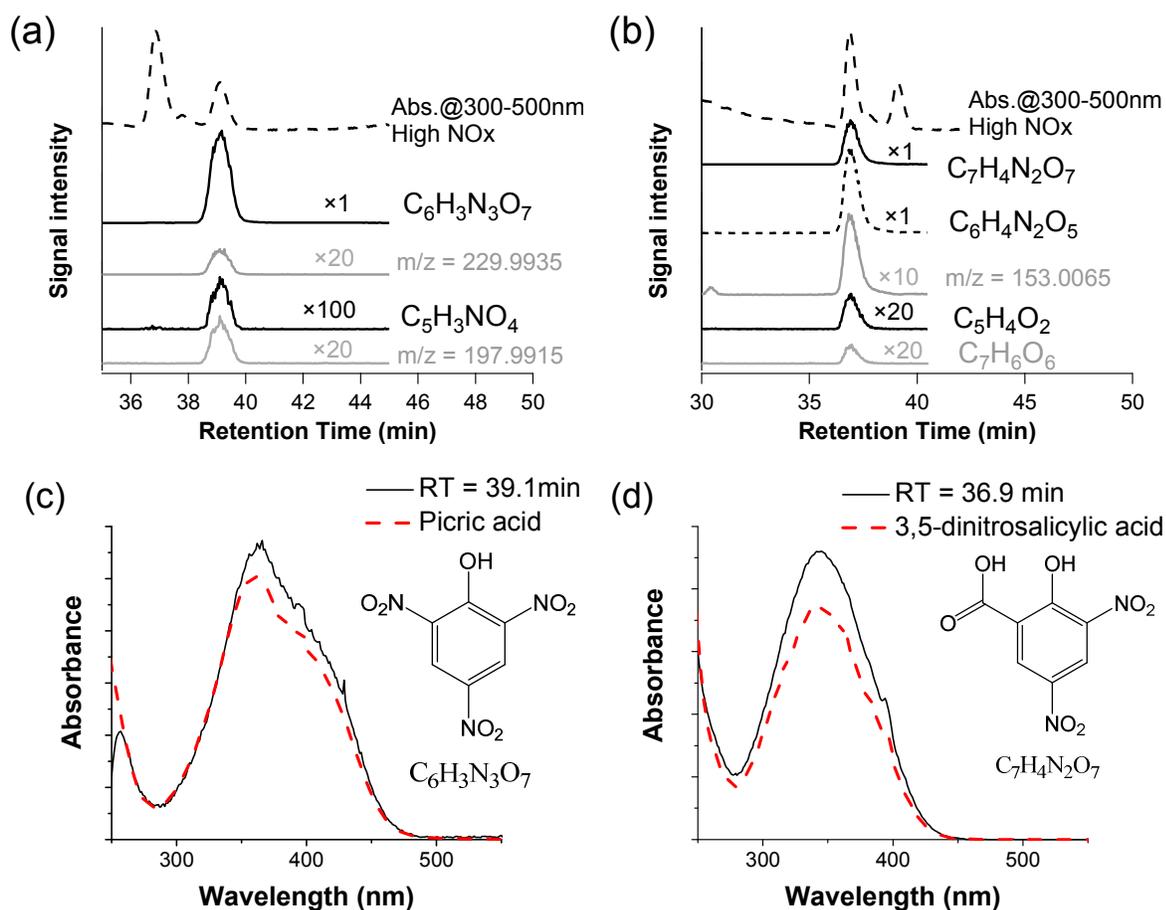
Figure 6. Extracted ion chromatograms (EIC) of molecules co-eluted at (a) 39.1 min and (b) 36.9min. Panel (c) compares the UV/Vis spectra of the BrC chromophore in high-NOx Tol-SOA sample eluting at 39.1min with the spectrum of picric acid measured by PDA. Panel (d) compares the UV/Vis spectrum of the BrC chromophore in high-NOx Tol-SOA sample eluting at 36.9min with the spectrum of 3,5-dinitrosalicyclic acid measured by PDA.

Figure 7
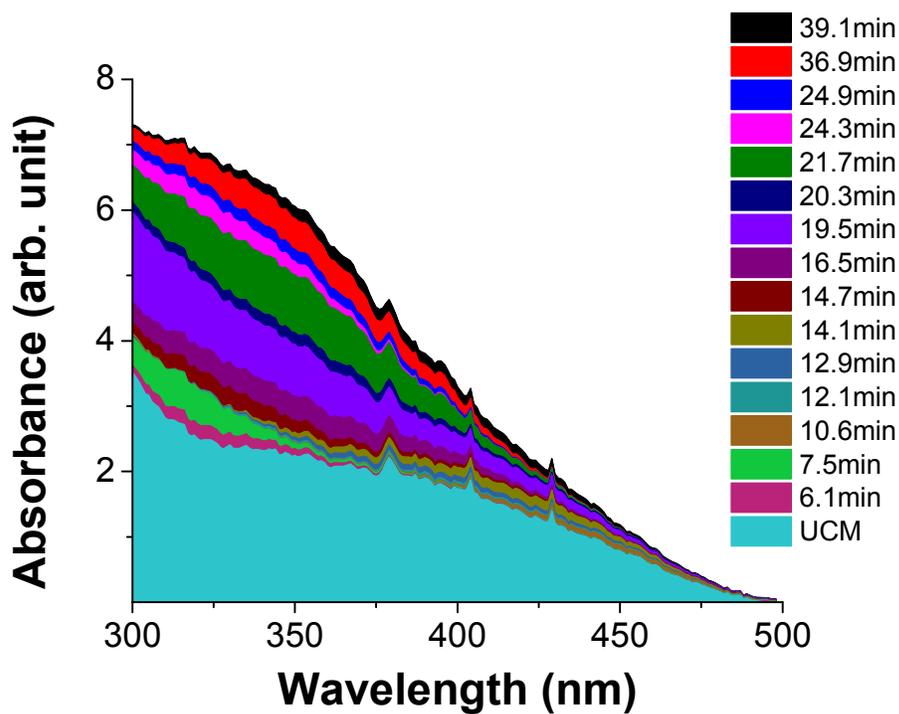
Figure 7. The relative contribution of the fifteen identified BrC chromophores and the unresolved complex mixtures (UCM, see text) with respect to the total light absorption by high-NOx Tol-SOA recorded in the HPLC-PDA measurement.

Table 1. Summary of the PDA spectra and retention times (RT) of major light-absorbing peaks and elemental formulas of the corresponding chromophoric compounds. The PDA spectra of some commercially available compounds or the maximum absorption wavelength (λ_{max}) of several organic compounds reported in the literature are also listed for comparison.

PDA spectrum @RT(min)	Formula and candidate compound	Proposed Structures	Comments
RT = 39.1min λ_{max} = 366nm	$C_6H_3N_3O_7$, picric acid		Identification of molecular structure was assisted by the analysis of commercially available standard of picric acid as shown in Figure 6a
RT = 36.9 min λ_{max} = 345nm	$C_7H_4N_2O_7$, 3,5-dinitrosalicylic acid		Identification of molecular structure was assisted by the analysis of commercially available standard of 3,5-dinitrosalicylic acid as shown in Figure 6b
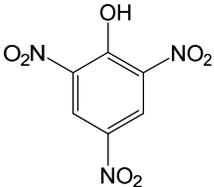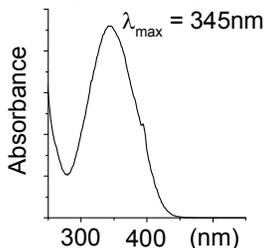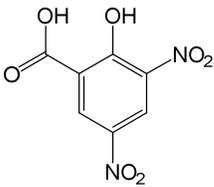
RT = 24.9min λ_{max} = 340nm Absorbance 300 400 (nm)	* $C_7H_6N_2O_6$, Methyl-dinitrocatechol		Specific positions of $-NO_2$ and $-OH$ groups in different isomers influence their absorption characteristics. Molecular structures with NO_2 groups in 1,4 (*para*) positions are likely to be most absorbing, followed by 1,3 (*ortho*) and 1,2 (*meta*) isomers. Positions of $-OH$ are expected to have additional, but less pronounced effect. For details, see comments to the cromophore at RT=21.7min.
RT = 24.3min λ_{max} = 325nm Absorbance 300 400 (nm)	$C_6H_4N_2O_5$, dinitrophenols (DNP)	 2,6-DNP **2,3-DNP** 2,4-DNP	Molecular structure of 2,3-dinitrophenol (2,3-DNP) is suggested as a plausible chromophore based on the literature report[30] of λ_{max}=329nm for 2,3-DNP, as opposed to λ_{max}=350nm for 2,6-DNP and λ_{max}=292nm for 2,4-DNP.
	$C_7H_7NO_3$, nitrocresols		Molecular structure of 4-nitro-o-cresol is suggested as a plausible chromophore based on the literature report of λ_{max}=319nm[30]
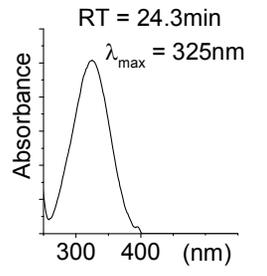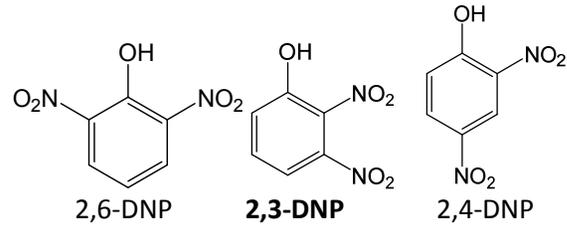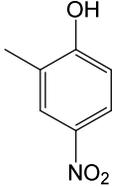
RT = 21.7min λ_{max} = 345nm Absorbance 300 400 (nm)	****** $C_7H_7NO_4$, Methyl- nitrocatechol (M-NC)	3M-6NC 3M-5NC 4M-5NC	Relative UV-Vis absorption of methyl-nitrocatechol (M-NC) and dinitrocatechol (DNC) isomers was evaluated using theoretical chemistry calculations of electronic structures for isolated molecules with the scope to assess effects of the functional groups positions (see Figure S2 for details). The results of these calculations are summarised below: 1) Presence or absense of $-CH_3$ group and its specific position on the aromatic ring have no coherent impact on the UV-Vis absorption (see structures 1-3 of Fig S2) 2) Specific positions of $-OH$ and $-NO_2$ groups influence the UV-Vis absorption of M-NC isomers. Molecular structures with 1,2-OH 3-NO_2 and 1,4-OH 3-NO_2 groups are predicted to have enhanced absorbtion in the Vis region (see structures 3-7 of Fig S2).
	$C_6H_4N_2O_6$, Dinitrocatechol		2) Specific positions of $-OH$ and $-NO_2$ groups influence the UV-Vis absorption of DNC isomers. Molecular structures with NO_2 groups in 1,4 (*para*) positions are
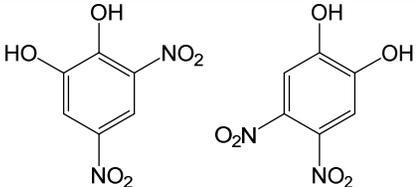
			predicted to be the most absorbing, followed by 1,3 (*ortho*) and 1,2 (*meta*) isomers. Positions of –OH groups have additional but less pronounced influence. (see structures 8-14 of Fig S2).
RT = 20.3min λ_{max} = 357nm	*** $C_7H_7NO_5$		
	$C_6H_5NO_3$, Nitrophenol	**2-NP** 3-NP 4-NP	Molecular structure of 2-Nitrophenol (2-NP) is suggested as a plausible chromophore based on the literature report of λ_{max}=351nm for 2-NP, as opposed to λ_{max}=333nm for 3-NP and λ_{max}=317nm for 4-NP.[30]
	** $C_7H_7NO_4$, Methyl-nitrocatechol		** see comments to the cromophore at RT=21.7min.
RT = 19.5min λ_{max} = 265nm	$C_7H_4N_2O_6$,		
	* $C_7H_6N_2O_6$, Methyl-dinitrocatechol		* see comments to the cromophore at RT=24.9min.
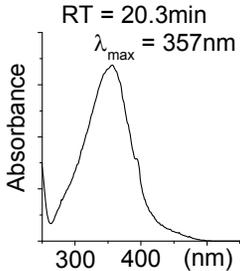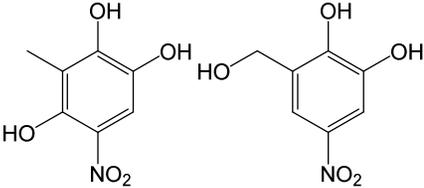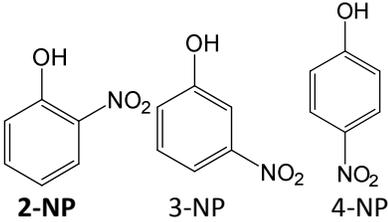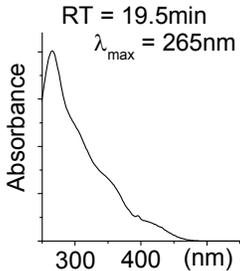
Spectrum	Formula / Name	Structure	Comments
	** $C_7H_7NO_4$, Methyl-nitrocatechol		** see comments to the cromophore at RT=21.7min.
RT = 16.5min λ_{max} = 347nm (Absorbance vs nm, 300–400)	$C_6H_5NO_4$, Nitrocatechol	3-NC **4-NC**	Molecular structure of 4-Nitrocatechol (4-NC) is suggested as a plausible chromophore based on the literature report of λ_{max}=345nm[66] for 4-NC, as opposed to λ_{max}=296nm for 3-NC.
RT = 14.7min λ_{max} = 321nm (Absorbance vs nm, 300–400)	$C_7H_5NO_6$		
	** $C_7H_7NO_4$, Methyl-nitrocatechol		** see comments to the cromophore at RT=21.7min.
RT = 14.1min λ_{max} = 412nm (Absorbance vs nm, 300–400)	$C_5H_4N_2O_5$;		
	*** $C_7H_7NO_5$		
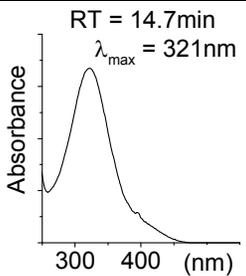
RT = 12.9min λ_{max} = 392nm (Absorbance vs nm plot, 300 400)	$C_7H_7NO_2$, nitro-toluene	 *p*-nitrotoluene, o-nitrotoluene	These two compounds have λ_{max} around 260nm, with a broad shoulder from 300nm to 400nm. (NIST Standard Reference Database Number 69, http://webbook.nist.gov)
	$C_8H_8N_2O_5$		
RT = 12.1min λ_{max} = 332nm (Absorbance vs nm plot, 300 400)	$C_7H_9NO_5$ DBE=4		Based on the low DBE value, corresponding molecular structure is likley non-aromatic
RT = 10.6min λ_{max} = 443nm (Absorbance vs nm plot, 300 400)	$C_7H_8N_2O_7$ DBE=5		Based on the low DBE value, corresponding molecular structure is likley non-aromatic
	$C_8H_{13}NO_8$ DBE=3		Based on the low DBE value, corresponding molecular structure is likley non-aromatic

RT = 7.5min, λ_{max} = 314nm (Absorbance vs nm, 300 400)	$C_7H_9NO_5$ DBE=4		Based on the low DBE value, corresponding molecular structure is likley non-aromatic
RT = 6.1min, λ_{max} = 309nm (Absorbance vs nm, 300 400)	$C_6H_5NO_2$ Nitrobenzene		Molecular structure of nitrobenzene (NB) is suggested as plausible chromophore. (λ_{max}=280nm has been reported[30] for NB).
	$C_6H_6N_2O_6$ DBE=5		

* potential chromophores with the same elemental formula ($C_7H_6N_2O_6$) appear at RT= 24.9 and 19.5min

** potential chromophores with the same elemental formula ($C_7H_7NO_4$) appear at RT= 21.7, 20.3, 19.5 and 14.7 min

*** potential chromophores with the same elemental formula ($C_7H_7NO_5$) appear at RT= 20.3, 14.1 min

Table 2. The acid dissociation constants (pKa) and maximum absorption wavelength of several nitro-phenolic compounds. ([m]the value is measured in this study for commercially available compounds. Other values are from literature reports)

Compound	pKa	λ_p(nm) of neutral molecule	λp(nm) of deprotonated molecule
2-nitrophenol	7.2[78]	350	430
3-nitrophenol	8.4[78]	330	420
4-nitrophenol	7.1[78]	315	425
4-nitrocatechol	6.7[66]	345	426
2,4-dinitrophenol	4.1[79]	292[m]	405 [m]
2,5-dinitrophenol	5.2[79]	360 [m]	450 [m]
3,5-dinitrosalicylic acid	3.0	345 [m]	360 [m]
picric acid	0.3	360 [m]	390 [m]